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Enhancement of electron-phonon interactions in the nonequilibrium solid solutions $Al_{1-x}Si_x$

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We report unusual behavior of the low-temperature electrical resistivity ρ of nonequilibrium substitutional solid solutions of the form $Al_{1-x}Si_x$. This behavior is thought to be similar to anomalies in d^2I/dV^2 observed in the tunneling or point-contact spectra of metals in the presence of disorder, and to result from strong electron-phonon interactions. The resistivity data, along with low-temperature heat-capacity measurements and Al $L_{\text{II-III}}$ x-ray-emission spectroscopy and NMR Knight shift experiments, strongly suggest that an enhancement of the electron-phonon interactions due to lattice instabilities is the main reason for the dramatic increase in the superconducting transition temperature T_c to ~ 11 K in $Al_{1-x}Si_x$ when $x = 0.2$.

The nonequilibrium substitutional solid solutions $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ have attracted much attention due to the dramatic variation of their superconducting transition temperatures T_c with composition; T_c can be as high as ~ 11 K in $Al_{0.8}Si_{0.2}$.[1] Moreover, both substances retain a face-centered-cubic (fcc) lattice up to the solubility limit for Si in Al, making them simple model systems for investigating the correlation between superconducting properties and, e.g., lattice instabilities induced by varying the composition. Following this idea, Chevrier *et al.*[2] used inelastic neutron scattering on $Al_{0.94}Si_{0.06}$ to demonstrate that softening of the phonon modes is a possible reason for the enhancement of T_c in $Al_{1-x}Si_x$; the softening of the transverse acoustic modes[2,3] is similar to that found in amorphous metals[4] and is probably connected with the nonequilibrium state of Si in the Al fcc lattice. A further glasslike feature[5] is a linear term in the specific heat below 0.5 K in the superconducting regime, suggesting that variations of the phonon density of states may be connected with the changes in T_c in these substances.

In spite of this interest in fcc $Al_{1-x}Si_x$, there have been no detailed studies of the variations of T_c combined with supporting measurements of the normal- and superconducting-state parameters in the important concentration range $x < 0.1$. Moreover, the drastic increase in T_c for $Al_{1-x}Si_x$ occurs in the fcc lattice instability regime, so that a large enhancement of electron-phonon coupling could also occur (see, e.g., Ref. 6). The aim of the present paper is to present the results of detailed resistivity, low-temperature specific heat, Al $L_{\text{II-III}}$ x-ray-emission spectroscopy and NMR Knight shift measurements for several samples in the $Al_{1-x}Si_x$ composition range $x < 0.1$ in order to clarify which of the above-mentioned mechanisms is most important for T_c enhancement. This is a first step towards understanding the behavior of amorphous superconductors in which large local atomic displacements and the softening of the phonon modes are believed to be important.

The solid solution samples of $Al_{1-x}Si_x$ were prepared by quenching under high pressure (up to 8 GPa) in a toroidal high-pressure chamber; details of the synthesis procedure, and sample characterization and preparation methods have been published elsewhere.[7] In addition, the heat capacity of the samples was determined by a quasiadiabatic technique using an isothermal shield; the computerized calorimeter used is capable of measuring samples of mass down to about 30 mg in the temperature range 1.6–40 K.

The temperature dependences of the resistivities $\rho(T)$ of three solid solution $Al_{1-x}Si_x$ samples are shown in Fig. 1 and compared with the resistivity of a polycrystalline Al sample before (curve 1) and after (curve 2) pressure-temperature treatment.

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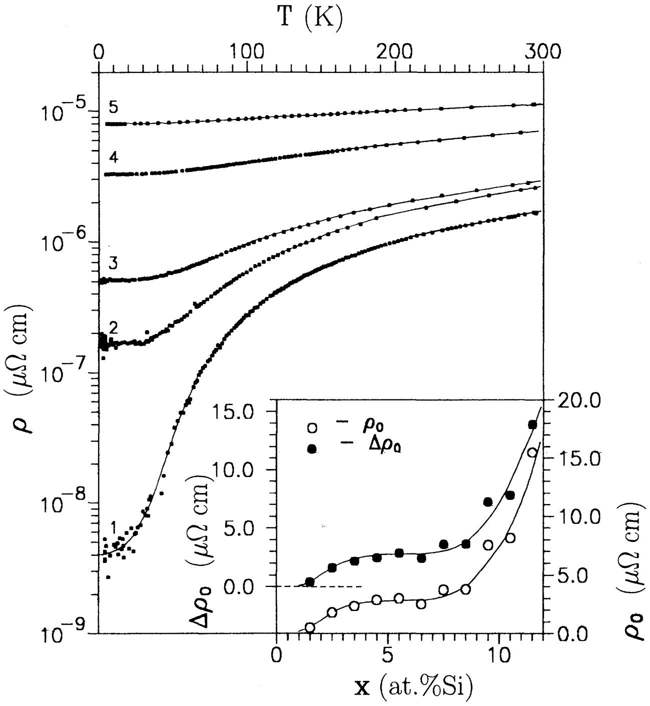

