Superconductivity and localization in thin polycrystalline tungsten-germanium films

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We report magnetoresistance measurements on a high-resistivity ($\approx 200 \mu\Omega \text{ cm}$) crystalline material that becomes superconducting. Our samples are thin polycrystalline $\text{W}_{100-x}\text{Ge}_x$ ($x=16-18$) films, measured above the superconducting transition temperature. This is an opportunity to test the predictions for electron-phonon scattering in the presence of strong elastic scattering. The films are deposited using a low-temperature chemical-vapor-deposition process and show the crystalline β -W structure (A15) with a T_c of around 3 K and H_{c2} near 8 T. Contributions from both superconducting fluctuations and weak localization to the magnetoresistance are discussed and the inelastic-scattering rate is found to be determined by electron-phonon scattering.

INTRODUCTION

The coexistence of superconductivity with a resistivity two orders-of-magnitude higher than in ordinary metals has made amorphous metal alloys such as Mo-Ge (Ref. 1) and Nb-Si (Ref. 2) model systems for the investigation of electron-localization effects. Similar alloys exist also in the case of tungsten alloyed with Si,³ Ge,⁴ and Re.⁵ These materials have been found to stabilize amorphous thin films and lead to transition temperatures in the range 2–5 K, substantially higher than the value of 11 mK in crystalline α -W. Using a low-temperature chemical-vapor-deposition (CVD) process we have been able to grow thin, crystalline W-Ge films. These films exhibit high normal-state resistivities of $200 \mu\Omega \text{ cm}$ and transition temperatures around 3 K, yet are characterized by the β -W (A15) crystal structure. Here we report on detailed magnetoresistance measurements.

Two effects determine the low-temperature magnetoresistance of thin, two-dimensional films; the electron localization effect and the effect of superconducting fluctuations. From the temperature and magnetic-field dependence of these contributions transport parameters, such as scattering lengths, can be determined. To our knowledge, the first magnetoresistance measurements on

W thin films are performed by Rosenbaum *et al.*⁶ Their samples are probably polycrystalline, but with further unspecified structure. Raffy *et al.*⁵ studied amorphous W-Re alloys. For crystalline β -W little is known about the low-temperature electronic transport properties besides the superconducting transition temperature.⁷ The crystalline W-Ge films investigated here allow a direct comparison with the electron-phonon scattering theory for the dirty crystalline limit.⁸

THEORY

For two-dimensional metal films detailed predictions for low-temperature quantum contributions to the classical residual resistance are available.⁹ There are different contributions to the magnetoresistance; here we use localization contribution and Maki-Thompson superconducting fluctuation contribution, other contributions are comparatively small in our case. This magnetoresistance we label in the following as

$$\Delta R/R = [R(T, B) - R(T, 0)]/R(T, 0).$$

Here B is an externally applied perpendicular magnetic field. The sign of the weak-localization contribution depends on the strength of spin-orbit scattering character-

ized by a spin-orbit scattering time τ_{so} , in the limit of small τ_{so} (as expected for high- Z materials) the sign is positive.

In addition to τ_{so} also the inelastic-scattering time τ_i and the magnetic impurity scattering time τ_s determine the magnetoresistance. It is common to write the expression for the magnetoresistance in terms of two effective magnetic fields B_ϕ and B_2 associated with relevant combinations of the scattering rates, namely the phase breaking rate $\tau_\phi^{-1} = \tau_i^{-1} + 2\tau_s^{-1}$ and the rate $\tau_2^{-1} = \tau_i^{-1} + \frac{4}{3}\tau_{so}^{-1} + \frac{2}{3}\tau_s^{-1}$. The corresponding fields B_x ($x = \phi, 2$) are then given by $B_x = \hbar/(4eD\tau_x)$, where D is the three-dimensional diffusion constant which is given by $D = v_F^2\tau/3$ with v_F the Fermi velocity. The weak-localization contribution to the two-dimensional magnetoresistance is then written as⁹

$$\frac{\Delta R^{\text{loc}}}{R} = \frac{3}{2}f_2(B, B_2) - \frac{1}{2}f_2(B, B_\phi), \quad (1a)$$

with

$$f_2(B, B_x) = -\frac{e^2 R_\square}{2\pi^2 \hbar} \left[\Psi \left(\frac{1}{2} + \frac{B_x}{B} \right) - \ln \frac{B_0}{B} \right]. \quad (1b)$$

