Stellingen behorend bij het proefschrift

Nanometer superstructuur in enkele vloeibare legeringen; een neutronenverstrooiingsonderzoek

1. De methode waarop de Reverse Monte Carlo (RMC) simulatie \(^1\) werkt (willekeurige verplaatsing van afzonderlijke atomen) in combinatie met het grote aantal vrije parameters zorgt ervoor dat, binnen een redelijke rekentijd, de 'best mogelijke fit' aan de data in het algemeen niet wordt bereikt.

2. De 'sterke ordening over korte afstanden' die wordt afgeleid uit de resultaten van een RMC simulatie aan de structuurfactor van vloeibaar CsTl \(^1\) is slechts een artefact welke het gevolg is van het aanpassen van het RMC model aan verkeerd genormeerde data.

3. Uit de zeer slechte resultaten van de RMC simulatie aan vloeibaar Cu\(_6\)Ce \(^1\) had geen andere conclusie getrokken mogen worden dan die er ergens een fout is gemaakt.

4. De relatie die wordt gelegd door C.A. Chatzidimitriou-Dreismann \(\text{et al}\) \(^1\) tussen de opzienbarenden resultaten van hun experiment aan H\(_2\)O-D\(_2\)O mengsels en een theorie over Quantum Entanglement, is totaal onbevestigd.

5. Het simuleren van diffractie data van complexe vloeibare legeringen als KTL met het "Structural Diffusion Model" \(^1\) (waarin een configuratie van 4 identieke atomen volgens een wiskundig formalisme gedempt periodiek worden voortgezet in de ruimte) lukt verbazingwekkend goed. Het levert echter evenveel inzicht op als een aanpassing van een polynoom aan de data.

6. De onmogelijkheid om experimenten op een onafhankelijke manier te reproduceeren is vaak een onderschat nadeel aan experimentele opstellingen die uniek zijn in de wereld en die zo complex (en, niet te vergeten, duur) zijn dat ze in alle redelijkheid niet kunnen worden nagebouwd.

7. Aangezien de kans op oorspronkelijke gedachten bij een X aantal geklooste mensen lager moet worden ingeschat dan bij een zelfde aantal genetisch verschillende mensen, is het klonen van mensen voor de vooruitgang van de wetenschap minder interessant.

8. Het feit dat F16's, tanks en ander militair materieel in de Nationale Rekening onder consumptieve bestedingen vallen in plaats van onder investeringen in vaste activa zegt iets over de risico's die militairen lopen in hun functie.

S.A. van der Aart
Propositions going with the thesis

Nanometer superstructure in some liquid alloys; a neutron diffraction study

1. The way in which Reverse Monte Carlo (RMC) modelling\(^1\) works (randomly moving individual atoms around) in combination with the large number of free parameters is the reason that the 'best fit' to the data is usually not achieved within a reasonable calculation time.

2. The strong ordering over short distances that was concluded from the results of RMC modelling on liquid CsTl\(^1\) is merely an artefact due to modelling on incorrectly normalized data with RMC.

3. From the RMC modelling of Cu\(_6\)Ce\(^1\) no other conclusion should have been drawn than the one that somewhere a mistake had been made.

4. The relation stated by C.A. Chatzidimitriou-Dreismann \textit{et al}\(^1\) between the remarkable results of their measurements on a H\(_2\)O-D\(_2\)O mixture and a theory about Quantum Entanglement is not proven at all.

5. The modelling of diffraction data of complex liquid alloys like KTi with the "Structural Diffusion Model"\(^1\) (where a configuration of 4 identical atoms is, according to a certain mathematical formalism, repeated in space with a damped periodicity) works amazingly well. However, it does not give much more insight into the structure of such an alloy as the fitting of the data with a polynomial function would.

6. The fact that it is impossible to reproduce measurements in an independent way is usually an underestimated disadvantage of experimental instruments that are unique in the world and are too complex (and costly!) to be duplicated in practice.

7. As the chance for original thoughts in an X number of cloned humans should be estimated lower than in the same number of genetically different humans, the cloning of humans is not very useful for the progress of science.

8. The fact that F16's, tanks and other military equipment are booked in the National Accounts as final consumption expenditure instead of investments in fixed assets says something about the risks involved in being in the military.

S.A. van der Aart
Nanometer superstructure in some liquid alloys; a neutron diffraction study

Nanometer superstructuur in enkele vloeibare legeringen; een neutronenverstrooilingsonderzoek
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Chapter 1

Liquid metals and alloys

1.1 General introduction

This thesis presents a study on nanometer superstructures that exist in some liquid alloys which belong to the group of so-called "Zintl-phases". The exact nature of this long-ranged ordering has been subject of study over the past decade [1, 2]. Most of the liquid alloys discussed in this thesis are quite extreme in that their ordering extends over distances larger than 1 nm. This ordering can be represented by a periodic volume which in some cases contains over \( \sim 30 \) atoms. Liquid intermetallic systems are evidently not as chaotic as one might expect at first impulse.

This thesis deals with neutron diffraction measurements carried out to further investigate this phenomenon of superstructure in liquid alloys. The interpretation of such measurements is however not straightforward nor unique, since we only measure statistical distribution functions, often of two or even three components at once. Modelling techniques help in assessing and extracting the information from the experimental data.

During this study it became clear that knowledge of the chemical aspects is crucial to understanding the (super)structure in the liquid alloy. We have therefore paid a fair amount of attention to the chemistry and bonding of Zintl-phases in the crystalline state.

In this introductory chapter we present the background and context of our work. Within the field of liquid metals and alloys the systems we have dealt with are structurally and chemically fairly complicated ones. Therefore the introduction will proceed from simple systems and notions to more complex ones. In the final section of this chapter the research program of this thesis will be given.
1.2 Solid and liquid metals

For obvious technological reasons interest in liquid metals dates from pre-historic times and a large body of empirical knowledge has been collected since then. However, a comprehensive understanding of their properties had to wait until the sixties of this century, when the so-called diffraction model was put forward by Ziman [3] and primitive, but usable pseudopotentials became available.

Three decades previously the fundamentals of the theory of solid metals had been established, offering a framework for the understanding of such diverse properties as electrical conductivity and cohesion. A central position in this theory is taken by the band structure, which is a direct consequence of the lattice periodicity in a metallic crystal.

Such periodicity is of course lacking in liquid metals. One can even not rely on the perfect lattice as a reference system because we do not know where the atoms "ought" to be. The structure of a liquid is given in terms of statistical distribution functions only. The most important ones are the pair distribution function $g(r)$ and the structure factor $S(q)$. $g(r)$ is defined such that $\rho_0 g(r)dr$ is the chance of finding a particle in a volume element $dr$ at distance $|\vec{r}|$ from another particle; $\rho_0$ is the average number of particles per unit volume. The counterpart of $g(r)$ in reciprocal space is the structure factor which is a function of the wavevector $q$

$$S(q) = \frac{1}{N} \left\langle \sum_{i,j} e^{-i\vec{q}(\vec{r}_i-\vec{r}_j)} \right\rangle$$  \hspace{1cm} (1.1)

where $\vec{r}_i$ is the position of particle $i$ and $N$ is the total number of particles in the volume considered.

1.3 Pseudopotentials, NFE model, diffraction model

A problem in the theory of metals is that the ionic potentials to which the conduction electrons are subject, are not small compared to the kinetic energy of a free electron. This would forbid the use of perturbation theory. A major step forward was made by the introduction of pseudopotentials [4]. The electron-ion potential is deepest inside the ion, where the electron wave function has large oscillations. A pseudopotential is designed such that it reproduces correctly the scattering of the conduction electrons, but still can
be treated as a perturbation. This leads to the so-called NFE (nearly-free-electron) model.

The introduction of the pseudopotential was crucial for the theory of liquid metals. This is easily demonstrated by considering the consequences of the so-called superposition principle. A conduction electron experiences a potential due to the total assembly of ion cores in a metal, \( W(\vec{r}, \vec{R}_1, ..., \vec{R}_N) \), where \( \vec{r} \) is the position of the electron and \( \vec{R}_i \) that of ion \( i \). The superposition principle states that \( W \) can be written as

\[
W(\vec{r}) = \sum_i w(\vec{r} - \vec{R}_i) \tag{1.2}
\]

Much of the physics and chemistry of metals is determined by the matrix elements of the kind

\[
\langle \vec{k} + \vec{q} | W | \vec{k} \rangle = V^{-1} \int e^{-i(\vec{k}+\vec{q}) \cdot \vec{r}} \sum_i w(\vec{r} - \vec{R}_i) e^{i\vec{k} \cdot \vec{r}} d\vec{r} \tag{1.3}
\]

where \( V \) is the total volume. The matrix element describes scattering from an electron state \( \vec{k} \) into a state \( \vec{k}' = \vec{k} + \vec{q} \). Performing the integral and neglecting boundary effects, it can be shown that

\[
\langle \vec{k} + \vec{q} | W | \vec{k} \rangle = V^{-1} \left( \sum_i e^{-i\vec{q} \cdot \vec{R}_i} \right) \langle \vec{k} + \vec{q} | w | \vec{k} \rangle
\]

\[
= V^{-1} \rho(\vec{q}) \langle \vec{k} + \vec{q} | w | \vec{k} \rangle \tag{1.4}
\]

If in equation 1.4 we replace the matrix elements of \( w \) by a form factor \( f(q) \) for X-ray diffraction or by a scattering length for neutron scattering it becomes equal to the scattered amplitude in a diffraction experiment. Therefore the theory of metals based on equation 1.4 is called the diffraction model. Evidently it is valid only in the first order perturbation approximation. It applies to solid as well as to liquid metals.

We notice that

\[
\frac{1}{N} \langle \rho^*(\vec{q}) \rho(\vec{q}) \rangle = S(\vec{q}) \tag{1.5}
\]

It is beyond the scope of this thesis to go into more detail. We mention only two important results of the diffraction model.

First one can calculate the electrical resistivity and other electronic transport properties from the matrix elements in equation 1.4. We notice here that the liquid state favours metallicity: liquid Ge, Si and Bi are good metallic conductors whereas the solid elements are not. Second, from the same matrix elements one can derive effective pair potentials \( V(\vec{r}) \) acting
between the ions. This potential can be used as input for calculations of the pair distribution function and the structure factor by means of analytical approximations known from the theory of liquids or by computer simulation. Thus the diffraction model provides a unified theory of such diverse properties as electronic transport and liquid structure. This description of the diffraction model could only be rudimentary. For a further account the reader is referred to, e.g., reference [5].

1.4 Order and disorder

New effects arise when we mix two metals, because then chemical effects occur, leading to preferential coordination. In the "order-disorder" theory [6] for binary solid solutions one considers a substitutional alloy. We restrict ourselves to nearest-neighbour interactions. The potential energy of an A-A pair is \( v_{AA} \), etc. We define an ordering energy by

\[
v = v_{AB} - \frac{1}{2} (v_{AA} + v_{BB})
\]

(1.6)

When \( v < 0 \) there is a tendency for an A-atom to have more B atoms in its first coordination shell than it would have in case of a random distribution. This is called ordering or heterocoordination. If \( v > 0 \) the opposite happens: atoms of the same kind tend to group together. There will be a tendency towards separation into two phases. In this theory this is called clustering.

What interests us are the structural consequences of such ordering. It can be shown that the scattered intensity in a diffraction experiment (with X-rays or neutrons) can be written as a sum of the sharp Bragg reflections and a continuous term, the so-called diffuse scattering [6]. When the distribution of the atom-types on the lattice points is random, the diffuse scattering is zero. In the case of ordering the diffuse scattering, even though it lacks the infinitely sharp Bragg reflections, may show broad peaks. One of them is the superstructure peak, associated with an increased periodicity and consequently situated in front of the first Bragg reflection.

It can be shown that the diffuse scattering corresponds to the contribution from the concentration-concentration partial structure factor, \( S_{CC}(q) \), to be introduced in section 3.2.3. The preference for heterocoordination is also called Chemical Short Range Order (CSRO). One example out of many is Cu-Au [7]. The low-\( q \) limit of \( S_{CC}(q) \), \( S_{CC}(0) \), gives the long wavelength composition fluctuations [8]. If \( S_{CC}(0) \) is high it indicates a tendency towards phase separation. An example of such an alloy is Cu-Ni [9].
In a liquid alloy also superstructure peaks can occur when there is a preference for heterocoordination of the atoms. An example of such an alloy is liquid Li-Pb, which will be discussed in more detail in section 1.5. Superstructure peaks are also called prepeaks or first sharp diffraction peaks.

The liquid alloys examined in this thesis are more complex and cannot simply be described by a preference for hetero or homocoordination. The superstructure peaks that occur in the structure factors of the investigated alloys are of a different nature than described above. They are due to the occurrence of clusters of atoms with a well-defined average size. These clusters cause an "Intermediate Range Ordering" (IRO) in the liquid alloy. Note that our use of the word "cluster" is different than the term clustering as used in the "order-disorder" theory, which merely indicates a preference for homocoordination. To avoid confusion we will describe the latter as "a tendency towards phase separation".

1.5 Coulomb interaction

Obviously, Coulomb forces are liable to produce ordering effects. This thesis deals with so-called ionic alloys in which the electronegativity difference between the components is moderate, smaller than in, e.g., NaCl but still large enough to be the primary driving force behind the chemical processes.

A good example is the system Li-Pb. It is intensively studied and forms an intermediate case between the NFE alloys and the more complicated alloys dealt with in this thesis. The electronegativity difference between Li and Pb is 1.35 on the Pauling scale. The diffraction pattern of liquid Li-Pb alloys exhibits a substantial prepeak suggesting strong Coulomb ordering [10, 11]. It is likely that Li transfers negative charge to Pb, so that the mixture becomes a bit salt-like. The electrical resistivity of Li-Pb alloys plotted as a function of composition has a sharp maximum at approximately 20% Pb. The value at the resistivity maximum is 440 $\mu\Omega$ cm, which is high enough to imply an electron mean free path which is slightly shorter than the nearest-neighbour distance between atoms. Formally, therefore, at this composition the material cannot be called a proper metal anymore, and the diffraction model is inadequate to describe it.

Chemically the resistivity peak at 20% Pb is associated with the formation of a compound Li$_4$Pb. In the purely ionic picture this can be formalized as (Li$^+$)$_4$Pb$^{4-}$, and the high resistivity can be interpreted as the onset of a "metal-to-salt transition". An ionic gap (or deep minimum in the density-of-states) has opened between the states deriving from the lead and the lithium orbitals. But also metallic and covalent bonding are mixed in
(Li₄Pb can easily be written as a Lewis structure). We will refer to this type of compound as "simple octet compound", in distinction from octet compounds obeying the more complicated Klemm-Busmann rules (see section 2.3.1).

1.6 Liquid compounds

Molten Li₄Pb is an example of a liquid compound. Liquid compounds, unlike solid compounds, are not delimited by phase boundaries (except for the liquidus) and they do not have a sharp stoichiometry. One of the advantages of liquid alloys is, that they can be investigated continuously as a function of composition. Examples of physical properties that have been measured as a function of composition are thermodynamic properties like the Darken stability function \((d^2G/dc^2)_{P,T,N}\), where \(G\) is the Gibbs free energy [12]), the heat and entropy of mixing and the specific heat, and electronical properties like the resistivity \(\rho\), its temperature derivative \(d\rho/dT\), the magnetic susceptibility and the Knight shift.

Liquid compounds can often be defined by extrema in their physical properties as a function of composition. The positions of these extrema will be considered as "stoichiometric compositions". Usually only one or two maxima are found in each binary system. If the extremum is "sharp enough" it indicates the existence of a chemical compound at that composition.

The case of Li-Pb system is quite unambiguous. At approximately 20% Pb it has maxima in the resistivity, the specific heat and the stability function and minima in the atomic volume and Knight shift. However, we will encounter exceptions in which a one-to-one correspondence between physical properties and compound formation does not exist.

1.7 Effects of disorder on the electronic properties

In liquid metals and alloys the behaviour of the electrons is not only dependent on the strength of the electron-ion interaction, also the effects of disorder can be appreciable. This is extensively discussed in the classical textbook "Electronic Processes in Non-crystalline Materials" by Mott and Davis [13]. In the liquid an electron experiences a random potential. P.W. Anderson (see references in [13]) showed that if the spatial fluctuations exceed certain limits localization of electrons may occur, i.e. the electrons can not move from one side of the sample to the other. This occurs particularly at electron
energies where the density of states is low, e.g. in band tails or in a deep
minimum of the density of states. In the latter case a so-called pseudogap is
formed, an energy gap in which some electron states have survived, but are
localized.

When the electrical resistivity is plotted as a function of composition, values
beyond the metallic range may occur for compositions involving compound
formation. Mott & Davis [13] defined the following regimes for the conduc-
tivity $\sigma$ in disordered materials:

Regime I: Nearly free electron behaviour (NFE); $\sigma > 3000 \text{ (\Omega cm)}^{-1}$

Regime II: Diffuse motion of electrons; $300 < \sigma < 3000 \text{ (\Omega cm)}^{-1}$

Regime III: Conduction by excitation; $\sigma < 300 \text{ (\Omega cm)}^{-1}$

These values should be considered as very approximate. The bor-
derline{d}erline between regime I and II is defined such that in regime I the electronic
mean free path is longer than the interatomic distance, while the opposite
applies to regime II. For this reason the electronic conduction in regime II
can not be classified as purely metallic anymore. Mott & Davis discern still
regimes IV and V, which are left out of discussion here. Most of the liquid
compounds discussed in this thesis fall into regime II. The binary systems to
which they belong all have additionally a negative $d\rho/dT$ for compositions
corresponding to the regimes II and III and $d\rho/dT$ has a sharp minimum at
the composition of the maximum in $\rho$. This can be explained in different,
non-conflicting, ways. The reader is referred to references [1] and [14].

1.8 Polyanion formation, Zintl-phases

The well-investigated alkali-Pb systems provide a good illustration of a search
for liquid compounds. The measured resistivities [15] as a function of com-
position, are plotted in figure 1.1. The resistivity maximum shifts from 20% Pb in Li-Pb and Na-Pb to 50% Pb for (K,Rb,Cs)-Pb, and it increases in
height along the series Li, Na, K, Rb, Cs. This indicates that for the heavier
alkalis the simple octet compound is no longer discernable and has given way
for an equiatomic compound. Geertsma [16] explained the existence of this
compound by a comparison with the solid state. The phase diagram of K-Pb
is dominated by an equiatomic compound KPb which melts congruently at
relatively high temperature (see figure 1.2). In the crystal structure of this
compound all Pb atoms occur in tetrahedral units Pb4 [18] (see figure 1.3).
Figure 1.1: Variation of resistivity with composition for liquid alkali-Pb measured 10 °C above the melting points.
Figure 1.2: Phase diagram of KPb. Reprinted from [17] with permission from ASM International.
Solid KPb is an example of a so-called Zintl phase.

The history of Zintl-phases goes back to 1932, when Eduard Zintl determined the crystal structure of NaTl and found that it consists of two interpenetrating diamond-type sublattices (B32 lattice), one for the Tl atoms and one for the Na atoms. He explained this as follows. In NaTl the less electronegative element (sodium) donates an electron to the more electronegative element (thallium). The Tl\(^-\) ions are isoelectronic (in their valence shell) with carbon in the next group of the periodic system and will tend to form the same structures, in this case a diamond lattice. The Na\(^+\) ions are small enough to occupy the empty positions in this lattice and form a second, interpenetrating, diamond lattice.

In KPb the electron transfer from potassium to lead results in \((\text{Pb}_4)^{-4}\) anions. (Because the charge transfer between K and Pb is not complete we use the notation \(\text{Pb}_4^{-4}\) where the superscript order denotes an oxidation state rather than an actual charge.) They are isoelectronic with \(\text{P}_4\) molecules as they appear in white phosphorus and obey the same chemical bonding rules. We call units of the kind \(\text{Pb}_4^{-4}\) polyanions and sometimes also clusters. The transition from a simple octet compound to an equiatomic clustered compound down the sequence Li-Pb to Cs-Pb has been confirmed by measurements of, among others, the density and the thermodynamic properties. Very important support came from neutron diffraction experiments. We will discuss them separately, as measurements of this kind form the subject of this thesis and need a more ample consideration.

Let us consider the electronic structure of the polyanions more closely. Notice that in KPb the Pb-Pb bonds are necessarily covalent and that all the electrons are in Pb-orbitals (or more precisely: in \(\text{Pb}_4^{-4}\) orbitals). Of the five valence electrons on each Pb-ion three participate in covalent bonds to other Pb-ions (electron sharing) while the remaining two form a lone pair. A covalent energy gap has opened between the bonding and antibonding states of the cluster. The band structure resembles the term scheme of As\(_4\) and P\(_4\) [19, 20]. This picture is confirmed by band structure calculations of NaSn and CsPb [21, 22]. Likewise the band structure of the Zintl-phases LiAl and NaTl resembles that of silicon, though the gap is bridged [23].

This model for the electronic structure formed the basis of the work of Geertsma [16] on the nonclustered-clustered transition from Li-Pb to Cs-Pb. His model strongly emphasizes the covalent interactions between Pb atoms (ions); in its most primitive form, it even completely neglects all other kinds of chemical bonding. The non-clustered situation is represented by a CsCl lattice. Geertsma then compares the energies of a clustered and a
Figure 1.3: The structure of solid NaSn [18], where the dark spheres represent Sn and the lighter ones Na atoms. The structure of KPb is isomorphous to that of NaSn.
Figure 1.4: The three regions in the phase diagram represent the different states in which equiatomic alkali-group 14 compounds can occur. Region I: no clustering, metallic; Region II\(^A\): clustering, overlapping bands, metallic; Region II\(^B\): clustering, nonoverlapping bands, nonmetallic. 1. LiSi; 2. LiGe; 3. LiSn; 4. LiPb; 5. NaSi; 6. NaGe; 7. NaSn; 8. NaPb; 9. KSi; 10. KGe; 11. KSn; 12. KPb; 13. RbSi; 14. RbGe; 15. RbSn; 16. RbPb; 17. CsSi; 18. CsGe; 19. CsSn; 20. CsPb [16].

nonclustered compound. The model is applicable to the solid as well as the liquid.

In this model it is assumed that there is complete electron transfer and the alkali elements thus obtain a noble gas electron configuration; their role is reduced to keeping the anions apart. Geertsmma compares two configurations, one containing tetrahedral clusters and another one with a salt-like structure (a CsCl type coordination). He introduced three parameters, U, V and T, which represent respectively interactions between Pb atoms within a cluster, Pb atoms in different clusters and between the Pb atoms as in the non-clustered CsCl structure. A phase diagram could be constructed with on the axes V/U and T/U, which is shown in figure 1.4. This diagram is divided in three regions separated by phase boundaries that indicate the division between clustered and CsCl type configuration. The position of real compounds in the diagram was calculated by scaling the interaction parameters with the inverse square of the interatomic distances. It turns out that the model describes the real situation for alkali-group 14 alloys perfectly well,
in spite of the serious approximations made.

According to this model clustering is essentially a size effect, as can be explained by the following considerations. The atomic diameter of the alkali metals changes by almost a factor 2 from Li to Cs. Large alkali ions in a CsCl type structure push the Pb atoms apart. The covalent interaction between Pb atoms becomes too small and a cluster type configuration is preferred where the Pb atoms can approach each other more closely. According to Geertsma’s model the clusters are relatively more stable when they are well-separated by large alkali atoms. It can thus be explained in a qualitative way that the maximum of e.g. the resistivity in alkali-Pb alloys increases along the series Li, Na, K, Rb, Cs.

Polyanion formation is a general characteristic of the Zintl-phases. Zintl-phases can be formed by a strongly electropositive metal and a ”metametal”. The term metametal refers to a class of moderately electronegative elements, ”a grey zone in the periodic system which divides nonmetallic elements from the typical metals” [24]. In practice one finds the anions in the groups 13, 14, 15 and 16 (post-transition groups III, IV, V and VI) of the periodic table. We will not give a precise definition of Zintl-phases, but a more elaborate description will be given in chapter 2. Well-known and typical examples of Zintl-phases are:

- NaTl, LiIn, NaIn, LiGa, LiAl.
  Polyanion: infinite diamond lattice, similar to Ge.

- All 16 equiatomic compounds of Na, K, Rb and Cs with Ge, Si, Sn and Pb.
  Polyanion: tetrahedron, similar to P₄ and As₄.

- All equiatomic compounds of Na, K, Rb and Cs with Sb.
  Polyanion: spirals, similar to the helical chains of tellurium.

- KTe.
  Polyanion: dumbbell (Te₂)²⁻, similar to the halogen molecule.

All these polyanions can be rationalized by electron counting in the same way as for Pb₄²⁻. This applies also to the Si₄ tetrahedra in BaSi₂ and the Tl₄ tetrahedra in Na₂Tl.

This list is far from exhaustive. More complicated structures arise in the alloys of K, Rb and Cs with the group 13 metals Ga, In and Tl, where the simple valence rules used above are no longer valid. In all these systems Geertsma’s rule that a large cation is favourable for polyanion formation proves to be valid empirically.
1.9 Structural investigations of liquid Zintl-phases

Polanyon formation is a structural phenomenon, even though the driving forces are of electronic nature. Therefore one of the most obvious ways to study them is by means of diffraction techniques. Neutron diffraction experiments form the main ingredient of this thesis. The technique and data analysis will be discussed in chapter 3. So far, diffraction experiments have largely confirmed the hypothesis of polyanions occurring in liquid alloys where they were expected from the measurements of electronic and thermodynamic properties.

We have seen that superstructure peaks occur in liquid Li-Pb. Its position for equiatomic LiPb is at $q_0 = 15.2 \text{ nm}^{-1}$ [10]. This peak is due to chemical short range order (CSRO) and it can be described by the partial structure factor $S_{\text{CC}}(q)$. Also in liquid K Pb, RbPb and CsPb a prepeak occurs, however they are positioned at substantially smaller wavevectors: $q_0 = 9.6, 9.3$ and $9.2 \text{ nm}^{-1}$ [25] respectively. This signals the occurrence of "Intermediate Range Order" (IRO). This order is related to cluster formation and is therefore of a more complicated nature than the order in Li-Pb (see also section 1.4). The prepeak in the structure factor of these alloys is not present in $S_{\text{CC}}(q)$ only, and it is usually easier to describe the structure with the Faber-Ziman partial structure factors (see section 3.2.3).

The following approach has shown to be useful. We identify the periodicity in the liquid with the average intercluster distance $d$. It relates to the position of the prepeak by $dq_0 = 7.7$ [26, 27]. The values of $d$ derived from the measured $q_0$ compare remarkably well with the intercluster distance in solid APb (where A=K,Rb or Cs). Moreover, modelling the liquid structure by means of computer simulations [28] or analytical [25] methods reproduces the measured intensities nicely if one presumes the existence of tetrahedra a priori.

Similar results were obtained for the alkali-tin alloys [29], the Cs-Sb alloys [27] and K-Te [30]. An overview is given in reference [1]. Turning to the alkali-group-13 alloys, the resistivity measurements show no signs of strong compound formation [31, 32] in contrast to some thermodynamic measurements [33, 34]. It came therefore as a big surprise that the neutron diffraction results of alloys of the K-Tl and Cs-Tl systems exhibit a prepeak at very low $q_0$, corresponding to distances in real space of about 1 nm [35]. The estimated average cluster size is about 8 Tl atoms [1]. During that time Tl$i^{-7}$
clusters were discovered in solid intermetallic compounds of the composition $A_8Tl_{11}$ ($A=K,Rb,Cs$) by groups in Ames [36] and Darmstadt [37], followed by $Tl_5^6$ clusters in KTi [38] and CsTi [39]. The analogy between the solid and the liquid state formed a stimulus for a further structural investigation of alkali-group 13 alloys.

1.10 Research program and organization of this thesis

This thesis is structured as follows. Chapter 2 will give a summary of some important points that concern the structure and bonding of Zintl-phases in solid alloys. The theory of neutron diffraction as well as the experimental aspects and "Reverse Monte Carlo modelling" will be discussed in chapter 3. In the chapters that follow the neutron diffraction results of several systems are described. The measurements made are summarized below.

The experimental investigations pertain primarily to the alkali-group 13 alloys. The choice of the particular systems to be investigated depends on experimental feasibility and expected scientific interest. Indium alloys were not taken into consideration, because the neutron absorption of In is too high.

The experimental part, analysis and conclusions of the measurements on liquid alkali-Tl systems are discussed in chapter 4. First the structure of equiatomic liquid KTi is reexamined by using a $^{205}$Ti substitution which allows for better, though not complete, separation of the partial structure factors. The structure of liquid KTi is compared to that of $K_8Tl_{11}$ and KTi in the solid [36, 38]. Further parallels between structures in solid and liquid alloys were sought in K-Tl systems with additional third elements: $K_{18}Tl_{20}Au_3$, $K_{10}Tl_{10}Pd$ and $K_9Tl_{10}Zn$. A composition study on the liquid Cs-Tl system was carried out, to investigate the composition dependence of the IRO.

In chapter 5 measurements of the alkali-Ga systems are presented, namely of liquid NaGa$_2$, KGa$_3$ and CsGa$_3$. In solid alkali-Ga structures have been found where large gallium cluster networks occur. One of the reasons why the structure of these liquid alloys had not been measured before was because of difficulties anticipated in experimentation. Gallium corrodes many container materials and not much is known about the chemical reactivity of the alloys.
The last set of measurements was on the liquid Cs-Bi alloys, viz. equiatomic CsBi and Cs$_3$Bi$_2$. The measurements carried out on this system are discussed in chapter 6. Bismuth belongs to group 15 of the periodic system. When applying the Zintl model to Bi, we can expect to see tellurium-like chains of Bi$^-$ ions in the alloy.

The alkali-Bi alloys are, as yet, badly understood. More particularly the indications for the stoichiometry of the presumed clustered compounds in the liquid are ambiguous. From Li-Bi to Cs-Bi the resistivity maximum changes gradually (i.e. via a double maximum) from the simple octet compound $A_3$Bi to $A_3$Bi$_2$. The maximum for Cs$_3$Bi$_2$ is very high, well into Mott’s regime III but also rather broad. Measurements of the Darken stability function indicate an equiatomic compound ABi rather than $A_3$Bi$_2$ (for references see section 6.1). The phase diagram displays congruently melting compounds at ABi$_2$ with a high melting point, not discernible in other physical measurements. Simple octet compounds occur in the solid state for all alkali-bismuth systems.

Relativistic effects are known to influence the chemical bonding properties of Bi [40]. It may be a possible cause for the puzzling behaviour in the liquid alloys. Further investigations seemed to be useful in order to clarify the situation.
Chapter 2

Structure and bonding of Zintl-phases

2.1 Introduction

As we have seen in chapter 1, solid Zintl-compounds display an astonishing richness in crystal structures. In this chapter the underlying principles of the structure and bonding in some of these solid alloys will be discussed as they are of fundamental importance for understanding the structure of the liquid alloys. Special attention will be paid to Zintl-phases with group 13 elements.

Most of this chapter is based on a recently published book: "Chemistry, Structure and Bonding of Zintl Phases and Ions" [41].

2.2 Structure and bonding in alloys

In many alloy-systems solid intermetallic compounds are formed, defined as phases with a sharp stoichiometry, i.e. they exist only in a discrete or very narrow composition range. Various interpretations have been given for the existence of intermetallic compounds. Hume-Rothery classified many intermetallic compounds on the basis of the number of valence electrons per atom [42]. Another important principle of compound formation is based on the relative sizes of the components, which was set forth by Laves [43]. The type AB₂ is known as Laves-phase. Pauling considered the differences in electronegativity which he correlated to the polarity of the bonds [44]. In the usual case, however, the observed structure of intermetallics is a result of the combined action of the three factors mentioned.

The transition between metallic and ionic bonding was extensively explored by Zintl. He observed significant contraction of the atomic volumes
Structure and bonding of Zintl-phases

in the examples that did not follow the classification according to the Hume-Rothery rules. This could be explained by assuming volume contraction of the electronegative atoms, due to the loss of an electron. We recall that he considered NaTl to consist of Na\(^+\) and Tl\(^-\) ions [45]. The extra electron for Tl makes it possible to form a diamond lattice of Tl\(^-\) ions, as Tl\(^-\) is isoelectronic to Ge and Si. The Tl\(^-\) ions form covalent bonds to each other to form what can be regarded as a three-dimensional macro-anion.

This idea was generalized by Klemm and Busmann [46]: The negatively charged atoms are iso-electronic to the neutral element in the next group of the periodic system, i.e. they possess the same number of valence electrons. Therefore they can form polyanions with structures similar to those of molecules of the corresponding elements. This is now known as the Zintl-Klemm concept (or sometimes referred to as the Zintl-Klemm-Busmann concept).

In the course of time numerous new compounds of alkali and alkaline earth metals with group 13-16 elements have been discovered. Many of them are denoted by the term "Zintl-phases". A number of them have been listed in section 1.8. Although they have some essential properties in common, they exhibit a rich variety in structure and bonding types. The term Zintl-phases is not sharply delimited. For attempts at a definition we refer to reference [41]. Characteristic is a moderate electronegativity difference between the components (0.4 to 1.3 on the Pauling scale), a tendency to form polyanions and little or no bonding between the cations. Zintl-phases are related to the so-called Zintl ions, aggregates like Pb\(_5^2^-\), Sn\(_9^4^-\), Ge\(_9^2^-\) and Bi\(_4^2^-\), which are made in liquid ammonia or cryptants. In the following we will denote the electronegative component by X and the electronegative component by A when a further specification is not needed.

2.3 Electronic structure of polyanions

In the Zintl-phases metallic, ionic and covalent bonds can coexist. Due to the structural complexity of many Zintl-phases, predominantly semiempirical electronic structure methods have been used to calculate the electronic structure (the density of states, DOS).

The real electron transfer between the atoms is not equal to that implied by the Zintl-Klemm concept. It depends on the electronegativity difference between the anions and the cations. Although the description in terms of complete charge transfer in for example NaTl is unrealistic (notice that each Tl\(^-\) ion is surrounded by as many Tl\(^-\) ions as Na\(^+\) ions in its first
coordination shell), it describes the structure very well. The reason that the Zintl-Klemm concept works at all is because the occupied electron states are counted, not the electrons. The charge on the ions can be regarded as an oxidation state, not as an actual charge.