FIG. 1. Temperature dependences of resistivity $\rho(T)$ for the Al samples ($RRR=470$)-(1), ($RRR=15$)-(2), and solid solutions $Al_{1-x}Si_x$: $x=0.015$-(3), 0.045-(4), 0.105-(5). The inset demonstrates the variation of the residual resistivity $\rho_0(T)$ and the metastable part of the resistivity $\Delta\rho_0(T)$ with Si concentration in $Al_{1-x}Si_x$.

There are two ways in which the changing composition x affects the resistivity. First, Fig. 1 shows that the residual resistivity ρ_0 in $Al_{1-x}Si_x$ increases because of the substitution of Si for Al (see the inset); for $x>0.015$ carrier-impurity scattering dominates and the temperature dependence of the resistivity becomes relatively small.[8] Second, the solid solutions of fcc $Al_{1-x}Si_x$ are metastable, and so, as indicated above, the phonon spectrum will be prone to quite dramatic composition-dependent changes; as a result, the carrier-phonon-scattering component of the resistivity will be affected. In order to separate these two effects, the fcc solid solution samples were annealed ($T_{an}=520$ K, $t=20$ min) converting them into fcc Al crystals containing well-separated submicron Si precipitates.[9] The resistivity measurements were then repeated and compared with the results obtained before annealing; as the samples used are the same, the effects of sample geometry and the total Si content are preserved.

The inset to Fig. 1 shows the composition dependence of $\Delta\rho_0=(\rho_0-\rho_{A0})$, where ρ_0 and ρ_{A0} are the residual resistivities of the fcc $Al_{1-x}Si_x$ and corresponding annealed samples, respectively; $\Delta\rho_0$ follows the variation of the absolute values of ρ_0 closely. In order to deduce the influence of the metastability of the fcc $Al_{1-x}Si_x$ on the carrier-phonon scattering, we assume that the components of the resistivity sum according to Matthieson's rule and plot

$$\Delta\rho_T=\{[\rho(T)-\rho_0]-[\rho_A(T)-\rho_{A0}]\}$$

in Fig. 2 for the samples in Fig. 1; here $\rho(T)$ and $\rho_A(T)$ are the total resistivities of the fcc $Al_{1-x}Si_x$ and annealed samples, respectively. $\Delta\rho_T$ therefore represents the additional component of carrier-phonon scattering introduced by the metastability of the fcc $Al_{1-x}Si_x$ samples. The peaks obtained in $\Delta\rho_T$ are very similar to features observed in the tunneling d^2I/dV^2 characteristics of Al films and point-contact spectra of Al (Ref. 10) in the presence of disorder; these particular features are characterized by very large amplitude changes in $\Delta(d^2I/dV^2)$ arranged around $k_BT\sim15$ meV. Note also that the height of the peak in $\Delta\rho_T$ increases as the Si concentration is raised (see the inset in Fig. 2); this correlates with the appearance of an additional component $\Delta G(\omega)$ in the phonon density of states as x increases, reported in fcc $Al_{1-x}Si_x$.[2,11]

In the case of an almost spherical Fermi surface and strong carrier-impurity scattering the resistivity is determined by the diffusive component[12]

$$\rho\sim\{[T^5|I_{k,k'}|]/[s^5p_F^3n]\}\log_e(T/p_Fs)\ , \tag{1}$$

where s is the velocity of sound, p_F is the Fermi momentum, and $I_{k,k'}$ is the electron-phonon interaction matrix element. Using this equation, it is therefore possible to connect the peak in $\Delta\rho_T$ with the temperature dependence of $I_{k,k'}$. As there are no anomalies in either the sound velocity or the elastic moduli for the metastable solid solutions $Al_{1-x}Si_x$ (Ref. 13) or for other similar materials such as Ti-M (Fe,Co,Ni) (Ref. 14) in the temperature range 50–300 K, the most likely explanation of the