Here $\Psi(x)$ is the digamma function, $R_\square$ is the sheet resistance of the film, and $B_0 = \hbar/4eD\tau$ is the characteristic field corresponding to elastic scattering. For strong spin-orbit scattering, i.e., $B_2/B \gg 1$, the B dependence of the term $f_2(B, B_2)$ in Eq. (1a) becomes much smaller than that of $f_2(B, B_\phi)$ and the magnetoresistance becomes insensitive to the spin-orbit scattering time.

For temperatures and magnetic fields such that $2\pi k_B(T - T_c) \gg \hbar/\tau_\phi$, $4eDB$ the Maki-Thompson contribution to the magnetoresistance^{9,10} is written as

$$\Delta R^{\text{MT}}/R = -\beta(T/T_c)f_2(B, B_\phi), \quad (2)$$

where $\beta(T/T_c)$ is a coefficient tabulated by Larkin.¹⁰ For fixed temperature, Eq. (2) displays the same structure as Eq. (1). The Maki-Thompson term thus contributes in a similar fashion to a positive magnetoresistance as the weak-localization term in the strong spin-orbit scattering limit.

SAMPLE PREPARATION

For sample fabrication a low-temperature chemical-vapor-deposition (CVD) process was employed based on the reduction of WF_6 with GeH_4 . Details of the CVD process were reported elsewhere.⁴ Substrate tempera-

tures during growth between 300 and 435°C resulted in films with a pure β -W crystal structure as seen in the x-ray-diffraction patterns. The crystalline structure was also revealed by transmission electron microscopy. Rutherford backscattering analysis showed a germanium content of 16–18 % in the films studied. The resistivity of these samples was about 200 $\mu\Omega \text{ cm}$ (Table I). This high value did not appear to be strongly dependent on the Ge content in the β -W phase but changed from 190 to 10 $\mu\Omega \text{ cm}$ at a deposition temperature of 435°C, above which α -W was deposited. The α -W phase has a Ge concentration of less than 5%. We did not detect any Ge segregation, e.g., at grain boundaries or at the films' surface, at temperatures below 700°C. This indicates that the Ge was uniformly incorporated into the film. We believe that the high resistivity of our films resulted from compositional disorder in the crystalline structure where all atoms sat on regular A15 places but randomly W atoms were replaced by Ge atoms.

The films were grown on a patterned amorphous silicon layer on an oxidized silicon substrate. The patterning was done by optical lithography. In the CVD process the W was deposited selectively on the amorphous silicon, it only grew on conducting surfaces and not on insulators. Typical film dimensions were 10- μm wide and 1000- μm long.

EXPERIMENTAL DATA AND FITTING RESULTS

In the following we discuss results on three different β -W films (see Table I). Using the measured upper critical field slope, $dB_c/dT = 2.37 \text{ T/K} - 2.64 \text{ T/K}$ near T_c , $D^{-1} = \pi e / 4k_B (dB_c/dT)$ gives the diffusion constant. If we assume $v_F = 1.5 \times 10^6 \text{ m/s}$, which is an average Fermi velocity for metals, this diffusion constant results in an elastic-scattering time $\tau = 0.06 \text{ fs}$, corresponding to a mean free path l of about 0.1 nm. This value for the Fermi velocity does not take into account the band structure of β -W or the influence of the high Ge content. Since no other data for β -W are available we assume $l = 0.1 \text{ nm}$ in the following. Equation $\tau/\tau_{so} = (\alpha Z)^4$ (Ref. 11) then leads to spin-orbit parameters $\tau_{so} = 0.7 \text{ fs}$, $l_{so} = (D\tau_{so})^{1/2} = 0.2 \text{ nm}$, and $B_{so} = \hbar/(4el_{so}^2) = 5 \times 10^3 \text{ T}$. These values place our films into the strong spin-orbit scattering regime. They should, however, only be considered rough estimates.^{6,9,12} The upper limit for the spin-orbit scattering length can be derived from the fits of the magnetoresistance.

