A study of the disorder in heavily doped $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ by neutron scattering, ionic conductivity and specific heat measurements

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Abstract. The ionic disorder in single crystals of the fluorite-type solid solutions $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ (with $x = 0.209$ and $x = 0.492$) has been studied in the temperature range from room temperature to 800°C by diffuse neutron scattering, ionic conductivity, and specific heat measurements. From the diffuse neutron scattering it was found that the disorder was dominated by 222 clusters, which at low temperatures ($T < 400$°C) were ordered along the (100) direction in aggregates of up to four 222 clusters. The correlation between the different 222 clusters in the aggregates is slowly lost when entering into the fast ion phase. The lifetime of the 222 clusters could not, even at the highest temperatures, be determined by neutron scattering ($\tau > 10^{-16}$ s), in agreement with NMR results which suggest a jump frequency below 75 MHz. The temperatures at which the steepest slopes are found in the loss of correlations and in the conductivity coincide at approximately 630°C. At this temperature no clear anomaly is observed in the specific heat. Based on these findings we propose a conduction mechanism where F⁻ ions are moving through the lattice by means of rearrangements of the 222 clusters.

1. Introduction

Metal halides with the fluorite ($\text{CaF}_2$) structure, notably the alkaline-earth fluorides and $\beta$-$\text{PbF}_2$, have interesting solid electrolyte properties. These materials attain values of ionic conductivity of the order of ionic melts a few hundred degrees below the actual melting point (O’Keeffe 1976). In the same temperature range a broad anomaly in the specific heat is observed (Belosludov et al. 1974, Schröter and Nölting 1980), and structural studies (Hutchings et al. 1984) have shown that the diffuse transition is connected with a partial disordering of the anion sublattice by formation of Frenkel defects.

Another interesting property of the fluorides is their high accessibility to doping with several metal-, tri- and tetrafluorides (e.g. $\text{REF}_3$, RE = $\text{Y}$, $\text{La}$–$\text{Lu}$; $\text{UF}_4$ and $\text{ThF}_4$), and the consequent substantial increase in the ionic conductivity at low and moderate temperatures. As a result of doping a strong suppression of the specific heat anomaly has been observed in heavily doped $\text{Pb}_{1-x}\text{U}_x\text{F}_{2+x}$ (Ouwerkerk et al. 1983, Andersen et al. 1983). Both groups of authors ascribe the suppression of the specific heat anomaly with increasing solute level to the lack of an undisturbed lattice. Ouwerkerk et al. (1983)
assume as a consequence that it becomes less probable for thermally generated defects to be formed. However, Andersen et al (1983) have shown, from a comparison with a model calculation, that interactions between defects may lead to increased concentrations of thermally generated defects at low temperatures despite the reduction in the configurational entropy on doping. According to the former suggestion the high values of the ionic conductivities may be interpreted as being a result of fast ionic mobility rather than to massive disorder in the anion array (Wapenaar and Schoonman 1979, Catlow 1980).

The defect structure of fluorite systems has been studied by many experimental techniques. In very dilute systems dielectric relaxation studies by small-signal AC response, and ion thermal current (ITC) techniques (Wapenaar and Schoonman 1981, Wapenaar et al 1982) have shown that the defect structure comprises simple dipoles of dopant cations and associated fluorines on nearest- or next-nearest-neighbour interstitial sites to preserve charge neutrality. With increasing dopant concentration there is a trend towards further association and clustering. Since the pioneering work by Cheetham et al (1971) and Catlow (1976a, b) several defect structure studies on heavily doped anion-excess systems have been implemented. Although no direct verification has been established until now, the occurrence of the so-called 222 cluster has often been proposed. The 222 cluster configuration, which was introduced by Cheetham et al (1971) and Catlow (1976a, b), is structurally quite similar to the major defect component found at high temperatures in several pure fluorite systems (Hutchings et al 1984).

Ba$_{1-x}$La$_x$F$_{2+x}$ forms a prototype fluorite system both as an intrinsic ionic conductor (x = 0), and with respect to doping (x \leq 0.55). The most significant property of the system is the substantial increase in the ionic conductivity in the low-temperature region. An enhancement of more than eight orders of magnitude has been observed at room temperature for x = 0.5.

