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Thermoelectric power anomalies and electron-phonon interaction in nonequilibrium solid solutions $\mathrm{Al}_{1-x}\mathrm{Si}_x$

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We report unusual behavior of the low-temperature thermopower of nonequilibrium $\mathrm{Al}_{1-x}\mathrm{Si}_x$ substitutional solid solutions. The thermopower and resistivity results suggest that the low-temperature anomalies of these parameters are likely due to electron-phonon interaction enhancement in the vicinity of the fcc lattice instability in these superconductors. [S0163-1829(97)03238-4]

Recent theoretical and experimental efforts have focused on the role of electron-phonon interactions in limiting the thermopower.[1,2] Interest in this area has originated from experiments on conductors with a strong electron-phonon interaction, such as glassy metals,[3] the Chevrel compounds,[4] fullerenes,[5] and high-T_c superconductors.[6] Here the most intriguing fact is that thermopower can be used to distinguish different superconductivity mechanisms and to establish the temperature dependence of the Eliashberg function.[4,6]

A simple and straightforward way to study the problem experimentally would be an investigation of Al-based nonequilibrium substitutional solid solutions fabricated using a high-pressure treatment. Indeed, in these compounds noticeable lattice instability is evidenced by the dramatic variation of the superconducting transition temperatures T_c with composition. T_c can be as high as ≈ 11 K in $\mathrm{Al}_{0.8}\mathrm{Si}_{0.2}$.[7] As established recently,[8] the main reason for the T_c increase is an enhancement of the electron-phonon interaction in these compounds. Hence one can consider these high-pressure synthesized solid solutions (that fcc lattice is retained up to the solubility limit for Si in Al; charge carriers are *s* and *p* electrons) as a simple ''model system'' for investigating the correlation between thermopower behavior and the strength of the electron-phonon interaction[8] in superconducting materials.

Thus an investigation of these compounds is a first step towards understanding the behavior of amorphous superconductors or superconductors arranged in the vicinity of lattice instability limit (such as fullerenes, high-T_c superconductors, etc.) where large local atomic displacements and the softening of the phonon modes are believed to be important. Thus the aim of the present paper is to introduce results from a detailed study of thermopower $S(T)$ and resistivity $\rho(T)$ measurements for several $\mathrm{Al}_{1-x}\mathrm{Si}_x$ substitutional solid solutions synthesized in the composition range $x \leqslant 0.08$ (e.g., below the spinodal boundary value[9]). Step-by-step annealing combined with $S(T)$ and $\rho(T)$ measurements clarifies the effects of the nonequilibrium state of Si atoms in the fcc lattice and the electron spectrum renormalization on the Seebeck coefficient in various temperature intervals.

The $\mathrm{Al}_{1-x}\mathrm{Si}_x$ solid-solution samples were prepared by quenching under high pressure (up to 8 GPa) in a toroidal high-pressure chamber. The details of the synthesis procedure and samples characterization have been published elsewhere.[10] Additionally, the thermopower of these samples was measured by conventional differential technique with 99.999%-pure Au wires used as a reference. A variable-temperature difference ΔT between two ends of a specimen was maintained at less than 1% of the fixed T_0 value for every temperature T_0 under investigation. In these limits of ΔT, special attention was paid to the linearity of the thermopower voltage dependence of $\Delta U(\Delta T, T_0)$ versus ΔT. To test and calibrate the experimental apparatus a sample of Bi-based high-T_c ceramics was measured within the temperature range 5–300 K using an Au-wire reference (inset in Fig. 1). These results indicate a superconducting transition near 80 K and allow one to compare the pure gold calibration (curve 3) with experimental data below T_c.

The temperature dependences of the thermopower $S(T)$ of four $\mathrm{Al}_x\mathrm{Si}_x$ solid solutions are shown in Fig. 1 and compared to pure Al data from Ref. 11. There are no significant changes in the concentration for $S(T)$, curves 1–3, although the amplitude of the phonon-drag minimum decreases slightly for these disordered solid solutions. These effects correlate with results of Ref. 12 for disordered Al and dilute

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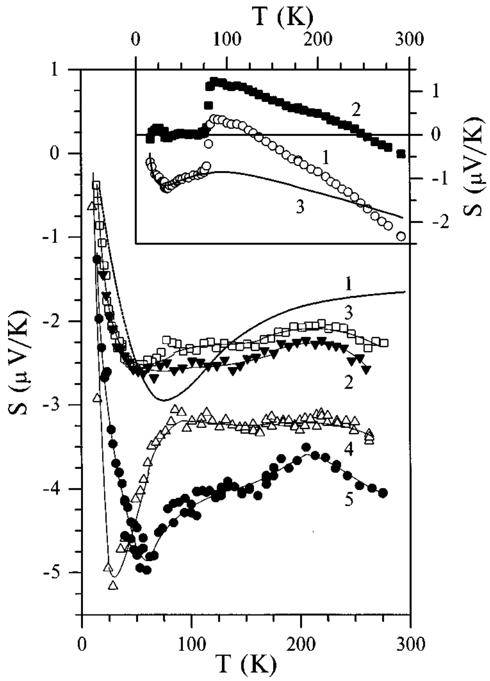