The resistance as a function of applied magnetic field for sample D is plotted in Fig. 1 for different tempera-

TABLE I. Relevant parameters for the studied $\text{W}_{100-x}\text{Ge}_x$ films, T_c and H_c are defined at the midpoint of the resistive transition.

Sample $\text{W}_{100-x}\text{Ge}_x$	d nm	$R_\square$ Ω	T_c K	H_c T	D m^2/s	τ_s^{-1} 10^9 s^{-1}	A $\text{s}^{-1} \text{ K}^{-p}$	p
I , $x = 16$	14	135	2.82	6.82	4.15×10^{-5}	2.6	3.17×10^6	4
D , $x = 17$	7.5	290	3.43	7.45	4.63×10^{-5}	13	4.92×10^6	4
F , $x = 17$ (best fit)	7.5	290	3.39	8.75	4.63×10^{-5}	9.9	13.8×10^7	3
						21	8.80×10^6	4
Rosenbaum <i>et al.</i>	5	306	2.75	≈ 5	6.7×10^{-5}	≈ 10

FIG. 1. Magnetoresistance curves $\Delta R/R = [R(T, B) - R(T, 0)]/R(T, 0)$ for a crystalline, 7.5-nm thick $\text{W}_{83}\text{Ge}_{17}$ film. The solid lines are fits to weak-localization and Maki-Thompson contributions [Eqs. (1) and (2)].

tures. The magnetoresistance is positive at all temperatures which clearly indicates strong spin-orbit scattering. The solid lines are fits of the Maki-Thompson and weak-localization functions as described by Eqs. (1) and (2) to the data using a nonlinear least-squares fitting procedure. From these fits the inelastic- and magnetic-scattering times are obtained. All values below 20 fs for τ_{so} give equally good fitting results, confirming the idea of a spin-orbit scattering length l_{so} below 1 nm. The fits in Fig. 1 extend over the range $|B| < k_B(T - T_c)/4eD$. In this range the sample is two dimensional with respect to weak localization, i.e., $d^2 \ll D\tau_0\hbar/(4eB)$, and the additional condition, $2\pi k_B(T - T_c) \gg \hbar/\tau_\phi$, for the applicability of the Maki-Thompson term are fulfilled. Other contributions like Aslamazov-Larkin fluctuations and the electron-electron interactions are neglected over the range of the fits as they are comparatively small.

We note that the fits to Eqs. (1) and (2) work remarkably well considering that these are results from a perturbation expansion relying on $(k_F l)^{-1} \ll 1$. In our case we find a product $(k_F l)^{-1} = 2.5$, using $k_F l = Dm^*/\hbar$ and taking the free-electron mass for m^* . However, weak-localization theory has also been found to successfully describe magnetoresistance data in related amorphous systems¹ such as amorphous Mo-Ge with comparable resistivity and Ge content.

SCATTERING RATE THEORY

In order to obtain the temperature dependence of the phase breaking rate, it is useful to represent τ_ϕ as a sum of three different contributions, namely electron-electron, electron-phonon, and magnetic scattering: $\tau_\phi^{-1} = \tau_{\text{ee}}^{-1} + \tau_{\text{ep}}^{-1} + 2\tau_s^{-1}$. While magnetic scattering is independent of temperature, in two-dimensional systems in the dirty limit the contribution of electron-electron scattering¹³ is dependent on T :

$$\tau_{\text{ee}}^{-1} = \left[\frac{e^2 R_\square}{2\pi\hbar^2} \right] k_B T \ln \left[\frac{\pi\hbar}{e^2 R_\square} \frac{(\hbar D/k_B T)}{d^2} \right]. \quad (3)$$

Equation (3) holds for film thicknesses d in the regime $\hbar D/k_B T \ll d^2 \ll \pi\hbar^2 D/k_B T e^2 R_\square$.