Later in this chapter more extended valence rules that describe polyanions will be given. To avoid confusion with actual ions the notation $X_m^{-n}$ will be used rather than $X_m^{n-}$, in which $-n$ refers to the oxidation state of the cluster $X_m$.

Below, the valence rules for Zintl-phases will be discussed. They all basically boil down to the application of the octet rule. There are two ways for an atom to obtain 8 electrons in its outer shell, one is through 'borrowing' electrons (ionic bonds) and the other way is to 'share' electrons with other elements (covalent bonds). When going from group 16 to 13 in the periodic system, the number of valence electrons decreases and, as a result, the atoms need to make more bonds to satisfy the octet rule. This leads to a change in bonding mechanisms, when one crosses the line separating the groups 13 and 14 in the periodic system. This line is often called the Zintl-line or Zintl-border. We will therefore in the following distinguish between electronegative atoms at the right and the left hand side of the Zintl-line and discuss them separately.

### 2.3.1 Zintl-Klemm description

Let us first consider anions at the right hand side of the Zintl-line.

Suppose we have an alloy of the composition $A_xX_z$, where $A$ is the electropositive and $X$ the electronegative metal. The number of valence electrons for elements $A$ and $X$ is respectively $e_a$ and $e_x$. Then the number of electrons in the outer shell per $X$ atom is

$$N_x = \frac{ae_a + xe_x}{x} = \frac{a}{x}e_a + e_x$$  \hspace{1cm} (2.1)

In the case of a so called "simple octet compound", $\frac{a}{x}e_a + e_x = 8$. An example of such a compound is Li$_3$Bi, where $N_x = 3 \times 1 + 5 = 8$. It has a cubic close packed structure of Bi atoms where all the tetrahedral and octahedral holes are filled with Li. No Bi-Bi bonds occur.

For most Zintl-phases $X - X$ bonds are needed to fill the outer shell of the $X$ atoms by formation of electron pairs. This leads to the well-known Lewis structures. These bonds are classical covalent bonds when 2 electrons are positioned in between 2 centers of atoms (2c:2e). In this case $\frac{a}{x}e_a + e_x < 8$,.
and the number of $2c:2e$ $X - X$ bonds per atom that is required to form a closed shell is

$$b_x = 8 - N_x$$  \hspace{1cm} (2.2)$$

This simply relates to the classical valence rule for insulators (the $(8 - N)$-rule). According to the Zintl-Klemm concept the $X^{-ae/2}$ unit can be regarded as a pseudoatom that shows the same structure as the isoelectronic element. For instance, in KPb every Pb receives one electron from K, so that it still needs $b_x = 8 - 5$ electrons from electron sharing in covalent bonds. Indeed, in the tetrahedral Pb$_4$$^-$ units that occur in KPb, each Pb atom makes 3 covalent bonds to other Pb atoms. Two electrons per Pb atom remain as a lone pair.

### 2.3.2 Crossing the Zintl-border, Wade rules

Choosing $X$ atoms with even less valence electrons, the number of classical covalent bonds per atom reaches a maximum. This is the case for Zintl-phases of group 13 elements, which possess only 3 valence electrons. In the case of NaTl, Tl receives one extra electron from Na, and has to form 4 covalent bonds (a diamond lattice) in order to satisfy equation 2.2. Since Na is small, it can form a second, interpenetrating, diamond lattice. This does not work for the larger alkali metals. In that case the electron-deficient group 13 elements form clusters that contain delocalized bonds, like e.g. $3c:2e$ bonds (3 centers sharing 2 electrons). The principles of electron counting for such systems are based on the Wade rules [47]. They will only be explained in short. These rules are, like all valence rules, based on closed shell requirements, only in this case some electron pairs are delocalized in bonds between more than 2 atoms at once and still contribute fully to the completion of their closed shells. They were originally applied to boranes, which contain deltahedral clusters, i.e. deltahedrons, of B-H units (named this way because they are made up of triangular faces each resembling a Greek delta, $\Delta$). By counting the electrons the cluster shape can be predicted. In the case of naked group-13 clusters the B-H unit is replaced by an element with a lone electron pair.

The Wade electron-counting rules are dependent on the shape of the cluster. We distinguish between closo, nido, arachno and hypno structures. We consider first a closo structure consisting of $n$ atoms. In the closo structure the $X$ atoms are all at the vertices of a closed deltahedron.

In the Wade picture each one of the $n$ atoms has an outer pair of electrons (lone pair), which replaces the B:H bond in a borane. It is non-bonding or can be used for binding the cluster to another cluster or to an
atom not belonging to the cluster. The remaining electrons (one per Ga, In or Tl atom) are skeleton electrons, which have to keep the cluster together. The Wade rule for the closo structure states that there are $2(n + 1)$ skeleton electrons. This, and the other Wade rules, can be justified by molecular orbital calculations. Here we will not go into such detail. The following crude picture for the closo structure may help to visualize the chemical bonding somewhat. The $s$ and $p$ electrons form $sp$ hybrids. There are 4 such orbitals per atom. One orbital is occupied by the lone pair, sitting on the outside of the cluster. Another one is pointing radially towards the center of the cluster and in addition there are 2 tangential orbitals, similar to $p$-states. The radial orbitals of all atoms combine to one orbital which is completely delocalized and is shared by all $n$ atoms. It is the lowest state of all. The $n-1$ remaining combinations of radial states are antibonding. The $2n$ tangential orbitals combine to $n$ bonding and $n$ antibonding orbitals. So there are $n+1$ bonding skeleton orbitals to be filled with $2(n + 1)$ electrons. There are, however, only $n$ electrons available for this purpose and therefore the cluster has to borrow $(n + 2)$ electrons from an electropositive component.

The nido structure can be obtained from a closo structure by taking one vertex atom away (to create a "vacancy"). The remaining arrangement is not a deltahedron. For a nido cluster the counting rule is: number of skeleton electrons = $2(n + 2)$. An arachno cluster is obtained by removing two atoms from a closo structure. Then the required number of skeleton electrons proves to be $2(n + 3)$. The Wade rules are summarized in table 2.1. An example of a closo $X_{12}$ cluster, a nido $X_{11}$ and an arachno $X_{10}$ is given in figure 2.1.

The names have the following meaning: closo is Greek for 'cage';
nido is Latin for ‘nest’; arachno is Greek for ‘spider’; hypho is Greek for ‘net’.

<table>
<thead>
<tr>
<th>cluster shape</th>
<th>number of skeleton electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Closo</td>
<td>2(n+1)</td>
</tr>
<tr>
<td>Nido</td>
<td>2(n+2)</td>
</tr>
<tr>
<td>Arachno</td>
<td>2(n+3)</td>
</tr>
<tr>
<td>Hypho</td>
<td>2(n+4)</td>
</tr>
</tbody>
</table>

Table 2.1: The number of bonding electrons necessary for a certain cluster shape according to the Wade rules.

Examples of such clusters as they occur in Zintl-phases are Tl\textsubscript{6}\textsuperscript{8} in Na\textsubscript{13}K\textsubscript{6}Tl\textsubscript{18} [48] and In\textsubscript{5}\textsuperscript{9} in La\textsubscript{3}In\textsubscript{5} [49]. Tl\textsubscript{6}\textsuperscript{8} has 6+8 electrons for the cluster framework (”skeleton”) which can be written as 2(6+1), and therefore it has a closo structure. Likewise, the 5+9 electrons in the In\textsubscript{5}\textsuperscript{9} cluster results in a nido structure since 14=2(5+2).

Other examples in section 2.4.1 will show that these Wade rules are not always strictly obeyed. Sometimes distortions in clusters can empty one of the bonding molecular orbitals (M.O.), or other deviations from the Wade rules may occur.

2.4 Structure of Zintl-phases at the Zintl-border

Many isolated clusters have been found in solid alkali-group 13 alloys, increasing in variety and frequency from Ga to In to Tl. The clusters are called "isolated" when they are not interlinked with each other; they are separated by the cations. The following isolated clusters have been observed:

- Tl\textsuperscript{5}, Tl\textsubscript{3}\textsuperscript{7}, Tl\textsubscript{4}\textsuperscript{8}, Tl\textsubscript{5}\textsuperscript{7}, Tl\textsubscript{6}\textsuperscript{6}, Tl\textsubscript{7}\textsuperscript{8}, Tl\textsubscript{9}\textsuperscript{9}, Tl\textsubscript{11}\textsuperscript{7}, Tl\textsubscript{13}\textsuperscript{10}, Tl\textsubscript{13}\textsuperscript{11}.

- In\textsuperscript{4}\textsuperscript{8}, In\textsubscript{11}\textsuperscript{7}.

- Ga\textsubscript{11}\textsuperscript{7}.

Many of these clusters were identified by groups in Ames and Darmstadt. More details about their structure and that of the Zintl-phases they occur in can be obtained from references in [41].

Only three of the smaller cluster types with the higher assigned charges follow the Wade rules (see subsection 2.3.2); nido X\textsuperscript{2}\textsuperscript{8} where X is Tl or In, closo
2.4 Structure of Zintl-phases at the Zintl-border

$\text{Tl}_5^{7-}$ and closo $\text{Tl}_6^{8-}$. The $X_4^{8-}$ cluster can however also be rationalized within the Zintl-Klemm concept.

For the larger clusters the assigned cluster charge becomes too high, and then the cluster description starts to deviate from the Wade rules. This will be explained in more detail in section 2.4.1.

2.4.1 Distorted clusters, size tuning

The deviations from the Wade rules usually imply distortions of the cluster shape in such a way that one of the M.O. is emptied. This leads to a lower cluster charge. The clusters $\text{Tl}_5^{6-}$ [38] and $\text{Tl}_{11}^{-7}$ [36] were the first examples of such hypoelectronic clusters. $\text{Tl}_6^{-6}$ can be regarded as a $\text{Tl}_6^{-8}$ cluster that is axially compressed as a result of which one bonding M.O. becomes antibonding. The $\text{Tl}_{11}^{-7}$ cluster can be derived from a $\text{Tl}_5^{-11}$ with two additional $\text{Tl}^+$ ions. The resulting $\text{Tl}_{11}^{-9}$ undergoes a distortion and again one M.O. is emptied to obtain $\text{Tl}_{11}^{-7}$. In figure 2.2 the structure of equiatomic K$\text{Tl}$ is drawn, the centers of the distorted $\text{Tl}_5^{-6}$ clusters appear in a FCC lattice. In figure 2.3 the $\text{Tl}_{11}^{-7}$ is drawn as it appears in K$_8\text{Tl}_{11}$, Rb$_8\text{Tl}_{11}$ and Cs$_8\text{Tl}_{11}$.

There is a strong influence of the cation packing around these clusters. For example, the afore mentioned $\text{Tl}_{11}^{-7}$ clusters require 8 cations (K, Rb or Cs), one of which is solely required for packing considerations. The one valence electron is not used in the Tl cluster and, to be precise, the cluster should be formulated as $\text{Tl}_{11}^{-7}+1\text{e}^-$. This is an example of a Zintl-phase with metallic character.

Probably many clusters do not occur in binary alloys because the packing constraints do not allow for it. This may be the reason why the undistorted $\text{Tl}_5^{-8}$ cluster has only turned up in the ternary compound Na$_{15}$K$_6\text{Tl}_{18}$ [48]. The average volume of the alkali metals is adjusted to accommodate the cluster, by using a mixture of alkali metals. This process is called "size-tuning" and has been used to obtain many of the cluster-types mentioned above.

2.4.2 Heterometallic clusters

A way to increase the stability of the clusters is to add a hetero element to gain central bonding, and in some cases add electrons to complete the electron count. In addition, these hetero elements often cause distortions of the cluster that lead to the emptying of one of the M.O.
Figure 2.2: The structure of KTL with Tl$_6^{-6}$ clusters [38]. The dark spheres are Tl and the lighter ones K atoms.

Figure 2.3: A Tl$_{11}^{-7}$ cluster as it occurs in K$_8$Tl$_{11}$ [36].
2.4 Structure of Zintl-phases at the Zintl-border

![Diagram of a clustered structure](image)

Figure 2.4: The central bonded In$_{10}$M$^{-10}$ cluster [50], where M is Ni, Pd or Pt, as occurs in K$_{10}$In$_{10}$M. The dark spheres represent In and the light one represents the M atom.

An example of central bonding in a cluster is given by In$_{10}$M$^{-10}$ in K$_{10}$In$_{10}$M [50], where M is Ni, Pd or Pt. The centering process in this cluster can be discussed in three steps. A tricapped trigonal prism, In$_9^{-11}$, is capped with an other In$^+$ ion to obtain an In$_{10}^{-10}$ cluster. The next step is a distortion that takes place resulting into a more spherical cluster shape, but nothing significant happens to the M.O. This cluster is then centered with M, whose $s$ and $p$ orbitals are of appropriate size and energy to overlap with the cluster M.O. The net result is stabilization of some of the cluster orbitals and gain of central bonding. In figure 2.4 the structure of In$_{10}$M$^{-10}$ is given.

In K$_8$Tl$_{10}$Zn [51] something similar happens, but in that case not only the energies of some of the cluster M.O. are lowered, also Zn provides two of the bonding electrons. The Tl$_{10}$Zn$^{-8}$ cluster is isoelectronic to In$_{10}$M$^{-10}$. The cluster shape however is different (Tl$_{10}$Zn$^{-8}$ is a bicapped square antiprism) and this is probably the result of the difference in the number of cations that have to be accommodated around the clusters.

An example where the hetero element is substituted for an X-element in the cluster, instead of centering it, is found in K$_{18}$Tl$_{20}$Au$_3$ [52]. The Tl$_9$Au$_2^{-9}$ cluster that appears in this alloy, can be derived from Tl$_{11}^{-7}$. Two Tl atoms are replaced by Au that would leave the cluster four electrons short of the closo Tl$_9$Au$_2^{-11}$. A strong axial compression leads to a short Au-Au bond in the cluster and one cluster M.O. is emptied. In this way the addition of two extra valence electrons from Au and the distortion lead to the Tl$_9$Au$_2^{-9}$
cluster. The packing of atoms, once again, requires one extra cation. The electron belonging to this cation is presumably delocalized and gives this compound a metallic character. Figure 2.5 displays the $\text{Tl}_9\text{Au}_{2}^{-9}$ cluster.

### 2.4.3 Interlinked clusters

A significant and common means of charge reduction for Ga, and to a lesser extent In and Tl, is intercluster bonding to form networks. Thallium shows predominantly isolated clusters and In provides a mix of both networks and isolated clusters. The trends down the group 13 elements reflect the change from strong and often localized bonds to more metallic-like longer and weaker bonds.

The intercluster bonds are shorter than the intrACLuster bonds, because they are stronger classical 2c:2e bonds. Each bond formed reduces the cluster charge by one. For instance the $\text{Ga}_6$ clusters in $\text{K}_2\text{Ga}_3$ [48] are linked to 4 other clusters in a two-dimensional network. This reduces the original closo $\text{Ga}_6^{-8}$ to $\text{Ga}_6^{-4}$. Another example is $\text{KGa}_3$ [53] which contains 8-bonded closo $\text{Ga}_8^{-10}$ clusters that thus reduce their charge to $\text{Ga}_8^{-2}$. But in this case the clusters are not all linked to each other, some are linked to $\text{Ga}^{-}$ atoms. These single Ga$^{-}$ atoms are 4-fold coordinated by clusters. In figure 2.6 the structure of $\text{KGa}_3$ is given.

Due to this interlinking of clusters, and the consequent charge reduction, much larger clusters can occur. $\text{Na}_7\text{Ga}_{13}$ for example contain 9-bonded $\text{Ga}_{12}^{-2}$ clusters and 18-bonded $\text{Ga}_{15}^{-11}$ connected to a three-dimensional net [54].
Figure 2.6: The structure of KGa₃ [53]. The dark spheres are Ga and the lighter ones K atoms.
Chapter 3

Neutron diffraction

3.1 Introduction

In this chapter the theory and practice of neutron diffraction on liquid alloys will be presented. The basic elements of the neutron diffraction theory which are necessary to understand the analysis and interpretation of the neutron diffraction experiments, are given in section 3.2. The textbooks of Lovesey [55] or Squires [56] provide further details on the theory of neutron scattering. The experimental technique and data correction procedures will be discussed in section 3.3. An important tool in the analysis of the neutron diffraction data is Reverse Monte Carlo modelling (RMC). For the evaluation of the results, it is important to understand the principles of RMC, which will be discussed in section 3.4.

3.2 Theory

The quantity measured in a neutron diffraction experiment is the differential scattering cross section

$$\frac{d\sigma}{d\Omega} = \frac{\text{flux scattered into solid angle } d\Omega \text{ at angle } 2\Theta}{\text{incident flux density } \cdot d\Omega}$$

(3.1)

where the incident neutron flux is considered to be of wavelength $\lambda$. If not only the direction but also the energy of the scattered neutrons is measured the double differential scattering cross section $d^2\sigma/d\Omega dE$ has to be used, defined as the fraction of neutrons scattered into an element of solid angle $d\Omega$ with an energy between the values $E$ and $E + dE$. In a diffraction experiment the detector integrates over all energies.
3.2.1 Scattering by a single atom

We start with the scattering of neutrons of wavelength $\lambda$ by a single atom. The incident beam is considered to be a plane wave described by a wavefunction of the form

$$\Psi_{\text{in}}(\vec{r}) = \frac{1}{\sqrt{v_0}} e^{-i\vec{k}_0 \cdot \vec{r}}$$  \hspace{1cm} (3.2)

The wavevector $\vec{k}_0$ is related to the velocity $\vec{v}_0$ of the neutrons according to $\hbar \vec{k}_0 = m \vec{v}_0$ and the absolute value is $|\vec{k}_0| = 2\pi/\lambda$. The wavelength of the neutrons is of the order of 0.1 nm and is much larger than the size of the scattering nucleus, which we can regard as a point object. Consequently, the scattering from a nucleus at the origin will be a spherically symmetric wave given by

$$\Psi_{\text{out}}(\vec{r}) = \frac{1}{\sqrt{v_0}} \frac{-b}{|\vec{r}|} e^{-i\vec{k} \cdot \vec{r}}$$  \hspace{1cm} (3.3)

where $\vec{k}$ is the wavevector of the scattered neutrons and $b$ is a constant called the scattering length of the nucleus. The flux of the scattered neutrons is given by $4\pi r^2 |\Psi_{\text{out}}(\vec{r})|^2 v_0$, hence using equation 3.1 we find:

$$\frac{d\sigma}{d\Omega} = r^2 \frac{|\Psi_{\text{out}}(\vec{r})|^2}{|\Psi_{\text{in}}(\vec{r})|^2}$$  \hspace{1cm} (3.4)

When we substitute equations 3.2 and 3.3 in equation 3.4 we obtain the differential scattering cross section for a single nucleus,

$$\frac{d\sigma}{d\Omega} = |b|^2$$  \hspace{1cm} (3.5)

In general $b$ is a complex number of which the absolute magnitude is of the order of the size of a nucleus, namely $10^{-15}$ m (1 fm). For most nuclei, however, $b$ is real and the absolute signs will be omitted from now on.

3.2.2 Scattering by a single-component system

The scattering from an ensemble of $N$ atoms is simply given by the sum over all the atoms $i$:

$$\Psi_{\text{out}}(\vec{r}) = \sum_{i=1}^{N} \frac{-b_i}{|\vec{r} - \vec{r}_i|} \frac{1}{\sqrt{v_0}} e^{-i\vec{k}_i \cdot (\vec{r} - \vec{r}_i)} e^{-i\vec{k}_0 \cdot \vec{r}_i}$$  \hspace{1cm} (3.6)

where the second exponential term on the right hand side is the phase factor of the incident wave at nucleus $i$. For large values of $\vec{r}$ compared to $\vec{r}_i$ (usually
3.2 Theory

the distance from the sample to the detector is in the order of meters and the sample dimensions in the order of cm) this equation can be written as:

$$\Psi_{out}(\vec{r}) = \frac{e^{-i\vec{q}\cdot\vec{r}}}{r} \sum_{i=1}^{N} b_i \frac{1}{\sqrt{\nu_0}} e^{-i\vec{q}\cdot\vec{r}_i}$$  \hspace{1cm} (3.7)

where $\vec{q} = \vec{k}_0 - \vec{k}$ is the scattering vector. The absolute value $|\vec{q}| = q = 2|\vec{k}_0|\sin(\theta) = 4\pi\sin(\theta)/\lambda$, where the scattering angle of the neutrons is defined as $2\theta$. Using equation 3.4 we obtain for $d\sigma/d\Omega$:

$$\frac{d\sigma}{d\Omega} = \langle \sum_{i,j} b_i b_j e^{-i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)} \rangle$$  \hspace{1cm} (3.8)

Here the brackets indicate an ensemble average. The above formulas are generally valid, e.g. for multi-component systems. For a system of chemically identical atoms we can proceed as follows.

Even if the atoms are chemically identical their scattering lengths may be different. First, generally a mixture of different isotopes is present in the sample, having different scattering lengths. Second, the scattering length also depends on the intermediate spin state $I - 1/2$ or $I + 1/2$ that the nucleus-neutron system can create during scattering, $I$ being the nuclear spin. Each state is characterized by its own scattering length. If there is no external field present and no magnetic sample in combination with a polarized neutron beam, the $I \pm 1/2$ spin states are distributed randomly. The isotopes are also distributed in a random way over the chemically identical particles. Since there is no correlation between the values of $b_i$ and $b_j$ when $i$ and $j$ refer to different sites, it is possible to write $\langle b_i b_j \rangle = \langle b_i \rangle \langle b_j \rangle = \langle b \rangle^2$. But if $i = j$, $\langle b_i b_j \rangle = \langle b^2 \rangle$, so that in general

$$\langle b_i b_j \rangle = \langle b \rangle^2 + \delta_{ij}(\langle b^2 \rangle - \langle b \rangle^2)$$  \hspace{1cm} (3.9)

The brackets $\langle \ldots \rangle$ indicate an average over isotopes and spin states. Equation 3.8 can be rewritten by using equation 3.9:

$$\frac{d\sigma}{d\Omega} = \langle b \rangle^2 \langle \sum_{i,j} e^{-i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)} \rangle + N(\langle b^2 \rangle - \langle b \rangle^2)$$  \hspace{1cm} (3.10)

The first term on the right hand side in the above equation depends on the mean scattering length, $\langle b \rangle$ and is called the coherent scattering since it represents the interference effects. The second term represents the incoherent scattering which depends on the mean square deviation of the individual
scattering lengths $b_i$. It does not contain a phase factor because the isotopes and spins are assumed to be randomly distributed.

Using the definition of the coherent scattering cross section $\sigma_c$

$$
\sigma_c = 4\pi \langle b \rangle^2
$$

(3.11)

the incoherent scattering cross section $\sigma_i$

$$
\sigma_i = 4\pi (\langle b^2 \rangle - \langle b \rangle^2)
$$

(3.12)

and the sum of the two which defines the total scattering cross section $\sigma_s$ per atom

$$
\sigma_s = 4\pi \langle b^2 \rangle
$$

(3.13)

we can write equation 3.10 as

$$
\frac{1}{N} \frac{d\sigma}{d\Omega} = \langle b \rangle^2 S(q) + (\langle b^2 \rangle - \langle b \rangle^2) = \frac{\sigma_c}{4\pi} S(q) + \frac{\sigma_i}{4\pi}
$$

(3.14)

where we introduced the structure factor $S(q)$, defined as:

$$
S(q) = \frac{1}{N} \sum_{i,j}^N e^{-iq(\vec{r}_i - \vec{r}_j)}
$$

(3.15)

Values for the scattering lengths and cross sections of the elements are tabulated in reference [58].

The distribution of atoms in real space can be described with the pair distribution function $g(\vec{r})$

$$
g(\vec{r}) = \frac{V}{N^2} \left( \sum_{i \neq j}^N \delta(\vec{r} - (\vec{r}_i - \vec{r}_j)) \right)
$$

(3.16)

It is defined such that $\rho_0 g(\vec{r})d\vec{r}$ is the probability of finding an atom between positions $\vec{r}$ and $\vec{r} + d\vec{r}$ with respect to another atom at the origin. $\rho_0$ is the average number density of the atoms. The definition implies that for small values of $|\vec{r}|$, $g(\vec{r})$ must be zero since atoms cannot completely interpenetrate. For large values of $|\vec{r}|$ the correlation between the atom pairs is lost and $g(\vec{r})$ will tend to 1. The relation between $S(q)$ and $g(\vec{r})$ can be derived using equation 3.15 and equation 3.16.

$$
S(q) - 1 = \frac{1}{N} \sum_{i \neq j}^N e^{-iq(\vec{r}_i - \vec{r}_j)} - N\delta(q)
$$
\[ \frac{1}{N} \int \int \left( \sum_{i \neq j} \delta(\vec{r}_1 - \vec{r}_i) \delta(\vec{r}_2 - \vec{r}_j) e^{-i\vec{q} \cdot (\vec{r}_1 - \vec{r}_2)} \right) d\vec{r}_1 d\vec{r}_2 \]
\[ - \frac{N}{V} \int e^{-i\vec{q} \cdot \vec{r}} d\vec{r} \]
\[ = \frac{1}{N} \int \left( \sum_{i \neq j} \delta(\vec{r} - (\vec{r}_i - \vec{r}_j)) e^{-i\vec{q} \cdot \vec{r}} \right) d\vec{r} - \frac{N}{V} \int e^{-i\vec{q} \cdot \vec{r}} d\vec{r} \]
\[ = \frac{1}{N} \int \frac{N^2}{V} g(\vec{r}) e^{-i\vec{q} \cdot \vec{r}} d\vec{r} - \frac{N}{V} \int e^{-i\vec{q} \cdot \vec{r}} d\vec{r} \]
\[ = \rho_0 \int (g(\vec{r}) - 1) e^{-i\vec{q} \cdot \vec{r}} \quad (3.17) \]

Where \( \vec{r} = \vec{r}_1 - \vec{r}_2 \), \( V = N/\rho_0 \) is the volume of the system and \( N \delta(\vec{q}) \) the forward scattering \((q = 0)\) which is subtracted because it is of no physical importance. \( \tilde{S}(\vec{q}) - 1 \) is the Fourier transform of \( g(\vec{r}) - 1 \) and the inverse transform is given by:

\[ g(\vec{r}) - 1 = \frac{1}{(2\pi)^3\rho_0} \int d\vec{q} (\tilde{S}(\vec{q}) - 1) e^{-i\vec{q} \cdot \vec{r}} \quad (3.18) \]

From equation 3.18 it follows that for large values of \(|\vec{q}|\), \( S(\vec{q}) \) tends to 1, since \( g(\vec{r}) \) is finite for all \( \vec{r} \). The long wavelength limit, \( q \to 0 \), of the structure factor needs some closer investigation. For this purpose fluctuations in the number of particles \( N \) have to be considered. The average number of particles is \( \langle N \rangle \), where the brackets \( \langle \ldots \rangle \) indicate a grand canonical average. In the definitions of \( S(\vec{q}) \) and \( g(\vec{r}) \) (equations 3.15 and 3.16) we can simply replace \( N \) by \( \langle N \rangle \). For the low wavelength limit of \( S(\vec{q}) \) we can write

\[ S(0) - 1 = \rho_0 \int (g(\vec{r}) - 1) d\vec{r} \]
\[ = \frac{1}{\langle N \rangle} \int \left( \sum_{i \neq j} \delta(\vec{r} - (\vec{r}_i - \vec{r}_j)) \right) d\vec{r} - \frac{\langle N \rangle}{V} \int d\vec{r} \]
\[ = \frac{\langle N(N - 1) \rangle}{\langle N \rangle} - \langle N \rangle = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} - 1 \quad (3.19) \]

By defining the particle number fluctuations as \( \Delta N = N - \langle N \rangle \) we obtain

\[ S(0) = \frac{\langle \Delta N^2 \rangle}{\langle N \rangle} \quad (3.20) \]

The mean square particle number fluctuation is connected to the isothermal compressibility \( \chi_T \) of the liquid. This relation is given by the compressibility
law:

\[ S(0) = \frac{\langle \Delta N^2 \rangle}{\langle N \rangle} = \rho_0 k_B T \chi_T \]  

(3.21)

where \( k_B \) is Boltzmann's constant.

The definitions of \( S(\vec{q}) \) and \( g(\vec{r}) \) (equations 3.15 and 3.16) are valid for all types of single-component systems whether they are crystalline or not. For liquids we can assume isotropy, then \( S(\vec{q}) \) and \( g(\vec{r}) \) depend only on the absolute values of the vectors \( \vec{r} \) and \( \vec{q} \). The integral can be performed directly over the angular part in polar coordinates giving the following results

\[ S(q) = 1 + 4\pi \rho_0 \int_0^\infty r^2 (g(r) - 1) \frac{\sin(qr)}{qr} \, dr \]  

(3.22)

and

\[ g(r) = 1 + \frac{1}{2\pi^2 \rho_0} \int_0^{\infty} q^2 (S(q) - 1) \frac{\sin(qr)}{qr} \, dq \]  

(3.23)

### 3.2.3 Scattering by a multi-component system

The theory can be extended to the more general case of multi-component systems. We introduce the partial pair distribution function, \( g_{\alpha,\beta}(r) \), which represents the average distribution of atoms of type \( \alpha \) around atoms of type \( \beta \) at the origin. For a system containing \( n \) atomic species there will be \( \frac{1}{2} n(n+1) \) partial pair distribution functions. According to the definition of Faber and Ziman [59] we can define the partial structure factor as:

\[ A_{\alpha,\beta}(q) = 1 + 4\pi \rho_0 \int_0^\infty r^2 (g_{\alpha,\beta}(r) - 1) \frac{\sin(qr)}{qr} \, dr \]  

(3.24)

and, in analogy with equation 3.23,

\[ g_{\alpha,\beta}(r) = 1 + \frac{1}{2\pi^2 \rho_0} \int_0^{\infty} q^2 (A_{\alpha,\beta}(q) - 1) \frac{\sin(qr)}{qr} \, dq \]  

(3.25)

We can use equation 3.8 where, in addition to summing over all the different isotopes and spin states we also sum over atom species with their specific scattering lengths. It is convenient to start with the definition of \( d\sigma /d\Omega \) for a single-component system (equation 3.14), now formulated as

\[ \frac{1}{N} \frac{d\sigma}{d\Omega} = \langle b \rangle^2 (S(q) - 1) + \langle b^2 \rangle \]  

(3.26)

where the first term on the right hand side represents the distinct scattering part and the second term the self scattering part. Equation 3.26 can
then be formulated for each pair of atom types \((\alpha, \beta)\) as a sum weighted for concentration and scattering so that
\[
\frac{1}{N} \frac{d\sigma}{d\Omega} = \sum_{\alpha,\beta} c_\alpha \langle b_\alpha \rangle c_\beta \langle b_\beta \rangle (A_{\alpha,\beta}(q) - 1) + \sum_{\alpha} c_\alpha \langle b_\alpha^2 \rangle \\
= F(q) + \langle b^2 \rangle
\] (3.27)

where \(c_\alpha\) is the atomic fraction and \(\langle b_\alpha \rangle\) the average coherent scattering length of element \(\alpha\). When there is no subscript to indicate the element type, the brackets \(\langle \ldots \rangle\) indicate averaging over the different elements present in the sample as well as over the isotopes and spins of the individual elements. The total structure factor, \(F(q)\), contains the structural information. Alternatively, often the Faber-Ziman total structure factor is used, defined as
\[
S^{FZ}(q) - 1 = \frac{F(q)}{\langle b \rangle^2}
\] (3.28)

Then, in analogy to the structure factor for a single-component system, we may write
\[
\frac{1}{N} \frac{d\sigma}{d\Omega} = \langle b \rangle^2 (S^{FZ}(q) - 1) + \langle b^2 \rangle = \frac{\sigma_c}{4\pi} S^{FZ}(q) + \frac{\sigma_i}{4\pi}
\] (3.29)

Again by Fourier transformation it can be shown that the total pair correlation function can be written as
\[
g^{FZ}(r) - 1 = \frac{1}{\langle b \rangle^2} \sum_{\alpha,\beta} c_\alpha \langle b_\alpha \rangle c_\beta \langle b_\beta \rangle (g_{\alpha,\beta}(r) - 1)
\] (3.30)

For a binary alloy with chemical constituents 1 and 2, \(S^{FZ}(q)\) may be written as:
\[
S^{FZ}(q) = \frac{1}{\langle b \rangle^2} (c_1^2 \langle b_1 \rangle^2 A_{11}(q) + c_2^2 \langle b_2 \rangle^2 A_{22}(q) + 2c_1c_2 \langle b_1 \rangle \langle b_2 \rangle A_{12}(q))
\] (3.31)

where we have used the fact that \(A_{12} = A_{21}\). The total pair distribution function likewise becomes:
\[
g^{FZ}(r) = \frac{1}{\langle b \rangle^2} (c_1^2 \langle b_1 \rangle^2 g_{11}(r) + c_2^2 \langle b_2 \rangle^2 g_{22}(r) + 2c_1c_2 \langle b_1 \rangle \langle b_2 \rangle g_{12}(r))
\] (3.32)

There are more possibilities for defining partial structure factors and their corresponding partial pair correlation functions. One other option that is
particularly useful for systems with strong ordering, like for example molten salts, is defined by Bhatia and Thornton [8]. Unlike the Faber-Ziman partial structure factors these are not associated with atomic species, but rather with density and concentration correlations, as will be explained below in more detail.

The total number of atoms in a binary alloy of species 1 and 2 is \( N = N_1 + N_2 \). Similar to the case of the single-component system, the particle number fluctuation of element \( \alpha \) is defined as \( \Delta N_\alpha = N_\alpha - \langle N_\alpha \rangle \), where the brackets indicate a grand canonical average. In the Faber-Ziman approach the fluctuations are described with the three quantities \( \langle (\Delta N_1)^2 \rangle \), \( \langle (\Delta N_2)^2 \rangle \) and \( \langle \Delta N_1 \Delta N_2 \rangle \), which are related to \( g_{\alpha,\beta}(r) \) according to

\[
\langle \Delta N_\alpha \Delta N_\beta \rangle = \langle N_\alpha \rangle \langle N_\beta \rangle \frac{1}{V} \int (g_{\alpha,\beta}(r) - 1) d\vec{r} + \delta_{\alpha,\beta} \langle N_\alpha \rangle
\]

which is a generalization of equation 3.19.