FIG. 1. Temperature dependence of the absolute thermopower $S(T)$ of (1) pure Al (Ref. 11) and $Al_{1-x}Si_x$ solid solutions for various Si contents: (2) $x=2$ at. %, (3) 4 at. %, (4) 6 at. %, and (5) 8 at. %. Inset shows (1) $\Delta S(T)=S_{\mathrm{BiSrCaCuO}}$-$S_{\mathrm{Au}}$ and (2) absolute $S(T)$ dependences for $Bi_{1.1}SrCa_{0.4}CuO_x$ and (3) negative $S(T)$ dependence for 99.999% gold wire.

Al-based alloys, and are in good agreement with well-known arguments on phonon-drag suppression in the presence of large structural scattering.[4]

One can observe the significant changes of $S(T)$ dependences when the Si concentration increases up to $x=0.06$ and 0.08 (Fig. 1), which are in the vicinity of a lattice instability.[9] There are two main features of thermopower changes that appear with an increasing Si content. The first is the increase of absolute $S(T)$ maximum by about a factor of 2 at low temperatures which occurs in combination with noticeable changes in its width and position (Fig. 1).

A convenient way to examine the nature of these low-temperature thermopower anomalies uses step-by-step annealing.[9] Indeed, for these nonequilibrium compounds the decay, by annealing of supersaturated $Al_{1-x}Si_x$ solid solutions allows one to study variable Si content using only one $Al_{1-x}Si_x$ sample.[9] Here the sample with $x=0.08$ was used. According to Ref. 13, incoherent and spherically coherent precipitates do not contribute to thermoelectric power. Thus, in the case of the formation of Si precipitates in the Al-based matrix,[9,14] one can expect that thermopower changes result from Si depletion in the matrix. Moreover, there is a proportionality between the x parameter and superconducting transition temperature T_c in $Al_{1-x}Si_x$[7] and so one can derive the Si content for any decay state.

$S(T)$ is shown in Fig. 2 for initial ($x=0.08$, curve 1, $T_c=5.4$ K) and intermediate stages of decomposition process. The assertions of Ref. 13 can be verified easily in the case of $Al_{1-x}Si_x$ by analyzing $S(T)$ curves 3 and 6 of Fig. 2 for intermediate stages of decomposition process, along with the $Al_{0.94}Si_{0.06}$ and $Al_{0.98}Si_{0.02}$ thermopower temperature dependences (Fig. 1, curves 4 and 2). The final $S(T)$ curve 7, Fig. 2 of the step-by-step annealing procedure, corresponds to a small concentration of Si atoms in the fcc lattice positions of the Al-rich matrix, with nearly spherical Si-rich inclusions surrounded by aluminum.[14] There is a large number of structural defects in the final state Al-Si alloy, and so one can expect an essential suppression of phonon-drag thermopower in that case. At the same time, the $S(T)$ plot of $Al_{0.98}Si_{0.02}$ (or relative decomposition curve 6, Fig. 2) produces a prominent reference to extract an additional (without phonon drag and ''bare'' diffusion) part of thermopower for these nonequilibrium fcc $Al_{1-x}Si_x$ solid solutions with $x \geqslant 0.04$.

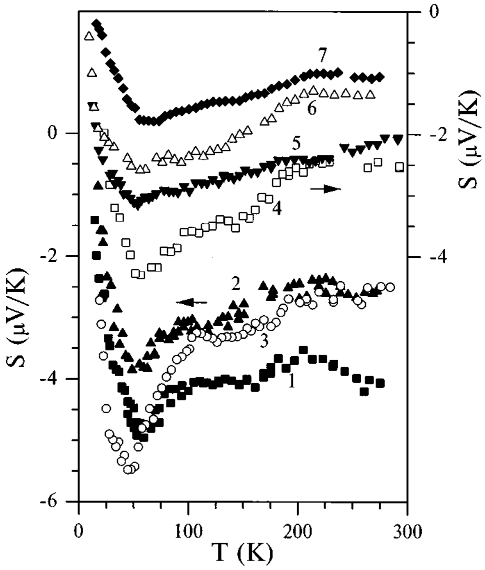

FIG. 2. Family of $S(T)$ dependences at various stages of the $Al_{0.92}Si_{0.08}$ solid-solution decomposition process: (1) initial state, $T_c=5.4$ K, (2) $T_c=5.0$ K, (3) $T_c=4.05$ K, (4) $T_c=3.75$ K, (5) $T_c=3.18$ K, (6) $T_c=1.87$ K, and (7) $T_c=1.2$ K.