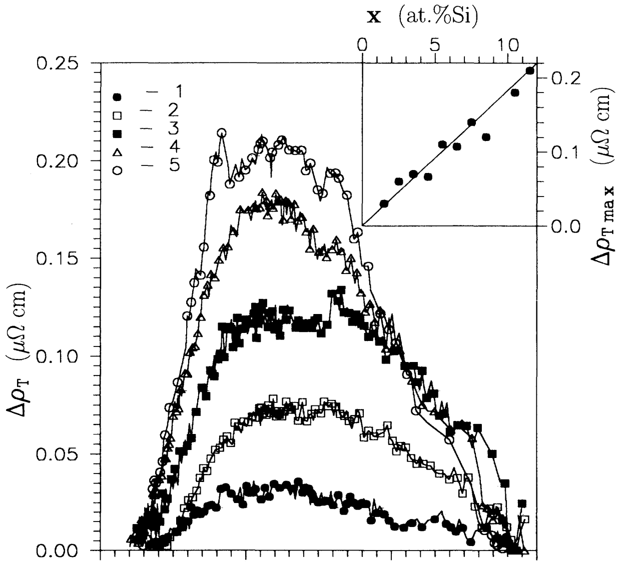

FIG. 2. The $\Delta\rho_T(T,x)$ dependences (see text) for substitutional solid solutions $Al_{1-x}Si_x$ for different Si concentration: $x=0.015$-(1), 0.045-(2), 0.075-(3), 0.105-(4), and 0.115-(5) Maximum amplitude $\Delta\rho_T(T,x)$ changes are shown in the inset.

above-mentioned anomaly in $\Delta\rho_T(T)$ is connected to the nonmonotonic behavior of $|I_{k,k'}|$.

An alternative approach, which gives information about the composition dependence of the electron-phonon interactions, involves the use of normal-state parameters to predict T_c. For example, one can use McMillan's equations

$$T_c=[\langle\omega_{\log}\rangle/1.2] \times\exp\{[1.04(1+\lambda)]/[1-\mu^*(1+0.6\lambda)]\} \quad (2)$$

and

$$\lambda=[N(E_F)\langle I^2\rangle]/[M\langle\omega^2\rangle]\ , \quad (3)$$

where μ^* is the Coulomb pseudopotential, $N(E_F)$ is the density of states at the Fermi energy, M is the mass of the ions, $\langle\omega_{\log}\rangle$ and $\langle\omega^2\rangle$ are the mean logarithmic phonon angular frequency and the mean-square phonon angular frequency, and $\langle I^2\rangle$ is the mean-square electron-phonon interaction matrix element. The mass of the ions M changes only slightly from Al to Si, practically eliminating any dependence of λ on M for the composition range studied in this work. Similarly, only slight T_c changes $\sim 1-3\%$ occur if Eqs. (2) and (3) are used with phonon frequency distribution softening taken into account and all other parameters held constant; in this case the data for $x=0.04$, 0.06, and 0.08 from Refs. 2 and 11 have been used to estimate the variations of $\langle\omega_{\log}\rangle$ and $\langle\omega^2\rangle$ with x. Furthermore, both the results of pressure-dependent experiments on $Al_{1-x}Si_x$ (Ref. 7) and the known x dependence of the lattice constants of $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ (Ref. 1) allow one to eliminate the specific volume decrease in these compounds as a significant influence on T_c. Therefore, the only remaining parameters that could cause the rapid changes of T_c with composition are $\langle I^2\rangle$ and $N(E_F)$; before information on $\langle I^2\rangle$ can be derived from T_c, some estimate of the variation of $N(E_F)$ must be made.

In order to provide further information on $N(E_F)$ and λ, we have measured the low-temperature heat capacity of the samples in the temperature interval ($T_c+0.1$ K) to 40 K by a quasiadiabatic technique using an isothermal shield.[7] The results in Fig. 3 allow the deduction of both the coefficient γ of the linear specific-heat term γT and the Debye temperature Θ_D of the fcc $Al_{1-x}Si_x$ solid solutions as a function of composition [see Figs. 4(b) and 4(c)]. The simple relationship

$$\gamma=\pi^2k_B^2N(E_F)(1+\lambda)/3\ , \quad (4)$$

where k_B is the Boltzmann constant, can be used to relate γ, $N(E_F)$, and λ. However, an independent estimate of $N(E_F)$ is still required. In this connection we have studied the Al $L_{\text{II-III}}$ x-ray-emission spectra of the fcc $Al_{1-x}Si_x$ samples on the Spectrozond instrument[15] (Fig. 5). There appears to be no qualitative modification of the conduction band structure with composition in these experiments; accurate measurements in the vicinity of the upper edge of the $I(E)$ spectra allowed the variation of E_F to be deduced. The results are shown in Fig. 4(a) and