The current neutron scattering, ionic conductivity, and specific heat studies on Ba$_{1-x}$La$_x$F$_{2+x}$ (x = 0.209 and x = 0.492) were undertaken in order to investigate the structural properties of heavily doped fluorites, and to correlate the structural information with the ionic conductivity, and the thermal properties. In the structural studies the basic idea was to investigate whether 222 clusters are present as significant defect structure components of heavily doped fluorite systems. Our results show that this is indeed the case. Additionally, we find evidence for short range correlations between the 222 clusters in both samples at low temperatures. Above 450 °C a decrease in these correlations is observed and they are gradually lost up to 800 °C. The influence of the short range correlations on the ionic conductivities has been studied by an extension of the previously performed measurements (Wapenaar et al 1981) to the temperature range above 600 °C. The specific heat measurements were performed in an attempt to evaluate the degrees of freedom involved in the loss of the short range correlations. A preliminary account of the structural data has been published earlier (Kjems et al 1983).

2. Experimental details

2.1. Sample preparation

The single crystals of Ba$_{1-x}$La$_x$F$_{2+x}$ were grown from mixed powders of BaF$_2$ (Merck, Suprapur) and LaF$_3$ (Alpha Division, 99.9%) using the Bridgman technique. Details have been reported before (Wapenaar et al 1981). Discs, 3–10 mm thick and 9 mm in
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diameter, were cut from single-crystalline ingots. For each concentration the sequence of experiments was: (1) neutron scattering, (2) ionic conductivity and (3) specific heat as a function of temperature.

2.2. Neutron scattering

The neutron scattering experiments were performed at the DR3 reactor at Risø National Laboratory using both a cold-neutron-source triple-axis spectrometer, and a four-circle diffractometer. The triple-axis spectrometer was equipped with pyrolytic graphite monochromator and analyser crystals oriented for the (002) reflection. The wavelength $\lambda$ for the triple-axis experiment was chosen to be $2.44\ \text{Å}$ where higher-order contaminations of the incoming beam could be removed by pyrolytic graphite filters. A typical choice for the collimation was $40'$ throughout the spectrometer. The four-circle diffractometer used a beryllium monochromator crystal mounted for the (002) reflection and a wavelength of $\lambda = 1.06\ \text{Å}$. With this set-up the higher-order contamination of the neutron beam is insignificant since the energies of higher-order reflections are in the range of vanishing thermal neutron intensities.

The neutron scattering experiments at elevated temperatures were performed under dynamic vacuum in a furnace equipped with a tantalum heating element, 0.12 m long and 0.025 m in diameter, surrounded by five concentric tantalum reflectors. The samples were wrapped in platinum foil and mounted on a stainless steel rod by use of tantalum wire.

Three types of neutron scattering experiments were performed. First the triple-axis spectrometer was used to make a thorough mapping at room temperature of the diffuse scattering of both samples ($x = 0.209$ and $x = 0.492$) in the scattering plane spanned by $(h00)$ and $(0kk)$ vectors in reciprocal space of the FCC fluorite lattice. This revealed an intense anisotropic diffuse scattering which tended to peak near diffuse satellite points $(hkl)\pm(00)$ in reciprocal space, especially for the $x = 0.492$ sample. A room-temperature scan of all the diffuse satellite points in the $q$-range up to the length of $(900)$ was then made on the $x = 0.492$ sample by use of the four-circle instrument. Finally, the temperature dependence, and energy width of the diffuse scattering at selected points in reciprocal space were determined by use of the triple-axis spectrometer.

2.3. Ionic conductivity

The bulk ionic conductivity was determined from standard admittance spectra investigations (see e.g. Bauerle 1969). A Solartron frequency response analyser 1174, equipped with a pre-amplifier system and a PDP 11/23 computer system was used for data collection and processing. The sample surfaces were polished to optical finish and subsequently platinum electrodes of approximately 1000 Å were sputtered onto the surfaces using a Balzer DC sputtering unit. Admittance parameters were recorded up to 800 °C in the frequency range from 0.1 to $10^6\ \text{Hz}$. A simple diagram corresponding to a geometrical capacitance in parallel with an almost perfect element due to the bulk resistance in series with a blocking electrode capacitance was found. This allowed the determination of the bulk conductivity from the intercept on the real axis of the high-frequency geometrical capacitance line. The measurements were performed in an atmosphere of high-purity nitrogen with a nominal content of oxygen below 2 ppm and water below 3 ppm.
2.4. Specific heat

The specific heat measurements were performed by use of a Perkin–Elmer DSC IIC scanning calorimeter which is operable between −175 and 725 °C. The experiments were performed in an atmosphere of high-purity nitrogen (see § 2.3 for specifications), and the sample was cleaned and polished to optical finish in a similar way to that for the conductivity investigations.