Electron-phonon scattering leads to a rate τ_{ep}^{-1} proportional to T^p with p between 2 and 4 depending on the ratio $k_B T l/\hbar c_s$. Here c_s is the velocity of sound and l is the electronic mean free path. For the dirty limit in crystalline materials Schmid and co-workers⁸ predict for $k_B T l/\hbar c_s \ll 1$ that

$$\tau_{\text{ep}}^{-1} = \eta \frac{(\pi k T)^4 l}{\hbar^2 m M c_s^5}, \quad (4)$$

where M is the ion mass, m is the electron mass, and $\eta = \frac{1}{20}$ for the transverse case and $\eta = \frac{1}{30}$ for the longitudinal. Because for longitudinal phonons c_s is usually larger than for transverse phonons, only scattering of electrons with transverse phonons is important.

DISCUSSION

The phase breaking rate τ_ϕ resulting from the fits is plotted in Fig. 2. The temperature dependence of τ_ϕ is fitted to

$$\tau_\phi^{-1} = 2\tau_s^{-1} + 5.07 \times 10^6 R_\square T \ln \left[\frac{10^{-7} D}{R_\square d^2 T} \right] + A T^p. \quad (5)$$

We find temperature-independent magnetic-scattering rates between $\tau_s^{-1} = 0.3 \times 10^{10} \text{ s}^{-1}$ and $1.3 \times 10^{10} \text{ s}^{-1}$. A power $p = 4$ for the electron-phonon scattering contribution gives the best fits for two samples, resulting in a coefficient A of $3.17 \times 10^6 \text{ s}^{-1} \text{ K}^{-4}$ and $4.92 \times 10^6 \text{ s}^{-1} \text{ K}^{-4}$. From Eq. (4) with a weighted average of the ion masses and $l = 0.1 \text{ nm}$ we obtain $1.3 \times 10^3 \text{ m/s}$ and $1.2 \times 10^3 \text{ m/s}$ for the transverse speed of sound. These values can be used to calculate an estimate for the Fermi velocity using the Bohm-Staver relation¹⁴ $v_F = c_s \sqrt{3M/Qm}$, where Q is the charge of the ions in units e . The resulting v_F on the order of 10^6 m/s serves as a consistency check for our earlier assumption of an average Fermi velocity, even without taking into account different longitudinal and transverse sound propagation. For film F a power $p = 3$ produces the best fitting results with a coefficient $A = 13.8 \times 10^7 \text{ s}^{-1} \text{ K}^{-3}$. Figure 2 compares the $p = 4$ fit with the $p = 3$ fit. In Table I also the $p = 4$ results are given. The difference between sample D and F is at present not understood. Using $c_s = 1.2 \times 10^3 \text{ m/s}$ we find $k_B T l/\hbar c_s = 10^{-2} T \ll 1$ over the relevant temperature range. Taking into account that the longitudinal sound propagation speed is usually larger than the transverse we conclude that all films are well within the dirty limit for electron-phonon scattering. Equation (4) may be used and $p = 4$ is the expected exponent.⁸

The temperature dependence with power 3–4 of τ_ϕ^{-1} in our data is in contrast to results on amorphous W-Re alloys. In these materials Raffy and Laibowitz⁵ find a linear temperature dependence of τ_ϕ^{-1} which they explain by assuming that τ_ϕ^{-1} is dominated by electron-electron scattering. An alternative explanation could be that in

FIG. 2. Temperature dependences of the phase breaking rate. The solid lines (—) are the best fits including contributions from magnetic, electron-electron, and electron-phonon scattering (Eq. 5). For comparison the broken line (---) shows a fit with $p=4$ to the *F* sample.

amorphous materials electron-phonon scattering has a different temperature dependence. Also shown in Fig. 2 are the data obtained by Rosenbaum *et al.*⁶ in granular W films. Their data indeed are of comparable magnitude with ours. Since also the inclusion of oxygen can stabilize the β -W phase it is conceivable that the films of Rosenbaum *et al.*, fabricated by vacuum arc deposition, contained a significant fraction of β -W grains. Our films, on the other hand, are formed in the presence of a strongly reducing CVD environment and showed no detectable oxygen content. However, it is possible that a thin layer of oxide formed on top of the films after fabrication.