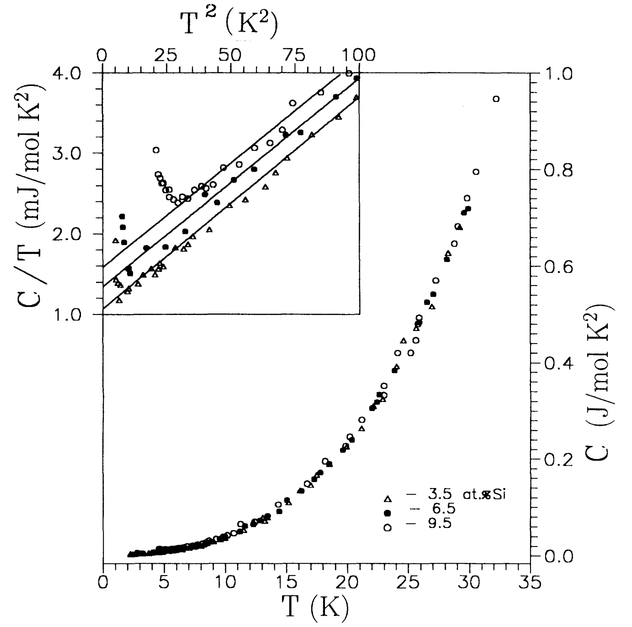

FIG. 3. Specific heat of $Al_{1-x}Si_x$ solid solutions for temperatures between T_c and 30 K. In the inset the $C/T=f(T^2)$ dependences are shown in the vicinity of liquid helium temperature.

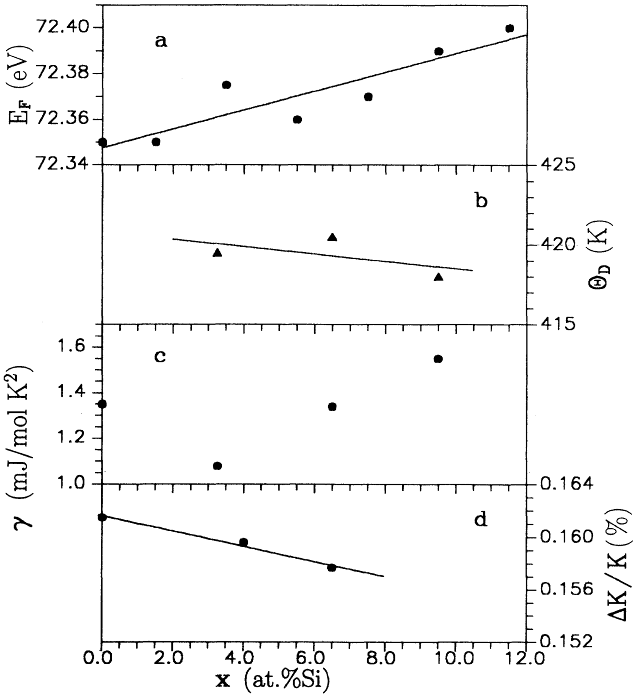

FIG. 4. Dependences on Si concentration for (a)-E_F parameter from Al $L_{\text{II-III}}$ XES, (b) and (c)-Debye temperature and linear coefficient γ from low-temperature-capacity measurements and (d)-NMR Knight shift $K(x)$ in substitutional solid solutions $Al_{1-x}Si_x$.

