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An enhanced superconductivity in the supersaturated Al–Si solid solutions

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Abstract. The Al L_{II-III} x-ray emission spectra, galvanomagnetic properties and superconductive-state parameters were investigated in supersaturated $Al_{1-x}Si_x$ FCC solid solutions obtained by a high-pressure treatment ($P \leq 8.0$ GPa). A drastic decrease in the charge carrier mobility and an anomalous behaviour of the hole concentration were found. The previous model which was used to describe the superconducting properties of Al–Si is reviewed. Anomalous galvanomagnetic properties and enhancement of the value of the superconducting temperature T_c are assumed to be connected with the local 'soft regions' in the vicinity of the lattice instability.

1. Introduction

The equilibrium value of the solubility of Si in an Al matrix under normal conditions is $x \leq 0.001$ [1]. Using a high-pressure high-temperature treatment ($P \leq 10$ GPa), metastable solid solutions with $x \simeq 0.2$ at liquid-nitrogen temperature were produced [2]. The reasons for the extremely large increase in T_c in such a metastable phase ($T_c \simeq 11$ K) [2] are not quite clear yet. The object of the present work was the detailed investigation of the galvanomagnetic and superconductive properties of the metastable FCC solid solutions $Al_{1-x}Si_x$ ($0 < x < 0.12$).

2. Experimental details

The samples of the FCC metastable solid solutions $Al_{1-x}Si_x$ (cylinder diameter, about 4 mm; height, about 4 mm) were produced in a 'toroid' high-pressure chamber [3] at 1–8 GPa and 800–1300 K. The value of the concentration x in the solid solutions was controlled by measuring the lattice parameter by x-ray diffraction (Cu Kα radiation) or with a Microzond MAR-1. The absence of foreign impurities was checked by mass spectrometry methods. No second-phase precipitation in the samples investigated was observed. Additional control of the inhomogeneity is provided by the susceptibility measurements which demonstrate a nearly total Meissner effect. The galvanomagnetic properties were investigated in magnetic

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fields up to 60 kOe and in the temperature range 1.6–300 K using a Van der Pauw four-point configuration. The Al L_{II-III} x-ray emission spectra were recorded with a Spectrozond instrument [4]. The magnetic susceptibility $\chi(T)$ was measured in a wide temperature range at pressures up to 0.7 GPa. The low-temperature heat capacity $C(T)$ was investigated in the range 2 K $< T <$ 40 K. The experimental details of the $C(T)$ measurement set-up will be published elsewhere. The procedure that we used to prepare the $Al_{1-x}Si_x$ samples for low-temperature experiments eliminates the possibility of decomposition.

3. Results and discussion

3.1. Galvanomagnetic properties

The Hall coefficient and magnetoresistance of pure Al have been investigated previously in detail (see, e.g., [5, 6]). For a description of the peculiarities of the behaviour of the galvanomagnetic properties, one can consider two kinds of charge carrier. The equations connecting the values of the Hall coefficient R and resistivity ρ with the corresponding partial values are presented for example in [7]:

$$R = [R_1\rho_2^2 + R_2\rho_1^2 + R_1R_2(R_1 + R_2)H^2]/[(\rho_1 + \rho_2)^2 + (R_1 + R_2)^2H^2] \tag{1}$$

$$\rho = [\rho_1\rho_2(\rho_1 + \rho_2) + (\rho_1R_2^2 + \rho_2R_1^2)H^2]/[(\rho_1 + \rho_2)^2 + (R_1 + R_2)^2H^2]. \tag{2}$$

For the isotropic case the following conditions hold:

$$\rho_1 = (en_1\mu_1)^{-1} \qquad \rho_2 = (en_2\mu_2)^{-1} \tag{3}$$

$$R_1(n_1ec)^{-1} \qquad R_2 = (n_2ec)^{-1}. \tag{4}$$

Using equations (1)–(4) and our experimental results (figure 1), one can evaluate the concentrations n of the electrons and concentrations p of the holes (figure 2(a), $x = 0$). These values are in good agreement with the previous results (see, e.g., [5]). The low values of the carrier mobilities μ_n^{Al}, $\mu_p^{Al} < 10^3$ cm^2 V^{-1} s^{-1} (figure 2(b), $x = 0$) are assumed to be caused by the preliminary pressure treatment of the Al samples.