Bhatia and Thornton discuss the properties of a binary system in terms of fluctuations in the total number \( N \) and the composition \( C \):

\[
\Delta N = \Delta N_1 + \Delta N_2
\]

and,

\[
\Delta C = \frac{1}{\langle N \rangle} (c_2 \Delta N_1 - c_1 \Delta N_2)
\]

In analogy with equation 3.19 we can find expressions for the mean square number fluctuation \( \langle (\Delta N)^2 \rangle \), the mean square concentration fluctuation \( \langle (\Delta C)^2 \rangle \) and the correlation between these fluctuations \( \langle \Delta N \Delta C \rangle \). They are related to \( g_{\alpha,\beta}(r) \) by the expressions

\[
\frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} = 1 + \rho_0 \int d\vec{r} [c_1^2 (g_{11}(r) - 1) + c_2^2 (g_{22}(r) - 1)
+ 2c_1c_2 (g_{12}(r) - 1)]
\]

\[
\langle N \rangle \langle (\Delta C)^2 \rangle = c_1c_2 + c_1^2c_2^2 \rho_0 \int d\vec{r} [g_{11}(r) + g_{22}(r) - 2g_{12}(r)]
\]

\[
\langle \Delta N \Delta C \rangle = c_1c_2 \rho_0 \int d\vec{r} [c_1g_{11}(r) - c_2g_{22}(r) + (c_2 - c_1)g_{12}(r)]
\]

(3.36)

The Bhatia-Thornton partial structure factors \( S_{NN}(q) \), \( S_{CC}(q) \) and \( S_{NC}(q) \) are

\[
S_{NN}(q) = 1 + \rho_0 \int (g_{NN}(r) - 1)e^{-i\vec{q}\cdot\vec{r}} d\vec{r}
\]
\begin{align*}
S_{\text{CC}}(q) &= c_1 c_2 + \rho_0 \int g_{\text{CC}}(r) e^{-i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r} \\
S_{\text{NC}}(q) &= \rho_0 \int g_{\text{NC}}(r) e^{-i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r}
\end{align*}
(3.37)

where
\begin{align*}
g_{\text{NN}}(r) &= c_1^2 g_{11}(r) + c_2^2 g_{22}(r) + 2c_1 c_2 g_{12}(r) \\
g_{\text{CC}}(r) &= c_1^2 c_2^2 [g_{11}(r) + g_{22}(r) - 2g_{12}(r)] \\
g_{\text{NC}}(r) &= c_1 c_2 [c_1 g_{11}(r) - c_2 g_{22}(r) + (c_2 - c_1) g_{12}(r)]
\end{align*}
(3.38)

Equations 3.36 can be regarded as the long wavelength limit of $S_{\text{NN}}(q)$, $S_{\text{CC}}(q)$ and $S_{\text{NC}}(q)$. This provides a relation to thermodynamic properties:
\begin{align*}
S_{\text{NN}}(0) &= \frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} = \rho_0 k_B T \chi_T + \langle N \rangle k_B T \delta \left( \frac{d^2 G}{dc^2} \right)^{-1}_{p,T,N} \\
S_{\text{CC}}(0) &= \langle N \rangle \langle (\Delta C)^2 \rangle = \langle N \rangle k_B T \left( \frac{d^2 G}{dc^2} \right)^{-1}_{p,T,N} \\
S_{\text{NC}}(0) &= \langle \Delta N \Delta C \rangle = -\langle N \rangle k_B T \delta \left( \frac{d^2 G}{dc^2} \right)_{p,T,N}
\end{align*}
(3.39)

where $k_B$ is Boltzmann's constant, $T$ is the temperature, $G$ is the Gibbs free energy, $\chi_T$ is the isothermal compressibility and $\delta$ is the dilatation factor:
\begin{align*}
\chi_T &= -\frac{1}{V} \left( \frac{dV}{dp} \right)_{T,N} \\
\delta &= \frac{1}{V} \left( \frac{dV}{dc} \right)_{p,T,N}
\end{align*}

$S_{\text{CC}}(0)$ is directly linked to the stability of the alloy via the Darken stability function $d^2 G/dc^2$ [12], which is a measure for the stability of the mixture with respect to fluctuations in the composition. The concentration fluctuations are smaller in a stable compound than in a less stable one. The derivation of equations 3.39 is given in reference [8]. They form an extension to the well known compressibility law for monatomic systems, given by equation 3.21.

The relation between the Bhatia-Thornton and the Faber-Ziman structure factors is given by:
\begin{align*}
S_{\text{NN}}(q) &= c_1^2 A_{11}(q) + c_2^2 A_{22}(q) + 2c_1 c_2 A_{12}(q)
\end{align*}
\[ S_{CC}(q) = c_1 c_2 [1 + c_1 c_2 (A_{11}(q) + A_{22}(q) - 2A_{12}(q))] \]
\[ S_{NC}(q) = c_1 c_2 [c_1 A_{11}(q) - c_2 A_{22}(q) + (c_2 - c_1) A_{12}(q)] \]

(3.40)

When there is a preference for hetero or homocoordination in the alloy this is visible in \( S_{CC}(q) \). Heterocoordination can give a prepeak (i.e. a peak in front of the main peak) in \( S_{CC}(q) \) because the Chemical Short Range Order (CSRO) causes correlations between atoms over larger distances than just the nearest neighbour distance. This is called ordering in the "order-disorder" theory [6], as is described in section 1.4. A preference for homocoordination can cause a rise in \( S_{CC}(q) \) for \( q \to 0 \), which implies a tendency towards phase-separation. In non-substitutional alloys effects in \( S_{CC}(q) \) can be accompanied by similar effects in \( S_{NN}(q) \) and \( S_{NC}(q) \). For \( q = 0 \) this can be seen in equations 3.39.

The total structure factor in the Bhatia-Thornton description reads:

\[
S_{BT}^{BT}(q) = \frac{1}{\langle b^2 \rangle} \frac{d\sigma}{d\Omega} = \frac{1}{\langle b^2 \rangle} \left( \langle b^2 \rangle^2 S_{NN}(q) + (\langle b_1 \rangle - \langle b_2 \rangle)^2 S_{CC}(q) + 2 \langle b \rangle (\langle b_1 \rangle - \langle b_2 \rangle) S_{NC}(q) \right) \]

(3.41)

When \( \langle b \rangle = c_1 \langle b_1 \rangle + c_2 \langle b_2 \rangle = 0 \), which is possible when \( \langle b_1 \rangle \) or \( \langle b_2 \rangle \) is negative, only \( S_{CC}(q) \) will contribute to the measured intensity. The alloy is then called a "zero-alloy". When the atoms in a zero-alloy are randomly distributed there is no structure in \( S_{CC}(q) \) and the total structure factor will be flat. This is the case in \( Ti_{0.69}Zr_{0.32} \) which, for this reason, is very convenient to use as a container material. When \( \langle b_1 \rangle - \langle b_2 \rangle = 0 \) only \( S_{NN}(q) \) will contribute to the total structure factor.

### 3.3 Experimental aspects

In this section some general experimental aspects of the neutron diffraction measurements on liquid alloys will be described. The more specific experimental details, like the preparation of the samples and experimental problems of individual measurements will be discussed in the appropriate chapters. Firstly, in the following section the sample container design will be discussed. Secondly, a description of the diffractometers SLAD and D4 will be given which were used for the measurements described in this thesis. To extract the structure factors from the measured intensities several corrections have to be performed, and the experimental data have to be normalized.
The procedure of obtaining the structure factors from the measurements will finally be described in section 3.3.3.

3.3.1 Sample container

The size of the sample should be adjusted to the width and the height of the neutron beam of the specific instrument that will be used (see section 3.3.2). Furthermore, the sample should not be too thick in order to prevent large corrections for multiple scattering. Generally, it is safe to aim for a single scattering fraction of about 10%. The fraction of those neutrons that scatter a second time is usually less than 10%, due to absorption and attenuation. The fraction of single scattering, $p$, by a cylindrical sample of radius $r$ with the axis perpendicular to the neutron beam can be approximated by [57]

$$p \approx \frac{\pi}{2} \Sigma_s r \left( 1 - \frac{16}{3 \pi} \Sigma_i r \right)$$

(3.42)

where $\Sigma_s = \rho_0 \sigma_s$ is the linear scattering coefficient of the sample. The total linear attenuation coefficient includes the absorption: $\Sigma_t = \Sigma_s + \Sigma_a$. The multiple scattering fraction can be calculated using the tabulated data for a cylindrical sample as calculated by Sears [57].

For the experiments described in this thesis a cylindrical container with a 0.5 mm thick wall, 8 mm inner diameter and 50 mm length was suitable. The containers were made of the alloy $\text{Ti}_{0.68} \text{Zr}_{0.32}$, which in this composition has zero coherent scattering length ($b_{Ti} = -3.3$ and $b_{Zr} = 7.1$ fm) and is therefore often called a zero alloy. The advantage is that it produces completely incoherent background scattering, which is flat without Bragg peaks. Furthermore, Ti-Zr is corrosion resistant against liquid alkali metals. The measuring temperatures, however, should be kept below $\sim 750$ °C, because the Ti-Zr alloy starts to soften and recrystallization can occur leading to Bragg peaks.

The containers were filled in a glovebox under argon atmosphere with $\text{O}_2$ and $\text{H}_2\text{O}$ levels less than 1 ppm. The sample preparation will be described in the appropriate chapters. Special care has to be taken to seal the containers leak tight, in particular at high temperatures. We have used two ways to accomplish this using different container designs. They are described below as the type I and the type II container.

The type I container is sealed in the following way. A tightly fitting lid was positioned on the filled sample container and the whole was enclosed in a
glass tube with a tap. The tube was flushed with He three times, and finally filled with 300 mbar He for reasons to be explained. To seal the container we used laser-beam welding, which was done at TNO in Apeldoorn (The Netherlands). The laser-beam, which is focused on the container, is transmitted by the wall of the glass tube and welds the lid onto the container. The He-pressure used was a compromise between vacuum and atmospheric pressure. Vacuum would lead to bad heat conduction and, consequently, welding failure due to alkali metal fumes. Welding at atmospheric pressure leads to a too high final pressure. To test if the containers are leak proof, and to mix the alloy properly, the containers were heated up to 700 °C inside the glovebox for half an hour. If the container isn't closed properly, fumes will appear from the leak. This actually did happen several times, probably due to pollution of the surface to be welded or to evaporation of the alkali metal during welding.

The success rate of this sealing method was poor. Therefore we designed the type II container which uses a knife-edge and a screw lid to close the container. A similar design was used in reference [60]. A schematical drawing of the container is given in figure 3.1. It should be noted that the dimensions of the container are slightly different from those of the type I container, the inner diameter is 7 mm and the wall thickness 0.6 mm. Between the knife-edge and the lid a slipping disk is placed which prevents the knife-edge from rotating. The rotating parts are coated with the lubricant MoS$_2$ (molykote). Tests showed that the containers were leak tight when a torque of 20 Nm had been applied to close the lid. The containers could even be re-used and closed a second time with the same knife edge using a slightly higher torque (30-40 Nm). Applying a torque of over 80 Nm may cause the seal to open again, because the knife edge may start slipping. Using a new knife-edge (possibly with an other diameter) the containers could be opened and closed more often. This of course is an additional advantage. Because the knife-edge is made of the same material as the container there were no problems due to thermal expansion. All of the type II containers were tested and proved to be leak proof at high temperature.

3.3.2 Diffractometers

Most of the neutron diffraction experiments described in this thesis were performed on SLAD (Studsvik Liquids and Amorphous materials Diffractometer) at the NFL (Neutronforskningslaboratoriet) in Studsvik, Sweden. The measurements on KTI and K$^{205}$TI were performed on D4 at the ILL
Figure 3.1: Schematic drawing of the type II sample container. The knife-edge and slipping disk are placed between the container and the lid. By screwing the lid with a specified torque (see text) the container is sealed. The inner diameter is 7 mm, the outer diameter 8.2 mm and the height of the thin walled part of the container is 50 mm.
Figure 3.2: Layout of SLAD (NFL, Studsvik, Sweden). 1. filter; 2. monochromator; 3. collimator; 4. evacuated sample chamber; 5. oscillating radial collimator; 6. detector shielding; 7. position sensitive detectors

(Institut Laue Langevin) in Grenoble, France. The latter diffractometer has a higher flux at the sample and the statistics of the data is about 10 times better than those of SLAD. It was very important to obtain accurate results for the isotope substitution experiment, especially in this case where the difference in the total scattered intensity is only 12%. For non-isotopic substitution experiments the SLAD diffractometer is very suitable.

SLAD has a medium resolution ($\Delta q/q \sim 0.01$) and a relatively high count rate. This angular resolution is more than sufficient for measuring the broad features in the structure factor of a liquid material. In figure 3.2 a schematic drawing of the diffractometer is given. The various parts are named in the legend. The monochromator we used was Cu (220) to select a wavelength of 0.11 nm. The collimator consists of radially oriented absorbing plates centered on the sample position, thus minimizing the background due to scattering of other objects than the sample. This collimator is oscillating to smear out the 'shadow' of the plates, which otherwise would be visible as a ripple in the data. There are 4 detector banks, each containing 3 Reuter-Stokes $^3$He linear position sensitive detectors with an active length of 60 cm. To cover the gaps between the 4 detector banks the detector box rotates about 10°. The angular range is $2^\circ < 2\theta < 125^\circ$, corresponding to an available $q$ range
of 4 to 93.6 nm\(^{-1}\). Usually 6 runs were collected (12 scans at alternating detector positions) of \(\sim 1.5\) hours to be able to check the stability of the system.

D4 is also specially adapted for structural investigations of liquids and amorphous materials. It provides a very wide range of momentum transfer: \(2 < q < 164\) nm\(^{-1}\) for \(\lambda = 0.07\) nm, with a resolution \(\Delta q/q \sim 0.02\). The wide \(q\) range is an advantage for obtaining an accurate Fourier transform of \(S(q)\). In figure 3.3 a schematical drawing of the instrument is given. A focussing Cu (200) monochromator is used in addition to a \(\lambda/2\) Ir filter to select a wavelength of 0.07 nm. The collimation is done by slits upstream of the sample and a series of absorbing rings between the sample and detectors. The efficiency of the incident-beam monitor and the detector-cell efficiencies within a given detector are stable to about \(1:10^4\) over several days, which is on average the duration of an experiment. Two independent \(2\theta\) arms move on air pads and cover the low and high angle ranges. Each arm has a 64-cell \(^3\)He multidetector with a size of 70 mm high and 160 mm wide. We used a setup with the low-angle detector (\(1.4^\circ < 2\theta_1 < 51^\circ\)) at a distance of 1.5 m from the sample position and the high-angle detector (\(46^\circ < 2\theta_2 < 132^\circ\)) at 0.75 m. For every sample 4 complete scans of \(\sim 3\) hours each were performed, where the low-angle detector covered the angular range with \(1.5^\circ\) steps and
the high-angle detector with steps of 2.6°.

SLAD and D4 are both diffractometers at a continuous source (reactor source). Diffraction can also be performed at a spallation source where the neutrons are created in pulses. These instruments use the so-called time-of-flight (TOF) method. The procedure of obtaining a corrected structure factor from a measurement performed on a TOF diffractometer is different in some aspects from what will be discussed in section 3.3.3.

3.3.3 Data correction procedures

Several steps have to be taken in order to obtain $S(q)$ from the measured intensity $I_s$. Corrections for attenuation, background, multiple scattering and inelasticity (Placzek) have to be performed and the data have to be normalized to obtain an absolute value for the scattered intensity. The data corrections and normalization were performed using the program CORRECT which is available at the NFL (Studsvik Neutron Scattering Center) [61]. A short description of the corrections and the procedure to obtain a normalized $S(q)$ will be given.

In order to obtain a corrected structure factor, measurements of the scattering should be taken from:

1. Sample (including the sample container) ($I_{sc}^E$)
2. Empty container ($I_c^E$)
3. Empty furnace ($I_f^E$)
4. Vanadium rod of same external dimension as the sample ($I_v^E$)
5. Background; without furnace or container ($I_b^E$)
6. Background with cadmium rod of same external dimensions as the sample ($I_{cd}^E$)

The superscript $E$ denotes that the intensities are experimentally obtained. Ideally all the runs, except for the background, should be taken at the same temperature as the sample. It is best to divide the runs into several shorter runs. In this way the stability of the combined system containing the sample, the sample environment and the instrument (detectors and monitor), can be checked.
attenuation corrections

The scattering contains contributions from the sample \((I_s)\), the container \((I_c)\), the furnace elements \((I_f)\) and the background \((I_b)\). The latter can be divided in two parts, \(I_b = I'_b + I''_b\), where \(I''_b\) is that part of the background that passes through the sample and the container. Usually, \(I'_{b}\) is relatively small and flat as a function of angle. It can be obtained by measuring the scattering with an absorber, usually cadmium, in a rod of the same outer dimensions as the sample container. \(I''_{b}\) is in general close to zero except at low angles. The different contributions to the scattering intensities are

\[
\begin{align*}
I_{sc}^E &= A_{s,scf}I_s + A_{c,scf}I_c + A_{f,scf}I_f + I'_b + A_{scf}I''_b \\
I_{c}^E &= A_{c,cf}I_c + A_{f,cf}I_f + I'_b + A_{cf}I''_b \\
I_{f}^E &= A_{f,f}I_f + I'_b + A_{f}I''_b \\
I_{b}^E &= I'_b + I''_b \\
I_{Cd}^E &= I'_b
\end{align*}
\]

(3.43)

where \(A_{i,j}\) are the attenuation coefficients for scattering in region \(i\) and attenuation in region(s) \(j\). The coefficients in equation 3.43 are determined from calculations involving multiple integrals over the specific geometries of the sample, container and furnace, using a scheme based on the method of Paalman and Pings [62]. Strictly speaking \(I'_b\) will be attenuated by the furnace. This is usually a small effect on an already small intensity, which can only be determined by doing an additional measurement of the cadmium rod inside the furnace. In many cases it is not worth the trouble.

normalisation

After correction for attenuation we have

\[
I_s(\theta) = \left[\frac{d\sigma_s(\theta)}{d\Omega} + N_s\langle b_s^2 \rangle \Delta_s\right]F(\theta)
\]

(3.44)

where \(N_s\langle b_s^2 \rangle \Delta_s\) is the multiple scattering correction that will be discussed shortly, and \(N_s\) is the total number of atoms in the sample. \(F(\theta)\) is a factor that is difficult to calculate and should therefore be normalized for. It depends on several aspects of the specific diffractometer, like the incident flux and the absolute detector efficiency. To normalize for \(F(\theta)\) a sample with a known structure factor is needed. For convenience, usually a largely incoherent scatterer like vanadium is used. The scattering from the vanadium rod
is

\[ I_v(\theta) = \left[ \frac{d\sigma_v(\theta)}{d\Omega} + N_v\langle b_v^2 \rangle \Delta_v \right] F(\theta) \]  \hspace{1cm} (3.45)

where \( d\sigma_v(\theta)/d\Omega \) is the differential cross section, but since vanadium almost totally scatters incoherently we may write

\[ \frac{d\sigma_v(\theta)}{d\Omega} = N_v\langle b_v^2 \rangle (1 - P_v(\theta)) \]  \hspace{1cm} (3.46)

where \( P_v(\theta) \) is the Placzek correction for vanadium, as will be discussed later in more detail. The scattered vanadium intensity \( d\sigma_v(\theta)/d\Omega \) is smoothed to minimize the statistical errors and to remove the small Bragg peaks that are present due to a remaining small amount of coherent scattering. Now \( F(\theta) \) can be calculated as follows

\[ F(\theta) = \frac{I_v(\theta)}{N_v\langle b_v^2 \rangle (1 - P_v(\theta)) + \Delta_v} \]  \hspace{1cm} (3.47)

This enables normalization of the scattered intensity \( I_s(\theta) \)

**multiple scattering corrections**

The multiple scattering fraction, \( \Delta_i \), can be numerically calculated for a specific sample \( i \) with a known scattering geometry. The multiple scattering fractions of the, in this case, cylindrical samples were interpolated from tabulated data calculated by Sears [57]. The multiple scattering correction is assumed to be independent of \( q \) and is given by \( N_i\langle b_i^2 \rangle \Delta_i \).

**inelasticity corrections**

In a neutron diffraction experiment \( \int_0^\infty \epsilon(k)d^2\sigma/((d\Omega dE)dE \) is measured, where \( \epsilon(k) \) is the detector energy. The definition of \( S(q) \) requires that the integral is performed at constant \( q \), whereas experimentally we measure at a constant angle 2\( \theta \). The inelasticity or Placzek correction [63] corrects for the difference between the two. It corrects for inelastic scattering due to the thermal motion of the particles, but not for inelastic scattering due to collective modes. The Placzek correction depends for instance on the mass \( M \) of the components and is larger for the lighter elements. We used the method of Yarnell et al [64] which takes the energy dependence of the detector efficiency explicitly into account. The differential cross sections we measure are related to the dynamic structure factors by

\[ \frac{1}{N_s} \frac{d\sigma_s(\theta)}{d\Omega} = \frac{\sigma_c}{\int_{-\infty}^{\omega_{max}} \frac{\epsilon(k)}{\epsilon(k_0)} \frac{k}{k_0} S(q, \omega) d\omega} \]
with the scattering angle $2\theta$ constant. $\hbar\omega_{\text{max}}$ equals the incident neutron energy $E_0$ and $k_0 = 2\pi/\lambda$. $S(q, \omega)$ is the dynamic structure factor and is related to the static structure factor by $S(q) = \int S(q, \omega) d\omega$. $S_{\text{self}}(q, \omega)$ is the 'self' part of $S(q, \omega)$ which describes the time correlation of one single particle [55]. In the analysis of Yarnell et al $S(q, \omega)$, $S_{\text{self}}(q, \omega)$, $k/k_0$ and $\epsilon(k)$ are all expanded as functions of $\omega$ and they take into account the first few moments of $S(q, \omega)$ and $S_{\text{self}}(q, \omega)$ which involve recoil effects to second order. The expression used for correction of the inelastic scattering can be written as

$$ P_i(q) = -\frac{m}{M_i} \frac{k_B T}{2E_0} - \left[ c_1 + c_2 \frac{k_B T}{E_0} - \frac{m}{2M_i} \left( \frac{q}{k_0} \right)^2 + c_2 \left( \frac{q}{k_0} \right)^4 \right] $$

(3.49)

where $m$ is the mass of the neutron, $M_i$ the mass of atom type $i$ and $k_B$ is Boltzmann's constant. The energy dependence of the detectors $\epsilon(k)$ can, in this case, be approximated by

$$ \epsilon(k) = 1 - e^{-A \frac{k_0}{x}} $$

(3.50)

with the constant $A$ depending on the specific detector that is used. The constants $c_1$, $c_2$ and $c_3$ are related to $\epsilon(k)$ and its first and second derivative with respect to $k$, $\epsilon_1(k)$ and $\epsilon_2(k)$.

$$ c_1 = 1 + \frac{k_0 \epsilon_1(k_0)}{2 \epsilon(k_0)} $$

$$ c_2 = \frac{3}{8} + \frac{5}{4} \frac{k_0 \epsilon_1(k_0)}{2 \epsilon(k_0)} + \frac{1}{4} \frac{k_0^2 \epsilon_2(k_0)}{2 \epsilon(k_0)} $$

$$ c_3 = -\left( \frac{3}{2} \frac{k_0 \epsilon_1(k_0)}{2 \epsilon(k_0)} + \frac{1}{2} \frac{k_0^2 \epsilon_2(k_0)}{2 \epsilon(k_0)} \right) $$

(3.51)

The differential cross section including the effects of recoil can now be written as

$$ \frac{1}{N_s} \frac{d\sigma_s(\theta)}{d\Omega} = \sigma_c \frac{S(q)}{4\pi} < P >_c + \sigma_i \frac{1}{4\pi} (1 - < P >_i) $$

(3.52)

and we find using equation 3.44

$$ S(q) = \left[ \frac{1}{F(\theta) N_s} I_s(q) - \langle b^2_s \rangle \Delta_s - \frac{\sigma_i}{4\pi} (1 - < P >_i) - \frac{\sigma_c}{4\pi} < P >_c \right] / \sigma_c $$

(3.53)
where, for a binary alloy with constituents 1 and 2, we have

\[
\langle P \rangle_i = \frac{(c_1 \sigma_{i,1} P_1(q) + c_2 \sigma_{i,2} P_2(q))}{(c_1 \sigma_{i,1} + c_2 \sigma_{i,2})}
\]

\[
\langle P \rangle_c = \frac{(c_1 \sigma_{c,1} P_1(q) + c_2 \sigma_{c,2} P_2(q))}{(c_1 \sigma_{c,1} + c_2 \sigma_{c,2})}
\]

(3.54)

### 3.4 Reverse Monte Carlo modelling

In general for a system with \( n \) atomic species there will be \( \frac{1}{2} n(n + 1) \) partial structure factors. It is desirable to find the individual partial structure factors \( S_{\alpha,\beta}(q) \) and hence the partial pair distribution functions \( g_{\alpha,\beta}(r) \). One route to obtaining this information is provided by the technique of isotope substitution, since the coherent scattering length \( b \) is isotope dependent. In the case of a binary alloy it is clear that at least three neutron diffraction experiments have to be performed with different isotopes or isotopic enrichment. Isotope substitution, however, is not applicable to all systems since only a limited number of suitable isotopes exists (more or less randomly distributed over the periodic system of the elements). The difference in the total scattering of the samples with different isotopic enrichment is usually small. Therefore, the measurements need to be accurate and good statistics is required to separate the partial structure factors \( A_{\alpha,\beta}(q) \) or partial pair distribution functions \( g_{\alpha,\beta}(r) \). An additional disadvantage is that some isotopes are extremely expensive, especially in the quantities that are needed for a neutron diffraction experiment (usually a few cm\(^3\)).

Other techniques such as anomalous X-ray scattering (AXS) and extended X-ray absorption fine structure (EXAFS) are also used to determine the partial structure of a disordered material. Advantages of such techniques are that only one small sample is needed which can have a natural abundance of isotopes. The development of these techniques is progressing fast which is due to the development of synchrotron sources with higher flux. For AXS, however, systematic errors can be significant due to beam stability problems. In the case of EXAFS a disadvantage is that the information obtained is limited to the short \( r \) range of the interaction. It would therefore not be possible to study intermediate range order. EXAFS, however, is a very powerful tool to study the local coordinations of components with a low concentration, which are difficult to study with diffraction techniques.

Reverse Monte Carlo (RMC) modelling [65] is a way to extract information on e.g. the partial structure factors from the measured total structure factor.
In this section the method of RMC will be explained and the advantages and disadvantages will be discussed.

### 3.4.1 The basic RMC method

Reverse Monte Carlo modelling is a method for producing three-dimensional models of usually disordered materials that agree quantitatively with the available diffraction data [65]. There is no interatomic potential required, the structural model is actually fitted to the data. Data from different sources (neutron, X-ray and EXAFS) may also be combined.

RMC is a variation of the standard Metropolis Monte Carlo procedure. The basic method of RMC is as follows. It is assumed that the measured structure factor \( A^E(q) \) contains only statistical errors that have a normal distribution. In order to model the structure of a system using \( A^E(q) \) a statistical ensemble of atoms is created whose structure factor is \( A^C(q) \). By moving the atoms one at a time in a random way the following function can be minimized

\[
\chi^2 = \sum_{i=1}^{m} \frac{(A^C(q_i) - A^E(q_i))^2}{\sigma(q_i)^2}
\]

(3.55)

The RMC program works according to the following steps:

1. Start with an initial configuration of atoms in a box with periodic boundary conditions. The positions of the atoms may be chosen randomly or it may be a crystal structure or any other model.

2. The radial distribution function \( g_0(r) \) is calculated for this configuration. The size of the configuration \( L \) should in principle be sufficiently large that there are no correlations across the cell, so that \( g(r > L/2) = 1 \). The radial distribution function is calculated up to \( r < L/2 \).

3. The pair distribution function is Fourier transformed to the total structure factor \( A^C_0(q) \).

4. The difference between the measured total structure factor and the calculated one is determined in the form of \( \chi_0^2 \) as defined in equation 3.55.

5. One atom is now moved at random. Again the radial distribution function is calculated and the total structure factor \( A^C_n(q) \). From the difference between \( A^C_n(q) \) and \( A^E(q) \), \( \chi_n^2 \) is obtained.
6. If $\chi_n^2 < \chi_0^2$ the move is accepted and the new configuration becomes the old configuration. If $\chi_n^2 > \chi_0^2$ then the move is accepted with probability $\exp(-\chi_n^2 - \chi_0^2)/2$. It will be rejected otherwise.

7. The steps repeat from point 5.

As the process is iterated $\chi^2$ will initially decrease until it reaches an equilibrium value about which it will fluctuate. The resulting configuration is a three-dimensional model that should be consistent with the experimental total structure factor within the experimental errors.

The standard deviation $\sigma$ of the experimental error depends on a combination of the statistical errors and possible systematic errors. In the RMC programme $\sigma$ is assumed to be constant for all data points. $\chi$ is inversely proportional to $\sigma$ and can therefore not be regarded as an absolute quantity, it is a relative number for comparing different fits to the same experimental data. If the fit is not good it could be an indication for systematic errors that are present in the data.

An important input parameter is the density, which has to be guessed when it is not experimentally available. Furthermore distances of closest approach have to be assumed in order to avoid unphysical configurations. The combination of these constraints greatly reduces the number of possible configurations that fit the data. Often realistic values for the closest approach between atoms can be obtained from the direct Fourier transform of the total structure factor, or from crystallographic considerations.

Other constraints may be applied, like for example a restriction on the coordination of the atoms. A coordination number $n_{\alpha\beta}$ is defined as being the number of atoms of type $\beta$ between two fixed distances from one of type $\alpha$. It can be used if there is a-priori knowledge of this type, or just to test if certain expected configurations fit the data.

3.4.2 Advantages and disadvantages

There are a number of advantages in using RMC of which we like to mention the following important ones:

1. RMC makes use of all the information available in diffraction data in a quantitative way. Because RMC models a three-dimensional structure with only simple constraints as excluded volume (distance of closest approach between atoms) and the density, the configuration must correspond to a physical structure that is feasible from a geometric point of view, and that is in agreement with the experimental data.
2. RMC provides a method to check the data for systematic errors. When RMC cannot fit the data, there is something wrong with the experimental data or with the choice of sample parameters such as the density.

3. By means of RMC partial structure factors can be obtained from a single measurement. The interpretation of the partials, however, requires caution, as they pertain effectively to a system with added entropy.

4. What is sometimes mentioned as an advantage is that the RMC solution has the characteristic of maximum configurational entropy, which is a result of the random moves the program makes. Any order that is found in the configuration must be due to information present in the data and the applied physical constraints.

Some remarks have to be made about points 3 and 4, regarding the uniqueness of the RMC solutions. This subject is also addressed in reference [66]. RMC does not give a unique solution, simply because the structure of the system, in terms of the correlation functions, is underdetermined by one total structure factor. This applies to a one-component liquid and even more so to a binary mixture. The volume in phase space delimited by RMC is therefore larger than that corresponding to the real system and consequently the statistical averages do not pertain to the physical system under investigation but to a system with added entropy. In general geometrical features may be less sharply defined in the RMC configuration than they are in the real system. It also follows that a configuration which is in agreement with the structure factor is not necessarily unique. The decomposition of the total structure factor into partials by RMC is also not necessarily correct, nor unique. Still the solutions of RMC can be considered as the most unbiased ones, given the restricted information available from the structure factor.

In principle a statistical ensemble of configurations should be collected to determine average features, like pair distribution functions or bond-angle distributions. In practice what we find is that all of these configurations are showing the same average features independent of the initial configuration. The user of RMC may be tempted to believe that, since the average features of the configurations are reproducible, they are representing a more or less unique solution. However, this is a result of the fact that RMC consequently finds the most random solution, i.e. a configuration with the highest entropy. There is only a negligible chance that RMC will incidentally find a solution with a higher degree of order even when it fits the data better. We actually found that the accuracy of the data, within certain limits, does not increase this chance of finding this higher ordered but better fitting configuration (see section 4.4.1). In short, RMC does certainly not probe all
minima in parameter space. A-priori knowledge or assumptions, therefore, have to be used to force RMC to find higher ordered configurations that fit the data.

For a binary or multi-component alloy the following effects might result from this characteristic of maximum configurational entropy. Peaks in the total structure factor may consist mostly of the partials with the highest weight factors, only because they have the highest weight factor. Another result can be that the peak positions in the structure factor are often represented by all partials with the same peak position, which is only very rarely the case in real structures. Only when the atom sizes of the different components are sufficiently different, and the cut-off distances are chosen accordingly, RMC will be better able to separate the partial structure factors (see for example the results in section 5.4).

With these considerations and limitations in mind, RMC is a useful tool for the analysis of structural data of disordered materials.
Chapter 4

Alkali-thallium alloys

In this chapter neutron diffraction measurements on several liquid alkali-Tl systems will be discussed. Attention will be paid to the more practical side of preparing the samples and specific details concerning data reduction. The general aspects of neutron diffraction experiments and data corrections were already addressed in section 3.3.

The experimental structure factors were analyzed by means of reverse Monte Carlo modelling (RMC), which was discussed in section 3.4. As we proceed with the discussion of the results of RMC modelling some general remarks will be made on its use in modelling non-crystalline multi-component systems. In order to better understand the structure in the liquid alkali-Tl alloys a link will be made with the available crystallographic information of these alloys; the necessary background material was presented in chapter 2. The presented data and analysis lead to better insight in the nature of the ordering in these liquid alloys, and on this basis we may speculate about the structure.