3. Results and analysis

3.1. Neutron scattering

The room-temperature contour maps of elastic scattering in the (011) plane for \( x = 0.209 \) and \( x = 0.492 \) are shown in figure 1. The energy distribution of the scattering was measured to be elastic to within the experimental resolution of 0.4 meV. Additional high-resolution investigations showed that the energy width is less than 0.05 meV. Between the Bragg peaks a significant anisotropic diffuse pattern is observed. The diffuse scattering arises from the deviations from the average periodic density of ions in the lattice and thus reflects the defect structure.

The patterns shown in figure 1 bear a strong resemblance to the high-temperature results of integrated quasi-elastic scattering intensities in CaF\(_2\) (Hutchings et al 1984) which could be reproduced very well by model calculations based on clusters similar to the 222 cluster defects. Model calculations based on 222 clusters formed on doping have been performed in the current study. The 222 cluster configuration is shown in figure 2. With the distances given in units of the lattice constant \( a \), the 222 cluster can be characterised by the following three defect components:

1. randomly substituted pairs of lanthanum ions on barium sites;
2. pairs of excess fluorine ions situated on interstitial sites but displaced \((\delta - \frac{1}{2}) \times \sqrt{2}\) along a (110) direction from the body centre of the simple fluorine interstitial cube; and

![Figure 1. Contour maps of the measured quasi-elastic diffuse neutron scattering intensities in the (011) plane of Ba\(_{1-x}\)La\(_x\)F\(_{3+x}\): (a) \( x = 0.209 \) and (b) \( x = 0.492 \). The indicated scale is arbitrary and different for the two samples.](image)
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(3) two relaxed fluorine ions displaced $3^{1/2}\varepsilon$ along the body diagonal from a regular fluorine site.

The model calculation follows the outline given by Hutchings et al (1984). It takes into account the various ways in which the cluster can be formed according to the lattice symmetry. The average density of ions in the lattice is derived as if all lanthanums are in 222 clusters. The result of the diffuse scattering arising from this ensemble average of single 222 clusters with displacement parameters, as derived below and given in table 1, is shown in figure 3. The qualitative agreement between the experimental data and the result of the model calculations is quite satisfactory. The major discrepancies, which are most pronounced for the $x = 0.492$ results, are the larger width in the calculated local maxima and the appearance of diffuse satellite intensities in the experimental data at $(hkl) \pm (000)$. We interpret these observations as a tendency towards ordering of the 222 clusters in more extended aggregates. The longitudinal width and the position of the

Figure 2. Single 222 cluster in the fluorite lattice. The lattice constant is two times the edge of the small cubes. Regular fluorine ions on the corners of the small cubes are not shown. Large full circle, $\text{La}^{3+};$ large open circles, $\text{F}^{-};$ small full circle, $\text{Ba}^{2+};$ small open circles, $\text{V}_1$.

Figure 3. Calculated contour map of the diffuse scattering from an average over the possible orientations of 222 clusters. The displacement parameters and the Debye–Waller factor used in the calculations are given in table 1. Intensities are on an arbitrary scale.
satellite peaks suggest that the correlations between the 222 clusters extend over 14 Å for $x = 0.209$ and 38 Å for $x = 0.492$ (corresponding to $2\xi$, where $\xi$ is the correlation length) and have an internal modulation period of $\frac{3}{2}a$ ($a = 6.20$ Å). One can deduce that the centres of the 222 clusters are situated on a FCC lattice similar to the cation lattice, because the satellites are found at all Bragg peaks. However, the large transverse widths of the satellites indicate that the clusters are essentially uncorrelated in the directions perpendicular to the modulation direction. This is consistent with an aggregate configuration of 222 clusters separated by $\frac{3}{2}a$ along the modulation axis and $\pm\frac{1}{2}a$ along any of the perpendicular (100) directions. With a spatial degeneracy of four in the transverse location of subsequent clusters and an average number of four clusters in an aggregate, as found for $x = 0.492$, a large number of different aggregate configurations exists (for the average aggregate $4^3 = 64$ for each modulation direction). An example of a cluster aggregate for $x = 0.492$ is shown in figure 4. Probably, the aggregate configurations are determined mainly by the pinning forces created by the random distribution of lanthanum pairs in the cation lattice.