It is well known from Refs. 1–6 that diffusion thermopower of metals is very sensitive to electron-phonon interaction effects. Following Kaiser and co-workers,[4,6] these anomalous low-temperature terms of the Seebeck coefficient shown in Fig. 3(a) can be considered as a renormalized temperature-dependent enhancement of the diffusion thermopower:

$$S-S_b=a\lambda\lambda_S(T), \tag{1}$$

where S_b is the ''bare'' diffusion thermopower, linear in temperature, and λ the dimensionless electron-phonon coupling constant:

$$\lambda\equiv 2\int(d\omega/\omega)\alpha^2F(\omega). \tag{2}$$

The function $\lambda_S(T)$ is the normalized enhancement factor:

$$\lambda_S = \int(d\omega/\omega)\alpha^2F(\omega)G_s(h\omega/k_BT) \Big/ \int(d\omega/\omega)\alpha^2F(\omega), \tag{3}$$

where $G_s(h\omega/k_BT)$ is a universal function from Ref. 4 and $\alpha^2F(\omega)$ the Eliashberg function. Moreover, from the detailed analysis of the anomalous resistivity (Fig. 2 of Ref. 8) and the derivative of the resistivity temperature dependences

[Fig. 3(b)], one can exclude any noticeable influence of phonon-drag effects in the low-temperature thermopower for both $Al_{1-x}Si_x$ and intermediate stages of $Al_{0.92}Si_{0.08}$ in the step-by-step annealing process. Indeed, as was established in Ref. 8, the electron-phonon interaction enhancement is possibly the main reason for not only the observed T_c increase, but also for the appearance of an anomalous diffusion component of the resistivity $\Delta\rho_T$. Thus both the low-temperature $\Delta S(T)$ anomalies [Fig. 3(a)] and $\Delta(d\rho/dT)=f(T)$ peculiarities [Fig. 3(b)] can possibly be attributed to the nonmonotonic behavior of the electron-phonon interaction constant in these compounds. It is worth noting that the peaks obtained in $\Delta\rho_T$ (Ref. 8) are very similar to features observed in the tunneling d^2I/dV^2 characteristics of Al films and point-contact spectra of Al (Ref. 15) in the presence of disorder. These particular features are characterized by very large amplitude changes in $\Delta(d^2I/dV^2)$ seen near $k_BT\approx 15$ meV. Moreover, the appearance of an additional component $\Delta F(\omega)$ in the phonon density of states was reported near 15 meV in data from inelastic-neutron-scattering experiments in fcc $Al_{1-x}Si_x$.[16]

It is necessary to point out that according to Eqs. (2) and (3) the λ and $\lambda_S(T)$ parameters are mainly determined by the Eliashberg function $\alpha^2F(\omega)$ behavior. As a result, while the phonon density of states $F(\omega)$ changes only slightly under Al to Si substitution,[16] the electron-phonon interaction enhancement can be considered as the main reason both for the λ increase between ~0.4 and ~0.9 (Ref. 8) and also for the appearance of diffusion thermopower anomalies [Fig. 3(a)] in the vicinity of fcc lattice instability in Al_xSi_x solid solutions. Thus the drastic increase of λ [see Eq. (2)] and the aforementioned anomalies of $\lambda_S(T)$ [see Eq. (3) and Fig. 3(a)] are possibly caused by the nonmonotonic behavior of $\alpha^2(\omega,T)$. It is also interesting that similar anomalies of α^2 have been predicted by Weber for high-T_c $La_{2-x}Sr_xCuO_4$ superconductors.[17]

At the same time, according to recent results,[18] the quantum interference between electron-phonon-impurity scattering plays a crucial role in the thermopower renormalization, especially for materials with substitutional disorder. As was shown by Sergeev and co-workers,[18] this effect dominates the pure phonon renormalization of the thermopower and other kinetic mechanisms, and describes the experimental data of $S(T)$ for ordinary metals with substitutional disorder, as well as for high-T_c superconductors. Finally, it is very important to examine quantitatively the low-temperature anomalies of the thermopower in the framework of the models[6,18] for the case of the nonequilibrium substitutional solid solutions $Al_{1-x}Si_x$. A detailed study is in progress and will be reported in a subsequent publication.