4.1 Introduction

Neutron diffraction measurements on several K-Tl and Cs-Tl alloys were carried out on the time-of-flight (TOF) diffractometer LAD at ISIS (Rutherford Appleton Laboratories, Didcot, UK) by Xu et al [67] and Verkerk et al [35]. In the structure factor a prepeak appeared at an unprecedented short wave vector, corresponding to a superstructure with a range of ~ 1 nm. Around the same time these diffraction measurements were made, crystal chemist groups at Ames and Darmstadt discovered interesting crystal structures in the solid phases. The structure of liquid KTL appears to exhibit similarities with the solid compounds KTL [38] and K8Tl11 [36] in which respectively Tl6
Figure 4.1: The resistivity $\rho$ of liquid alkali-Tl alloys as a function of composition, taken from references [31, 68, 69]

and Tl$_{11}$ clusters exist (see figures 2.2 and 2.3). In section 2.3 the crystal structure of these alloys was discussed. The average distance between the clusters in the solid (1.01 and 0.87 nm in K$_5$Tl$_{11}$ and KTi respectively) is similar to the range of the superstructure in the liquid (0.96 nm). Peaks in the resistivity of the liquid binary alloys of K, Rb or Cs with Ti [31, 68, 69] suggest compound formation at the equiatomic composition (see figure 4.1), though the indications are weak.

We decided to investigate this, for a liquid, extremely long-ranged superstructure of $\sim$ 1 nm more closely. To this end we carried out a neutron diffraction experiment on liquid KTi using $^{205}$Tl isotope substitution, which allows for a better determination of the partial structure factors. The same measurements were also done at a higher temperature (660 °C instead of 360 °C) to obtain an indication on the stability of these large clusters in the liquid alloy.

We searched for possible parallels between crystal structures and structure in the corresponding liquid alloys. More and more types of Tl
clusters in solid binary and ternary alloys were identified [41], and we chose
to measure the structure of the following ternary alloys in the liquid state:
$K_{96}Tl_{97}Pd_2$, $K_{10}Tl_{10}Pd$, $K_{10}Tl_{10}Ni$, $K_8Tl_{10}Zn$ and $K_{18}Tl_{20}Au_3$. In these al-
loys hetero-metallic clusters occur in which the hetero-element either centers
the cluster (as is the case in the clusters $Tl_{10}Pd$, $Tl_{10}Ni$ and $Tl_{10}Zn$) or it is
interstitial (in the $Tl_8Au_2$ cluster). The crystal structures of these alloys are
more elaborately described in chapter 2). A crystal structure of $K_{96}Tl_{97}Pd_2$
has not been established, but, theoretically, it is isoelectronic to $Na_{96}In_{97}Ni_2$
[70] which displays a very complex structure. It contains Ni-centered $In_{10}$
clusters which are surrounded by 39 Na atoms and the whole is enclosed in
an $In_{74}$ "fullerene". It is, of course, not likely that such large structural units
survive in the liquid. This example illustrates that there is a tendency to
form shells around the clusters.

The chemical implications of the presence of a hetero-element in the
clusters are basically that the charge on the clusters is lowered and/or that
the clusters become more stable because they gain central bonding. This is
discussed in more detail in section 2.4.2. We set out to investigate if any of
these chemical aspects would affect the structure in the liquid alloys.

To study ordering as a function of composition we measured several
Tl-rich Cs-Tl alloys. Cs was chosen rather than K because the inter-cluster
distances are greater and according to Geertsma’s rule (see section 1.8) the clusters
are therefore expected to be more stable. An extensive structural
study on the composition dependence had already been performed on Na-Tl
by Takeda et al [71]. The intermediate range order (IRO) in this system
however is not very strong, only a small prepeak was found at 11.5 nm$^{-1}$
which was highest at the composition Na$_2$Tl.

In figures 4.2 and 4.3, the phase diagrams of K-Tl and Cs-Tl are given [17].
They indicate where the tendency to compound formation is strongest (i.e.
the stoichiometric compositions). The congruently melting phase "$K_4Tl_6$" is
now known to be $K_8Tl_{11}$ [38], and "$Cs_5Tl_7$", "$Cs_4Tl_7$" and $CsTl_3$ are now
more precisely known as $Cs_8Tl_{11}$, $Cs_{15}Tl_{27}$ and $Cs_4Tl_{13}$ [39].

4.2 Sample preparation

The samples were prepared in an argon-filled glovebox with O$_2$ and H$_2$O ($g$)
levels that are typically lower than 1 ppm. The following metals were used:

- K: vial 99.95%, Aldrich (Steinheim, Germany).
- Cs: vial 99.98%, Cabot (Revere, USA).
Figure 4.2: Phase diagram of K-Tl. Reprinted from [17] with permission from ASM International.

- Tl: rod 99.999%, Highways International (Baarn, The Netherlands).
- Pd: wire 99.95%, Balzers (Zaventem, Belgium).
- Zn: foil 99.999%, Aldrich (Milwaukee, USA).
- Au: chunks >99.8%, unknown origin, the purity was checked using X-ray absorption.

For the container material we used the zero-alloy Ti_{0.68}Zr_{0.32}, that has the advantage that it does not produce any Bragg peaks. The material was obtained from the Rutherford Appleton Laboratories (Didcot, UK). The containers were made according to the two designs described in section 3.3.1.

The alkali metals easily oxidize in air, even within the glovebox some oxidation did occur. Before starting to prepare the sample containers the atmosphere was purified by melting some lithium or other alkali metal inside the glovebox.

K and Cs were delivered in glass ampoules under a noble-gas atmosphere. These ampoules were opened inside the glovebox using a glass
knife. Cs may melt before the ampoule is opened as the melting point is only 29 °C. Cooling it in a refrigerator before use is very practical in this case. Solid alkali metals are rather soft and sticky and it is therefore easiest to melt the metals and transfer the necessary quantities into the container using a glass pipette. If some potassium oxide forms, it floats on top of the liquid and clean K can always be sucked into the pipette from under this thin oxide layer. In Cs however the oxides and nitrides are dissolved. It is therefore crucial to work fast and in a very clean atmosphere.

Thallium is an extremely toxic material, and should be treated with utmost care, especially since its black powdery oxides can dissolve in water and penetrate the skin. The surface of the Tl rods was therefore cleaned inside the glovebox by using a scalpel, until its surface was silvery. Small pieces can be cut off quite easily.

In the few samples that were prepared in the type I containers (see section 3.3.1) we dissolved the Tl chunks in the K inside the container which was kept at a temperature well above the liquidus (see phase diagram in figure 4.2). The alloy was heated for about 15 minutes at 500 °C and cooled to room temperature again. The lid was positioned and the whole was en-
closed in a glass tube. The sealing of the containers by means of laser-beam welding was described in section 3.3.1 as well. To test if the containers were leak proof they were heated up to 700 °C inside the glovebox.

The samples using the other containers (type II) were prepared at a lower temperature, just high enough to melt the alkali metal. The Tl chunks and other elements were added but not yet dissolved. After closing the containers with a torque-wrench (see section 3.3.1 for the applied torques) they were heated to 700 °C in order to mix the metals properly. This technique was especially useful for the Cs-Tl alloys because it prevents strong Cs evaporation. For some Zintl-phases the reaction between the elements is very violent and in these cases it is not possible to prepare the samples this way. (An example is KGa₃ which will be discussed in section 5.2.)

The compositions of the alkali-Tl samples are given in table 4.1. The amounts of metal were weighed with an accuracy of 1 mg, except for the CsTl₃ sample which was prepared with an accuracy of 10 mg. The KTL sample in the type I container was the one used in the experiment carried out on LAD [35], and which we also measured on SLAD for comparison. For the measurements with $^{205}$Tl substitution a KTL and a K$^{205}$Tl sample were both prepared in a type II container.

<table>
<thead>
<tr>
<th>sample</th>
<th>type</th>
<th>m_Tl (g)</th>
<th>m_A (g)</th>
<th>m_M (g)</th>
<th>composition, in at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>KTL</td>
<td>II</td>
<td>7.388</td>
<td>1.413</td>
<td>-</td>
<td>K₄₉.₉₉Tl₅₀.₀₁</td>
</tr>
<tr>
<td>K$^{205}$Tl</td>
<td>II</td>
<td>7.464</td>
<td>1.424</td>
<td>-</td>
<td>K₄₉.₉₉Tl₅₀.₀₇</td>
</tr>
<tr>
<td>KTL</td>
<td>I</td>
<td>sample used in reference [35]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₉₆Tl₉₇Pd₂</td>
<td>I</td>
<td>7.825</td>
<td>1.508</td>
<td>0.081</td>
<td>K₄₉.₆₆Tl₄₉.₃₃Pd₀.₉₈</td>
</tr>
<tr>
<td>K₁₀Tl₁₀Pd</td>
<td>I</td>
<td>7.592</td>
<td>1.454</td>
<td>0.397</td>
<td>K₄₇.₆₄Tl₄₇.₅₅Pd₀.₇₈</td>
</tr>
<tr>
<td>K₈Tl₁₀Zn</td>
<td>II</td>
<td>7.636</td>
<td>1.169</td>
<td>0.243</td>
<td>K₄₂.₁₂Tl₵₂.₆₆Zn₅.₂₄</td>
</tr>
<tr>
<td>K₁₈Tl₂₀Au₃</td>
<td>II</td>
<td>6.641</td>
<td>1.14₃</td>
<td>0.96₂</td>
<td>K₴₃.₈₉Tl₴₉.₇₈Au₇.₃₃</td>
</tr>
<tr>
<td>K₅Tl₁₁</td>
<td>II</td>
<td>7.87ₘ</td>
<td>1.₀₉₆</td>
<td>-</td>
<td>K₄₂.₁₆Tl₵₇.₉₀</td>
</tr>
<tr>
<td>Cs₁₅Tl₁₈₃</td>
<td>II</td>
<td>1.₈₉ₘ</td>
<td>1.₇₀₄</td>
<td>-</td>
<td>Cs₁₄.₉₇Tl₸₅.₃₃</td>
</tr>
<tr>
<td>CsTl₃</td>
<td>II</td>
<td>9.₇₆</td>
<td>2.₁₂</td>
<td>-</td>
<td>Cs₂₅.₀₄Tl₷₄.₉₆</td>
</tr>
<tr>
<td>CsTl₂</td>
<td>II</td>
<td>1.₀₇₆₆</td>
<td>3.₄₉₈</td>
<td>-</td>
<td>Cs₹₃.₃₂Tl₶₆.₆₈</td>
</tr>
<tr>
<td>Cs₈Tl₁₁</td>
<td>II</td>
<td>7.₇₇₆</td>
<td>3.₆₈ₘ</td>
<td>-</td>
<td>Cs₴₂.₁₈Tl₶₇.₈₂</td>
</tr>
<tr>
<td>CsTl</td>
<td>II</td>
<td>5.₇₄₄</td>
<td>3.₇₃ₘ</td>
<td>-</td>
<td>Cs₵₀.₀₂Tl₴₉.₉₈</td>
</tr>
</tbody>
</table>

Table 4.1: The compositions of the alkali-Tl samples. Here m_i is the mass of element i, i=A represents the alkali element K or Cs and i=M represents the third element M=Pd, Zn or Au. The container types are described in section 3.3.1.
4.3 Neutron diffraction measurements

We have tried to prepare a Na$_{95}$Tl$_{97}$Pd$_2$ sample as well, however it turned out that this material expands when it solidifies in the sample container. The container had swollen and a large crack had appeared. A different technique is required in this case to successfully prepare a sample. A sample with K$_{10}$Tl$_{10}$Ni had also been prepared because it was a good candidate for a $^{62}$Ni isotope substitution experiment. Nickel however did not seem to dissolve in the alloy as could be deduced from Bragg-peaks that were still present in the diffraction pattern of the liquid sample. A disadvantage was that we could not heat the sample beyond $\sim$750 °C, because then softening and recrystallization of the container material would occur.

4.3 Neutron diffraction measurements

Most of the measurements on the liquid alkali-Tl alloys were carried out on SLAD (Studsvik Liquid and Amorphous materials Diffractometer) at the NFL (Neutronforskningslaboratoriet) in Studsvik, Sweden. This instrument is described in section 3.3.2. For the experiment on KTL and K$^{205}$Tl however we needed a higher statistical accuracy and therefore this isotopic substitution experiment was done on D4, a diffractometer at the ILL (Institut Max von Laue - Paul Langevin) in Grenoble, France. This instrument is described in section 3.3.2 as well.

In this chapter the results of the measurements will be presented in the form of fully corrected structure factors. We have used the program CORRECT [61] for calculating the data corrections that were described in section 3.3.3.

4.3.1 KTL and K$^{205}$Tl

The isotopic substitution experiment on KTL was carried out on D4 at the ILL (c.f. section 3.3.2) using a neutron wavelength of $\lambda = 0.07$ nm. We measured the structure factors of KTL and K$^{205}$Tl at 360 °C and at 660 °C [72]. Each measurement took about 12 hours at the lower temperature and 8 hours at the higher temperature. They were divided in at least 3 separate runs with which the stability of the instrument and the sample were checked by looking at the relative differences between the runs. They were smaller than 0.5% except at small $q$ values where sometimes deviations occurred up to 1%. We have taken additional measurements from the empty furnace, the empty can, the empty sample chamber (i.e. the background), the empty container, a vanadium rod and a cadmium rod both of the same outer diameter as the sample. The empty can was measured at room temperature
for $\sim 1$ hour and at 360 °C for 9 hours. The other measurements took $\sim 1$
hour each. For the corrections of the data taken at 660 °C we multiplied the
empty container scattering by a factor of 0.987 in order to take the linear
expansion of Ti-Zr into account. (This number was obtained using the dif-
ference in scattering intensity of the empty container at room temperature
and at 360 °C.)

The data corrections were made according to section 3.3.3. The number
density of KTl at 360 °C is 23 nm$^{-3}$ according to reference [73]. When this
density was used in the data correction procedure the scattering intensity
($N^{-1}d\sigma/d\Omega$) for large $q$ values was 2% below the expected level of 0.47 barns
(as can be calculated using equation 3.27 and the values of $\sigma_s$ given in ta-
table A.1). The data were multiplied with a factor of 1.02 in which case also
K$^{205}$Tl obtained the theoretically expected level of 0.53 barns. The origin
for this deviation of 2% may be an error in the used density, or an error in
the calculated scattering level caused by the inaccuracy of the coherent
scattering lengths presented in table A.1.

After Fourier transforming the data, the low $r$ limit in $g(r)$ oscillated
about zero, indicating that the data analysis and normalization is carried out
correctly with the right density. An advantage of D4 is that the $q$ range is
very wide ($2 < q < 164$ nm$^{-1}$ for the wavelength used) which makes it
possible to determine the low $r$ limit of $g(r)$ after direct Fourier transforming
the data. The density of KTl at 660 °C was 9.5% lower than at 360 °C (21
instead of 23 nm$^{-3}$), as could be determined from the ratio of their scattering
intensities.

Other important values that are used in the corrections are: the
beam size (44 mm high and 15 mm wide); the zero angles of detector 1 and
2 (-0.14° and -0.168°); the parameters for the Placzek correction ($c_1 =0.878,$
$c_2 = 0.211$ and $c_3 = 0.206$, c.f. equation 3.49). The scattering lengths and
cross sections of the elements composing the samples are given in table A.1
in appendix A. In figure 4.4 the size and $q$ dependence of the attenuation
coefficients is displayed in the upper part of the graph (see equation 3.43).
In the lower part the multiple scattering and the Placzek corrections are
plotted. These values were calculated for the KTl sample at 360 °C.

After the data corrections the structure factors of KTl and K$^{205}$Tl
at 360 °C and 660 °C were obtained. We noticed a systematical error of
$\sim 1\%$ visible as a slope in the data. The slope became even more apparent
when $F(q)$ (defined in equation 3.27) of KTl was subtracted from that of
K$^{205}$Tl because the systematical error then becomes relatively large. The
origin of the slope could not be determined. To eliminate this problem we
Fourier transformed the data back and forth in the following way. $S(q) - 1$
4.3 Neutron diffraction measurements

Figure 4.4: Upper part, from top to bottom: $A_{f,f}; A_{f,scf}; A_{f,scf}; A_{c,cf}; A_{c,scf}; A_{s,scf}$ (see equation 3.43). Lower part, from top to bottom: multiple scattering; inelasticity (Placzek). The values are calculated for the KTI sample at 360 °C.
Figure 4.5: The structure factor of KTL at 360 °C as measured (solid line) and the one obtained after Fourier transforming it back and forth (dashed line).

was extended at large $q$ to zero-level and was extrapolated at low $q$ by a straight line that smoothly fits the data. The Fourier transform, $g(r) - 1$, was calculated up to 5 nm and for $r < 0.25$ the values were set to -1. This function was Fourier transformed a second time to obtain the structure factor again. In figure 4.5 the two structure factors of KTL at 360 °C, before and after Fourier transforming back and forth, are shown. The same procedure was followed for the isotopic data and the data at high temperature.

The final structure factors obtained for KTL and K$^{205}$Tl at 360 °C and at 660 °C can be seen in figure 4.6. The difference in scattering intensity of the samples is visible because the function $F(q) + \langle b^2 \rangle$ is plotted (see equation 3.27).

The $F(q)$'s of KTL and K$^{205}$Tl can be combined in different ways, such that one of the three partial structure factors $A_{\alpha,\beta}(q)$ is eliminated. The resulting
Figure 4.6: Top graph: the structure factors of KTL (lower one) and $^{205}$KTL (higher one) at 660 °C. Bottom graph: the structure factors of KTL (lower one) and $^{205}$KTL (higher one) at 360 °C.
Figure 4.7: The experimental data of liquid KTI and K$^{205}$Tl combined to give the $\Delta F_i(q)$ wherein one of the three partial structure factors is eliminated. $\Delta F_1(q)$, $\Delta F_2(q)$ and $\Delta F_3(q)$ (defined in equation 4.7) are shifted vertically by +2, +1 and 0 respectively. Upper graph: 660 °C and lower graph: 360 °C. Functions are given in equation 4.1.

$$
\begin{align*}
\Delta F_1(q) &= 1.1972A_{Tl,Tl}(q) - 0.19272A_{K,K}(q) \\
\Delta F_2(q) &= 0.7115A_{Tl,Tl}(q) + 0.2885A_{K,Tl}(q) \\
\Delta F_3(q) &= 0.7111A_{K,Tl}(q) + 0.2889A_{K,K}(q)
\end{align*}
$$

(4.1)

The coefficients are normalized in such a way that their total is 1. These $\Delta F_i(q)$ functions contain only 0.6%, 12% and 1.1% (for $\Delta F_1(q)$, $\Delta F_2(q)$ and $\Delta F_3(q)$ respectively) of the intensity of the total structure factor of KTI. They are plotted in figure 4.7. It is directly clear from this experimental data that the prepeak is only present in $A_{Tl,Tl}(q)$. Further analysis of the data is described in sections 4.4.1 and 4.6.1.
4.3.2 K-Tl with additional third elements

Experiments on K-Tl alloys with additional third elements were carried out on SLAD at the NFL (c.f. section 3.3.2) using a neutron wavelength of \( \lambda = 0.11 \) nm. We measured the structure factors of \( K_{10}Tl_{10}Pd \) [74, 75], \( K_{96}Tl_{97}Pd_2 \) [74, 75], \( K_{8}Tl_{10}Zn \) [76] and \( K_{18}Tl_{20}Au_3 \) [76] at temperatures of 35 °C above the melting point of KTI (320 °C, see phase diagram in figure 4.2). In addition we measured the structure factors of KTI and \( K_{8}Tl_{11} \) as references. The experiments took on average 8 hours each, divided in runs of 1 hour. The stability of the combined system of the instrument and sample was checked statistically.

In the case of KTI and KTI+Pd these statistical checks showed that some of the detectors in banks 2, 3 and 4 were not stable. The detectors in the first bank, however, which measured the prepeak and the main peak, were stable. The intensities of the other detectors could be adjusted to the intensity of the detectors in the first bank. The intensity corrections made were about 5%. As KTI had been measured previously on LAD [35] at ISIS and, later, on D4 (ILL), we could compare the results with the SLAD-measurement. There are small differences that can be seen in figure 4.8 but in general the data sets compare very well.

During the other measurements the detectors remained stable. At first another problem occurred because the sample stick, which we used to position the sample in the beam, appeared to be bent. The structure factors clearly did not oscillate around a horizontal line at high \( q \) values, which was a result of the fact that the oscillating collimator was not focussed on the sample anymore. As we could not correct for this, the experiments had to be repeated. This time a boron-nitride cup had been positioned at the bottom of the furnace in order to center the sample containers from below as well as from the top, and the problem was remedied.

The beam width was 1 cm and the height 4 cm during the experiment on KTI and KTI+Pd. For the other experiments discussed in this section it was 1 cm wide and 3.5 cm high. The measurements were corrected, again using the program CORRECT [61]. The parameters for the Placzek correction (equation 3.49) were for the detectors used: \( c_1 = 0.793 \), \( c_2 = 0.139 \) and \( c_3 = 0.265 \). The inelasticity correction varied from -0.0001 to 0.0108 (for \( q = 2 \) and 100 nm\(^{-1} \) respectively) for the sample and from -0.0046 to 0.0594 for the vanadium rod. The multiple scattering was 0.078 for the sample and 0.169 for the vanadium rod. The attenuation coefficients were typically: \( A_{v,v} = 0.644 \) for the vanadium rod, \( A_{s,sc} = 0.850 \), \( A_{c,sc} = 0.857 \) and \( A_{cc} = 0.914 \) at wavevector \( k = 100 \) nm\(^{-1} \). The attenuation of the thin heating element was not taken into account, as it is negligible in this case.
Figure 4.8: The structure factors of liquid KTI as measured on LAD (dashed line) [35], SLAD (dotted line) and D4 (solid line).
The densities used in the correction procedure were 23 nm$^{-3}$ for KTI, and KTI+Pd, 24 nm$^{-3}$ for $K_8Tl_{11}$, $K_8Tl_{10}Zn$ and $K_{18}Tl_{20}Au_3$. The densities were estimated by taking the average atomic volume of the liquid elements at 370 °C and applying the volume contraction occurring in the solid alloy. For Pd, Au and Zn the atomic volume of the dissolved atoms was assumed to be equal to that of Tl. The density used has influence on the normalization of the data and on the multiple scattering corrections. Fortunately, the latter effect is very small.

The scattering level for the measurements on $K_8Tl_{11}$, $K_8Tl_{10}Zn$ and $K_{18}Tl_{20}Au_3$ came out to be $\sim$ 15% too high. This cannot be explained by a wrong estimate of the densities, as it would require a density of the liquid greater than that of the solid. We concluded there must have been something wrong with the normalization, probably with the vanadium measurement. We had used an empty container filled with vanadium flakes for the normalization, and possibly the vanadium density in this container was not as well-defined as it should be. We had also measured KTI again, which could be used as a reference to the earlier measurements. It turned out that multiplying the data with a constant to obtain the right scattering level, resulted in good agreement with earlier measurements of KTI. This method was therefore applied to the measurements of $K_8Tl_{11}$, $K_8Tl_{10}Zn$ and $K_{18}Tl_{20}Au_3$ as well.

The final structure factors are plotted in figure 4.9. Figure 4.10 zooms in on the prepeak of KTI + 0%, 1% and 5% Pd, and it can be seen that the position shifts to lower $q$ values with increasing Pd content. An analysis of the prepeak positions and heights will be given in section 4.6.2.

### 4.3.3 Cs-Tl

The structure factors of the alloys Cs$_3$Tl$_{17}$, CsTl$_3$, CsTl$_2$, Cs$_8$Tl$_{11}$ and CsTl were also measured on SLAD [77], right after the measurements of $K_8Tl_{11}$, $K_8Tl_{10}Zn$ and $K_{18}Tl_{20}Au_3$. The structure factors of Cs-Tl were also about 15% too high, probably due to the same reason i.e. an error in the density of the vanadium sample. The further data analysis was taken care of in the same way as described in section 4.3.2. The densities used are mentioned in section 4.4.3.

The structure factors were measured at 450 °C except for Cs$_3$Tl$_{17}$ which was measured at 400 °C. The corrected structure factors of Cs-Tl are displayed in figure 4.11.

The most conspicuous feature in this data is the prepeak which gradually shifts to smaller $q$ values and decreases in height, with increasing Tl-
Figure 4.9: $S(q)$ of liquid KTI, K$_{96}$Tl$_{97}$Pd$_2$, K$_{10}$Tl$_{10}$Pd, K$_5$Tl$_{11}$, K$_5$Tl$_{10}$Zn and K$_{18}$Tl$_{20}$Au$_3$, in this order from bottom to top vertically shifted by steps of 0.5.
Figure 4.10: The prepeaks in the structure factors of KTI (squares), KTI + 1% Pd (circles) and KTI + 5% Pd (triangles)
content. In sections 4.4.3 and 4.6.3 this will be further examined.

4.4 Reverse Monte Carlo modelling

We used RMC modelling in order to find a three-dimensional configuration of atoms that reproduces the measured structure factor within the statistical accuracy of the data. The principle of RMC is explained in section 3.4. From this three-dimensional configuration of atoms we obtain partial structure factors, average coordination of the elements and bond-angle distributions.

In addition, an important reason to use RMC is to check the data for systematical errors. RMC can usually not fit a structure factor with unphysical features, or when the value of the density is wrong. There is often uncertainty on the density of the liquid alloys, and RMC can be of help to find a better estimate.

As isotopic data are available for KTI we used this opportunity to examine how this extra information influences the results of RMC. It is important to find out how reliable the RMC results are for a binary alloy if no isotopic data are available.

4.4.1 KTI and K\textsuperscript{205}Tl

For modelling the liquid KTI system a random initial configuration was prepared of 3000 atoms. The particle number density is taken equal to $\rho = 23$ nm\textsuperscript{-3} and the cut-off distances (i.e. distances of closest approach) between all atom pairs are 0.25 nm. This cut-off distance is somewhat shorter than the shortest Tl-Tl distance in solid KTI or K\textsubscript{8}Tl\textsubscript{11} (0.306 nm) and for K-K the ionic radius of 0.266 nm was kept in mind. The Fourier transform of the structure factor, $g(r)$, shows that the main peak starts at a value only a little higher than 0.25 nm (as can also be seen in $g_{\alpha\beta}(r)$ displayed in figures 4.13 and 4.17).

Using equation 3.27 and the values of $b_c$ given in table A.1 the weights of the three partial structure factors (in barns) can be calculated:

$$F_1(q) = 0.1925(A_{\text{Tl,Tl}}(q) - 1) + 0.1628(A_{\text{K,Tl}}(q) - 1) - 0.0344(A_{\text{K,K}}(q) - 1)$$

$$F_2(q) = 0.2266(A_{\text{Tl,Tl}}(q) - 1) + 0.1766(A_{\text{K,Tl}}(q) - 1) - 0.0344(A_{\text{K,K}}(q) - 1)$$

where $F_1(q)$ is the structure factor of natural KTI and $F_2(q)$ of K\textsuperscript{205}Tl.

The parameter that indicates the quality of the fit is $\chi^2$, defined in equation 3.55. $\chi$ is inversely proportional to the estimated standard deviation $\sigma$ of the experimental errors. As $\sigma$ is not known exactly, $\chi^2$ can only be used for relative evaluation of different fits to the same experimental data, with
Figure 4.11: $S(q)$ of liquid Cs-Tl. From bottom to top: CsTl, Cs$_8$Tl$_{11}$, CsTl$_2$, CsTl$_3$ and Cs$_3$Tl$_{17}$, with vertical shifts of 0, 0.5, 1, 1.5 and 2 respectively.
the same $\sigma$. As $\sigma$ determines the acceptance ratio of the steps generated by RMC, it can be used as a parameter in the fit. The values of $\sigma$ and the $\chi^2$ for the different fits that will be discussed in this section are given in table 4.2.

<table>
<thead>
<tr>
<th>RMC fit to:</th>
<th>$\sigma$ used in fit</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_1$ (LAD [35])</td>
<td>0.003</td>
<td>2.56</td>
</tr>
<tr>
<td>$F_1$ (SLAD)</td>
<td>0.01</td>
<td>2.06</td>
</tr>
<tr>
<td>$F_1$ (D4)</td>
<td>0.001</td>
<td>1.58</td>
</tr>
<tr>
<td>$F_1 + F_2$ (D4)</td>
<td>0.001, 0.001</td>
<td>2.88, 2.67</td>
</tr>
<tr>
<td>$\Delta F_1 + \Delta F_2 + \Delta F_3$ (D4)</td>
<td>0.013, 0.042, 0.03</td>
<td>1.51, 1.57, 2.77</td>
</tr>
<tr>
<td>$F_1 + F_2 + \Delta F_1 +$</td>
<td>0.001, 0.001, 0.013,</td>
<td>1.60, 1.67, 2.48,</td>
</tr>
<tr>
<td>$\Delta F_2 + \Delta F_3$ (D4)</td>
<td>0.042, 0.03</td>
<td>2.74, 2.99</td>
</tr>
</tbody>
</table>

Table 4.2: $\chi^2$ for several RMC fits on the structure factors of liquid KTL ($F_1(q)$), K$^{205}$Tl ($F_2(q)$) and on linear combinations of the two defined by the $\Delta F_i(q)$ functions in equation 4.1, for data taken at 360 °C.

We did RMC modelling on the three different measurements of $F_1(q)$, namely the ones measured on D4, LAD [35] and SLAD (see sections 4.3.1 and 4.3.2). These data have different statistical (and probably also systematical) accuracies and we estimated $\sigma$ to be 0.001, 0.003 and 0.01 respectively. The three different final configurations that fitted the data were analyzed and we found that the partial structure factors $A_{\alpha,\beta}(q)$ and the partial pair distribution functions, $g_{\alpha,\beta}(r)$, were similar for the three fits; the peak positions and heights agree within the accuracy of the simulation for all partials. In figures 4.12 and 4.13 $A_{\alpha,\beta}(q)$ and $g_{\alpha,\beta}(r)$ obtained from the simulation of the D4 data are given.

The structure factors of KTL and K$^{205}$Tl, $F_1(q)$ and $F_2(q)$, were modelled to produce one configuration that gives a fit to both structure factors. The $\chi^2$ obtained in the fit to $F_1(q)$ and $F_2(q)$ simultaneously is larger than $\chi^2$ obtained for a fit to $F_1(q)$ or $F_2(q)$ separately (see table 4.2). The peak positions in $A_{\alpha,\beta}(q)$ and $g_{\alpha,\beta}(r)$ obtained from this fit are within 1% the same to those of the fit to $F_1(q)$ only (figures 4.12 and 4.13). When we plot the $\Delta F_i(q)$ functions that were defined in equation 4.1, differences between the fit and the data are displayed very clearly (figure 4.14). We temporarily increased $\sigma$ in the RMC fit to $F_1(q)$ and $F_2(q)$ to permit RMC to accept more particle moves that do not increase $\chi^2$ (see section 3.4.1). If the system were in a local minimum of $\chi^2$, it might be possible to 'climb' out this way. However we did not succeed in obtaining a better fit.
Figure 4.12: $A_{\alpha,\beta}(q)$ produced by RMC for KTi measured on D4 (360 °C). $A_{Ti, Ti}(q)$: solid line; $A_{K, Ti}(q)$: dashed line; $A_{K, K}(q)$: dotted line.

Figure 4.13: $g_{\alpha,\beta}(r)$ produced by RMC for KTi measured on D4 (360 °C). $g_{Ti, Ti}(r)$: solid line; $g_{K, Ti}(r)$: dashed line; $g_{K, K}(r)$: dotted line.
Figure 4.14: The $\Delta F_i(q)$ functions (equation 4.1) calculated for the measured data at 360 °C (dotted lines) and the RMC fit (solid lines). From top to bottom: $\Delta F_1$, $\Delta F_2$ and $\Delta F_3$, vertically shifted by +2, +1 and 0 respectively.

We then proceeded by fitting to $\Delta F_1$, $\Delta F_2$ and $\Delta F_3$ simultaneously, instead of to $F_1$ and $F_2$. In principle these functions contain the same information as the total structure factors of KTl and K$^{205}$Tl together. Using the $\sigma$'s given in table 4.2, good fits were obtained. Consequently, the resulting configuration was used as a starting point to fit to five functions simultaneously, namely $F_1 + F_2 + \Delta F_1 + \Delta F_2 + \Delta F_3$. Now $\chi^2$ for $F_1$ and $F_2$ is clearly better than that of the fit to $F_1 + F_2$ only and on average even slightly better than that of the fits to $F_1$ and $F_2$ separately, the values are given in table 4.2. The result of this fit can be seen in the following figures: the fits to $\Delta F_1$, $\Delta F_2$ and $\Delta F_3$ in figure 4.15; $A_{\alpha,\beta}(q)$ in figure 4.16; $g_{\alpha,\beta}(\tau)$ in figure 4.17. The fits to the total structure factors $F_1$ and $F_2$ are not shown because the fits coincide with the data. In figure 4.18 a section of the three-dimensional configuration is shown.

The partial structure factors in figure 4.16 differ considerably from those of the fits to $F_1$ only (figure 4.12) or of $F_1$ and $F_2$ simultaneously (the peak positions are within 1% similar to those in figure 4.12). Now the position of the main peak is different for the three partial structure factors. In figure 4.17 it can be seen that $g_{\text{TI-TI}}(\tau)$ is very well-defined and is indicating a short Tl-Tl distance of 0.315 nm.
Figure 4.15: RMC fits (solid lines) to $F_1$, $F_2$, $\Delta F_1$, $\Delta F_2$ and $\Delta F_3$ (dotted lines) simultaneously, of which only the last three are shown (360 °C). From top to bottom: $\Delta F_1$, $\Delta F_2$ and $\Delta F_3$, vertically shifted by +2, +1 and 0 respectively.

Figure 4.16: $A_{\alpha,\beta}(q)$ (360 °C) of the fit displayed in figure 4.15. $A_{\text{T}_{\text{I}},\text{T}_{\text{I}}}(q)$: solid line; $A_{\text{K},\text{T}_{\text{I}}}(q)$: dashed line; $A_{\text{K},\text{K}}(q)$: dotted line.
Figure 4.17: $g_{\alpha,\beta}(r)$ (360 °C) of the fit displayed in figure 4.15. $g_{\text{Tl,Tl}}(r)$: solid line; $g_{\text{K,Tl}}(r)$: dashed line; $g_{\text{K,K}}(r)$: dotted line.