For the homogeneous solid solutions the following additional assumption was used:

$$n(x_{Si}) = n(Al)(1 + x_{Si}). \tag{5}$$

It is necessary to point out that the magnetic field range which we used ($H < 60$ kOe) is not quite enough to estimate the H^2-term coefficients in equations (1) and (2) and hence the additional assumption (5) is needed to complete equations (1)–(4). The x-ray emission spectra Al L_{II-III} of the $Al_{1-x}Si_x$ samples were investigated to test equation (5). The data obtained are identical with the Al L_{II-III} spectra from [4]. The upper edge vicinity of the $I(E)$ spectra is presented in figure 3 and qualitatively confirms assumption (5). However, it should be mentioned that the Al L_{II-III} spectra were investigated at room temperature whereas the Hall and magnetoresistance measurements were made at $T \simeq 4.2$ K. Also additional smoothing of the spectra takes place at high excitation energies because of the creation and annihilation of phonons [8]. Thus one cannot exclude the presence of some fine structure in the electron density of states near the Fermi level.

From equations (1)–(5) the concentration dependences of the values of μ_n, μ_p, n and p for the solid solution were obtained (figure 2).

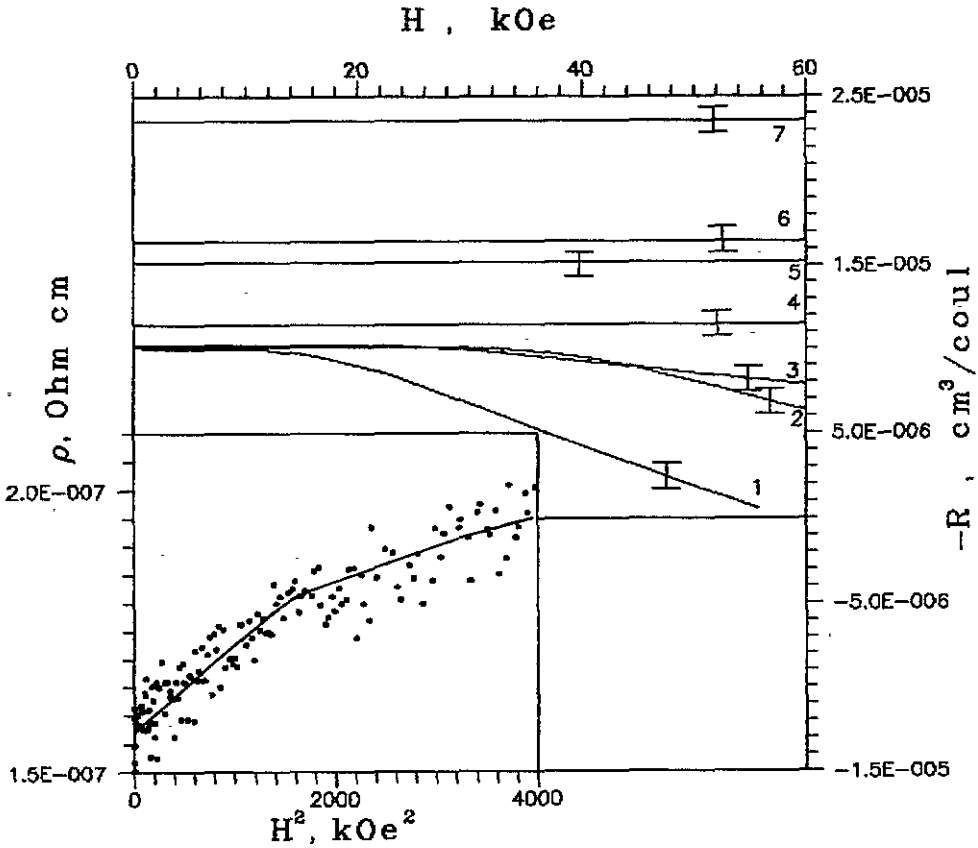

Figure 1. Magnetic field dependences of the Hall coefficient $R(H, T = 4.2\ \mathrm{K})$ in $Al_{1-x}Si_x$ solid solutions: curve 1, $x = 0$; curve 2, $x = 0.01$; curve 3, $x = 0.015$; curve 4, $x = 0.045$; curve 5, $x = 0.075$; curve 6, $x = 0.095$; curve 7, $x = 0.115$. In the inset the $\rho(H^2, T = 4.2\ \mathrm{K})$ dependence for the Al sample is presented.