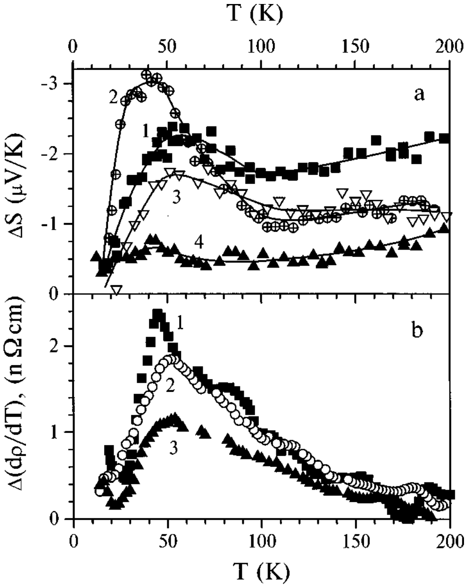

FIG. 3. (a) Temperature-dependent thermopower enhancement $\Delta S(T)$ of $Al_{0.92}Si_{0.08}$ with step-by-step annealing stages: (1) $T_c=5.4$ K, (2) $T_c=4.05$ K, (3) $T_c=3.75$ K, and (4) $T_c=3.18$ K relative to $T_c=1.87$ K stage as reference (see text); (b) Temperature-dependent metastable part of resistivity derivative $\Delta(d\rho/dT)=(d\rho/dT)_n-(d\rho/dT)_{\mathrm{final}}$ for some stages of the $Al_{0.92}Si_{0.08}$ decomposition process: (1) $T_c=5.4$ K, (2) $T_c=3.75$ K, and (3) $T_c=1.87$ K.

In summary, we have used thermopower and resistivity data to show that the low-temperature anomalies of these parameters are likely due to an electron-phonon interaction enhancement in the vicinity of the fcc lattice instability in the substitutional solid solutions $Al_{1-x}Si_x$.

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[1] M. Jonson and G. D. Mahan, Phys. Rev. B **42**, 9350 (1990); J. L. Opsal, B. J. Thaler, and J. Bass, Phys. Rev. Lett. **36**, 1211 (1976).

[2] M. A. Howson and B. L. Gallagher, Phys. Rep. **170**, 266 (1988).

[3] B. L. Gallagher and D. Greig, J. Phys. F **12**, 1721 (1982); T. Matsuda and U. Mizutani, *ibid.* **12**, 1877 (1982); A. B. Kaiser and G. E. Stedman, Solid State Commun. **54**, 91 (1985).

[4] V. Vasudeva Rao, G. Sangarajan, and R. Srinivasan, J. Phys. F **14**, 973 (1984); A. B. Kaiser, Phys. Rev. B **35**, 4677 (1987).

[5] T. Inabe *et al.*, Phys. Rev. Lett. **69**, 3797 (1992); D. T. Morelli, Phys. Rev. B **49**, 655 (1994).

[6] A. B. Kaiser and G. Mountjoy, Phys. Rev. B **43**, 6266 (1991); E. C. Jones *et al.*, Phys. Rev. B **52**, R743 (1995).

[7] V. F. Degtyareva *et al.*, Phys. Status Solidi A **89**, K127 (1985).

[8] N. E. Sluchanko *et al.*, Phys. Rev. B **51**, 1112 (1995).

[9] N. E. Sluchanko *et al.*, J. Phys.: Condens. Matter **6**, 9079 (1994).

[10] V. V. Brazhkin *et al.*, J. Phys.: Condens. Matter **5**, 5933 (1993).

[11] R. P. Huebener, Phys. Rev. **171**, 634 (1968).

[12] G. Sieber, G. Wehr, and K. Boning, J. Phys. F **7**, 2503 (1977); A. W. Dudenhoeffer and R. R. Bourassa, Phys. Rev. B **5**, 1651 (1972).

[13] J. M. Pelletier *et al.*, Acta Metall. **32**, 1069 (1984); R. Borrelly *et al.*, *ibid.* **26**, 1863 (1978).

[14] O. Barkalov, Ph.D. thesis, Institute of Solid State Physics, Chernogolovka, 1990 (unpublished).

[15] I. K. Yanson and O. I. Shklarevskii, Fiz. Nizk. Temp. **12**, 899 (1986) [Sov. J. Low Temp. Phys. **12**, 509 (1986)]; A. Leger and J. Klein, Phys. Lett. **28A**, 751 (1969).

[16] J. Chevrier *et al.*, Phys. Rev. Lett. **61**, 554 (1988); J. Chevrier *et al.*, Phys. Rev. B **49**, 961 (1994).

[17] W. Weber, Phys. Rev. Lett. **58**, 1371 (1987); **58**, 2154 (1987).

[18] M. Yu. Reizer and A. V. Sergeev, Zh. Eksp. Teor. Fiz. **93**, 2191 (1987) [Sov. Phys. JETP **66**, 1250 (1988)]; D. V. Livanov and A. V. Sergeev, Phys. Rev. B **48**, 13 137 (1993); A. V. Sergeev, M. Yu. Reizer, and D. I. Livanov, *ibid.* **50**, 18 694 (1994).