Probably the RMC model we fitted to $F_1$, $F_2$, $\Delta F_1$, $\Delta F_2$ and $\Delta F_3$ simultaneously, is nearer to the real structure in liquid KTL than the other models. This is based on the facts that $\chi^2$ is on average smaller for $F_1$ and $F_2$, and the structure seems to be more structured (i.e. less close to a random configuration).

We conclude that RMC can not be used to obtain the partial structure factors of liquid KTL from a single measurement [78]. This might be due to a combination of the facts that in general RMC tends to the most random configuration and that in this particular case the distances of closest approach of K and Tl are very similar.

Apparently one should always be aware of the fact that the results strongly depend on the way in which a fit to the data is obtained.

For the data at 660 °C we have followed exactly the same procedure as above, except that a number density of 21 nm$^{-3}$ was used. Again we obtained the best fit by fitting to $F_1$, $F_2$, $\Delta F_1$, $\Delta F_2$ and $\Delta F_3$ simultaneously. The resulting $A_{\alpha,\beta}(q)$ and $g_{\alpha,\beta}(r)$ are given in figures 4.19 and 4.20.

We used these best-fitting configurations to calculate the coordination numbers and the bond-angle distributions. The Tl-Tl coordination number is
Figure 4.18: A part (1/8 th) of the three-dimensional configuration produced by RMC in the fit to $F_1$, $F_2$, $\Delta F_1$, $\Delta F_2$ and $\Delta F_3$ simultaneously (KTI at 360 °C). The dark spheres are Tl and the light spheres K atoms. A connecting line is drawn between Tl atoms that are closer than 0.4 nm.
Figure 4.19: $A_{\alpha,\beta}(q)$ (660 °C) obtained by fitting to $F_1$, $F_2$, $\Delta F_1$, $\Delta F_2$ and $\Delta F_3$ simultaneously. $A_{\text{TI,TI}}(q)$: solid line; $A_{\text{K,TI}}(q)$: dashed line; $A_{\text{K,K}}(q)$: dotted line.

Figure 4.20: $g_{\alpha,\beta}(r)$ (660 °C) obtained by fitting to $F_1$, $F_2$, $\Delta F_1$, $\Delta F_2$ and $\Delta F_3$ simultaneously. $g_{\text{TI,TI}}(r)$: solid line; $g_{\text{K,TI}}(r)$: dashed line; $g_{\text{K,K}}(r)$: dotted line.
Figure 4.21: The distribution of coordination numbers for Tl-Tl \((r < 0.4 \text{ nm})\) and K-K \((r < 0.5 \text{ nm})\), circles and squares respectively.

the average number of Tl atoms around other Tl atoms, within the first coordination shell. In figure 4.17 it can be seen that the first minimum of \(g_{\text{Tl-Tl}}(r)\) occurs at about 0.4 nm, which we interpret as the outer bound of the first coordination shell. The first minimum in \(g_{\text{K-K}}(r)\) is at 0.5 nm. The coordination number distribution of Tl-Tl and K-K for \(r \leq 0.4\) and 0.5 nm respectively is shown in figure 4.21 for the data measured at 360 °C and at 660 °C. The average Tl-Tl coordination number is 3.95 at 360 °C and 3.85 at 660 °C. The bond-angle distributions of Tl-Tl-Tl and K-K-K were also calculated up to distances of \(r = 0.4\) and 0.5 nm respectively. The result is displayed in figure 4.22.

In section 4.6.1 the structural information obtained with RMC modelling for liquid KTL at 360 °C will be interpreted via a comparison to crystallographic data. In section 4.5 the temperature dependence of KTL will be discussed further.

### 4.4.2 K-Tl with additional third elements

The data of KTL with additional third elements were modelled with RMC and gave good fits. No effect of the third elements were observed on e.g. the bond-angle distributions or the coordination numbers. Due to the small
quantities and therefore the small weight factors of the Pd, Zn or Au partials nothing can be concluded about their position in the alloy.

In the previous section we found that RMC could not be used to find the partial structure factors of liquid KTl from a single measurement. The RMC results are therefore also not reliable for KTl with additional third elements. We have, however, used RMC to test certain expected structures against the data. KTl + 5% Pd was used as a test case, because there is a clear effect visible of Pd on the structure of the liquid alloy [75].

As before we started from random configurations of 3000 atoms, with cut-off distances of 0.25 nm between both the K and Tl atoms. For the minimum Pd-Pd distance we chose 0.5 nm because we wanted to test a configuration in which the Pd atoms were clearly separated as is the case in the crystal structures. The number density used was 23.2 nm$^{-3}$, derived from the crystal structure with 4% linear expansion taken into account. A good fit was obtained that coincided with the data within the statistical errors.

In additional RMC simulations on KTl + 5% Pd we used extra constraints: in the first simulation every Pd atom was forced to be surrounded by six Tl atoms within a radius of 0.4 nm; in another simulation every Pd atom was forced to have 10 Tl neighbours within 0.45 nm. There are some free Tl atoms left in this last configuration first because only 85% of the
4.4 Reverse Monte Carlo modelling

Pd atoms could be forced to be surrounded by the required number of 10 Tl atoms in their first coordination shell and, second, because clusters can partially overlap and then share Tl atoms. With these constraints it is very difficult for RMC to move a whole cluster of 11 atoms around in the cell. In such a case the result is also dependent on the initial configuration. All three fits (with PdTl6, 85% PdTl10, and no constraints) agree with the experimental data within the errors. The values of $\chi^2$ were 8.1 ($\sigma = 0.003$), 69.6 ($\sigma = 0.001$) and 72.9 ($\sigma = 0.001$) for KTL+5%Pd with no clusters, PdTl6 and 85% PdTl10 clusters respectively. A closer inspection of the three configurations showed that the configurations resulting from the simulation without constraints and from the simulation with PdTl6-cluster constraints, produce indistinguishable results for both the Tl and K atoms. The coordination numbers, bond-angle distributions and partial pair distribution functions, are the same within the statistical fluctuations. Although the PdTl10-cluster configuration fits the total structure factor of the data very well, the partial structure factors widely diverge at small wavevectors. The prepeak is only formed when the partial structure factors are summed together with the right weight factors. It is highly unlikely, though not completely impossible, that this PdTl10-cluster configuration is correct. The constraints might be too severe, and we probably ended in a local minimum of $\chi^2$.

These results may be suggestive towards the existence of Tl-clusters in the liquid alloy with a size of somewhere between 6 and 10 atoms. We have to be careful however because many more structures may give a fit to the data, which we cannot all try.

4.4.3 Cs-Tl

The structure factors of Cs-Tl were measured for several compositions, namely with 15%, 25%, 33%, 42% and 50% Cs. As cesium is significantly larger than thallium, the first peak in $g(r)$ must be mostly due to Tl-Tl coordination. Imposing the expected different cut-off distances to RMC will give a better separation of the partial structure factors. This is an advantage that we did not have in the case of the KTL system, because the closest approaches of K and Tl atoms are almost equal. Of course, since we do not have three independent measurements for the Cs-Tl alloys, the partial structure factors are not uniquely defined.

The cut-off distances we applied are 0.27, 0.33 and 0.35 nm for Tl-Tl, Cs-Tl and Cs-Cs respectively. The choice of these cut-off distances involves some speculation and some trial-and-error when modelling with RMC. It is however important because the results depend on the cut-off distances.
applied. The Tl-Tl cut-off chosen is larger than the one we used in modelling
the KTI system (0.25 nm) because \( g(\tau) \), and also \( g_{\text{TI-TI}}(\tau) \) after the modelling,
show it is possible. We based the choice of the cut-off distances on the
following data. In the solid CsTI crystal the shortest distances are 0.303 (Tl-
Tl), 0.381 (Cs-Tl) and 0.39 nm (Cs-Cs) [39]. For the liquid we have to take
the widths of the distributions into account and estimate the cut-off distance
to be somewhat smaller. The diameters of Tl and Cs\(^+\) are respectively 0.342
[80] and 0.334 nm [81]. We can expect the diameter of Tl\(^-\) to be more or
less equal to that of Tl, as the addition of one extra electron to a shell that
contains already three electrons does not make much difference. The shorter
Tl-Tl distance in the crystalline structure is the result of a covalent Tl-Tl bond.

The densities were estimated in the following way. The densities of
solid Tl, Cs\(_{15}\)Tl\(_{27}\), Cs\(_8\)Tl\(_{11}\), CsTI and Cs are known from the crystal struc-
tures (35.1 [82], 24.24 [83], 21.98 [84], 21.36 [39] and 8.5 nm\(^{-3}\) [82], respec-
tively) and for Tl and Cs also in the liquid state as a function of temperature
[82]. The average atomic volumes of the solid alloys were linearly interpo-
lated. An expansion coefficient to take melting and heating up to 450 °C
into account was calculated by averaging the expansion of pure Cs and Tl. It
varied between 15% volume expansion for CsTI and 11% for Cs\(_{15}\)Tl\(_{85}\). The
resulting values for the number density of the liquid Cs-Tl alloys are: 26.7,
23.7, 21.8, 19.2 and 18.6 nm\(^{-3}\) for Cs-Tl with 15%, 25%, 33%, 42% and 50%
Cs respectively. These values made reasonably good RMC fits to the struc-
ture factors possible. They could however be improved (a smaller \( \chi^2 \) when
the densities were assumed to be somewhat lower: 26.0, 23.0, 21.0, 18.5 and
17.5 nm\(^{-3}\) respectively.

The weight factors for the partial structure factors can be calcu-
lated using equation 3.27 and the average coherent scattering lengths of the
elements which are given in table A.1. The weight factors are normalized
by \( \langle b \rangle^2 \), so that their total equals 1 (see equation 3.31). They are given in
table 4.3. The fits are shown in figure 4.23.

<table>
<thead>
<tr>
<th>alloy</th>
<th>( w_{\text{TI-TI}} )</th>
<th>( w_{\text{Cs-TI}} )</th>
<th>( w_{\text{Cs-Cs}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsTI</td>
<td>0.3822</td>
<td>0.4721</td>
<td>0.1457</td>
</tr>
<tr>
<td>Cs(<em>8)Tl(</em>{11})</td>
<td>0.4762</td>
<td>0.4277</td>
<td>0.0961</td>
</tr>
<tr>
<td>CsTl(_2)</td>
<td>0.5838</td>
<td>0.3606</td>
<td>0.0556</td>
</tr>
<tr>
<td>CsTl(_3)</td>
<td>0.6876</td>
<td>0.2832</td>
<td>0.0292</td>
</tr>
<tr>
<td>Cs(<em>3)Tl(</em>{17})</td>
<td>0.8131</td>
<td>0.1772</td>
<td>0.0097</td>
</tr>
</tbody>
</table>

Table 4.3: The weight factors \( w_{\alpha,\beta} \) for the partial structure factors \( A_{\alpha,\beta}(q) \)
and partial pair correlation functions \( g_{\alpha,\beta}(\tau) \).
Figure 4.23: $S(q)$ of liquid Cs-Tl (dotted lines) with their respective RMC fits (solid lines). From bottom to top: CsTl, Cs$_5$Tl$_{11}$, CsTl$_2$, CsTl$_3$ and Cs$_3$Tl$_{17}$, with vertical shifts of 0, 0.5, 1, 1.5 and 2 respectively (measured at 450 °C except Cs$_3$Tl$_{17}$ which was measured at 400 °C).

$A_{a,b}(q)$ and $g_{a,b}(r)$ of equiatomic CsTl are displayed in figures 4.24 and 4.25. The position of the main peak in $g_{Tl,Tl}(r)$ is at 0.315 nm, which is the same as in the KTl case. A spurious small spike can be seen at 0.27 nm. When we used a higher density in the modelling ($\rho = 18.6$ nm$^{-3}$) this spike was as large as the main peak. Probably it is a result of the fact that RMC does not know a better position for the atoms when the density assumed is too high to make a good fit to the data. The bond-angle distribution of Tl-Tl-Tl in CsTl with $r < 0.4$ nm is shown in figure 4.26. The distance of $r = 0.4$ nm is chosen to be able to compare with the KTl case. The average Tl-Tl coordination number for $r < 0.4$ nm is 3.65 in CsTl, compared to 3.95 in the KTl case. As is to be expected the coordination number strongly depends on the composition: 3.65, 4.017, 5.012, 5.803, 7.123 for CsTl, Cs$_5$Tl$_{11}$, CsTl$_2$, CsTl$_3$ and Cs$_3$Tl$_{17}$ respectively. In figure 4.27 a part (1/8 th) of the three-dimensional configuration is shown. Between Tl atoms that are closer to each other than 0.4 nm a connecting line is drawn.

Figure 4.28 shows the $A_{Tl,Tl}(q)$ obtained from the RMC fits for all compositions measured. Prepeaks in the partial structure factors were exclusively present in these $A_{Tl,Tl}(q)$. In figure 4.29 it can be seen that the height of the prepeak in $A_{Tl,Tl}(q)$ increases more or less linearly with the ratio of...
Figure 4.24: $A_{\alpha,\beta}(q)$ of CsTl as produced by RMC. $A_{Tl,Tl}(q)$: solid line; $A_{Cs,Tl}(q)$: dashed line; $A_{Cs,Cs}(q)$: dotted line.

Figure 4.25: $g(r)$ (upper graph) and $g_{\alpha,\beta}(r)$ (lower graph) of CsTl as produced by RMC. $g_{Tl,Tl}(r)$: solid line; $g_{Cs,Tl}(r)$: dashed line; $g_{Cs,Cs}(r)$: dotted line.
the Cs and Tl concentration, $c_{Cs}/c_{Tl}$. This height was determined from the height of the prepeak in the total structure factor divided by $w_{Tl,Tl}$, as this is a little bit more reliable than the height of the prepeak of $A_{Tl,Tl}(q)$ obtained from RMC modelling. We assumed that, in analogy to the KTI case, the prepeak is only due to the Tl-Tl correlations. The position of the prepeak in $S(q)$ as a function of $c_{Cs}/c_{Tl}$ is plotted in figure 4.30. In section 4.6.3 a model will be proposed to interpret these features and a comparison to the structure of liquid KTL will be made.

## 4.5 Temperature and pressure dependence

In this section we will further discuss the temperature dependence of the structure of KTL. And, although we have not mentioned this in the experimental section of this chapter, we have also measured the structure of CsTl at a higher temperature (600 °C instead of 450 °C) and Cs$_8$Tl$_{11}$ at a higher pressure (354 bar and 450 °C). About the measurement at higher pressure we can be short, because we did not see any pressure dependence of the structure factor within the error of about 5%.

The results of the RMC modelling on KTL and $K^{205}Tl$ were presented in
Figure 4.27: A part (1/8 th) of the three-dimensional configuration produced by RMC in the fit to $S(q)$ of CsTl. The dark spheres are Tl and the light spheres Cs atoms. A connecting line is drawn between Tl atoms that are closer than 0.4 nm.
Figure 4.28: $A_{\text{Tl,Tl}}(q)$ obtained from the RMC fits for CsTl, Cs$_8$Tl$_{11}$, CsTl$_2$, CsTl$_3$ and Cs$_3$Tl$_{17}$, in order of decreasing prepeak height.

Figure 4.29: The height of the prepeak in $A_{\text{Tl,Tl}}(q)$ obtained from RMC fits to the Cs-Tl alloys, as a function of the number of Cs atoms per Tl atom.
section 4.4.1. We have seen that the Tl-Tl coordination number decreases from 3.95 at 360 °C to 3.85 at 660 °C, which is a small change compared to the difference in density at the two temperatures (23 and 21 nm\(^{-3}\) respectively). The Tl-Tl bond-angle distribution also changes only slightly for higher temperatures (see figure 4.22). At 660 °C, \(g_{\text{Tl-Tl}}(r)\) is still well-defined (as is seen in figure 4.20) and peaks at the same short Tl-Tl distance of 0.315 nm that was observed for the data taken at 360 °C. This indicates a strong short range ordering (SRO) which is still present at 660 °C.

The intermediate range ordering (IRO), however, undergoes a change with increasing temperature. The prepeak is broader and lower at high temperature, which indicates that the cluster sizes and/or inter-cluster distances are less well-defined. The prepeak position shifts from 8.0 to 7.3 nm\(^{-1}\) at higher temperature. This is probably not only due to the change in density but also to an increase of the structure factor at lower \(q\) values. The width of the prepeak, \(\Delta q\), governs the extent of the correlations in real space, given by the correlation length \(R_c = 2\pi/\Delta q\) [79]. We see that the SRO remains intact but the IRO starts to diminish as \(R_c\) changes from \(\sim 1.7\) nm to \(\sim 0.9\) nm.

The temperature dependence of the structure factor of CsTl is analogous to that of KTL. The prepeak shifted to lower \(q\) value (from 7.4 to 7.0 nm\(^{-1}\)), broadens and decreases in height. For KTL the effect is somewhat stronger because the temperature difference is larger. In figure 4.31 the measurements for CsTl and KTL at different temperatures are shown.
4.5 Temperature and pressure dependence

Figure 4.31: The structure factor of KTL (upper graph) and CsTl (lower graph) measured at different temperatures.

We can compare these results to other temperature dependent measurements that were obtained for e.g. KPb [85] and CsTl [86]. In the first case the prepeak exists up to the highest temperature measured (1600 °C), it shifts to a lower $q$ value ($8.8 \geq q \geq 7.3 \text{ nm}^{-1}$) and its height decreases roughly by a factor 3 while the width doubles. The Pb$_4$ poly-anions and the network in which they exist are gradually breaking down with increasing temperature. In the measurements of CsTl at high temperature and pressure [86] it is seen that the prepeak gets lower and broader at 627 °C and its position shifts 0.5 nm$^{-1}$ to the left with respect to the measurement at 457 °C. At higher temperature (up to 1427 °C and 60 bar) the prepeak deforms until there is no maximum visible any more due to a strong increase of small-angle scattering, which, according to [86], is due to an increase in concentration fluctuations. As far as we can tell, our results on the KTL and CsTl systems are quite similar.

We mention that there are differences in the measurement of CsTl at 457 °C
from reference [86] and our measurements of CsTl at 450 °C. An inaccuracy both in the angle calibration and in normalization of the measurements has been detected in [86], and re-analysis of this data is in progress.

4.6 Interpretation of the structure

The measured structure factors of alkali-Tl alloys show a prepeak at a wavevector between ~8 and ~6 nm\(^{-1}\). From the measurements in which \(^{205}\)Tl isotope substitution was applied, it can be concluded in a direct way that this prepeak is only present in \(A_{\text{TI,TI}}(q)\). The crystal structures of alkali-Tl Zintl-phases contain Tl-clusters and, moreover, the distance between them is similar to the periodic distance found in the liquid. This correlation between the solid and liquid phase is also present in alkali-Pb alloys, which were mentioned as an example in section 1.8. In a review article of Van der Lugt [1] more alloys are discussed and he shows there is a more or less linear relation between the periodic distances in the solid \((d_s)\) and in the liquid alloys \((d_l)\).

Given these resemblances it seems worthwhile to further investigate the structure in the liquid Zintl-phases by comparing it to the structure of their solid counterparts and using the crystal chemical knowledge that is available. In chapter 2 several crystalline structures of relevant materials were already discussed.

By using RMC modelling we have obtained three-dimensional configurations of atoms that have the same structure factor as the data, within the experimental error. From these configurations, average atomic distances, bond-angle distributions and coordination numbers can be obtained. However, we have to keep in mind that these data are not uniquely defined (see section 3.4.2). They are obtained using RMC modelling as described in section 4.4.

We will compare the structure in the liquid phase to that of the corresponding solid by investigating the intermediate range and the short range ordering (IRO and SRO) in the following way:

1. IRO: the size of the clusters is estimated via the position of the prepeak.

2. SRO: the average distribution of atoms on the short range scale is obtained from the outcome of RMC modelling.

The method with which the first item is approached needs some further explanation, which will be given below.
4.6 Interpretation of the structure

Model for the IRO

The prepeak position, \( q_0 \), relates to a periodic distance, \( d_i \), in real space via the relation [26]

\[
q_0 d_i = 7.7 \tag{4.2}
\]

It seems to be empirically valid within \( \sim 5\% \) [27, 1], also for the positions of the main peaks in \( g(r) \) and \( S(q) \) of the alloys described in this thesis and of e.g. liquid Cs.

The IRO in the liquid can be thought of as spheres of volume \( 1/6 \pi d_i^3 \) that are positioned on an FCC lattice, as this best represents the isotropy of the liquid. The volume available to the sphere is:

\[
\Omega_{\text{cell}} = \frac{\frac{1}{6} \pi d_i^3}{P_{\text{FCC}}} = \frac{\frac{1}{6} \pi d_i^3}{\frac{1}{6} \pi \sqrt{2}} = \frac{d_i^3}{\sqrt{2}} \tag{4.3}
\]

where \( P_{\text{FCC}} \) is the packing fraction of a close packed FCC ordering of spheres. In analogy to the name "periodic distance" for \( d_i \) we will sometimes denote \( \Omega_{\text{cell}} \) as a "periodic volume". Equation 4.3 can also be used to estimate the periodic distance \( d_e \) between the clusters in the solid, as it would be when the clusters were positioned on an FCC lattice. In that case \( \Omega_{\text{cell}} \) is taken equal to the average volume available to a cluster in the crystal structure.

Using equation 4.2 we find:

\[
\Omega_{\text{cell}} = \frac{1}{\sqrt{2}} \left( \frac{7.7}{q_0} \right)^3 \tag{4.4}
\]

The number of atoms \( N \) in this \( \Omega_{\text{cell}} \) can be found using the number density \( \rho_0 \) of the alloy:

\[
N = N_A + N_B + N_M = \rho_0 \frac{1}{\sqrt{2}} \left( \frac{7.7}{q_0} \right)^3 \tag{4.5}
\]

Here \( N \) is divided into the number of alkali atoms \( (N_A) \), the number of polyvalent atoms \( (N_B, \) where in this case B denote Tl atoms) and, if applicable, the number of third elements \( (N_M) \), according to the composition of the alloy.

This very simple model depends on the validity of the rules \( q_0 d_i = 7.7 \) [26, 27] and \( \Omega_{\text{cell}} = d_i^3/\sqrt{2} \) [1]. Apart from a possible systematical error induced in this way, we have to consider the accuracy with which the value \( N \) can be obtained. The error in \( q_0 \) is estimated to be \( \sim 1\% \) and the error in the density of a liquid alloy we guess is \( \sim 5\% \). The estimated error in \( N \) therefore is \( \sim 8\% \). The calculated values for \( N, N_A, N_B \) and \( N_M \), are summarized for several different alloys in table 7.1.
4.6.1 KTI and $K^{205}Tl$

The position of the prepeak in KTI is $q_0 = 8.0$ nm$^{-1}$ and, according to equation 4.5, there are $N = 14.5$ atoms in $\Omega_{\text{cell}}$, with an error of about 8%. The periodic volume contains on average $\sim 7.3$ Tl and $\sim 7.3$ K atoms, which indicates the Tl-clusters are on average larger than the Tl$_6$ clusters in solid KTI and smaller than the Tl$_{11}$ clusters in solid K$_8$Tl$_{11}$. This also follows from the fact that the periodicity in the liquid obtained by using equation 4.2 is $d_l = 0.96$ nm, in comparison to the average distances between the clusters in solid K$_8$Tl$_{11}$ and KTI (calculated by using equation 4.3) which are 1.01 and 0.87 nm respectively.

The Tl-clusters can not exist without the alkali atoms that surround them, because they provide the electrons for the bonds in the cluster and shield the negative cluster-charge. The Tl-cluster including the alkali atoms will be called a cluster-unit. The cluster-units in solid KTI can be written formally as $(K^{-1})_6Tl_6^6$ but will in the following often be denoted by K$_6$Tl$_6$. Likewise the cluster-unit in solid K$_8$Tl$_{11}$ is denoted as K$_7$Tl$_{11}$ (because the oxidation state of the Tl$_{11}$ cluster is -7, see section 2.4.1).

The partials of KTI are relatively well-defined by the isotopic data in combination with RMC modelling and we may have a look at the short range ordering of the liquid alloy. The Tl-Tl coordination number was found to be 3.95 which is very close to 4, the value we expect in a classical covalent bonded Zintl-phase (see section 2.3). In Tl$_6$ clusters the coordination number is also 4 and in Tl$_{11}$ clusters 3.82, in these cases there is delocalized (but closed-shell) bonding.

Strong evidence for the presence of covalent bonding in the liquid alloy is given by the short Tl-Tl nearest neighbour distance of 0.315 nm (see figure 4.17) which is nearly equal to the average Tl-Tl distances found in Tl$_6$ and Tl$_{11}$ clusters of 0.318 and 0.314 nm respectively. The bond-angle distribution shows a maximum near 60°, which is, however, not unusual because all relatively closed-packed systems show many of these bond-angles. Perhaps the dip near 90° excludes the presence of many Tl$_6$ clusters (like they occur in solid KTI), because they contain several right angles in addition to angles near 60°. The Tl$_{11}$ clusters have bond-angles near 60° and near 110°. In figure 4.32 the bond-angle distributions in the solid phases and in the liquid phase of KTI are compared.
Figure 4.32: The Tl-Tl-Tl bond-angle distribution of liquid KTL compared to that of the Tl$_6$ clusters in solid KTL (upper graph) and the Tl$_{11}$ clusters in solid K$_8$Tl$_{11}$ (lower graph). The absolute height of the vertical bars is chosen arbitrarily.
4.6.2 K-Tl with additional third elements

In table 4.4 the average inter-cluster distances in the crystal ($d_s$) and the periodic distance in the liquid ($d_l$) are given for the K-Tl alloys with additional third elements. For comparison KTI and K₈Tl₁₁ are included. In addition, the height of the prepeak is given in this table, which gives an indication to the stability of the IRO.

The value of $d_s$ marked with * is obtained from $K_{10}I_{10}Pd$ instead of the isomorphous alloy $K_{10}Tl_{10}Pd$. The existence of $K_{10}Tl_{10}Pd$ is known [41], however crystal structure data are not yet available. It is known that the atomic distances in In and Tl phases are almost equal, e.g. the calculated $d_s$ for $K_8I_{10}Zn$ and $K_8Tl_{10}Zn$ are 1.014 and 1.012 respectively.

<table>
<thead>
<tr>
<th>alloy</th>
<th>cluster-type</th>
<th>$d_s$ (nm)</th>
<th>$d_l$ (nm)</th>
<th>height prepeak</th>
</tr>
</thead>
<tbody>
<tr>
<td>KTI</td>
<td>Tl₆⁻⁶</td>
<td>0.87</td>
<td>0.96</td>
<td>0.765</td>
</tr>
<tr>
<td>$K_{96}Tl_{97}Pd_2$</td>
<td>-</td>
<td>1.01</td>
<td>0.96</td>
<td>0.775</td>
</tr>
<tr>
<td>$K_{10}Tl_{10}Pd$</td>
<td>PdTl₁₀⁻¹⁰</td>
<td>1.05*</td>
<td>1.07</td>
<td>0.877</td>
</tr>
<tr>
<td>$K_8Tl_{11}$</td>
<td>Tl₁₁⁻⁷</td>
<td>1.01</td>
<td>0.96</td>
<td>0.746</td>
</tr>
<tr>
<td>$K_8Tl_{10}Zn$</td>
<td>ZnTl₁₀⁻⁸</td>
<td>1.01</td>
<td>0.96</td>
<td>0.775</td>
</tr>
<tr>
<td>$K_{18}Tl_{20}Au_3$</td>
<td>Au₂Tl₃⁻⁹</td>
<td>0.96</td>
<td>0.96</td>
<td>0.641</td>
</tr>
</tbody>
</table>

Table 4.4: Comparison of the inter-cluster distances in the crystals ($d_s$) and in the liquid ($d_l$). These values are calculated using formulas 4.3 and 4.2 respectively. The height of the prepeak is the absolute value of the maximum in $S(q)$. The value of $d_s$ marked with a * is based on the isomorphous alloy with In instead of Tl.

The position of the prepeak for $K_{96}Tl_{97}Pd_2$ indicates average cluster sizes that lie in between those in KTI and $K_{10}Tl_{10}Pd$, although the difference in prepeak position between KTI and $K_{96}Tl_{97}Pd_2$ is remarkably large given the addition of only 1% Pd. The prepeak position of KTI with 0%, 1% and 5% Pd shifts to lower $q$ values (8.0, 7.6 and 7.2 nm⁻¹ respectively) and the height of the prepeak increases down this series (see table 4.4). These are indications that Pd stabilizes the clusters. This shows a strong analogy to the solid crystal structure of $K_{10}Tl_{10}Pd$ where Tl₁₀⁻¹⁰ clusters are stabilized because of the centering with Pd (see section 2.4.2).

We expected similar behaviour for the alloy with Zn. However there is no change in prepeak position between $K_8Tl_{11}$ and that of $K_8Tl_{10}Zn$. There is only a slight increase in the height of the prepeak with respect to $K_8Tl_{11}$, but by far not as drastic as in the case of $K_{10}Tl_{10}Pd$. We do not have an explanation for this difference.

For the alloy $K_{18}Tl_{20}Au_3$ we see that the prepeak position also does
not change with respect to KTL or K₈Tl₁₁. The decrease in height of the prepeak indicates the clusters in the liquid become less stable in the presence of Au. The crystallographic data of solid K₁₈Tl₂₀Au₃ (see section 2.4.2) shows there is a short Au-Au bond present (0.296 nm) in Au₉Tl₉⁻⁹ that deforms the cluster. It might make the clusters less stable.

The number of atoms in the periodic volumes Ω_{cell} can be calculated using the prepeak position and the density, according to equation 4.5. The results are summarized in table 4.5. The most striking result in this table is the good agreement of the number of atoms in Ω_{cell}, N ≈ 20, in liquid K₁₀Tl₁₀Pd with that of the solid cluster-units (K⁻¹)₁₀PdTl₁₀⁻¹⁰. Furthermore, it can be seen that K₉₆Tl₉₇Pd₂ is not just 20% K₁₀Tl₁₀Pd cluster-units swimming around in liquid KTL. The average cluster size increases in a non-linear way: 15% upon addition of 1% Pd and 37% upon addition of 5% Pd.

### Table 4.5: The number of atoms N present in a periodic cell Ω_{cell} calculated using equation 4.5. N_A is the number of alkali atoms, N_B the number of Tl atoms and N_M the number of third elements in Ω_{cell}. The inaccuracy of q₀, ρ₀ and N_i is estimated to be ~1%, ~5% and ~8%, respectively.

<table>
<thead>
<tr>
<th>sample</th>
<th>q₀ (nm⁻¹)</th>
<th>ρ₀ (nm⁻³)</th>
<th>N</th>
<th>N_A</th>
<th>N_B</th>
<th>N_M</th>
</tr>
</thead>
<tbody>
<tr>
<td>KTL</td>
<td>8.0</td>
<td>23.0</td>
<td>14.5</td>
<td>7.3</td>
<td>7.3</td>
<td>-</td>
</tr>
<tr>
<td>K₉₆Tl₉₇Pd₂</td>
<td>7.6</td>
<td>23.0</td>
<td>16.9</td>
<td>8.4</td>
<td>8.4</td>
<td>0.2</td>
</tr>
<tr>
<td>K₁₀Tl₁₀Pd</td>
<td>7.2</td>
<td>23.0</td>
<td>19.9</td>
<td>9.5</td>
<td>9.5</td>
<td>1.0</td>
</tr>
<tr>
<td>K₈Tl₁₁</td>
<td>8.0</td>
<td>23.6</td>
<td>14.9</td>
<td>6.3</td>
<td>8.6</td>
<td>-</td>
</tr>
<tr>
<td>K₈Tl₁₀Zn</td>
<td>8.0</td>
<td>23.6</td>
<td>14.9</td>
<td>6.3</td>
<td>7.8</td>
<td>0.8</td>
</tr>
<tr>
<td>K₁₈Tl₂₀Au₃</td>
<td>8.0</td>
<td>24.0</td>
<td>15.1</td>
<td>6.6</td>
<td>7.4</td>
<td>1.1</td>
</tr>
</tbody>
</table>

4.6.3 Cs-Tl

The measurements on Cs-Tl show a gradual decrease of the prepeak position with increasing Tl content. The values of the prepeak position are included in table 4.6. In analogy to solid K-Tl alloys, the structures of the binary phases Cs₈Tl₁₁ [36] and CsTl [39] are known, which contain Tl₁⁻⁷ and Tl₆⁻⁶ clusters as well. Also Cs₁₃Tl₂₇ [83] is known, which is built out of Tl₁₁⁻⁷ clusters. The prepeak of equiatomic CsTl is positioned at 7.4 nm⁻¹ which is at a lower value than that of KTL (8.0 nm⁻¹) because the Cs atoms that separate the Tl-clusters are larger. As a result of this the clusters are expected to be more stable (see Geertma's rule in section 1.8). The prepeak in CsTl is clearly higher than in KTL, which we think is due to this higher cluster
stability. The corresponding periodicity in the liquid obtained by using equation 4.2 is $d_l = 1.04$ nm for CsTl and $d_l = 1.06$ nm for Cs$_8$Tl$_{11}$. The average distances between the clusters in solid CsTl and Cs$_8$Tl$_{11}$ are 0.93 and 1.07 nm respectively.

<table>
<thead>
<tr>
<th>sample</th>
<th>$q_0$ (nm$^{-1}$)</th>
<th>$\rho_0$ (nm$^{-3}$)</th>
<th>$N$</th>
<th>$N_A$</th>
<th>$N_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsTl</td>
<td>7.4</td>
<td>17.5</td>
<td>13.9</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Cs$<em>8$Tl$</em>{11}$</td>
<td>7.3</td>
<td>18.5</td>
<td>15.4</td>
<td>6.5</td>
<td>8.9</td>
</tr>
<tr>
<td>CsTl$_2$</td>
<td>7.0</td>
<td>21.0</td>
<td>19.8</td>
<td>6.6</td>
<td>13.2</td>
</tr>
<tr>
<td>CsTl$_3$</td>
<td>6.6</td>
<td>23.0</td>
<td>25.8</td>
<td>6.5</td>
<td>19.4</td>
</tr>
<tr>
<td>Cs$<em>{15}$Tl$</em>{85}$</td>
<td>6.2</td>
<td>26.0</td>
<td>35.2</td>
<td>5.3</td>
<td>29.9</td>
</tr>
</tbody>
</table>

Table 4.6: The number of atoms $N$ present in a periodic cell $\Omega_{cell}$ calculated using equation 4.5. $N_A$ is the number of alkali atoms and $N_B$ the number of Tl atoms in $\Omega_{cell}$. The inaccuracy of $q_0$, $\rho_0$ and $N_i$ is estimated to be $\sim 1\%$, $\sim 5\%$ and $\sim 8\%$, respectively.