A decrease in the carrier mobility occurs in two stages at 1–3 and 8–11 at.% Si. The range $x \simeq 0.06$–0.08 corresponds to a significant number of Si–Si pairs and triple Si clusters in the FCC lattice [9]. In this Si concentration region (6–8 at.%) an increase in hole concentration takes place. The increase in p is probably connected with the appearance of some defects in the FCC lattice. At the same time, one can note that an additional peak of heat release appears in this concentration region [9] during the high-temperature annealing of these samples.

3.2. Superconductive properties

The $\rho(T)$ dependences for the $Al_{1-x}Si_x$ samples are similar to those obtained in [10]. The linear decrease in ρ at $T \simeq 80$–300 K changes in the saturation regime at $T \leq 30$ K. However, the value of $(d\rho/dT)|_{80\ \mathrm{K}<T<300\ \mathrm{K}} \simeq 1.4 \times 10^{-8}\ \Omega\ \mathrm{cm\ K^{-1}}$ is conserved for all concentrations of Si in the solid solutions in our experiments, while in [10] different $d\rho/dT$-values were obtained for the different Si contents. We assume that the discrepancy is connected with the inhomogeneity of the solid solutions reported in [10] and with the

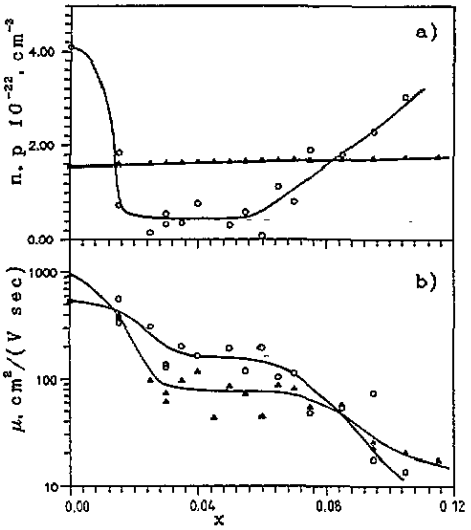

Figure 2. The Si content dependences of (*a*) concentration and (*b*) mobility in $Al_{1-x}Si_x$ ($T = 4.2$ K) of electrons (△) and holes (○).

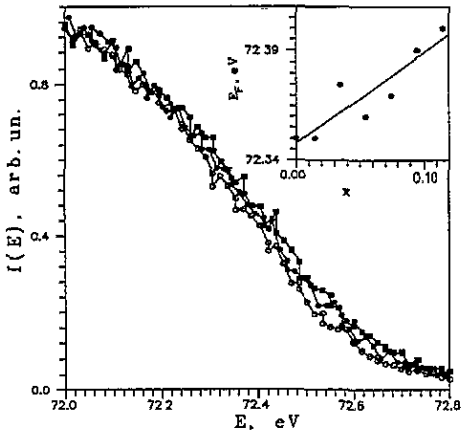

Figure 3. The experimental Al L_{II-III} x-ray emission spectra corresponding to the upper edge of the band in $Al_{1-x}Si_x$: ○, $x = 0$; ●, $x = 0.055$; ■, $x = 0.095$. In the inset the concentration dependence of E_F is presented.

presence of the large share of pure diamond-like crystalline Si in the samples obtained by the multimode melt-spinning method [10]. Also it should be mentioned that the changes in $d\rho/dT$ were used in [10] to evaluate the changes in the Debye temperature Θ_D in the solid solutions.

At low temperatures for all samples, a sharp transition to the superconductive state was observed. The resistivity $\rho(T)$ and magnetic susceptibility $\chi(T)$ data are shown in figures 4(*a*) and 4(*b*), respectively. The H–T diagram was constructed from the $\rho(T, H)$ data and is presented in figure 5.