Quantitative support for the presence of 222 cluster aggregates has been obtained by a comparison between the theoretical expression for the scattering peak intensities, and the intensities of the observed satellite peaks along the (100) direction in reciprocal space which have scattering vectors smaller than (900). The model calculation treats the satellite peaks as if they were Bragg peaks. That is, the structure factors are calculated...
from the enlarged cell (cell dimensions: \( \frac{3}{2} a \times a \times a \)) shown in figure 2 with scattering amplitudes equal to the scattering amplitudes of the actual ions and vacancies of the 222 cluster relative to the average amplitudes of all possible sites. Thereby, the model contains the following parameters: the two positional parameters \( \delta \) and \( e \) for interstitial and relaxed fluorine ions, as described above, a Debye–Waller factor \( B \) and a scaling factor \( I_0 \). The result of a least-squares fit of the model to the experimental data is shown in Table 1. As indicated, the fit turned out to be rather insensitive to the \( \delta \)-parameter. Considering that our model only allows for defect structures which may be formed from regular and 222 cluster sites, the agreement is quite satisfactory. The result verifies that 222 cluster aggregates are formed and suggests that a considerable number of the lanthanum ions are part of 222 clusters. The full set of satellites might, in principle, be included in the comparison with the model calculation. However, this requires an average over all the possible ways in which the aggregates may be formed, and thereby very elaborate calculations. A rigorous model should also treat the correlation between the 222 clusters in agreement with the experimental observations. A more thorough analysis of the structural data on the basis of extended model calculations is planned.

Although both the intensity distribution of the broad diffuse scattering and the intensities of the diffuse satellite peaks suggest the 222 cluster as the basic defect component we have considered other possibilities. The positions of the satellite peaks confine the possibilities to defects with longitudinal extensions smaller than \( \frac{3}{2} a \). This means that defect structures that include large clusters, for example, those formed by association of cubo-octahedral and fluorite-type cells as suggested by Matar et al. (1984), are not very probable in \( \text{Ba}_{1-x}\text{La}_x\text{F}_{2+x} \). The 342 cluster discussed by Cheetham et al. (1971) has been considered. However, the calculated intensities from 342 clusters give poor agreement both with the broad intensity distribution shown in figure 1, and the diffuse satellite peak intensities given in Table 1. The main discrepancies observed from the calculated values are low diffuse scattering intensities between (111) and (222), and strong satellite peaks at \((3.3300)\) and \((4.6700)\) relative to those at \((2.6700)\) and \((5.3300)\). Association of simpler defect components like a lanthanum–fluorine pair to a 222 cluster has also been considered, but only minor changes were observed in the calculated diffuse pattern. This means that only minor concentrations of 342 clusters may be present but randomly distributed simpler associates are possible defect components.

<table>
<thead>
<tr>
<th>( h \pm \frac{1}{2} )</th>
<th>( I_{\text{obs}} ) (counts)</th>
<th>( I_{\text{expt}} )</th>
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<td>0.67</td>
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<td>8.67</td>
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*Table 1.* Comparison of observed satellite peak intensities \((h \pm \frac{1}{2} 00)\) in \( \text{Ba}_{0.93}\text{La}_{0.04}\text{F}_{2.492} \) and a least-squares fit to a theoretical model based on 222 cluster aggregates with finite longitudinal correlation length. The defect cluster coordinates \( \delta \) and \( e \) relate to interstitial and relaxed fluorine ion positions as described in the text. The Debye–Waller factor is defined as \( B = 8\pi^2(a^2) \). \( I_0 \) is a model calculation scale factor. \( \chi^2 = 1.96 \) (quality of fit); \( I_0 = 24.7 \pm 1.7 \); \( B = 0.23 \pm 0.12 \text{ A}^2 \); \( \delta = 0.15 \pm 0.5 \); \( e = 0.127 \pm 0.002 \).
The presence of 222 cluster aggregates has been studied as a function of temperature by measurements of the most intense satellite peak at \( Q = (2.69 \, 0.0) \) for both \( x = 0.209 \) and \( x = 0.492 \). The results for the peak intensities are given in figure 5. Concomitant with the decrease in the peak intensity above 450 °C an increase in the \( q \)-widths is observed. We interpret this result as a loss of correlation between the 222 clusters. The 222 clusters themselves are probably intact since the broad distribution around \( (2.69 \, 0.0) \), which is representative of the individual 222 clusters, remains.