In table 4.6 it can be seen that the number of atoms present in $\Omega_{cell}$ (calculated using equation 4.5) increases with increasing Tl fraction to $\sim 35$ atoms for Cs$_{15}$Tl$_{85}$, of which $\sim 30$ atoms are Tl atoms. It is doubtful that clusters as large as Tl$_{30}$ occur in the liquid. A possible explanation is that the separation between the clusters increases, not the cluster-size. This "swimming-cluster model" was proposed in [77]. Assuming that only one type of cluster-units, like e.g. Cs$_7$Tl$_{11}$ or Cs$_8$Tl$_6$, occur in all compositions the increase in inter-cluster distances can qualitatively be described by the excess of Tl atoms that surrounds these units.

A strong indication that this may indeed be the case, follows from the fact that the number of Cs atoms in $\Omega_{cell}$, $N_A$, varies remarkably little over the composition range. Only for Cs$_{15}$Tl$_{85}$, $N_A$ starts to deviate significantly. There is no reason for this number to be constant, unless there is one preferred type of cluster-unit that specifically needs $N_A$ Cs atoms. In solid Zintl-phases the number of alkali atoms in a cluster-unit bears a direct relationship to the formal charge (i.e. the oxidation state) of the Tl-cluster, as they provide electrons for the bonds in the cluster. The fact that the number of Cs atoms in $\Omega_{cell}$ is constant over a significant composition range would indicate the existence of a valence rule in the liquid alloys, associated with rather well defined cluster units.

In this view the number of Cs atoms is the limiting factor in the number of clusters that occur, the cluster-size, however, is independent of the Cs fraction. The left-over Tl atoms surround the cluster-unit (e.g. Cs$_8$Tl$_6$) as a sort of third layer which makes $d_l$ larger. This picture is confirmed by the
results displayed in figure 4.29, where the height of the prepeak in $A_{\text{Tl},\text{Tl}}(q)$ was plotted as a function of composition. The height of the prepeak, which is an indication for the number of clusters in the alloy, increases more or less linearly with $c_{\text{Cs}}/c_{\text{Tl}}$.

Interestingly enough the values of $N_A$ calculated for CsTl and Cs$_8$Tl$_{11}$ (7.0 and 6.5 respectively) are close to those obtained for KTI and K$_8$Tl$_{11}$ (7.3 and 6.3 respectively, see table 4.5), even though the density and prepeak position of Cs-Tl and K-Tl differ considerably. This indicates the cluster-units present in liquid K-Tl and Cs-Tl are alike, and it confirms the idea that there is a valence rule that governs the IRO in these liquid alloys.

The absolute values of $N_i$ depend of course on the rules of thumb $q_0 d_i = 7.7$ and $\Omega_{\text{cell}} = d_i^3/\sqrt{2}$, as was already mentioned in section 4.6. The relative variation of $N_i$ between different alloys is perhaps more meaningful, although one has to be aware of the large errors that originate from errors in the densities and the error in the position of the prepeak (see table 4.6).

A speculation will be made on the type of clusters that occur in the liquid alkali-Tl alloys. To do this we assume that there is indeed a direct relation between $N_A$ and the oxidation state of the cluster. Furthermore we assume that the absolute value of $N_i$ is reliable within an error of $\sim 10\%$.

The nearly constant value of $N_A$ in a large part of the composition range implies that one type of cluster-unit is dominantly present. The oxidation state of the Tl-cluster could be -6 or -7 according to the calculated number of alkali atoms, $N_A$, present in $\Omega_{\text{cell}}$ and the estimated error of $\sim 10\%$. Of these clusters only Tl$_{11}^{-7}$, Tl$_5^{-7}$ and Tl$_6^{-6}$ exist in solid phases of alkali-Tl. Tl$_{11}^{-7}$ is clearly too large as $N = 11 + 7 = 18$ and not $\sim 14$ as is the case for KTI and CsTl. The clusters Tl$_5^{-7}$ and Tl$_6^{-6}$ are possible candidates. Although a Cs$_8$Tl$_6$ cluster-unit is a little bit small to account for $d_i$ in the liquid, it could be a solution given the possible errors in the calculations. However, the right angles that occur in a Tl$_6^{-6}$ cluster were not reproduced in the RMC model of KTI or that of CsTl. Tl$_5^{-7}$ is a cluster with its electron count conforming to the Wade rules (see section 2.3). It is therefore probably a stable cluster that, surrounded by 7 alkali atoms, may survive in the liquid phase. In this case two Tl-atoms are left in $\Omega_{\text{cell}}$ which are not clustered.

In this speculation the possibility of the existence of clusters in the liquid phase that do not occur in the solid, was ruled out. There might however be cluster-units that are electronically stable but do not fit in a periodic crystal lattice. Given the results of the above calculations a Tl$_7^{-7}$ cluster for example could explain our experimental results as well. Unfortunately there are no data available on the electronic stability of such a cluster.
4.7 Conclusions

In this chapter neutron diffraction measurements are described taken from several liquid alkali-Tl alloys. The purpose of these measurements was to investigate the intermediate and short range order (IRO and SRO) in these alloys. The following alloys were measured:

1. KTL and K\textsuperscript{205}Tl at 360 °C [72] and 660 °C.

2. KTL, K\textsubscript{90}Tl\textsubscript{97}Pd\textsubscript{2}, K\textsubscript{10}Tl\textsubscript{10}Pd, K\textsubscript{6}Tl\textsubscript{11}, K\textsubscript{8}Tl\textsubscript{10}Zn and K\textsubscript{18}Tl\textsubscript{20}Au\textsubscript{3} [74, 75, 76].

3. CsTl, Cs\textsubscript{3}Tl\textsubscript{11}, CsTl\textsubscript{2}, CsTl\textsubscript{3} and Cs\textsubscript{3}Tl\textsubscript{17} [77].

From the isotopic measurements we could directly observe the following. The prepeak in KTL is exclusively present in \( A_{\text{Tl-Tl}}(q) \), which indicates that Tl-Tl correlations produce the, for a liquid, long-ranged periodicity of 0.96 nm in liquid KTL. We assume this is also the case for the other alkali-Tl and Cs-Tl alloys measured. The measurements of KTL at 660 °C show that the prepeak decreases in height and increases in width. It is a sign that the IRO starts breaking down at higher temperature, but it is still fairly stable.

The position and/or height of the prepeak is influenced by the addition of third elements like Pd, Zn and Au. The prepeak in the structure factors of KTL + 0%, 1%, and 5% Pd shifts from 8.0 to 7.2 nm\textsuperscript{-1} with increasing Pd content. Also the height of the prepeak increases (~ 14%) which indicates a stronger ordering and more stable clusters. The alloy with Zn shows only a slight increase in prepeak height (~ 4%) and in the alloy with Au a significant decrease of ~ 19% occurs. The addition of Au to KTL clearly makes the clusters less stable.

The most significant feature in the series of the Cs-Tl data is the gradual shift of the prepeak position towards smaller \( q \) values with increasing Tl content (from 7.4 to 6.2 nm\textsuperscript{-1}). This means the periodicity in real space increased from 1.04 to 1.24 nm. The prepeak in CsTl is much higher than in KTL which, in accordance with Geertsma’s rule, indicates that the clusters in CsTl are more stable.

We have analyzed these phenomena by looking at the SRO via RMC modelling and at the IRO via an evaluation of the position and size of the prepeak.

Reverse Monte Carlo modelling

As we are in the possession of several data sets of KTL including isotopic data, we used this opportunity to test the results of RMC modelling [78].
4.7 Conclusions

The following observations were made:

1. RMC does not give different results for our data sets measured on SLAD and D4 even though the accuracy of the measurement on D4 is about a factor 10 better.

2. RMC cannot be used to obtain the partial structure factors from one single measurement of KTl.

3. The results of RMC modelling on both KTl and K\textsuperscript{\textit{205}}Tl measurements depend on the way the fit is obtained.

One major problem, of course, is that the partials are not uniquely defined by one structure factor. Another problem appeared to be the tendency of RMC to find the most random configuration (i.e. the one with highest configurational entropy). RMC cannot, without help, reach the higher ordered, but better fitting configurations.

Due to the isotopic information the SRO of KTl is relatively well-defined. The best fitting configuration we could find for KTl and K\textsuperscript{\textit{205}}Tl provided us with partial pair correlation functions that differed quite a lot from the ones we found when modelling on KTl only. A sharp peak in $g_{\text{Tl, Tl}}(r)$ occurs with a maximum at 0.315 nm, indicating a short average Tl-Tl distance nearly equal to the distances found in the clusters of the solid phases KTl and K\textsubscript{8}Tl\textsubscript{11} (0.318 and 0.314 respectively). This provides strong evidence for the occurrence of covalent bonding in the liquid alloy. The Tl-Tl coordination number is 3.95 which is very close to 4, the value which we would expect if the alloy was a classical covalent-bonded Zintl-phase. In solid KTl and K\textsubscript{8}Tl\textsubscript{11} the coordination numbers are 4 and 3.82 respectively.

Because we observed that RMC can not be used to obtain reliable structural information from only one structure factor, we used extra constraints to test certain structures for K\textsubscript{10}Tl\textsubscript{10}Pd\textsuperscript{[75]}. We applied constraints such that only Pd-centered Tl\textsubscript{6} clusters were present or only Pd-centered Tl\textsubscript{10} clusters. These configurations both gave good fits to the data. From this we can conclude that the idea of Tl clusters in the liquid alloy, of a size between 6 and 10 Tl atoms, is not unlikely. We can not conclude anything for the position of Pd in these clusters as the weight of the Pd-partial is too small. This information can perhaps be obtained through Pd-EXAFS measurements.

We have also used RMC to analyze the Cs-Tl measurements. Cs atoms are larger than Tl atoms and by applying the expected cut-off distances the number of configurations that fit the data is strongly restricted.
This is an advantage over the KTI case where the minimum distance between the different elements is very similar. Like in the case of KTI, CsTl has a peak in $g_{\text{Tl,Tl}}(r)$ at 0.315 nm. The coordination number however is 3.65 which is less than 3.95 for KTI. The prepeak is in all Cs-Tl measurements only present in $A_{\text{Tl,Tl}}(q)$. The height of the prepeak in this partial as a function of $c_{\text{Cs}}/c_{\text{Tl}}$ is more or less linear. It shows that the number of clustered Tl atoms increases linearly with the number of Cs atoms that is available per Tl atom.

**Temperature and pressure dependence**

The coordination number for KTI measured at 660 °C is 3.85, which is still relatively high given the decrease in density from 23 nm$^{-3}$ at 360 °C to 21 nm$^{-3}$ at 660 °C. Also the first peak in $g_{\text{Tl,Tl}}(r)$ remains sharp and peaks at 0.315 nm. We therefore conclude that the Tl-Tl SRO is not effected by the higher temperature. This in contrast to the IRO which clearly decreases as could be derived from the lowering and broadening of the prepeak. Similar effects were seen in a measurement of CsTl at 600 °C. The results are similar to those of [86] on the temperature and pressure dependence of the structure factor of CsTl, or of [85] on the temperature dependence of the structure in Kpb.

We also made a measurement of Cs$_8$Tl$_{11}$ at 354 bar and 450 °C, which shows no differences with respect to the measurement at normal pressure.

**Analogies to solid phases**

In many cases analogies exist between the structure in the liquid alloys and their solid counterparts. We have seen this analogy in the SRO of KTI for example in the coordination number and in the average Tl-Tl distances. The IRO also provide strong analogies to the solid phases when we look at e.g. the distances between the clusters and compare these to the periodicity in the liquid. The analogy to the solid was further investigated with the use of the available crystal chemical information.

We have used a model to represent the IRO. Using the density of the alloy and the prepeak position we can estimate the number of atoms $N$ that are present in a periodic volume, $\Omega_{\text{cell}}$. In chapter 7 all results are summarized in a table.

For KTI the periodic volume, $\Omega_{\text{cell}}$, contains 7.3 Tl and 7.3 K atoms, and for CsTl 7.0 Cs and Tl atoms respectively. These values are the same within the
estimated error of $\sim 8\%$. This shows that the difference in prepeak position between KTL and CsTl is only due to a different density of the alloy, not to different cluster sizes. The crystal structures of KTL and $K_8Tl_{11}$ contain $K_6Tl_6$ and $K_7Tl_{11}$ cluster-units respectively, and similar units also occur in the solid CsTl and $Cs_8Tl_{11}$ alloys. It seems however that the cluster-units in the liquid ATl alloys are a little larger than $A_6Tl_6$ but definitely smaller than $A_7Tl_{11}$.

The alloy $K_{10}Tl_{10}Pd$ shows an increase in periodic volume of 37% relative to KTL; it contains 9.5 Tl atoms, 9.5 K atoms and 1 Pd atom. This is very similar to the $K_{10}Tl_{10}Pd$ unit that occurs in the solid alloy. Perhaps this similarity is somewhat fortuitous given the very simple model that is used. In crystal chemistry it is known that the centering of the Tl$_{10}^{10}$ cluster with Pd makes this cluster more stable by providing central bonding. Because the height of the prepeak increases with increasing Pd content, we see that also in the liquid the clusters gain stability. This is one example where there is a strong analogy between the structure in the liquid and that in the solid phase.

For $K_8Tl_{10}Zn$ the relation is less obvious. The number of atoms in $\Omega_{cell}$ is the same as in $K_8Tl_{11}$ and there is only a slight increase in prepeak-height visible. Also the prepeak position of $K_{18}Tl_{20}Au_3$ is the same as that of $K_8Tl_{11}$. In this case however the height of the prepeak decreases significantly. This can perhaps be explained via a relation to the solid. In solid $K_{18}Tl_{20}Au_3 Tl_{11}$ clusters occur and $Tl_9Au_2$ clusters. The last contain 2 Au atoms that replace 2 Tl atoms. The bond between the Au atoms is very short and deforms the cluster, it therefore might make it less stable.

The analysis of the IRO in the Cs-Tl data shows that the periodic volume increases in size from $\sim 14$ atoms for CsTl to $\sim 35$ atoms for the Tl richest alloy. It was noticed however that the number of Cs atoms, $N_A$, in $\Omega_{cell}$ remained remarkably constant for all compositions ($N_A \approx 7$), only for Cs$_{15}$Tl$_{85}$ this number starts to deviate significantly ($N_A \approx 5$). To explain the results the "swimming-cluster model" is used [77]. In this model one type of cluster-unit, like e.g. Cs$_6Tl_6$ or Cs$_7Tl_{11}$, swims around in the excess Tl atoms in the alloy. We might picture the excess Tl in a sort of shell around the cluster-units. (Perhaps in analogy to the alloy Na$_{96}$In$_{97}$Pd$_2$ which also contains a layered structure around a central cluster-unit.) The fact that $N_A$ is constant over a large composition range would indicate that even in the liquid alloy a valence rule is obeyed, because the number of Cs atoms in $\Omega_{cell}$ is directly related to the number of valence electrons that can be used for bonds in the Tl-cluster.

There are indications that the same type of cluster-units exists in liquid KTL, CsTl, Cs$_8Tl_{11}$, CsTl$_2$ and CsTl$_3$. There is a considerable inaccuracy in the
number of atoms in the cluster-units ($N_i$) and we have to be aware of a systematic error that is induced in the, very likely oversimplified, model of the IRO. It is therefore difficult to conclude on the exact type of cluster-units that 'swim' around in the liquid K-Tl and Cs-Tl alloys. When we rely on this oversimplified model and assume that the absolute value of $N_i$ is reliable within 10% we can speculate about the cluster-types.

The oxidation state of the $\text{Tl}_n$ cluster is -6 or -7 according to the calculated number $N_A$. Of these clusters only $\text{Tl}_{11}^{-7}$, $\text{Tl}_{15}^{-7}$ and $\text{Tl}_{5}^{-6}$ exist in solid alkali-Tl phases. The $\text{Tl}_{11}^{-7}$ is too large to fit in $\Omega_{\text{cell}}$, and $\text{Tl}_{5}^{-6}$ perhaps a little too small although it would be possible given the errors. An argument against $\text{Tl}_{5}^{-6}$ is that no indications for the existence of 90° angles are found in the results of RMC modelling, which do occur in the solid phase. $\text{Tl}_{15}^{-7}$ is a cluster with its electron count conforming the Wade-rules [47], and given the size (including the 7 alkali atoms) it is a possible choice. An argument against the latter is that the stoichiometry is not at 50%, which we expect because resistivity measurements clearly indicate this (see figure 4.1). Of course, we can not rule out the possibility that clusters occur which do not exist in the solid phases. Given the above calculation e.g. $\text{Tl}_{7}^{-7}$ clusters would explain our experimental results best.

This $\Omega_{\text{cell}}$ model will be more generally discussed in the final chapter of this thesis.
Chapter 5

Alkali-gallium alloys

In this chapter neutron diffraction measurements on liquid alkali-Ga alloys are described. The preparation of the samples, the experiment and the data analysis will be discussed. For a further analysis of the structure we use RMC modelling and a comparison to the solid crystal structures (c.f. section 2.4.3) will be made. In chapter 3 the general data-analysis procedure and the RMC method were already presented.

5.1 Introduction

Alkali-Ga systems are difficult to investigate experimentally because liquid alkali metals as well as liquid gallium are very reactive with many common metals. Reaction crucibles have to be manufactured of refractory metals (like tantalum, niobium or molybdenum) and even then slight corrosion can generally not be avoided. Corrosion complicates the determination of the liquid-solid phase equilibrium, which is reflected in the differences between the various phase diagrams that have been published over the years. Evaporation may offer serious experimental problems as well. In figures 5.1, 5.2 and 5.3 the most recent phase diagrams of Na-Ga [87], K-Ga [88] and Cs-Ga [17] respectively are shown.

The Na-Ga phase diagram shows a relatively flat liquidus in a considerable part of the concentration range. This indicates large concentration fluctuations (high \( S_{CC}(0) \), see equation 3.30) and therefore a tendency to phase separation [16]. In the K-Ga phase diagram we observe a zone of liquid immiscibility at high temperature. The indications for this, however, are not very strong and in disagreement with resistivity measurements which do not display any anomalies as a function of composition [89] (see figure 5.4). However, the possibility that some of the resistivity measurements of the
Figure 5.1: Phase diagram of Na-Ga. Reprinted from [87] with permission from Elsevier Science.

K-Ga system pertain to a phase-separating area can not completely be ruled out. Liquid immiscibility is certainly present in the alloys with heavier alkali metals, Rb-Ga [90] and Cs-Ga (see figure 5.3) above 621 °C.

The resistivity measurements of the liquid K-Ga [89] system are shown in figure 5.4, as well as the measurements for the Li-Ga [91] and the Na-Ga [87] systems. The resistivities of Rb-Ga and Cs-Ga have not been measured. The resistivities of Ga and Tl alloys for a given alkali metal are rather similar (compare figures 5.4 and 4.1). A distinct difference however is that the resistivity of K-Ga peaks at 45% Ga and not at 50% as is the case for K-Tl, Rb-Tl and Cs-Tl.

Neutron diffraction measurements have been made only for the liquid Li-Ga system [92]. In the structure factor there is a prepeak visible that is almost as high and as broad as the main peak and is positioned at wavevector $q_0 = 15.7$ nm$^{-1}$. It was ascribed to the persistence of elements of the crystal structure (isostructural to NaTl with a double diamond structure, B32) and is also in agreement with computer simulations on this system [93].

Other liquid alkali-Ga systems have not been investigated yet by
Figure 5.2: Phase diagram of K-Ga. Reprinted from [88] with permission from Elsevier Science.

means of neutron diffraction. Not because of lack of interest; the structures found in the solid phases are very fascinating and strong intermediate range ordering in the liquid alloys can be anticipated. The expected experimental difficulties (like high corrosiveness and high evaporation), however, do not make this the first choice of systems to be investigated.

It is interesting to compare the structures of liquid alkali-Tl and alkali-Ga. The solid phases both contain clusters, but in alkali-Tl the clusters are isolated in contrast to alkali-Ga where they are generally interlinked into a three-dimensional network. We measured the structure factors of liquid NaGa, KGa$_3$ and CsGa$_3$. It indeed presented us with some experimental difficulties, which will be described in the following sections.

Originally, we did not intend to measure a Cs-Ga alloy. During sample preparation a mistake was made, as we intended to prepare a CsBi sample and mistook gallium for bismuth. The result was a Cs-Ga sample of almost equiatomic composition. As we see in figure 5.3, liquid CsGa separates into liquid CsGa$_3$ and liquid Cs. We decided to measure the sample anyway, because we can obtain information on the structure of liquid CsGa$_3$. 
Figure 5.3: Phase diagram of Cs-Ga. Reprinted from [17] with permission from ASM International.

5.2 Sample preparation

The samples were prepared in an argon-filled glovebox with O$_2$ and H$_2$O levels that are typically lower than 1 ppm. The following metals were used:

- Na: rod (under paraffin) 99.93%, Merck (Darmstadt, Germany).
- K: vial 99.95%, Aldrich (Steinheim, Germany).
- Cs: vial 99.98%, Cabot (Revere, USA).
- Ga: ingots 99.999%, Alfa (Karlsruhe, Germany).

Ti$_{0.68}$Zr$_{0.32}$ was used as a container material. Ti and Zr have a good resistance against liquid Ga at low temperatures, but a limited to poor resistance to liquid Ga at higher temperatures [94]. The measurements on Li-Ga [92], however, were also made in Ti-Zr containers and no signs of corrosion were observed. It could well be that alkali-Ga mixtures are less corrosive than pure liquid Ga, however there are no data available on this. We have tried to do a corrosion test by heating a mixture of K and Ga in a quartz tube together with a thin piece of Ti-Zr, but due to high evaporation we had to abandon
Figure 5.4: The electrical resistivities of liquid alkali-Ga alloys as a function of composition for temperatures close to the liquidus.
this experiment. Other container materials are optional. Quartz, for example, can be used, however it involves a risk because it can easily break when the liquid alloy solidifies (Ga expands when it freezes). Containers of materials like tungsten, niobium or molybdenum would be a better choice. The disadvantage of these materials, apart from the Bragg-peaks they produce, is that they are difficult to machine. Preparing and closing the containers would require welding with a laser or electron-beam, and this will cost a lot of time and money because this can only be done by specialized companies. Relying on the positive results in the experiment on Li-Ga in Ti-Zr containers [92] we used this container material for NaGa, KGa$_3$ and Cs-Ga as well.

During the sample preparation the alkali metals K and Cs were treated in the same way as described in section 4.2. The sodium we used was contained under paraffin oil and had to be cleaned outside the glovebox with petroleum. Na oxidizes very fast in air and was put in the glovebox immediately after cleaning. The white oxide layer can easily be skimmed of the surface after the metal has melted (melting point 98 °C). It can be transferred most easily in the liquid state, using a pipette. Ga only very slightly oxidizes in air. It melts at 30 °C and it was put in a wide pyrex beaker in order to prevent the glass from breaking when Ga solidifies.

The samples were prepared by adding the appropriate amounts of metal in the Ti-Zr containers. They were closed and then heated up very slowly, especially around the melting point of the alkali metal. This method worked for NaGa and Cs-Ga, not for KGa$_3$. The latter reacted in such a fierce way that the container cracked. Therefore we made an other sample in a different way. We transferred K and Ga in a pyrex beaker and when the K started to melt a highly exothermic reaction took place (with 'flames' in all colours). A dark-gray powder had formed of which the volume was about three times as large as before. The container was filled with this powder which seemed to be a homogeneous mixture. In this way we could not get much of the sample in the container and the diffraction data have to be corrected for that.

In table 5.1 the exact compositions of the samples are given. As mentioned in the introduction of this chapter, we did not intend to make a Cs-Ga alloy, as we mistook Ga for Bi. From the analyzed data of Cs-Ga, which according to the phase diagram (see figure 5.3) is phase separated into CsGa$_3$ and Cs, we will subtract an appropriate fraction of the structure factor of liquid Cs. In this way we obtain the structure factor of CsGa$_3$.

The Ti-Zr containers used were of type II and are described in section 3.3.1. All samples were heated up to 650 °C to test if the containers were leak tight. The samples were cooled in horizontal position, in order to
avoid damage to the containers due to expansion of the samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>type</th>
<th>(m_c) (g)</th>
<th>(m_A) (g)</th>
<th>composition, in at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaGa</td>
<td>II</td>
<td>4.023</td>
<td>1.327</td>
<td>Na(<em>{49.99})Ga(</em>{50.01})</td>
</tr>
<tr>
<td>KGa(_3) *</td>
<td>II</td>
<td>total: 4.487</td>
<td></td>
<td>K(<em>{25})Ga(</em>{75})</td>
</tr>
<tr>
<td>Cs-Ga</td>
<td>II</td>
<td>1.733</td>
<td>3.849</td>
<td>Cs(<em>{53.84})Ga(</em>{46.19})</td>
</tr>
</tbody>
</table>

Table 5.1: The compositions of the alkali-Ga samples. Here \(m_i\) is the mass of element \(i\), \(i=A\) represents the alkali element Na, K or Cs. Only the total weight of the alloy marked with a * is known because the container has been filled with the reacted alloy. The container types are described in section 3.3.1.

5.3 Neutron diffraction measurements

The measurements on the alkali-Ga alloys were carried out on SLAD (Studsvik Liquid and Amorphous materials Diffractometer) at the NFL (Neutronforskningslaboratoriet) in Studsvik, Sweden. This instrument is described in section 3.3.2. We encountered some experimental problems, for instance a corrosion of the sample containers which was most severe for the KGa\(_3\) alloy. Despite this and other experimental difficulties that influenced the quality of the data, we find the results are worthwhile and quite interesting.

Measurements were taken of the following samples: NaGa (560 °C), KGa\(_3\) (625 °C) and Cs-Ga (620 °C), just above the corresponding melting points (see phase diagrams in figures 5.1, 5.2 and 5.3). The Cs-Ga alloy melted at about 610 °C which is a lower melting point than indicated by the phase diagram. The latter is however not very well established due to problems with oxidation and volatilization of Cs. From the measurement on liquid Cs-Ga we obtained the structure factor of liquid CsGa\(_3\), as will be discussed in more detail later.

The first measurement was on KGa\(_3\), which took 8 hours and was measured in 9 runs alternating between detector positions A and B. Bragg peaks in the diffraction data of the liquid alloy were immediately apparent. Increasing the temperature up to 670 °C did not result in the disappearance of the Bragg peaks. They were therefore not due to crystalline K-Ga. A closer investigation on the data showed that the Bragg peaks had appeared quite early in the experiment and had not changed very much in height from then on. The shape and intensity of the scattering from the liquid did not change noticeably during the measurement. Probably some alloying of
Ga with Ti and/or Zr had taken place which prevented the container from further reacting with the alloy. In figure 5.5 the (corrected) diffraction data are shown, including the mentioned Bragg peaks.

A second problem with this measurement was that the sample was slightly bent in an 'S' shape, from top to bottom it was 3 mm off-center. The sample stick appeared to be about 5 mm off-center (over a total length of 26 cm), and since the bottom of the container was fixed in a boron-nitride cup a strain was applied on the sample. With increasing temperature the container material softens and is easily deformed. The sample stick was carefully straightened before the other measurements were made. There is a slight upward slope visible in the corrected structure factor of KGa₃ at high q values (see figure 5.5), which is probably caused by this distortion of the sample container.

For the other experiments the samples remained straight. NaGa was measured for 13 hours in 18 runs. Also in this case corrosion occurred, but only in a very mild way (see figure 5.5). The Bragg peaks are very small and they have the same positions as in the KGa₃ case. This indicates that probably the same Ga-(Ti/Zr) alloy has formed. The phase diagrams of the Ga-Ti and Ga-Zr systems show many possible compounds (the melting points exceed 1000 °C) of which Ga₃Ti and Ga₃Zr are the Ga richest phases. The Bragg peaks appeared also in the Cs-Ga measurement. They were slightly larger than in the NaGa measurement, as can be seen in figure 5.5 as well. Cs-Ga was measured for 7 hours in 7 separate runs. The stability of the instrument and sample were checked statistically for all measurements.

We have also made one short scan of the solid Cs-Ga sample. The diffraction pattern of solid Cs-Ga is compared to that of liquid CsGa₃ in figure 5.6. The sharp high peak at small q-values indicates the intermediate range order that is present in the crystalline structure. It might be that remnants of this structure are the origin of the strong intermediate range order in the liquid alloy. The data of solid Cs-Ga do not form a perfect powder diffraction pattern; the peaks varied in height for different detectors due to texture in the sample.

During these experiments the reactor power varied, basically in 4 periods of 37, 33, 47 and 37 MW in chronological order. It turned out that this was not well corrected for by the monitor in the incident beam. The intensity of a vanadium rod measured for 5000 monitor counts at 47 MW was 3.9% higher than the intensity of the same rod measured with the same number of monitor counts at 33 MW. This is probably a saturation effect of the monitor. The statistical checks on the data brought this to light quite early in the experiment. We therefore made vanadium runs at all the different
Figure 5.5: The structure factors of liquid alkali-Ga alloys. From bottom to top: NaGa (560 °C), KGa₃ (625 °C) and CsGa₃ (620 °C), with vertical shifts of 0, +1 and +2 respectively. The Bragg peaks are present due to corrosion of the Ti-Zr sample container.
Figure 5.6: The structure factor of liquid CsGa$_3$ at 620 °C (upper graph) and of the solid Cs-Ga sample (lower graph). The small Bragg peaks that are present in the the structure factor of liquid CsGa$_3$ are due to corrosion on the Ti-Zr sample container.
reactor powers. The empty can however was measured at 37 MW only, and for the corrections of the measurement taken at 47 MW the intensity of the empty can measurement was multiplied by the difference in scattering intensities of the vanadium runs at the respective reactor powers (3.6%).

Another problem in the data corrections was that the empty container was a type I container (see section 3.3.1) and the sample containers were of type II. (Our last empty type II container had to be used in an other experiment at that time). The type I container has an inner radius of 3.5 mm and an outer radius of 4.1 mm, for type II it is 3.5 and 4.0 mm respectively. The scattering intensity of the type I container was therefore divided by 1.216. As this is only an approximate correction in the data analysis this adds some inaccuracy to the final data. The further data analysis procedure was done as described in section 4.3 using the program CORRECT [61]. For the KGa$_3$ sample we took a filling fraction of 0.6 into account, as the container was not completely filled with the sample. The beam-size we used was 1 x 3.5 cm.

A quite uncertain factor is the density of the liquid alkali-Ga alloys. The average volume contraction of the solid phases relative to the unmixed components, was also applied to the liquid alloy. We used the known densities of the following solid compounds: CsGa$_3$ (38 nm$^{-3}$ [95]), KGa$_3$ (41.3 nm$^{-3}$ [95]) and Na$_{22}$Ga$_{39}$ (48.4 nm$^{-3}$ [96]). The densities of the pure liquid metals at the appropriate temperatures were obtained from reference [94]. The following densities were obtained for the liquid alloys: NaGa: 38 nm$^{-3}$, KGa$_3$: 36 nm$^{-3}$ and CsGa$_3$: 32 nm$^{-3}$.

The scattering intensities ($N^{-1}d\sigma/d\Omega$) for large $q$ values were 0.413 and 0.45 for NaGa and KGa$_3$ respectively, to be compared to the theoretically expected levels of 0.396 and 0.476 barns (as can be calculated using equation 3.27 and the values of $\sigma_s$ given in table A.1). Given the uncertainties mentioned this is reasonable. The data were multiplied with a factor to obtain the expected scattering level. The results of the data analysis are the structure factors that are displayed in figure 5.5.

The measured Cs-Ga alloy is phase separated into a CsGa$_3$ phase and a Cs phase on top. From the densities of these phases and the position of the sample in the beam we know there is 1.12 cm of CsGa$_3$ in the beam and 2.38 cm of Cs. Taking account of the relative densities of the phases (32 nm$^{-3}$ for liquid CsGa$_3$ and 6.77 nm$^{-3}$ for liquid Cs [82]) we find that the measured structure factor $F(q)^{Cs-Ga} = 0.69F(q)^{CsGa_3} + 0.31F(q)^{Cs}$. The high $q$ limit of $F(q)^{Cs-Ga}$ was 0.39, which was multiplied by a factor to obtain the expected level of 0.425. As the structure factor of liquid Cs is known (at 600 °C [97]) we can obtain that of CsGa$_3$. In figure 5.7 the result of this manipulation is shown. There may be an inaccuracy in the obtained
Figure 5.7: The structure factor of CsGa₃ (solid line) is obtained by subtracting an appropriate fraction of the structure factor of liquid Cs (dotted line) from the measured structure factor of Cs-Ga (dashed line).

structure factor of CsGa₃ because the fraction of $F(q)^{\text{Cs}}$ subtracted depends on the estimated densities. Also some errors must be caused in the data corrections as we assumed the alloy to be a homogeneous mixture.

In the next section these structure factors will be used with the Bragg peaks removed, in order to be able to do RMC modelling.

5.4 Reverse Monte Carlo modelling

RMC modelling was used in order to obtain information on the structure in these liquid alkali-Ga alloys. The way RMC works is already explained in section 3.4.

An experimental problem was that an alloying reaction between the sample and the container took place, which was most severe for the KGa₃ alloy. We have removed the resulting Bragg peaks from the structure factors, and fitted with RMC only to the remaining data points. The weight factors
for the partial structure factors can be calculated using equation 3.27 and the average coherent scattering lengths of the elements which are given in table A.1. The weight factors are normalized by \( \langle b \rangle^2 \), so that their total equals 1 (see equation 3.31). They are given in table 5.2.