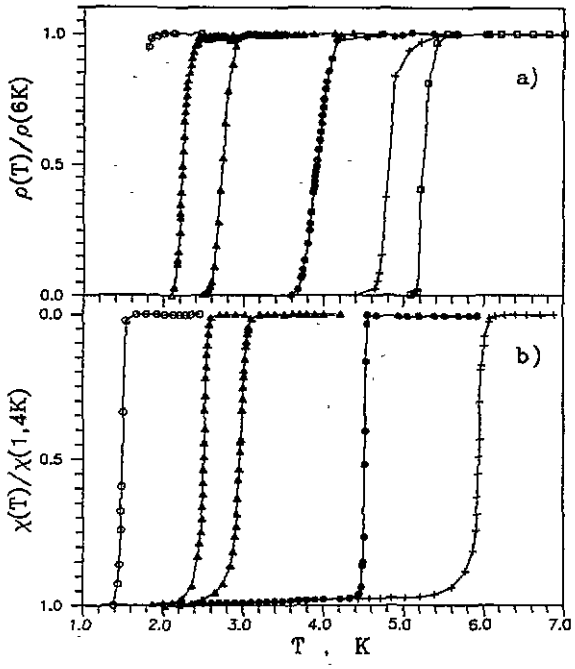

Figure 4. The temperature dependences of (*a*) resistivity ρ and (*b*) diamagnetic susceptibility χ near T_c in $Al_{1-x}Si_x$ solid solutions: (*a*) ○, $x = 0.035$; △, $x = 0.04$; △, $x = 0.05$; ●, $x = 0.065$; +, $x = 0.08$; □, $x = 0.095$; (*b*) ○, $x = 0.03$; △, $x = 0.05$; △, $x = 0.055$, ●, $x = 0.08$; +, $x = 0.11$.

The $Al_{1-x}Si_x$ FCC solid solutions are the type II superconductors for $x \geq 0.01$. The dependences of the upper critical field $H_{c2}(0)$ and the derivative $(dH_{c2}/dT)(T = T_c)$ on T_c are presented in the inset in figure 5. At $T_c \simeq 5.0$ K ($x \simeq 0.08$–0.09) there are noticeable changes in the slopes of these dependences, probably connected with a modification of the superconductive state. It should be noted that the anomalies of the concentration dependences of the charge carrier mobility and hole concentration mentioned above occur in the same region.

The values of coherence length $\xi = (\Phi_0/2\pi H_{c2})^{1/2}$ (Φ_0 is the magnetic flux quantum) were evaluated and presented in the same inset in figure 5.

The measurements of the low-temperature heat capacity allow us to define the values Θ_D and γ (γ is the linear coefficient of the electron part of the specific heat). The experimental $C(T)$ curve was approximated by the dependence $C(T) = \gamma T + \beta T^3$. The γ-value is increased by a factor of 1.5 for $x = 0.08$ (figure 6(*a*)), whereas Θ_D is changed insignificantly. This behaviour of Θ_D contradicts the results in [11], where a decrease in Θ_D (about 10%) was found for $Al_{0.94}Si_{0.06}$ in comparison with pure Al. The discrepancy is possibly caused by two main factors. One is the narrow experimental temperature interval (3 K $< T <$ 7 K) which was used in [11] and the other is connected with the traces of Al–Si superconductive phases with $T_c > 3$ K in the samples investigated in [11]. In [12], softening of the phonon modes was established for $Al_{0.94}Si_{0.06}$ by investigation of the inelastic neutron scattering. The enhancement of T_c is probably connected with the softening. It should be mentioned that a similar softening of the phonon spectra takes place in many metallic glasses (see for example [13]). However, the value of Θ_D is almost invariable in Al–Si for $x \leq 0.08$, and the models being used for quantitative evaluations