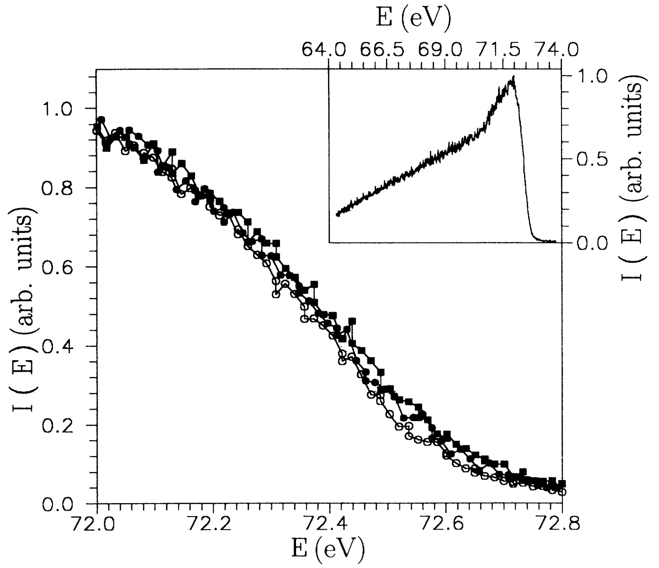

FIG. 5. The experimental Al $L_{\text{II-III}}$ x-ray emission corresponding to the upper edge of the band in $\text{Al}_{1-x}\text{Si}_x$: ○, $x=0$; ●, $x=0.055$; ■—$x=0.095$. In the inset the $I(E)$ XE's curve for pure Al sample is shown.

indicate that the $\text{Al}_{1-x}\text{Si}_x$ band structure and the value of $N(E_F)$ have little dependence on composition in the region $x<0.1$, which applies to the present experiments. In passing, it should be mentioned that the Al $L_{\text{II-III}}$ spectra were recorded at room temperature and that additional smoothing of the spectrum takes place at high excitation energies because of the creation and annihilation of phonons.[16]

Another way of obtaining of $N(E_F)$ is supplied by Al NMR Knight shift $K(x)$ measurements; data were extracted from NMR spectra recorded on a Bruker CXP-300 spectrometer and are shown in Fig. 4(d). According to the relationship

$$K=a\chi_s/(g\mu_B\gamma_I h)\sim aN(E_F)\ , \tag{5}$$

where a is the hyperfine interaction constant, χ_s is the electron spin susceptibility, γ_I is the nuclear gyromagnetic ratio, and μ_B is the Bohr magneton, variations in Knight shift value may be attributed to changes in $N(E_F)$ or a. The latter parameter is determined by the magnitude of the electron's wave function near the nucleus; one can thus connect the decline of $K(x)$ with increasing Si content with the noticeable decrease of the electronic charge density close to the Al nuclei (i.e., the progressive transfer of electron density from Al to Si atoms as substitution takes place). Therefore, $N(E_F)$ is probably approximately constant in $\text{Al}_{1-x}\text{Si}_x$, with a declining with increasing x.

Both Knight shift and x-ray-emission data appear to indicate that $N(E_F)$ is approximately independent of composition. If one therefore assumes that only the changes in λ in Eq. (4) are significant in determining γ and uses $\lambda_{\text{Al}}=0.38$,[5] one obtains $\lambda_{\text{Al}_{0.92}\text{Si}_{0.08}}=0.9$.

It should be mentioned that additional proof of the enhancement of the electron-phonon interactions could be obtained from measurements of the Seebeck coefficient, as has been shown in Ref. 17 for pure Al samples. A detailed study of the thermoelectric power of the substitutial solid solutions $\text{Al}_{1-x}\text{Si}_x$ is in progress and will be reported in a subsequent publication.

The latest experimental data by Chevrier *et al.*[11] on $\text{Al}_{1-x}\text{Si}_x$ agree qualitatively with our results. The main discrepancy appears in the Debye temperature $\Theta_D(x)$; this is possibly caused by two factors. First, only a narrow experimental temperature interval ($4.5\text{ K}<T<7\text{ K}$) was used in the heat-capacity measurements in Refs. 5 and 11 and, second, small traces of Al-Si superconducting phases with $T_c>3$ K were present in the samples used in that work.[5,11] Moreover the T_c values for $x=0.08$ and 0.1 samples are rather higher in reality[1,7] than the values reported in Ref. 11. According to preliminary investigations,[18] the room-temperature spinodal boundary in these solid solutions of $\text{Al}_{1-x}\text{Si}_x$ occurs at about $x=0.08$. Therefore, the discrepancies in the values of T_c are very likely connected with the start of the decomposition of the samples investigated in Ref. 11.

In summary, we have used a variety of data to argue that the electron-phonon interaction enhancement in the vicinity of the fcc lattice instability is likely to be the main reason for the drastic increase in the superconducting transition temperature in the substitutional solid solutions $\text{Al}_{1-x}\text{Si}_x$. The substitution of Si for Al causes strong local atomic displacements and phonon mode softening. This behavior is possibly connected with the local "soft microregions" less than 1 nm in size in the fcc lattice that are destroyed under pressure.[7] These microregions correspond to the nonequilibrium states of Si atoms in the solid solution and give rise to the noticeable enhancement of the electron-phonon interaction.

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