<table>
<thead>
<tr>
<th>alloy</th>
<th>( w_{A,A} )</th>
<th>( w_{A,Ga} )</th>
<th>( w_{Ga,Ga} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaGa</td>
<td>0.1105</td>
<td>0.4439</td>
<td>0.4456</td>
</tr>
<tr>
<td>KGa_3</td>
<td>0.0209</td>
<td>0.2527</td>
<td>0.7264</td>
</tr>
<tr>
<td>CsGa_3</td>
<td>0.0395</td>
<td>0.3185</td>
<td>0.6421</td>
</tr>
</tbody>
</table>

Table 5.2: The weight factors \( w_{\alpha,\beta} \) for the partial structure factors \( A_{\alpha,\beta}(q) \) and partial pair correlation functions \( g_{\alpha,\beta}(r) \).

We used configurations of 3000 atoms and the cut-off distances and densities that were used are given in table 5.3. The cut-off distances are chosen somewhat smaller than the shortest distance in the solid phases. The ionic radii of the alkali atoms give a minimum value of the cut-off distance that could be used. A value of twice the atomic radius of Ga \( (r = 0.153 \text{ nm} \ [80]) \) is not suitable as cut-off distance because the Ga atoms form covalent bonds to each other. Even the average Ga-Ga distance, which turns out to be 0.27 nm in the liquid alloy, is smaller than the diameter of Ga. The radius of Ga\(^-\) probably does not differ much from that of Ga.

There is still a lot of flexibility to choose cut-off distances between those limits. We have based the choice of the cut-off distances on the shape of the pair distribution function, and on the interatomic distances in the crystal phases. Usually a shoulder is present on the first peak of \( g(r) \) that indicates the A-Ga or the A-A distance of closest approach. As an illustration we show \( g_{\alpha,\beta}(r) \) for Na-Ga with different cut-off distances used in the RMC fit. The \( \chi^2 \) was identical in both cases, however the shape of the partials differs a lot as is shown in figure 5.8. This shows the results depend very much on the choice of the cut-off distance.

<table>
<thead>
<tr>
<th>alloy</th>
<th>( r_{\min} ) A-A (nm)</th>
<th>( r_{\min} ) A-Ga (nm)</th>
<th>( r_{\min} ) Ga-Ga (nm)</th>
<th>( \rho_0 ) (nm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaGa</td>
<td>0.29</td>
<td>0.29</td>
<td>0.20</td>
<td>36</td>
</tr>
<tr>
<td>KGa_3</td>
<td>0.30</td>
<td>0.30</td>
<td>0.20</td>
<td>36</td>
</tr>
<tr>
<td>CsGa_3</td>
<td>0.34</td>
<td>0.34</td>
<td>0.20</td>
<td>28</td>
</tr>
</tbody>
</table>

Table 5.3: Cut-off distances and the number densities \( \rho \) used in RMC modelling for the alkali-Ga alloys.

In figure 5.9 the RMC fits to the data are shown. Given the possible in-
Figure 5.8: The partial pair correlation functions $g_{\alpha,\beta}(r)$ for NaGa obtained with RMC using the cut-off values of 0.29, 0.29 and 0.20 for Na-Na, Na-Ga and Ga-Ga respectively (upper graph) and the cut-off values 0.25, 0.25 and 0.20 respectively (lower graph). Solid line: $g_{\text{Ga,Ga}}(r)$; dotted line: $g_{\text{Na,Ga}}(r)$; dashed line: $g_{\text{Na,Na}}(r)$. 
accuracies in the data the fits are quite good. To obtain a good fit for the NaGa alloy we had to lower the number density to 36 nm\(^{-3}\), instead of the density of 38 nm\(^{-3}\) we estimated in section 5.3. For a fit to the CsGa\(_3\) alloy we had to use a density of 28 nm\(^{-3}\) (instead of 32 nm\(^{-3}\)). It could be that we overestimated the average volume contraction in the liquid alloy. In the case of CsGa\(_3\), the data correction depends on the estimated density of the alloy because we have to know how much Cs should be subtracted from the data. The data was corrected with a CsGa\(_3\) density of 28 nm\(^{-3}\) as well, which led to a slightly lower structure factor at low \(q\) (\(~5\%\)). In principle an iterative process of data corrections and RMC could be started, however we think it is beyond the accuracy of the data to go into such detail. The estimated densities of the KGa\(_3\) alloy (36 nm\(^{-3}\)) gave a reasonably good fit, and we therefore did not try other values of the density. In figure 5.10 and figure 5.11 \(A_{\alpha,\beta}(q)\) and \(g_{\alpha,\beta}(r)\) are plotted. Figure 5.10 shows that the strong ordering is primarily due to Ga-Ga correlations. Note that the alkali-alkali correlations have a very low weight factor and therefore a prepeak in \(A_{A,A}(q)\) is not a significant feature.

In figure 5.11 we see that in the case of CsGa\(_3\) it is easy to separate the partials because of the large differences in cut-off distances. We can be sure the first peak in \(g(r)\) is due to the Ga-Ga nearest neighbour distance. Also for the other alloys we tried to separate the first peaks by applying the cut-off distances mentioned in table 5.3. The average Ga-Ga distance in the alkali-Ga alloys is 0.27 nm, which is only a little bit larger than the average Ga-Ga distance of 0.265 nm in solid AGa\(_3\) (A= Cs, Rb, K ).

The Ga-Ga coordination numbers for NaGa, KGa\(_3\) and CsGa\(_3\) are 3.78, 5.64 and 5.17 respectively. They are calculated for \(r < 0.33\) nm, which is a reasonable choice for the outer bound of the first coordination shell of the Ga-Ga distribution for all measured alkali-Ga alloys (see figure 5.11). The Ga-Ga-Ga bond-angle distributions are shown in figure 5.12, which are also calculated for \(r < 0.33\) nm. Figure 5.13 shows that Ga atoms are grouping together in CsGa\(_3\). Lines are drawn between Ga atoms that are closer than 0.33 nm.

### 5.5 Interpretation of the structure

Unlike the alkali-Tl alloys the alkali-Ga alloys do not have a very well-defined sharp prepeak. The prepeaks are broad but quite prominent and are positioned at very low \(q\) values. It is, especially in the cases of liquid NaGa and CsGa\(_3\), not clear if the prepeak is really a peak as we could not measure smaller \(q\) values. The cluster-size is therefore not well-defined. The broadness
Figure 5.9: The structure factors (dotted lines) of the alkali-Ga alloys where the Bragg peaks, that were present due to a reaction of the alloys with the container material, are removed. The solid lines are the corresponding RMC fits to the data. From bottom to top: NaGa (560 °C), KGa₃ (625 °C) and CsGa₃ (620 °C), with vertical shifts of 0, +1 and +2 respectively.
Figure 5.10: The partial structure factors $A_{\alpha\beta}(q)$ for the alkali-Ga alloys. From bottom to top: NaGa, KGa$_3$ and CsGa$_3$, with vertical shifts of 0, +5 and +10. Solid line: $A_{\text{Ga,Ga}}(q)$; dotted line: $A_{\text{Ga,A}}(q)$; dashed line: $A_{\text{A,A}}(q)$, where A denotes the alkali element.
Figure 5.11: The partial pair correlation functions $g_{\alpha,\beta}(r)$ for the alkali-Ga alloys. From bottom to top: NaGa, KGa$_3$ and CsGa$_3$. Solid line: $g_{Ga,Ga}(r)$; dotted line: $g_{Ga,\alpha}(r)$; dashed line: $g_{\alpha,\alpha}(r)$, where $\alpha$ denotes the alkali element.
Figure 5.12: The Ga-Ga-Ga bond-angle distribution of the alkali-Ga alloys. Dotted line: distribution of CsGa₃; dash-dotted line: NaTI; dashed line KGa₃.
Figure 5.13: A part (1/8 th) of the three-dimensional configuration produced by RMC in the fit to $S(q)$ of CsGa$_3$. The dark spheres are Ga and the light spheres Cs atoms. A connecting line is drawn between Ga atoms that are closer than 0.33 nm.
of the prepeak shows the correlation length is relatively short \( R_c = 2\pi/\Delta q \) [79]), which indicates there is only a diffuse network of clusters present in the liquid. As we expect the clusters to be interlinked, the oxidation state of the clusters is not only dependent on the alkali atoms that surround them but also on the neighbouring clusters. A discussion like the one given in section 4.6.3 to obtain an indication for the oxidation state of the clusters is therefore not feasible.

We can however roughly estimate the cluster-size with the prepeak position, according to equation 4.5 derived in section 4.6. For \( q_0 \) we take the highest value for which the prepeak is still at its maximum. In table 5.4 the number of atoms \( N \) in a periodic volume \( \Omega_{cell} \) are given.

<table>
<thead>
<tr>
<th>sample</th>
<th>( q_0 ) (nm(^{-1}))</th>
<th>( \rho_0 ) (nm(^{-3}))</th>
<th>( N )</th>
<th>( N_A )</th>
<th>( N_B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaGa</td>
<td>6.9</td>
<td>36</td>
<td>35</td>
<td>17.5</td>
<td>17.5</td>
</tr>
<tr>
<td>KGa(_3)</td>
<td>6.4</td>
<td>36</td>
<td>44</td>
<td>11</td>
<td>33</td>
</tr>
<tr>
<td>CsGa(_3)</td>
<td>6.0</td>
<td>28</td>
<td>41</td>
<td>10.5</td>
<td>30.5</td>
</tr>
</tbody>
</table>

Table 5.4: A rough estimate for the number of atoms \( N \) present in a periodic cell, \( \Omega_{cell} \), calculated using equation 4.5. \( N_A \) is the number of alkali atoms and \( N_B \) the number of Ga atoms in \( \Omega_{cell} \). The value of \( q_0 \) is not well-defined as the prepeaks are quite broad. The derivation of the values for the densities was discussed in section 5.3 and section 5.4.

There is no direct relationship between the structure in the liquid alkali-Ga alloys and that of the solid. For example, the periodic distance \( d_s \) (see section 4.6) between the Ga-clusters in KGa\(_3\) and CsGa\(_3\) is 0.743 and 0.763 respectively. This is much shorter than the periodic distances in the liquid alloys: \( d_l = 1.20 \) and 1.28 nm respectively.

We will now have a look at the SRO information obtained through RMC modelling. The Ga-Ga coordination numbers in liquid KGa\(_3\) and CsGa\(_3\) are 5.64 and 5.17. In Ga\(_{11}\) clusters the Ga-Ga coordination is on average \( (r < 0.3 \) nm) 4.4, and 5 for a Ga\(_{12}\) cluster, when no interlinking is taken into account. The structures KGa\(_3\) (see figure 2.6) and CsGa\(_3\), which is isostructural, have an average Ga-Ga coordination number of 5. The coordination number of NaGa we obtained via RMC modelling is 3.78 which is quite low compared to the solids. A reason for this may be that the IRO is not strong and very diffuse. Also, we have to keep in mind that the reliability of the RMC result is less than in the CsGa case because the atomic diameters of Na and Ga are relatively close.

The bond-angle distributions show a peak near 60\(^\circ\), which is consistent with the deltahedral clusters in the solid phases. It is however quite
common for RMC to produce peaks near this angle; they occur in any densely packed system.

5.6 Conclusions

The structure factors of liquid NaGa, KGa₃ and CsGa₃ have been measured at temperatures just above the melting points. We encountered some experimental problems, for example corrosion of the container material (Ti-Zr) which was visible as Bragg-peaks in the diffraction pattern. The corrosion was most severe for the KGa₃.

The structure factors that were obtained show some very interesting features. There is a strong IRO indicated by a high prepeak at very low wavevector. This peak is however broad and $S(q)$ remains quite high for the lowest $q$ value measured. The KGa₃ measurement, however, shows a clear maximum of the prepeak and starts to decrease again at lower $q$ values. This is also, although only weakly, the case in the CsGa₃ measurement. We can therefore not draw any conclusions on the expected size of $S(0)$, as yet.

There is no correspondence between periodicities in liquid KGa₃ or CsGa₃ (1.20 and 1.28 nm) and those in the respective solid phases (0.743 and 0.763 nm). Because the prepeaks are broad the cluster-sizes are not well defined. This indicates a relatively short correlation length and therefore a quite diffuse network of these large clusters. Solid alkali-Ga alloys most usually consist of inter-connected Ga clusters. Due to the connections to other clusters the charge on the Ga-clusters can be lowered and therefore it is possible to form larger clusters (up to ~15 Ga atoms). This in contrast to the solid alkali-Tl alloys which predominantly form isolated clusters of which the largest consist of 11 Tl atoms (i.e. for binary compounds, clusters of 13 Tl atoms can be obtained with size-tuning). This difference in the solid structures of alkali-Ga and alkali-Tl is reflected in the liquid phase. The prepeaks in the alkali-Tl alloys are much sharper and situated at a higher $q$ value than that of the corresponding gallium alloy.

The results from RMC modelling indicate the existence of covalent Ga-Ga bonds with average distances (0.27 nm) close to those in the solid phases (0.265 nm). The IRO is predominantly due to Ga-Ga correlations. An increase of the prepeak height in $A_{Ga,Ga}(q)$ along the series Na-Ga, K-Ga, Cs-Ga, is observed. This is a manifestation of Geertsma's rule (see section 1.8) which states that the clusters are more stable when the size of the alkali element is larger.
Chapter 6

Cesium-bismuth alloys

Up to now our measurements pertained only the alkali-group 13 alloys. In this chapter measurements on the Cs-Bi system will be discussed. Bismuth belongs to group 15 of the periodic system and with its 5 valence electrons is less electron-deficient than e.g. Tl. We therefore do not expect compact clusters in the liquid alloy but rather Te-like chains, according to the Zintl-Klemm principle.

The neutron diffraction measurements were made on SLAD (NFL, Studsvik, Sweden). Again part of the analysis of the data was done using RMC modelling. An extensive comparison to the solid alloys is unfortunately not possible because only very little is known about the crystalline structures of alkali-Bi alloys.

6.1 Introduction

The phase diagram of Cs-Bi (figure 6.1) indicates two congruently melting compounds: CsBi₂ and the simple octet compound Cs₃Bi. There is a deep eutectic at the equiatomic composition. Cs₃Bi₂ melts peritectically near 500 °C, however according to reference [17] congruent melting is equally likely within the experimental limits. The phase diagrams of K-Bi [17] and Rb-Bi [17] are similar to that of Cs-Bi but the 3:2 composition is congruently melting. The maximum in the liquidus is however very small and almost disappears under the high and broad maximum of the simple octet compounds.

The indications for compound formation in the liquid alkali-Bi alloys are rather confusing. The resistivity measurements show a gradual change from Li-Bi [99] and Na-Bi [100], with only a peak at the simple octet compound composition, towards Cs-Bi [101] with a peak at 40% Bi. K-Bi [101] and Rb-Bi [100] display peaks at both compositions. The resistivities of the
alkali-Bi compounds are shown in figure 6.2. Measurements of the Darken stability function confirm the existence of the simple octet compound, but there is a second peak at the equatomic composition in Na-Bi [102, 103], K-Bi [104] and Rb-Bi [105] (Cs-Bi has not been measured over the whole composition range). This offers a discrepancy in stoichiometry with the resistivity data.

The relation to the phase diagrams is also not very clear, except for the occurrence of a simple octet-phase. The congruently melting compounds KBi$_2$, RbBi$_2$ and CsBi$_2$ do not show up as liquid compounds in the resistivity measurements, probably because they are Laves-phases of which the ordering is to a greater extent dominated by packing requirements than by electronic requirements. Perhaps the congruently or peritectically melting compound at the composition with 40% Bi could possibly be associated with the maximum in the resistivity data. Unfortunately the structure of solid Cs$_3$Bi$_2$ has not been resolved yet, although an X-ray powder pattern was obtained [106].

The behaviour of alkali-Bi alloys is very different from that of alkali-Sb, even though Bi and Sb belong to the same group of the periodic system. The phase diagrams of the alkali-Sb alloys for example show a congruently melting com-
Figure 6.2: The electrical resistivities of liquid alkali-Bi alloys as a function of composition for temperatures close to the liquidus.
compound at the equiatomic composition. Measurements of the susceptibility, the Darken stability function and resistivities of the alkali-Sb alloys mostly have been carried out only in the alkali-rich regions. But the peaks that have been found, apart from those at the simple octet compound composition, are at equiatomic composition. These include the Darken stability function of K-Sb [107] and the resistivity of Cs-Sb [108], although the latter is badly established as the measurements cover only the range of 0-50% Sb. Also neutron diffraction measurements on the Cs-Sb system were made [27] on alloys containing 85, 75, 65 and 50% Cs. In the alloys with 75, 65 and 50% Cs a small but distinct prepeak was observed which was highest for the equiatomic composition. The results of this structural investigation suggest that there are Sb\textsuperscript{-} chain segments present in the liquid.

The difference in structure between alkali-Bi and alkali-Sb alloys arises from the more extended nature of the Bi 5p orbitals compared to the Sb 4p orbitals [40]. Due to relativistic contraction the valence s orbitals provide better shielding and this results in an expansion of the p, d and higher orbitals. Relativistic effects also occur for other heavy elements like Pb or Tl, however it seems that in the case of Bi they have a particularly strong effect on the bonding properties. The bonding properties of alkali-Pb and alkali-Sn or alkali-Tl and alkali-In are much more closely related than those of alkali-Bi and alkali-Sb.

We have seen that resistivity and thermodynamic measurements on liquid alkali-Bi indicate that a clustered compound exits, although the problem of the stoichiometry of 40% or 50% is still unresolved. We decided to measure the structure of Cs\textsubscript{3}Bi\textsubscript{2} and CsBi to obtain more information on the size and shape of the Bi-polyanions in the liquid compound. Another group at Argonne National Laboratory already started measurements on the structure of liquid K-Bi alloys, which would be interesting to compare to our Cs-Bi data.

### 6.2 Sample preparation

The following metals were used for the preparation of the samples:

- Cs: vial 99.98%, Cabot (Revere, USA).
- Bi: ingots 99.999%, Ventron GmbH (Karlsruhe, Germany).

The samples were made in an argon-filled glovebox with O\textsubscript{2} and H\textsubscript{2}O levels that are typically lower than 1 ppm.
6.3 Neutron diffraction measurements

Like liquid gallium, bismuth is a corrosive material. Ti and Zr both have a poor resistance to liquid bismuth [94]. We can however imagine that the Cs-Bi mixture is less corrosive than the pure elements, because there is a strong compound formation. This is, for instance, indicated by the fast reaction between liquid Cs and solid Bi chunks. Unfortunately, no information on the corrosiveness of the Cs-Bi alloy is available. Due to high Cs evaporation from the liquid alloy, it was too complicated to do a corrosion test.

The sample preparation was done in the way as described in chapter 4. The proper amounts of metal were added in the sample container. After closing, the container was heated up to 650 °C. Near the melting point of bismuth (271 °C) the heating was done very slowly in order to avoid a sudden fierce reaction which could destroy the container. The container was cooled in horizontal position, which diminishes the chance of breaking the container when the alloy starts to crystallize. (However, this turned out to be an unnecessary precaution because the containers were not destroyed by cooling in a vertical position after the experiment.) Only the Cs₃Bi₂ sample was initially prepared. After the measurement on SLAD the container was reopened inside a glove-box and small pieces of Bi were added to obtain the equiatomic composition. The container was closed again using a different knife-edge with a slightly smaller diameter than the former one. The compositions of the samples are given in table 6.1. The Ti-Zr container is of type II, which is described in section 3.3.1.

<table>
<thead>
<tr>
<th>sample</th>
<th>type</th>
<th>m₇Bi (g)</th>
<th>mCs (g)</th>
<th>composition. in at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs₃Bi₂</td>
<td>II</td>
<td>3.150</td>
<td>3.002</td>
<td>Cs₄₀.₀₂Bi₅₉.₉₈</td>
</tr>
<tr>
<td>CsBi</td>
<td>II</td>
<td>4.725</td>
<td>3.002</td>
<td>Cs₅₀.₀₂Bi₄₉.₉₈</td>
</tr>
</tbody>
</table>

Table 6.1: The compositions of the alkali-Bi samples. The container types are described in section 3.3.1.

6.3 Neutron diffraction measurements

The measurements on the Cs-Bi alloys were carried out on SLAD (Studsvik Liquid and Amorphous materials Diffractometer) at the NFL (Neutronforskningslaboratorium) in Studsvik, Sweden. This instrument is described in section 3.3.2. The measurements were made in the same beam-time period as the measurements on the alkali-Ga systems. We therefore had the same problems with the neutron flux as described in section 5.3. The sample measurements were taken at a reactor power of 47 MW and they were normalized by a vanadium run taken at the same reactor power. The empty can was
measured at 37 MW which needed to be corrected for the difference in monitor efficiency at the respective reactor powers (3.6%, see section 5.3). The empty container was a type I container, as our last type II container had to be used in another experiment at that time. We needed to correct for this by dividing the scattering of the empty container by a factor of 1.216 as is also described in section 5.3.

There were no signs of container corrosion with the Cs-Bi samples. The samples were measured at 550 °C. Cs$_3$Bi$_2$ was measured in 13 runs for 9 hours, alternating the detector positions. After adding extra bismuth to this sample in a glovebox we obtained an equiatomic composition. This sample was heated up in the SLAD-furnace where we could see from the diffraction pattern that bismuth melted at 271 °C and immediately after that we saw new Bragg-peaks appear at a different position. At around 440 °C these Bragg-peaks disappeared. CsBi was measured for 11 hours in 16 runs.

The densities of the liquid alloys are rather uncertain. We have estimated them by applying the same volume contraction as we find for solid Cs$_3$Bi. This contraction is very large: 52.8% with respect to the ideal mixture. At a temperature of 550 °C we estimated 20.2 at. nm$^{-3}$ for Cs$_3$Bi$_2$ and 20.5 at. nm$^{-3}$ for CsBi. The densities and expansion coefficients of the pure liquid metals were taken from reference [82]. We probably overestimate the density of the liquid alloys Cs$_3$Bi$_2$ and CsBi when this volume contraction is applied. We might get a better indication of the density with the use of RMC modelling.

The data were corrected for background, multiple scattering and inelasticity using the program CORRECT [61], in the way described in section 3.3.3. The beam size used was 3.5x1 cm. After normalization, using the densities mentioned above, the scattering levels for large q values were 0.428 barns for Cs$_3$Bi$_2$ (using a filling fraction of the sample of 0.79) and 0.444 barns for CsBi (using a filling fraction of 0.94). The theoretically expected levels are 0.478 and 0.519 barns respectively. The difference may be partly due to a too high estimated density. The density only has a noticeable effect on the normalization, the effect of the density on the multiple scattering correction is negligible. We therefore multiplied the data by a factor to obtain the theoretically expected scattering level.

The structure factors of Cs$_3$Bi$_2$ and CsBi measured at 550 °C are shown in figure 6.3. Notice that they both show prepeaks at 10.6 nm$^{-1}$. 
Figure 6.3: The structure factor of liquid $\text{Cs}_3\text{Bi}_2$ and CsBi at 550 °C, shifted vertically +1 and 0 respectively.
6.4 Reverse Monte Carlo modelling

We used RMC modelling to obtain information on the structure of these liquid Cs-Bi alloys. In section 3.4 a description of the RMC-method is given.

The weight factors for the partial structure factors, $A_{\alpha,\beta}(q)$, can be calculated using equation 3.27 and the average coherent scattering lengths of the elements which are given in table A.1. The weight factors are normalized by $\langle b \rangle^2$, so that their total equals 1 (see equation 3.31). They are given in table 6.2.

<table>
<thead>
<tr>
<th>alloy</th>
<th>$w_{\text{Cs, Cs}}$</th>
<th>$w_{\text{Cs, Bi}}$</th>
<th>$w_{\text{Bi, Bi}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$_3$Bi$_2$</td>
<td>0.2381</td>
<td>0.4997</td>
<td>0.2622</td>
</tr>
<tr>
<td>CsBi</td>
<td>0.1509</td>
<td>0.4751</td>
<td>0.3740</td>
</tr>
</tbody>
</table>

Table 6.2: The weight factors $w_{\alpha,\beta}$ for the partial structure factors $A_{\alpha,\beta}(q)$ and partial pair correlation functions $g_{\alpha,\beta}(r)$.

The densities we used in the RMC simulation are 15.4 at. nm$^{-3}$ for Cs$_3$Bi$_2$ and 15.6 at. nm$^{-3}$ for CsBi. These values are lower than the values of 20.2 and 20.5 at nm$^{-3}$ estimated in the previous section, with which we could not get a good fit to the data. The new values of the density are based on the density of the solid CsBi alloy, which we estimated by measuring the height of the sample in the container on an X-ray photograph. The cut-off distances used were 0.33, 0.32 and 0.27 nm for Cs-Cs, Cs-Bi and Bi-Bi respectively. Bi with $r = 0.170$ nm has about the same atomic radius as Tl ($r=0.171$ nm).

The results of RMC modelling were two fits that almost coincided with the data. The partial structure factors and the partial pair correlation functions are shown in figures 6.4 and 6.5. Figure 6.4 shows that the prepeak is mainly due to the Bi-Bi correlations. The $g_{\text{Bi, Bi}}(r)$ in figure 6.5 shows a distinct peak at 0.30 nm. Cs ions are too large to be able to contribute in this region. Beyond about 0.34 nm, RMC can probably not separate the contributions of the different partials as they are all of the same shape from that point on. The first minimum in $g_{\text{Bi, Bi}}(r)$ occurs at 0.34 nm. We therefore took this value as the maximum $r$ value for the calculation of the Bi-Bi coordination number. For Cs$_3$Bi$_2$ this number is 0.84 and for equiatomic CsBi 0.99. The values are close to 1, which indicates that there are dumbbells or short chains present in the liquid alloy. The Bi-Bi-Bi bond-angle distributions have also been calculated up to a maximum distance of $r = 0.34$ nm. They are shown in figure 6.6. There is a maximum at 60°, which is usually present, but there is also a significant peak near 83°. We will discuss this further in section 6.5.
Figure 6.4: The partial structure factors $A_{\alpha\beta}(q)$ for Cs$_3$Bi$_2$ (shifted vertically by +1) and CsBi. Solid line: $A_{\text{Bi,Bi}}(q)$; dotted line: $A_{\text{Bi,Cs}}(q)$; dashed line: $A_{\text{Cs,Cs}}(q)$. 
Figure 6.5: The partial pair correlation functions \( g_{a,\beta}(r) \) for \( \text{Cs}_3\text{Bi}_2 \) (shifted vertically by +5) and \( \text{CsBi} \). Solid line: \( g_{\text{Bi},\text{Bi}}(r) \); dotted line: \( g_{\text{Bi},\text{Cs}}(r) \); dashed line: \( g_{\text{Cs},\text{Cs}}(r) \).
Figure 6.6: The Bi-Bi-Bi bond-angle distribution of Cs$_3$Bi$_2$ (dashed line) and CsBi (solid line).
Figure 6.7: A part (1/8 th) of the three-dimensional configuration produced by RMC in the fit to $S(q)$ of Cs$_3$Bi$_2$. The dark spheres are Bi and the light spheres Cs atoms. A connecting line is drawn between Bi atoms that are closer than 0.34 nm.

A part of the three-dimensional configuration of liquid Cs$_3$Bi$_2$ obtained with RMC is shown in figure 6.7. Apart from quite a few single Bi atoms, there are many Bi-dumbbells present and some small chains not longer than 4 atoms.

At first glance there seems to be little difference between the structure factors of Cs$_3$Bi$_2$ and CsBi. The height of the prepeak in Cs$_3$Bi$_2$ is almost the same as that in CsBi (0.555 and 0.559 respectively). However, with regard to the weight factors of the Bi-Bi partials (see table 6.2), we would expect the prepeak to be 1.43 times higher for CsBi. We can conclude that in Cs$_3$Bi$_2$ the ordering is more pronounced than in CsBi.

The Bi-Bi coordination number decreases from 0.99 in CsBi to 0.84
in Cs₃Bi₂. It is rather risky to draw conclusions from this difference, as the coordination number can depend on the composition as well as on the structure. It is however clear that in a disordered system (random mixture) the Bi-Bi coordination number would be higher. Or, in other words, a high degree of order is needed to obtain a coordination number between 0 (heterocoordination) and 1 (dumbbells). Perhaps the lower average Bi-Bi coordination number in Cs₃Bi₂ is therefore in agreement with our earlier conclusion, which we derived from the height of the prepeak, that there is a higher degree of order in Cs₃Bi₂ than in CsBi.

The positions of the prepeak in Cs₃Bi₂ and CsBi are identical. This implies that the distance between the Bi-polyanions is more or less the same in both alloys. Measurements on the Cs-Sb system by Lamparter et al [27], also show that the prepeak remains at about the same position for CsSb and Cs₃₃Sb₃₅ namely 9.5 and 9.7 nm⁻¹ respectively. This is in contrast to the Cs-Tl case (see section 4.6.3) where we saw that the prepeak increased in height and the position shifted to higher q₀ with increasing Cs concentration. A further discussion on this difference is given in section 7.3.

6.5 Interpretation of the structure

There is not much known on the crystal structure of alkali-Bi alloy. It seems to be difficult to obtain well-defined single crystals of these alloys that are suitable for X-ray diffraction [109].

One structure that is known is NaBi [110]. It contains planar square nets of Bi⁻⁻ atoms. This is in contrast to the structure of NaSb, which follows the classical Zintl-Klemm concept by forming spiral chains of Sb atoms [111]. The difference between the structures has been attributed to relativistic effects of Bi.

The Bi₃⁻ ion has been synthesized in a polar solvent [112]. According to the Wade rules (see section 2.3.2) these clusters should have an arachno structure, as they posses (4x5) + 2 - (4x2) = 14 skeletal electrons, which is equal to 2(n+3). However this polyanion does not have the expected 'butterfly' shape of the arachno structure with 4 atoms, but it is a square planar. It is isoelectronical and isostructural to the Se₄²⁺ ion, which again illustrates the Zintl-Klemm concept.

Using the method described in section 4.6 we can estimate the size of the Bi-polyanions in the liquid Cs-Bi alloys. The prepeak of Cs₃Bi₂ as well as that of CsBi is positioned at 10.6 nm⁻¹, which implies an intermediate range order with a characteristic distance of 0.73 nm. By using equation 4.5 we
find a total of \( N = 4.2 \) atoms that are present in the periodic volume \( \Omega_{\text{cell}} \). This would indicate a \( \text{Bi}^- \) polyanion of about 2 atoms on average. This has also been suggested by the coordination number of \( \sim 1 \) that was obtained from the RMC simulation.

There are a few Bi-chains present that are longer than 2 Bi-ions. Interestingly enough those short \( \text{Bi}^- \)-chains show an unusual angle distribution. There is a significant peak near \( \sim 83^\circ \). This is unusual because for randomly closed-packed structures RMC will normally find a minimum near this angle. It might indicate that the \( 90^\circ \) angles which are found in solid NaBi and also in the \( \text{Bi}_4^{2-} \) ion are perhaps preferred in the liquid Cs-Bi alloys as well.

### 6.6 Conclusions

We have measured the structure factors of liquid \( \text{Cs}_3\text{Bi}_2 \) and CsBi at \( 550 \, ^\circ \text{C} \). In both cases there is a prepeak visible at \( q_0 = 10.6 \, \text{nm}^{-1} \) which indicates that there is an IRO present with a characteristic distance of 0.73 nm. In analogy to measurements on the Cs-Sb system [27] and according to the results we obtained with RMC modelling, we conclude that the IRO is due to covalently bonded Bi-polyanions. According to the Zintl-Klemm principle the Bi-polyanions should be Te-like chains of \( \text{Bi}^- \) atoms. The Bi-Bi coordination number we found was 0.84 for \( \text{Cs}_3\text{Bi}_2 \) and 0.99 for CsBi, which implies the existence of Bi-dumbbells or a mixture of short chains and isolated \( \text{Bi}^- \) ions in the liquid. The position of the prepeak also indicates that \( \sim 4 \) atoms are present in a periodic cell, of which about 2 are Bi atoms.

The bond-angle distribution obtained from RMC modelling shows that quite some angles occur near \( 83^\circ \), which is rather unusual. Perhaps they are remnants of the \( 90^\circ \) angles that are found in NaBi or \( \text{Bi}_4^{2-} \) ions.

From the height of the prepeak we may conclude that there is a stronger polyanion formation in liquid \( \text{Cs}_3\text{Bi}_2 \) than in CsBi. The resistivity measurements on the Cs-Bi system [101] show a very high maximum at this composition as well. However, we still do not understand why the composition with 40% Bi is more stable than the equiatomic one. A structural determination of solid \( \text{Cs}_3\text{Bi}_2 \) would be of much help to interpret our findings.
Chapter 7

Conclusions

We have studied the intermediate range order (IRO) in several liquid alloys by means of neutron diffraction measurements. In the alloys investigated there are covalently bonded clusters present which cause a large spatial periodicity. The size and position of the prepeak in the structure factor give information on the degree of ordering (stability) and on the cluster size, respectively. The structure factors measured were further analyzed with Reverse Monte Carlo modelling. In many cases we could see a clear relation between the structure in the liquid and that in the solid alloy.

In this final chapter a summary will be given of the results we obtained and we try to generalize our ideas. The prepeak positions, densities and number of atoms in the periodic volumes of the investigated alloys will be summarized in table 7.1, including some alloys that have been measured by others.

But first, in the next section, our findings on the use of RMC modelling will be discussed.

7.1 RMC modelling

We frequently used RMC modelling to obtain information on the structure in real space of the liquid alloy. We have made measurements using isotopic substitution (K^35Tl and K^205Tl) which we used as a test case for RMC modelling. The conclusion was that RMC does not find the best fit possible to the data. When the better fitting configurations have a higher degree of order, the chance of RMC finding this configuration (by randomly moving atoms) is very small.

The relatively small difference in atomic diameters of K and Tl, however, makes this a rather difficult case for RMC. For alloys like Cs-Ga
or Cs-Bi the different distances of nearest approach between the atom-pairs make a better separation of the partial pair distribution functions possible, at least in the first coordination shell. However, we noticed that the result depends on the cut-off distance we choose.