3.2. Ionic conductivity

The ionic conductivities from 300 to 800 °C of \( \text{Ba}_{1-x}\text{La}_x\text{F}_{2+z} \), with \( x = 0.209 \) and \( x = 0.492 \) are shown in figure 6 as an Arrhenius plot. The result obtained for \( \text{BaF}_2 \) by Oberschmidt and Lazarus (1980) is shown for reference. Wapenaar (1980) has performed similar investigations on heavily doped \( \text{Ba}_{1-x}\text{La}_x\text{F}_{2+z} \) in the temperature range from room temperature to 600 °C. In the overlapping temperature region there is good agreement between our results for \( x = 0.492 \) and those of Wapenaar for \( x = 0.448 \) since an activation energy of 0.57 eV and an absolute value of \( \sigma T = 100 \, \text{S} \, \text{m}^{-1} \text{K} \) was found at 300 °C for both samples. For the \( x = 0.209 \) sample, however, Wapenaar finds an activation energy of 0.645 eV and an absolute value of \( \sigma T = 40 \, \text{S} \, \text{m}^{-1} \text{K} \) at 300 °C whereas the similar results from our data give an activation energy of 0.54 eV and \( \sigma T = 100 \, \text{S} \, \text{m}^{-1} \text{K} \). We have not pursued the source of these discrepancies for the \( x = 0.209 \) results since our main effort in the conductivity study was to trace the possible influence of the disappearance of the short range correlations between the 222 clusters.

The most significant features in our results are the anomalous behaviour found in both samples in the temperature region above 500 °C. By a comparison with the temperature variation of the \( (2.69 \, 0.0) \) satellite peak intensities shown in figure 5 there is a striking coincidence in the temperature regions of the two events. This observation strongly supports the assertion that the short range correlations between the 222 clusters have significant influence on the conductivity mechanisms.
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A thorough explanation for the anomalous deviation from the simple linear Arrhenius behaviour of the conductivity results has not yet been fully established. The observed initial slight decline of the slope between 500 and 620 °C is especially difficult to account for as an inherent property on the basis of the present understanding of the system. However, it has previously been proposed (Wapenaar and Schoonman 1979) that irreversible incorporation of oxygen might be responsible for the decrease in conductivity observed in samples which have been heated to in excess of 440 °C. Such aging phenomena are observed in figure 6 for the $x = 0.492$ sample in the temperature region above 590 °C. It should be recalled, however, that the sample had already been heated several times in dynamical vacuum to temperatures as high as 900 °C during the neutron scattering experiments. The observed aging effect might therefore result from a part of the irreversible oxygen incorporation process. Whether a reversible oxygen incorporation process also takes place in the temperature region above 500 °C, and thereby might be responsible for the initial declination of the slope remains speculative at present. However, there is close agreement between the temperature of steepest slope in the loss of correlations between 222 clusters and the temperature of steepest slope in the ionic conductivity. Such behaviour is clearly expected if the fluorine ions involved in the formation of the 222 clusters also contribute to the ionic conduction process. In this case the correlations between the 222 clusters limit the degree of freedom for at least some of the mobile fluorine ions and thereby reduce the conductivity. In the enhanced ionic motion model (Wapenaar 1980), which has been successfully applied to account for the ionic conductivity of heavily doped $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ $(0.05 < x < 0.5)$ below 600 °C, the fluorine ions in the 222 clusters are considered to be immobile. The rationale for this assumption is the high binding energies of 222 clusters calculated by Catlow (1976b). However, the large concentrations of lanthanums in the current systems give rise to several equivalent configurations of the defect structure composed of 222 clusters and maybe also of simpler defect components. If, therefore, the processes consisting of a rearrangement of 222 clusters eventually combined with an adjustment of adjacent
simpler defects have a low activation energy, they are likely to play an important role in the conduction mechanism. Since the cluster–cluster correlations observed in our neutron scattering experiments obstruct these rearrangement processes it is expected that the loss of the correlations with increasing temperature would lead to an anomalous increase in the ionic conductivity. However, deciding whether this mechanism in the ionic transport process is responsible for the experimental observations awaits a comparison with a model calculation based on the microscopic properties of the system.