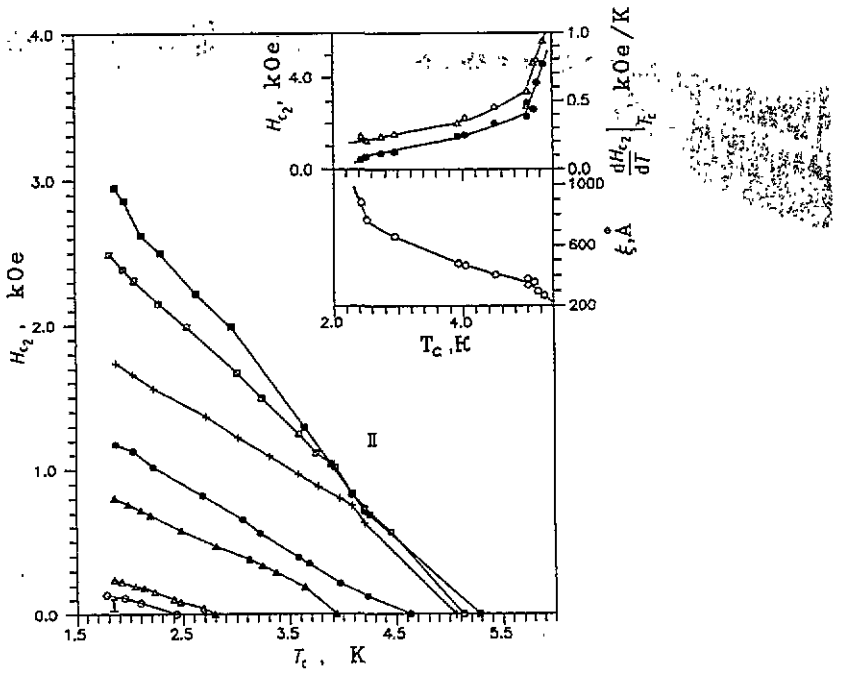

Figure 5. H–T diagram for $Al_{1-x}Si_x$: ○, $x = 0.045$; △, $x = 0.055$; △, $x = 0.065$; ●, $x = 0.07$; +, $x = 0.075$; □, $x = 0.085$; ■, $x = 0.095$. I is the superconductive state, and II is the normal state. The inset contains the following dependences: ●, upper critical field H_{c2} (T_c); △, $(dH_{c2}/dT)|_{T=T_c} = f(T_c)$; ○, coherence length $\xi(T_c)$.

of T_c [11, 12] are not very accurate. It is necessary to use McMillan's equation [14] for the correct evaluation of T_c enhancement from the softening of a phonon spectrum for the $Al_{1-x}Si_x$ solid solutions:

$$T_c = (\langle\omega_{log}\rangle/1.2)\exp\{1.04(1+\lambda)/[\lambda - \mu^*(1+0.62\lambda)]\} \tag{6}$$

where $\langle\omega_{log}\rangle$ is the logarithmically averaged phonon frequency, λ is the constant of electron–phonon interaction and μ^* is the Coulomb pseudopotential constant. However, there are some difficulties in this method connected with the absence of any information on the function $\alpha^2(\omega)G(\omega)$ for $Al_{1-x}Si_x$ in equations

$$\lambda = 2\int_0^\infty \frac{\alpha^2(\omega)G(\omega)\,d\omega}{\omega} \tag{7}$$

$$\langle\omega_{log}\rangle = \exp\left(2\int_0^\infty \frac{d\omega}{\omega}\alpha^2(\omega)G(\omega)\frac{\ln\omega}{\lambda}\right). \tag{8}$$

It is also necessary to take into account the possible influence on T_c of the electron density-of-state variations. Additional investigations are essential to deduce the values of λ and $N(E_F)$ separately from the equation $\gamma = \frac{1}{3}\pi^2 k_B N(E_F)(1+\lambda)$.

The phonon mode softening is possibly connected with the non-equilibrium state of Si atoms in the solid solutions. It is assumed in [2] that Si atoms in FCC solution are in the metallic state. The non-equilibrium factor for the states of Si atoms must obviously decrease