The reproducibility of the results from RMC may give the impression that the results are reliable and in the vicinity of the 'truth'. This is generally not the case. RMC invariably ends in a local minimum with a large configurational entropy. We need to keep this in mind in order to evaluate the results obtained with RMC.

Nevertheless, we have used RMC for the reason that any typical order that is found must be due to the information in the data in combination with the chosen cut-off distance and the density. The result gives a hint towards the real structure in the liquid alloy. If desired, coordination constraints can also be applied in order to test certain expected configurations against the data.

It is also important to fit the data with RMC in order to detect systematic errors in the data and/or errors in the density. RMC should be able to fit to correctly analyzed data; the other way around, however, a good fit does not necessarily mean there are no errors in the data.

### 7.2 Summary of results

The main research subject of this thesis has been the structure of alkali-Tl alloys. We measured K\textsubscript{Tl} and K\textsuperscript{205}Tl from which we could get accurate information on the partial structure factors. The average Tl-Tl distance we found for the liquid alloy is nearly equal to that of the solid. This is a strong indication that the covalent Tl-Tl bonds are present in the liquid. The Tl-Tl coordination number is 4, very similar to that in the solid phases K\textsubscript{Tl} and K\textsubscript{8}Tl\textsubscript{11} (4 and 3.85 respectively).

The position of the prepeak indicates a periodic volume \( \Omega_{\text{cell}} \) with an average of 14.5 atoms of which \( \sim 7.3 \) are Tl atoms. This gives an indication of the size of the clusters, although we have to keep in mind that the error in this number is about 8%, and that the assumptions we made to calculate this number are very crude. The size of the clusters is in between the size of the Tl\textsubscript{6} clusters present in solid K\textsubscript{Tl} and of the Tl\textsubscript{11} clusters in K\textsubscript{8}Tl\textsubscript{11}.

K\textsubscript{Tl} and K\textsuperscript{205}Tl were also measured at 660 °C instead of 360 °C. The analysis led to the conclusion that the Tl-Tl short range order hardly changed, despite the difference in average densities. The prepeak however shifted to a lower \( q \)-value: 7.3 instead of 8.0, which is more than we would expect on the
basis of the density difference alone. The prepeak also decreases in height and gets broader, but it is still clearly present. The results are similar to those obtained for other measurements at higher temperature, like on CsTl [86] and KPb [85].

We measured the structure of liquid K₈Tl₁₁ and of liquid K-Tl with additional third elements: K₉₆Tl₉₇Pd₂, K₁₀Tl₁₀Pd, K₁₈Tl₂₀Au₃, and K₆Tl₁₀Zn. The analogy with the corresponding solid structures was strongest for K₁₀Tl₁₀Pd. The size of the Pd-centered Tl₁₀Pd⁻¹₀ clusters in the crystal almost exactly fits the large periodicities in the liquid (see table 7.1 for the number of atoms in Ω_{cell}). The increased prepeak height indicates that Pd increases the stability of the clusters. The alloy with less Pd showed that the cluster volume increases more than linearly with the Pd concentration: 15% upon addition of 1% Pd and 37% upon addition of 5% Pd. For the alloy with Zn the prepeak did not shift position and the height increased only slightly. We would have expected a stronger ordering in this alloy, because the solid compound is quite stable and congruently melting [115]. The clusters in the alloy with Au became less stable. In the solid phase clusters occur which can be understood as Tl₁₁ clusters with two Tl atoms replaced by Au atoms. The short Au-Au bond deforms the cluster, which might be a cause for the lower cluster stability.

A composition study was made for Tl-rich Cs-Tl alloys. We measured liquid CsTl, Cs₈Tl₁₁₁, CsTl₂, CsTl₃ and Cs₁₅Tl₈₅. We observed that the prepeak shifted position to lower q values with increasing Tl content. A calculation of the number of atoms in Ω_{cell} showed that the number of Tl atoms in Ω_{cell} increased, but the number of Cs atoms remained remarkably constant. Only for the Tl-richest alloy Cs₁₅Tl₈₅ a significant deviation is noticed. The values are summarized in table 7.1.

Our interpretation is that the Tl-clusters have the same size in all compositions (except the Tl-richest) and that they are separated by the excess of Tl, which makes the average intercluster distance larger for the Tl-richer alloys. With increasing Cs content the number of clusters increases, not their size. This interpretation also explains the almost linear increase of the height of the prepeak in A_{Tl,Tl}(q) with increasing Cs/Tl fraction. The number of Cs atoms present in Ω_{cell} indicate an oxidation state of -6 or -7 for the Tl-clusters. Furthermore the number of atoms in Ω_{cell} in CsTl is 13.9 which is within the error of 8% equal to 14.5 in KTL. This confirms the idea that a specific valence rule for Tl-clusters is obeyed in the liquid alloy.

We consider Tl₇⁷ and Tl₈⁶ as possible structures that may be present in liquid KTL and Cs-Tl because they also exist in solid phases of alkali-Tl.
alloys. A Tl\textsubscript{6} cluster might explain the periodic distance just within the error. However this cluster contains right angles, which we have not observed in the results of RMC modelling. The Tl\textsubscript{5} cluster could explain the intercluster distance, but in this case the stoichiometry of the K-Tl alloy is 7:5 and, according to resistivity measurements, it should be at 50\%. A hypothetical cluster like e.g. Tl\textsubscript{7} could also explain the results. Such a cluster has unfortunately never been detected in the solid. A theoretical evaluation of the stability of such a cluster would be very interesting.

Measurements on alkali-Ga systems were made as well. We measured the structure factors of liquid NaGa, KGa\textsubscript{3} and CsGa\textsubscript{3} just above the melting points. The prepeaks in these alloys are higher and much broader than those in the alkali-Tl alloys. At the lowest q-value measured the structure factor is still very high. The IRO in these alloys is strong, but not very well-defined by the measurement. In analogy to the solid alkali-Ga phases known we may expect that large Ga-clusters interlinked in a network survive in the liquid. There is, however, no direct relationship to the solid counterparts of the measured alkali-Ga alloys. The periodic volumes in liquid KGa\textsubscript{3} and CsGa\textsubscript{3} are much larger (roughly about 30 Ga atoms) than the clusters in the solid phases (8 Ga atoms). The Ga-Ga average nearest neighbour distance is 0.27 nm which is very close to the average Ga-Ga distance in the solid alkali-Ga phases of 0.265 nm.

The alloys CsBi and Cs\textsubscript{3}Bi\textsubscript{2} have been measured because there were unresolved differences in stoichiometry between several measured physical properties (either at 40\% or 50\% Bi). Our measurements showed that the ordering in Cs\textsubscript{3}Bi\textsubscript{2} is slightly more stable than CsBi. However, a reason for this could not be found. The Zintl-phases we would expect in the liquid are linear chains of Bi\textsuperscript{-} ions or, more likely, fragments of those. However, we found several indications that Bi-dumbbells occur in the liquid alloy. The Bi-Bi coordination number was very close to 1, and the number of atoms in Ω\textsubscript{cell} was 4.2, which indicates about 2 Bi atoms per cell. The configuration obtained with RMC clearly showed many Bi\textsubscript{2} dumbbells, and a few longer chains of not more than 4 atoms.

Crystallographic data on the alkali-Bi alloys are unfortunately hardly available. Only the structure of NaBi is known and that of a Bi\textsubscript{4} Zintl-ion. The angles in these structures between the Bi atoms are 90°. A peak at 83° was present in the Bi-Bi-Bi bond-angle distribution, which is an unusual result for an RMC simulation as most randomly close packed systems show a minimum near this angle. This may indicate that remnants of those mentioned 90° angles persist in the liquid phase.
7.3 General conclusions

We have seen that there are many similarities between the structures in the investigated liquid alloys and their solid counterparts. Because there are less packing constraints and there are no symmetry requirements in a liquid, its structure reveals perhaps even more directly the electronic structure.

The most intriguing example we found is the structure of liquid Cs-Tl. The fact that the Tl-cluster size is almost unaffected by the composition of the alloy shows that there is a strong preference for one type of cluster which obeys a certain valence rule. The same clusters also appear in liquid KTI.

The very simple \( \Omega_{\text{cell}} \) model gives an indication towards the size of these Tl-clusters. We have also applied this model to previous measurements of other alloys. The results are summarized in table 7.1. The number of atoms present in the periodic volume \( \Omega_{\text{cell}} \) in e.g. liquid KPb is 7.9 of which \(~4\) are Pb atoms. It confirms the idea that Pb_{4}^{-4} clusters, which exist in the crystalline structure, are present in the liquid alloy as well. These clusters are surrounded by, on average, 4 K^{+} ions. The model also seems to work for RbPb, CsPb, KSn and CsSn, where Pb_{4}^{-4} or Sn_{4}^{-4} tetrahedra are expected to exist in the liquid. We are quite surprised by these uniform results with this very simple model. Also remarkable is the number of atoms in \( \Omega_{\text{cell}} \) of K_{10}Tl_{10}Pd, which is very similar to the Pd-centered PdTl_{10}^{10} cluster as it appears in the solid phase. The model was also applied to liquid KTe. In the solid alloy Te_{2}^{-2} ions are present and according to reference [30] they also exist in the liquid alloy. There are 4 atoms in \( \Omega_{\text{cell}} \) which is consistent with the occurrence of K_{2}Te_{2} units.

Of course, there are also alloys for which this model does not apply. Some Na-X alloys appear to be deviating. This can be explained with Geertsma's rule, which states that the cluster structure is less stable for smaller alkali metals. This rule seems to be generally valid. For the alkali-Ga alloys this \( \Omega_{\text{cell}} \) model does not make much sense because the prepeaks are very broad. It is obvious that there are no compact clusters of one size present in the alloy. They are probably interlinked into some three-dimensional structure, as they are in the solid. In any case the position of the prepeaks indicate much larger periodicities than present in the respective solid phases. We also can not simply use the model for e.g. the Cs-Sb alloys, even though they exhibit well-defined prepeaks. The polyanions that are expected are parts of linear chains. It is somewhat dubious to apply the \( \Omega_{\text{cell}} \) model to this system, because the ordering of chains in a liquid is very different from that of more-or-less spherically shaped polyanions.
<table>
<thead>
<tr>
<th>alloy</th>
<th>reference</th>
<th>( q_0 ) (nm(^{-1}))</th>
<th>( \rho_0 ) (nm(^{-3}))</th>
<th>( N )</th>
<th>( N_A )</th>
<th>( N_B )</th>
<th>( N_M )</th>
</tr>
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<td>7.3</td>
<td>-</td>
</tr>
<tr>
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<td>[75], this work</td>
<td>7.6</td>
<td>23.0</td>
<td>16.9</td>
<td>8.4</td>
<td>8.4</td>
<td>0.2</td>
</tr>
<tr>
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<td>[75], this work</td>
<td>7.2</td>
<td>23.0</td>
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<td>9.5</td>
<td>1.0</td>
</tr>
<tr>
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<td>23.6</td>
<td>14.9</td>
<td>6.3</td>
<td>8.6</td>
<td>-</td>
</tr>
<tr>
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<td>6.3</td>
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<td>5.3</td>
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<td>-</td>
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<td>4.3</td>
<td>-</td>
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<td>2.1</td>
<td>2.1</td>
<td>-</td>
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<tr>
<td>Cs(_2)Bi(_2)</td>
<td>this work</td>
<td>10.6</td>
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<td>4.2</td>
<td>2.5</td>
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<td>-</td>
</tr>
<tr>
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<td>4.1</td>
<td>2.0</td>
<td>2.0</td>
<td>-</td>
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</table>

Table 7.1: The number of atoms \( N \) present in a periodic cell \( \Omega_{cell} \) calculated using equation 4.5. \( N_A \) is the number of alkali atoms, \( N_B \) the number of polyvalent atoms and \( N_M \) the number of third elements in \( \Omega_{cell} \). The inaccuracy of \( q_0 \), \( \rho_0 \) and \( N_i \) is estimated to be \( \sim 1\% \), \( \sim 5\% \) and \( \sim 8\% \), respectively.

The model implies a homogeneous distribution of clusters in the alloy. This is not necessarily the case if the alloy is not at its stoichiometric composition. For instance when we have an alloy \( A_x X_y \) at its stoichiometric composition and we add some extra \( A \) (or \( X \)). There are two possibilities, either
the two phases \( A_x X_z \) and A (or X) are ordered or the two phases display a tendency towards phase separation. This description is analogous to the "order-disorder theory" discussed in section 1.4. Only when the two phases are ordered, there is a homogeneous distribution of clusters in the alloy.

For Cs-Tl, the clusters proved to be homogeneously distributed in a large part of the composition range; the average cluster separation depends on the space which the 'free' Tl atoms between the clusters occupy. We can therefore conclude that CsTl and Ti form an ordered mixture. A comparison with other available composition studies shows that this is more of an exception than a rule. In K-Pb [113] (with 20%, 35%, 50% and 75% Pb), Cs-Sb [27] (with 50%, 35%, 25% and 15% Sb) and for the Cs-Bi alloys we measured (with 50% and 40% Bi), the prepeak remains on the same position when viewed as a function of composition. This can be explained by assuming there is a tendency towards phase separation between the stoichiometric alloy and the excess element. This idea is supported by the fact that the composition studies on Cs-Sb and K-Pb show a gradual increase of small angle scattering, away from the stoichiometric composition. According to the Bhatia-Thornton relations a large zero-wavevector limit indicates large concentration fluctuations, i.e. a tendency towards phase separation.

The \( \Omega_{\text{cell}} \) model describes the absolute number of atoms that are present in a cluster unexpectedly well, at least when the alloy is at its stoichiometric composition. Despite these nice and systematic results, we have to remember that we cannot interpret the structure in these liquid alloys as consisting of rigid well-defined clusters [114]. This also becomes clear from the measurements. For example in liquid KTL and CsTl, the average cluster-size and the volume fraction of clusters are the same. Yet, the prepeak height in \( A_{\text{Tl,TL}}(q) \) of liquid KTL is clearly lower than that of CsTl. We imagine this is due to a difference in cluster stability. The average cluster size is the same in KTL as in CsTl, which accounts for the same periodicity, but the distribution in cluster-sizes is broader in KTL than in CsTl, which accounts for the smaller prepeak. The difference in prepeak size is then a manifestation of Geertsma’s rule.

It is clear that the intermediate range ordering in the investigated alloys is determined by covalently bonded polyanions. The surprise is that the average size of the polyanions in each alloy is very well-determined by a specific valence rule, and is, to a large extent, independent of the stability of these polyanions. The liquid alloys are ordered in a more systematical way than we expected at the beginning of our investigation.
7.4 Further investigations

There are at least a few things that follow from this research which need further investigation. The Alkali-Bi alloys, for example, remain a puzzle. Their stoichiometry is uncertain and it depends on the physical properties that are measured. The investigations showed that liquid Cs-Bi alloys contain many Bi$_2$ dumbbells, which is chemically not understood. A determination of the crystal structure of Cs$_2$Bi$_2$ is therefore very much desired.

A large part of this thesis dealt with the structure of alkali-Tl alloys with or without additional third elements. E.g. the measurement on K$_{10}$Tl$_{10}$Pd gave an extraordinary result. In order to verify the existence of Pd centered Tl$_{10}$Pd clusters in the liquid, Pd EXAFS measurements could be made. The Pd-Tl coordination number should give an indication on the average cluster structure. Different Pd-fractions in KTI may give an indication of the stoichiometry of the alloy. And, as CsTl clusters more strongly than KTI, what happens if Pd is added to CsTl?

It also would be very instructive to measure the structure factors of the alkali-Ga alloys at lower wavevectors, in order to see the whole prepeak. For further measurements on these systems the use of a different container material than Ti$_{0.68}$Zr$_{0.32}$ should be considered (e.g. tungsten, niobium or molybdenum).

There is still more room for experimental investigations. By comparing different measurements, and making composition studies, perhaps more systematical trends will be discovered. Also theoretically still much work can be done. There is need for a statistical description of structures in liquid alloys, taking the valence rules into account.

And many times we have wished that more fundamental data existed on liquid alloys. For example densities have to be guessed, the phase-diagrams are less than perfect, or practical data on corrosiveness etc. are not available. The problem is that such experiments are often difficult and the prestige they lend to the scientist is relatively low.
## Appendix A

### Cross sections

<table>
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<th>element</th>
<th>$b_c$</th>
<th>$\sigma_c$</th>
<th>$\sigma_i$</th>
<th>$\sigma_s$</th>
<th>$\sigma_a$</th>
<th>$M$</th>
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<tbody>
<tr>
<td>Na</td>
<td>3.63(2)</td>
<td>1.66(2)</td>
<td>1.62(3)</td>
<td>3.28(4)</td>
<td>0.530(5)</td>
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<td>K</td>
<td>3.71(2)</td>
<td>1.73(2)</td>
<td>0.25(10)</td>
<td>1.98(10)</td>
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<tr>
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<td>5.42(2)</td>
<td>3.69(15)</td>
<td>0.21(5)</td>
<td>3.90(6)</td>
<td>29.0(1.5)</td>
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<td>7.2879(16)</td>
<td>6.674(3)</td>
<td>0.00(2)</td>
<td>6.7(2)</td>
<td>2.9(1)</td>
<td>69.7</td>
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<td>9.678(9)</td>
<td>0.15(15)</td>
<td>9.83(15)</td>
<td>3.43(6)</td>
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</tr>
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<td>11.39(17)</td>
<td>0.0021(10)</td>
<td>11.39(17)</td>
<td>0.104(17)</td>
<td>205</td>
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<tr>
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<td>0.0084(10)</td>
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<td>0.43(5)</td>
<td>7.75(13)</td>
<td>98.65(9)</td>
<td>197</td>
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Table A.1: Average coherent scattering lengths (in fm) and the coherent, incoherent, total and absorption cross sections (in barns = 100 fm$^2$) for some elements, based on values tabulated by Sears [58]. The absorption cross section is given for 0.18 nm neutrons (2200 ms$^{-1}$) and depends linearly on the wavelength. The atomic mass $M$ of the elements is given in the last column.
Bibliography


[115] Z.-C. Dong, private communication.
Nanometer superstructure in some liquid alloys; a neutron diffraction study

by Suzan A. van der Aart

Summary

In this thesis an experimental study on structure in several liquid alloys is described. The alloys investigated are neither metallic-like nor salt-like, but somewhere in between. The so-called "Zintl-phases" to this group. They are characterized by strong chemical interactions that lead to the formation of polyanions.

In this summary we use the oversimplified purely ionic notation for polyanions; $(X_n)^{m-}$. The solid phases display complex crystal structures containing such polyanions. They can be effectively described by chemical valence rules [41]. The chemical interactions also play an important role in the liquid phase. Physical properties that are measured as a function of the composition usually display one or sometimes two "sharp" maxima, each indicating the existence of a "liquid compound".

Using the technique of neutron diffraction it is possible to look directly at the structure of such liquid compounds. This has been done, for example, for liquid alkali-lead alloys [25]. It became clear that the $(\text{Pb}_4)^{4-}$-tetrahedra existing in the solid phase, partly "survive" in the liquid phase. Many other liquid Zintl-phases have been investigated in the past decade [1]. In the systematic search through the periodic system, alkali-thallium alloys were encountered that showed ordering over extremely large distances
of ~ 1 nm [35]. This intriguing phenomenon of (super)structure in liquid alloys formed the stimulus to the investigations described in this thesis.

We have made neutron diffraction measurements on several alkali-group 13 alloys, in order to investigate this ordering and to search for analogies to their solid counterparts. The measured structure factors were analysed with the use of "Reverse Monte Carlo" (RMC) modelling in order to extract information on the Short Range Ordering (SRO), like coordination numbers and bond-angle distributions. The prepeak in the structure factor gives information on the superstructure or the "Intermediate Range Ordering" (IRO). Using the position of the prepeak and the density of the alloy we can estimate how many atoms are present in a periodic volume, $\Omega_{\text{cell}}$, which can be regarded as a kind of unit-cell in the liquid alloy that represents the IRO.

Neutron diffraction measurements on liquid KTL using $^{205}$Tl isotope substitution show that the IRO is only present in the Tl-Tl correlations of the structure. The short Tl-Tl nearest neighbour distances indicate that relatively strong covalent bonds are present in the liquid. The distances are identical to those in the solid phases KTL and $K_5Tl_{11}$. These phases contain $(Tl_6)^{6-}$ and $(Tl_{11})^{7-}$ clusters, respectively. Also the obtained Tl-Tl coordination number of 4 is in agreement with the solid phases. It is therefore plausible that Tl-clusters, like those in the solid phases, partly survive in the liquid phase. Also at higher temperature (660 °C instead of 360 °C) the short range Tl-Tl correlations hardly change. The lowering and broadening of the prepeak tells us that the IRO decreases, but it is still clearly present at higher temperature. The clusters seem to be fairly stable even at high temperatures. The results on the temperature dependence are similar to those in reference [86] for the CsTl system.

Several Tl-rich Cs-Tl alloys were measured to investigate the IRO as a function of the composition. The results are surprisingly systematic. The height of the prepeak increases, over a large composition range, linearly with the Cs/Tl fraction and its shift in position can be described with a very simple model. The model entails cluster-units of $(Tl_n)^{m-}(Cs^+)_m$, which are separated by the excess of Tl atoms. Using the "$\Omega_{\text{cell}}$ model" we estimate $n$ and $m$ to be ~ 7 with an error of about 10%. This cluster size is in between that of a $(Tl_6)^{6-}$ cluster and a $(Tl_{11})^{7-}$ cluster, although the first cannot be excluded given the estimated errors. Applying the same model to the KTL alloy we find the same values, within the errors, for $n$ and $m$. The fact that identical cluster-units occur in liquid Cs-Tl alloys with different compositions, as well as in KTL, gives strong indications for the existence of a valence rule governing the structure of these liquid alloys.
We have made several measurements on K-Tl alloys with additional third species elements like Pd, Zn and Au. The relationship to the respective solid phases is strongest for the alloy K₁₀Tl₁₀Pd. The solid phase contains Pd-centered (Tl₁₀)¹⁰⁻ clusters, where Pd stabilizes the cluster by providing central bonding. The prepeak in the structure factor of liquid K₁₀Tl₁₀Pd also indicates larger and more stable clusters than in liquid KTI. The Ω₁₀ model shows that the periodic volume contains ~20 atoms, which is very close to the number of atoms in a K₁₀Tl₁₀Pd unit.

We have also measured the liquid alloys NaGa, KGa₃ and CsGa₃. The structure factors show a strong, but not very well defined IRO. The prepeaks are very broad and occur at very low wavevector. It seems that there is quite a diffuse network of large Ga atoms present in the liquid alloys. This in contrast to well defined IRO in the alkali-Tl alloys. The differences between the alkali-Ga and the alkali-Tl alloys are probably similar to the differences that show up in their solid phases. In solid alkali-Ga phases large Ga clusters occur (up to 15 Ga atoms) that are usually interlinked in three-dimensional networks, whereas in the alkali-Tl alloys the clusters are isolated from each other.

The structure of liquid CsBi and Cs₃Bi₂ was also measured. Unexpectedly, we found many Bi₂ dumbbells in our configuration of atoms obtained with RMC and a coordination number of ~1. For chains longer than 2 atoms we found that angles near 83° frequently occurred. Perhaps this is related to the square planar shape of the few Bi-polyanions that have been found. In agreement with resistivity data on this system [101], we found that polyanions in liquid Cs₃Bi₂ are relatively more stable than in CsBi.

Applying the Ω₁₀ model to previous measurements shows that the results are quite systematically in agreement with the valence rules. For equiatomic liquid alkali-Pb alloys it indicates ~8 atoms present in Ω₁₀ in accordance with cluster-units like (Pb₄)⁴⁻(A⁺)₄. The same is true for the alkali-Sn alloys. Consistent results are also obtained for KTe where (Te₂)²⁻ dumbbells are present. The model does usually not apply for Na-alloys, in those cases the IRO is only very weak.

We may conclude that the relation to the solid phases is even stronger and more systematic than what we expected at the beginning of our investigation. Even though the stability of the IRO in all those alloys is different it appears that the average structure is very well-determined by the valence rules that apply.
Nanometer superstructuur in enkele vloeibare legeringen; een neutronenverstrooingsonderzoek

door Suzan A. van der Aart

Samenvatting

In dit proefschrift wordt een experimenteel onderzoek beschreven aan verschillende vloeibare legeringen. De onderzochte legeringen bezitten eigenschappen die inliggen tussen die van metalen en die van zouten. In deze legeringen komen sterke chemische interacties voor die kunnen leiden tot de formatie van polyanionen. Ze worden dan "Zintl-fasen" genoemd. In deze samenvatting zal een versimpelde notatie worden gebruikt voor de polyanionen, namelijk $(X_n)^{m-}$, als waren het echte ionen. In de kristalstructuren van de Zintl-fasen komen ook zulke polyanionen voor. Ze kunnen goed beschreven worden aan de hand van chemische valentieregels [41]. De chemische interacties blijven een belangrijke rol spelen in de vloeibare fase. Als bepaalde fysische grootheden gemeten worden als functie van de concentratie komen vaak één of soms twee "scherpe" maxima voor, welke een voorkeurscompositie aangeven.

Met behulp van neutronenverstrooiing is het mogelijk om direct naar de structuur van zulke vloeibare legeringen te kijken. Dit is in het verleden gedaan voor vloeibare alkali-lood legeringen [25]. Uit deze meetingen bleek dat $(Pb_4)^{4-}$ tetrahedra, die ook voorkomen in de kristallijne fase, gedeel-
telijk blijven bestaan in de vloeibare fase. Vele andere vloeibare Zintl-fasen zijn in de afgelopen tien jaar onderzocht [1]. Op een gegeven moment werd ontdekt dat in alkali-thallium legeringen een ordening optreedt over een extreem grote afstand van ongeveer 1 nm [35]. Dit boeiende verschijnsel van (super)structuur in vloeibare legeringen vormde de inspiratie voor dit onderzoek.

We hebben neutronendiffractie metingen gedaan aan verschillende alkali-groep 13 legeringen om deze ordening te onderzoeken en eventuele relaties te vinden met de bekende kristalstructuren. De gemeten structuurfactoren werden geanalyseerd met behulp van "Reverse Monte Carlo" (RMC) modelberekeningen. Hiermee kan informatie uit de data worden gehaald, met name over de korte afstands ordening van de atomen zoals coördinatiegetallen en bindingshoekverdelingen. De zogenaamde "prepeak" in de structuurfactor geeft informatie over de intermediare afstands ordening, ofwel de superstructuur. Met behulp van de positie van deze prepeak en de dichtheid van de legering kunnen we een schatting maken van het aantal atomen dat zich in een zogenaamd periodiek volume, $\Omega_{cell}$, bevindt. $\Omega_{cell}$ kan beschouwd worden als een soort eenheidscel in de vloeibare legering die de superstructuur beschrijft.

Er zijn neutronendiffractie metingen gedaan aan vloeibaar KTL waarbij $^{205}$Tl isotoop substitutie werd toegepast. Deze metingen laten eindelijk zien dat de superstructuur alleen bepaald wordt door de Tl-Tl correlaties. De korte Tl-Tl naaste buur afstand geeft aan dat er covalente bindingen voorkomen in de vloeistof. De gemiddelde afstanden tussen de Tl atomen zijn zelfs gelijk aan die in de kristalstructuren KTL en K$_2$Tl$_{11}$. In deze vaste stoffen komen respectievelijk (Tl$_6$)$^{6-}$ en (Tl$_{11}$)$^{7-}$ clusters voor. Ook het Tl-Tl coordinatie getal van 4 dat voor de vloeistof werd gevonden is in overeenstemming met dat van de genoemde vaste stoffen. Waarschijnlijk wordt de periodiciteit in de vloeibare legering veroorzaakt door het gedeeltelijk 'overleven' van zulke Tl-clusters. Ook bij hogere temperatuur (660 °C in plaats van 360 °C) is er nauwelijks verandering te zien in de korte afstands ordening van de Tl atomen onderling. De prepeak wordt bij hogere temperatuur wel lager en breder. De superstructuur is echter nog duidelijk aanwezig, hetgeen aangeeft dat de clusters redelijk stabiel zijn, zelfs bij hoge temperaturen. Deze resultaten van de temperatuurafhankelijkheid zijn soortgelijk aan die in referentie [86] voor het CsTl systeem.

Enkele Tl-rijke Cs-Tl legeringen werden gemeten om de superstructuur te onderzoeken als functie van de samenstelling. De resultaten laten een verrassende systematiek zien. De hoogte van de prepeak neemt, over een zeer groot gedeelte van het composietbereik, lineair toe met de Cs/Tl
fractie en de verschuiving van de prepeakpositie kan verklaard worden met een simpel model. Dit simpele model houdt in dat bepaalde clustereenheden \((\text{Tl}_n)^{m-}(\text{Cs}^+)_m\) in de vloeistof bestaan, van elkaar gescheiden door de overige Tl atomen. Met gebruik van het "\(\Omega_{\text{cell}}\) model" kunnen we schatten dat \(n\) en \(m\) ongeveer 7 zijn (± 10%). De clustergrootte ligt tussen die van \((\text{Tl}_6)^6-\) en \((\text{Tl}_{11})^7-\) in, hoewel de eerste binnen de geschatte fout overeen zou kunnen komen. Als we dit model toepassen op vloeibaar KTL vinden we dezelfde waarden voor \(n\) en \(m\). Het feit dat identieke clustereenheden voorkomen in verschillende vloeibare Tl-rijke Cs-Tl legeringen en in KTL is een sterke indicatie dat een valentiepactie van deze structuur bepaalt.

Ook zijn er verschillende metingen gedaan aan K-Tl waaraan nog een derde element is toegevoegd, zoals Pd, Zn of Au. Een zeer duidelijke relatie tussen de kristalstructuur en de structuur in de vloeibare legering werd gevonden voor K\(_{10}\)Tl\(_{10}\)Pd. In de vaste fase komen Pd-gecentreerde \((\text{Tl}_{10})^{10-}\) clusters voor, waarin het Pd atoom de cluster stabiliseert door centrale bindingen mogelijk te maken. De prepeak in de structuurfactor van vloeibaar K\(_{10}\)Tl\(_{10}\)Pd geeft ook aan dat de clusters groter en stabielier zijn dan in vloeibaar KTL. Het \(\Omega_{\text{cell}}\) model laat zien dat het periodieke volume uit ongeveer 20 atomen bestaat, hetgeen goed overeenkomt met het aantal atomen in een K\(_{10}\)Tl\(_{10}\)Pd eenheid.

We hebben ook metingen gedaan aan vloeibaar NaGa, KGa\(_3\) en CsGa\(_3\). Aan de structuurfactor is te zien dat er een sterke, maar niet erg goed gedefinieerde, superstructuur bestaat. De prepeaken zijn erg hoog en breed en ligggen bij een kleine golfvector. Het lijkt erop dat er een diffuus netwerk van grote Ga-clusters bestaat in deze vloeibare legeringen. Dit is in tegenstelling tot de goed gedefinieerde superstructuur in de alkalii-Tl legeringen. De verschillen zijn waarschijnlijk gerelateerd aan de verschillen die in de vaste stoffen bestaan. In de kristalstructuur van alkalii-Ga legeringen komen grote Ga-clusters voor (tot ongeveer 15 atomen groot) die in de meeste gevallen met elkaar verbonden zijn tot een driedimensionaal netwerk. In de kristalstructuren van de alkalii-Tl legeringen komen de Tl-clusters altijd los voor.

De structuurfactor van vloeibaar CsBi en Cs\(_3\)Bi\(_2\) werd ook gemeten. Verwonderend was dat we veel Bi\(_2\) haltes aantroffen in de configuratie van atomen die we verkregen door middel van een RMC modelberekening. Het gemiddelde Bi-Bi coördinatiegetal was ook \(~ 1\). In de enkele ketentjes die langer dan 2 atomen waren, bleken hoeken van ongeveer 83° veelvuldig voor te komen. Dit is misschien gerelateerd aan de vierkante platte vorm van de enkele Bi-polyanionen die bekend zijn. In overeenstemming met weerstands- metingen aan dit systeem [101] vonden we dat de polyanionen in vloeibaar
Cs₃Bi₂ relatief gezien iets stabielere zijn dan in CsBi.

Het toepassen van het $\Omega_{\text{cell}}$ model op eerdere metingen geeft aan dat de resultaten systematisch zijn en in overeenstemming met de valentierregels. Er zijn bijvoorbeeld $\sim$8 atomen aanwezig in $\Omega_{\text{cell}}$ van alle vloeibare equiatomaire alkali-Pb legeringen (behalve NaPb) hetgeen in overeenstemming is met clustereenheden als (Pb₄)⁴⁺(A⁺)₄. Hetzelfde geldt voor de alkali-Sn legeringen. Ook voor vloeibaar KTe, waarin (Te₂)²⁻-halters voorkomen, zijn de resultaten consistent. Over het algemeen geldt het model niet voor de Na-legeringen omdat daarin de superstructuur erg zwak aanwezig is.

We kunnen concluderen dat de relatie tussen de vaste fase en de vloeibare fase nog duidelijker en systematischer is dan wat we verwachtten aan het begin van dit onderzoek. Ook al is de stabiliteit van de superstructuur in de verschillende legeringen anders, het blijkt dat de gemiddelde structuur erg goed gedefinieerd is door de valentieregels die gelden.
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Curriculum Vitae

I was born the 20th of July 1969 in Leiden. From 1982-1985 I attended the HAVO at the Rijksscholengemeenschap Prof. Zeeman in Zierikzee. In 1987 I graduated from the HAVO at Instituut Blankesteijn in Utrecht and in 1988 from VWO. In the same year I started to study experimental physics at the University of Utrecht. On the 30th of August 1993 I obtained my masters degree and graduated on the subject: "Interference effects of electron-excited autoionising states of He" in the department of Atom Physics. After a short intermezzo of studying Sinology in Leiden, I started my work as a PhD. student in April 1994 at the Interfacultair Reactor Instituut of the Delft University of Technology. Here I investigated the structure in liquid alloys, using the technique of neutron scattering. This work is described in this thesis, and was supervised by dr. P. Verkerk, prof. dr. W. van der Lugt and prof. dr. ir. L. A. de Graaf.
List of publications

1. The effect of adding a tea-spoon of palladium to liquid potassium-thallium.
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