3.3. Specific heat studies

The specific heat measurements on Ba$_{80.59}$La$_{19.40}$F$_{2.42}$ in the temperature range from 225 to 725 °C are shown in figure 7. From 225 to 675 °C the results show an almost linear increase, most likely caused by anharmonic lattice effects. An expected additional contribution from the entropy involved in the loss of correlation between the 222 clusters could not be detected with certainty within the resolution and accuracy of the scanning calorimeter, although a very weak and broad anomaly might be present. Above 675 °C an additional anomaly starts to develop but since only the tail of this distribution is within the accessible temperature range of our instrument the conclusion may only be speculative. However, 675 °C is clearly in the upper limit of the temperature range where the 222 cluster aggregates disintegrate. It is therefore not very likely that the developing anomaly is related to the loss of correlations in the 222 cluster aggregates. Rather, it results from the diffuse onset of the fast ionic phase. This interpretation agrees with the result of similar studies on Pb$_{1-x}$U$_x$F$_{2+x}$ (Andersen et al 1983, Ouwerkerk et al 1983) where a weak specific heat anomaly was observed in the temperature range where the ionic conductivity levels off (Ouwerkerk and Schoonman 1983) often referred to as the onset of the fast ionic conducting phase.

4. Discussion

From quasi-elastic diffuse neutron scattering studies we have established the presence of 222 clusters, and cluster aggregates as major defect components in heavily doped fluorite systems. Qualitatively the type of 222 cluster found in Ba$_{1-x}$La$_x$F$_{2+x}$ is quite similar to the thermally generated 222 clusters in the pure systems except that the interstitial fluorine ions are charge-compensated by cation excess charges instead of vacancies in the regular fluorine lattice. There are significant differences, however, particularly in the dynamic properties of the two types of defect structure. In the pure
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systems the energy width of the diffuse scattering in the fast ion phase is $q$-dependent (Hutchings et al 1984) and, in all cases, it could be resolved experimentally. A rough estimate of the average lifetime of a thermally generated 222 cluster would therefore give values of the order of $10^{-13}$ s. In contrast we have found no observable energy width in the spectra from the doped type of 222 clusters ($\Delta E \approx 0.05$ meV), which means that at the temperatures studied these clusters are static on a time scale shorter than $10^{-10}$ s. The difference between the characteristic lifetimes of the cluster configurations most probably results from pinning of clusters at the available pairs of lanthanums in the heavily doped systems. The pinning forces effectively increase the energy barrier for change of the cluster configuration, and thereby stabilise the clusters. Apparently the forces between the 222 clusters are relatively weak in both the pure and the doped systems. In the pure systems there has not been any observation of cluster aggregates, probably because the couplings between the 222 clusters are overcome by thermal fluctuations in the temperature region where appreciable numbers are generated. In the doped systems a sufficient number of 222 clusters are present at low temperatures for the couplings between them to become effective. The couplings tend to form orderings of 222 clusters in the directions of the cube axes with a period of $\frac{1}{2}$ lattice units but apparently the pinning forces, which are randomly distributed, dominate and prevent long range ordering.