Vranken, Haesendonck, and Bruynseraede¹⁵ showed that such surface layers enhance τ_s^{-1} . Our thinner films indeed exhibit an increased rate τ_s^{-1} .

CONCLUSIONS

In summary we find that the magnetoresistance data on crystalline W-Ge films can be well understood in terms of weak-localization and Maki-Thompson contributions. The calculated phase breaking rate can be explained using magnetic scattering, electron-electron scattering, and electron-phonon scattering. The electron-phonon scattering follows the theory of Schmid⁸ reasonably well. These crystalline films are comparable to amorphous transition metal alloys such as Mo-Ge and Nb-Si, with respect to the high resistivity and the strong spin-orbit scattering. In contrast to amorphous W-Re alloys, however, the temperature dependence of the inelastic-scattering rate can certainly not be explained on the basis of electron-electron interactions and significant electron-phonon scattering is found.

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¹J. M. Graybeal, *Physica* **135B**, 113 (1985).

²M. Denhoff and S. Gyax, *Phys. Rev. B* **34**, 151 (1986).

³S. Kondo, *J. Mater. Res.* **7**, 853 (1992).

⁴C. A. van der Jeugd, G. J. Leusink, G. C. A. M. Janssen, and S. Radelaar, *Appl. Phys. Lett.* **57**, 354 (1990).

⁵H. Raffy and R. B. Laibowitz, *Phys. Rev. B* **30**, 5541 (1984); H. Raffy, R. B. Laibowitz, P. Chaudhari, and S. Maekawa, *ibid.* **28**, 6607 (1983).

⁶R. Rosenbaum, M. Ben-Shlomo, S. Goldsmith, and R. L. Boxman, *Phys. Rev. B* **39**, 10009 (1989).

⁷W. L. Bond, A. S. Cooper, K. Andres, G. W. Hull, T. H. Geballe, and B. T. Matthias, *Phys. Rev. Lett.* **15**, 260 (1965); S. Basavaiah and S. R. Pollack, *J. Appl. Phys.* **39**, 5548 (1968).

⁸A. Schmid, *Z. Phys.* **259**, 421 (1973); B. Keck and A. Schmid, *J. Low Temp. Phys.* **24**, 611 (1976); A. Schmid, *Localization, Interaction and Transport Phenomena* (Springer-Verlag, Berlin, 1985), p. 212; S. Chakravarty and A. Schmid, *Phys. Rep.* **140**, 193 (1986).

⁹B. L. Al'tshuler, A. G. Aronov, M. E. Gershenson, and Yu. V.

Sharvin, *Sov. Sci. Rev. A Phys.* **9**, 223 (1987), and references therein.

¹⁰A. I. Larkin, *Pis'ma Zh. Eksp. Teor. Fiz.* **31**, 239 (1980) [*JETP Lett.* **31**, 219 (1980)].

¹¹A. Abrikosov and L. P. Gor'kov, *Zh. Eksp. Teor. Fiz.* **42**, 1088 (1962) [*Sov. Phys. JETP* **15**, 752 (1962)].

¹²J. Romijn, R. M. G. Boesten, T. M. Klapwijk, and J. E. Mooij, in *Proceedings of the University of Tokyo International Symposium on Anderson Localization*, edited by T. Ando and H. Fukuyama, Springer Proceedings in Physics Vol. 28 (Springer-Verlag, Berlin, 1987), p. 198.

¹³B. L. Al'tshuler, A. G. Aronov, and D. E. Khmel'nitskii, *J. Phys. C* **15**, 7367 (1982).

¹⁴N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1976); D. Bohm and T. Staver, *Phys. Rev.* **84**, 836 (1950).

¹⁵J. Vranken, C. Van Haesendonck, and Y. Bruynseraede, *Phys. Rev. B* **37**, 8502 (1988).