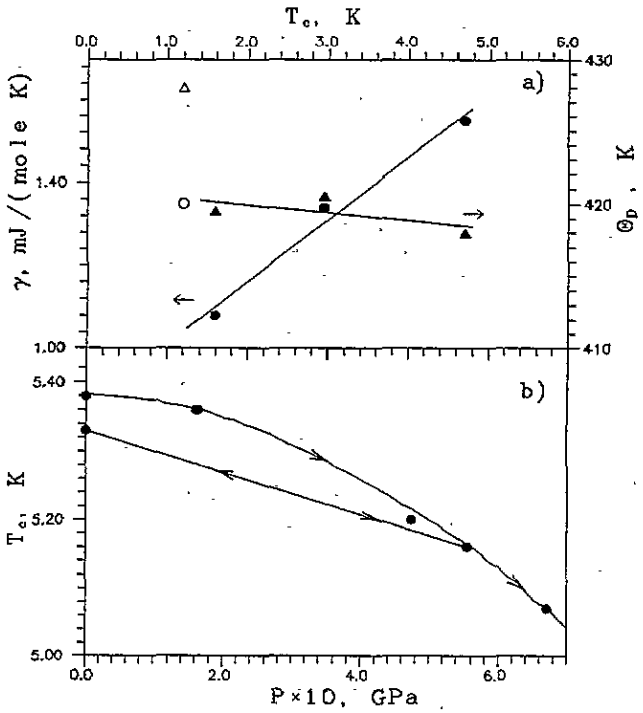

Figure 6. (*a*) The values of the parameter γ (●) and the Debye temperature Θ_D (△) from T_c for $Al_{1-x}Si_x$ (●, △) and its values for pure Al [10] (○, △). (*b*) The pressure dependence of T_c for $Al_{0.89}Si_{0.11}$.

with increasing pressure. The experimental results obtained confirm this (see figure 6(*b*)). The pressure coefficient of T_c – dT_c/dP is found to be 0.5 K GPa^{-1}.

At $x > 0.06$–0.08 a large number of nearest-neighbour Si–Si pairs appear in the FCC lattice, and these pairs are probably the second kind of 'soft' region less than 10 Å in size. For $x \geq 0.08$ a noticeable number of three- and four-Si-atom configurations must arise. These configurations are more unstable than Si–Si pairs and the rigidity percolation limit must be achieved during the subsequent increase in Si content. The local 'soft' regions possibly correspond to the 'local soft modes' in the phonon spectrum. Probably the third source of the softening is connected with the 'disordering' of Al and Si atom positions in the FCC lattice of the $Al_{1-x}Si_x$ solid solutions.

4. Conclusion

The resistivity, magnetoresistivity, Hall coefficient, magnetic susceptibility, heat capacity and x-ray emission spectra of $Al_{1-x}Si_x$ solid solutions have been experimentally investigated at different temperatures, magnetic fields and Si contents. It was found that in spite of softening of phonon spectra the Debye temperature is not significantly changed. We assume that the anomalies of the galvanomagnetic and superconductive properties are possibly connected with the local 'soft' microregions less than 10 Å in size in the FCC lattice, corresponding to the non-equilibrium states of Si atoms in the solid solution, and are

destroyed under pressure. However, the usual dilemma remains: is the enhancement of superconductive properties inevitably connected with the instability of the lattice? Investigations to establish separately the values of the electron density of states and the constant of electron–phonon interaction are now in progress.

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References

[1] Mii H, Senoo M and Fujishiro I 1976 *Japan. J. Appl. Phys.* **15** 777
[2] Degtyareva V F, Chipenko G V, Belash I T, Barkalov O I and Ponyatovskii E G 1985 *Phys. Status Solidi* a **89** K127
[3] Khvostancev L G, Vereschagin L F and Novikov A P 1977 *High Temp.–High Pressures* **9** 16
[4] Maslenkov S B, Koslenkov A I, Filin S A and Shulgin A I 1984 *Phys. Status Solidi* b **123** 605
[5] Borovic E S 1952 *Zh. Eksp. Teor. Fiz.* **23** 83, 91
[6] Forswoll K and Holwech I 1964 *Phil. Mag.* **10** 921
[7] Askerov B M 1985 *Electronnye Yavleniya Perenosa v Poluprovodnikah* (:) p 160 (in Russian)
[8] Shevchik N J 1977 *J. Phys. C: Solid State Phys.* **10** L555
[9] Brazhkin V V, Lyapin A G, Popova S V and Voloshin R N 1992 *J. Mater. Sci.* at press
[10] Chevrier J, Pavuna D and Cyrot-Lackmann F 1987 *Phys. Rev.* B **36** 9115
[11] Chevrier J, Lasjaunias J S, Zougmore F and Caponi J J 1989 *Europhys. Lett.* **8** 173
[12] Chevrier J, Suck J V, Caponi J J and Perroux M 1988 *Phys. Rev. Lett.* **61** 554
[13] Suck J B, Rudin H, Güntherodt H J and Beck H 1984 *J. Non-Cryst. Solids* **61–2** 295
[14] Allen P B and Dynes R C 1975 *Phys. Rev.* B **12** 905