At temperatures above approximately 800 °C the short range correlations between the 222 clusters in both the systems studied are destroyed by thermal fluctuations. Estimates of the degrees of freedom involved in the loss of correlations in the defect structures could not be resolved from the specific heat studies below 675 °C. This means that only a minor fraction of 222 clusters disintegrate in this temperature region. In agreement with the conclusions from the neutron scattering studies the loss of correlations is therefore most probably related to the couplings between the 222 clusters rather than to the clusters themselves. Qualitatively, the lack of a specific heat anomaly in the temperature region where the aggregates disintegrate into individual 222 clusters may be due to the one-dimensional character of the correlations and the small configurational entropy associated with reorientation of 222 clusters when most of the lanthanum ions are part of 222 clusters. A similar type of argument has been used in the interpretation of the relatively small specific heat anomalies observed in heavily doped $\text{Pb}_{1-x}\text{U}_x\text{F}_{2+\delta}$ (Andersen et al 1983).

The presence of the cluster aggregates influences the ionic conductivity significantly. From our conductivity data we have found strong evidence for a conduction mechanism which directly includes at least some of the fluorine ions in the 222 clusters as mobile species. In the enhanced ionic motion (EIM) model (Wapenaar and Schoonman 1979, Wapenaar 1980), it is suggested that the ionic conduction is established by a few per cent of effective mobile charge carriers outside the more static defect components like the 222 clusters. The enhancement of the ionic conductivity is related solely to an increase in the mobility due to lowering of the migration enthalpy. From a simple extrapolation of the EIM model results to the temperature region above 600 °C we might argue that the effective number of mobile charge carriers roughly doubles by the loss of correlations between the 222 clusters. It should be recalled, however, that the anomaly in the conductivity is observed close to the high-temperature region where the increase in the conductivity levels off. In the high-temperature region, which in the pure systems is often referred to as the fast ionic phase, the conductivity mechanism is still subject to discussion. Evaluations of the number of free charge carriers in the transition region are therefore not well established. Apparently, there is a controversy over the large number
of defects deduced from studies of specific heat (Andersen et al 1983), neutron diffraction and diffuse neutron scattering (Hutchings et al 1984), and the relatively few conducting defects deduced from the EIM model (Wapenaar and Schoonman 1979, Wapenaar 1980), molecular dynamics simulations (Dixon and Gillan 1980, Gillan and Dixon 1980a, b), and x-ray diffraction studies based on effective anharmonic single-ion potentials (Bachman and Schulz 1983). It should be recalled, however, that the definition of a defect differs among the authors as a result of both the experimental conditions and the level of details from which they are derived. From specific heat studies the derived number of thermally generated defects includes both interstitial and relaxed ions. The same definition is used in the interpretation of the neutron scattering data whereas molecular dynamics results give the number of defects with their associated strain fields. Since the interstitial and relaxed fluorine ions are strongly correlated, it is not surprising that the effective number of free charge carriers derived from the EIM model is found to be in better agreement with the result from molecular dynamics simulations than those of specific heat and neutron scattering studies.

Another interesting property of the heavily doped systems is the time scale of the 222 cluster rearrangements. The present observations that the short range correlations between the 222 clusters have completely disappeared above 800 °C without significantly affecting their concentration indicate that the cluster configuration may not be stable in longer time scales (t ≃ 10^{-19} s). A slow dynamical rearrangement of 222 clusters on the possible lanthanum pairs in the lattice is therefore a plausible suggestion for the process which leads to the break of the short range cluster–cluster correlations. The cluster configuration rearrangements in heavily doped fluorides has been studied via the fluorine NMR linewidth (Panhuysen et al 1981). The results from Ba_{0.52}La_{0.48}F_{2.48} suggest a jump frequency around 36 MHz at 485 °C and an activation energy of 0.21 eV. The possibility of studying rearrangement lifetimes of cluster aggregates within the accessible range of a neutron scattering experiment might exist in lightly doped fluorites. Whether cluster aggregates are formed in these systems or even the pure ones depend on the competition between the formation energy of the 222 clusters relative to the correlation energy and the thermal disorder.

Although the current work has imparted significant information concerning the defect structure of heavily doped fluorites it also opened many questions to be answered from future experimental studies. The ionic conductivity studies indicate a strong dependence on the defect structure configuration which cannot be accounted for on the basis of established theories. In the temperature region above 600 °C our findings lend support to a conduction mechanism where rearrangements of 222 clusters mediate the effective transport of the F^- ions through the lattice. However, more elaborate theoretical models are required before the relations between the defect structure and the ionic conductivity in these systems are fully understood.

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