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Structural effects on the superconducting and magnetic behavior of aluminum-rich metallic glasses

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We have performed specific heat, resistivity, and magnetic measurements on a series of glassy aluminum alloys containing up to 93 at.% Al. In addition to the fact that we can extrapolate from our data the values of superconducting temperature (>5 K) and resistivity ($\sim 20\ \mu\Omega$ cm) for amorphous Al, our results also provide evidence that significant softening of phonon modes (in the case of glassy $Al_{92}La_8$, a drastic reduction is observed with a Debye temperature of ~ 242 K as compared with ~ 428 K in crystalline Al) is responsible for the enhanced superconductivity of up to 8.5 K observed in some metastable Al alloys. For glassy Al alloys containing a few at.% Gd, the maximum in specific heat is observed at more than twice the magnetic ordering temperature defined by the cusp in susceptibility, markedly different from that of canonical spin glasses. The structural differences between these glassy Al alloys and other magnetic alloys are pointed out. Ce in glassy Al shows a large valence instability, yielding an effective moment of $1.37\mu_B$ at room temperature to $\sim 0.25\mu_B$ at 5 K, which was not observed previously in an amorphous metal.

Recently, aluminum-rich metallic glasses (containing up to 93 at.% Al have been found in a variety of rapidly quenched binary and ternary systems.[1,2] We have begun to investigate the electronic, vibrational, transport, magnetic, and structural properties of these materials. In this Rapid Communication, we present resistivity, specific heat, and magnetic susceptibility measurements on several Al-based amorphous alloys. The amorphicity of these Al-rich alloys offers an excellent opportunity for addressing the long-standing question on the degree of enhanced superconductivity due to softening of phonon modes in granular Al (Ref. 3) and some metastable Al alloys.[4-6] The superconducting and transport properties for the amorphous Al phase will be investigated by a systematic study of $Al_{100-x}La_x$ ($x=7,8,9,10$) and $Al_{100-x}Y_x$ ($x=9,10,11,12$) alloys from which trends in the resistivity and T_c will allow us to discuss the properties of amorphous Al. These Al-rich alloys also provide an ideal system for studying interesting magnetic properties (e.g., spin-glass and mixed-valence behavior) of dilute magnetic moments dissolved in a simple metal matrix and their associated electronic properties. As will be discussed later, these amorphous phases have a structural advantage over systems previously studied.

Amorphous ribbons of $Al_{100-x}La_x$ ($7 \le x \le 10$), $Al_{100-x}Y_x$ ($9 \le x \le 12$), $Al_{87}Ni_{8.7}Y_{4.3}$, and $Al_{87}Fe_{8.7}R_{4.3}$ (R=La,Ce,Gd) were obtained by melt spinning, as discussed in Ref. 2. Electrical resistivity was measured using the standard four-terminal technique in the temperature range 0.35 K to room temperature. Specific-heat measurements were performed on small samples (10–50 mg) in the temperature range 0.6–20 K in a relaxation calorimeter, which has previously been described.[7] dc magnetic measurements were carried out in a SHE superconducting quantum interference device (SQUID) model 905 susceptometer. The applied field was 5 kOe. ac susceptibility was measured by the standard mutual induction method with a 1-Oe, 100-Hz field in a ^{4}He probe.

For the binary alloys of $Al_{100-x}M_x$ (M=La,Y), the results of the resistivity and superconducting measurements are shown in Fig. 1 with room-temperature resistivity and T_c plotted as a function of x. The $\rho_{300\,K}$, T_c values ranged from 42 $\mu\Omega$ cm, ~ 5 K for $Al_{93}La_7$ to 61 $\mu\Omega$ cm, 3.54 K for $Al_{88}Y_{12}$, respectively. As can be seen, the resistivity for the samples measured increases monotonically with x and is similar for both Al-La and Al-Y alloys. The trend in the data suggests a resistivity of $\sim 20\ \mu\Omega$ cm for the

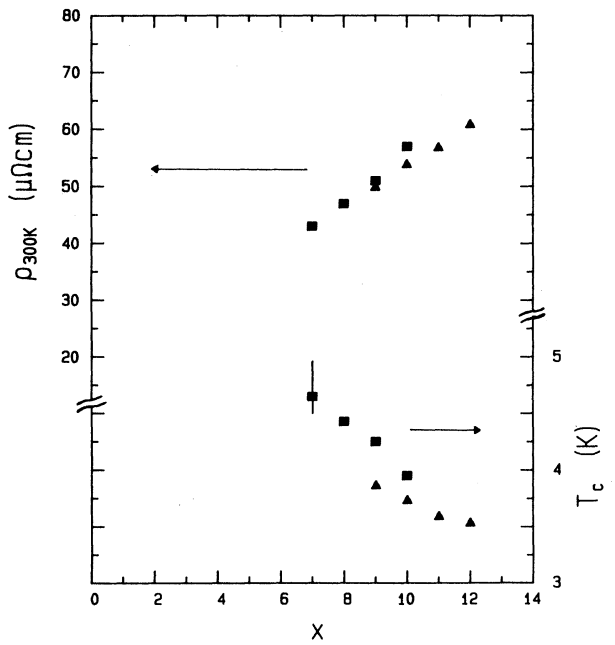

FIG. 1. Resistivity and superconducting temperature as a function of composition for amorphous (■) Al-La and (▲) Al-Y. All superconducting transitions were sharp ($\Delta T_c < 20$ mK) except that of $Al_{93}La_7$, where the line drawn represents the width of the transition (90%–10% point) and T_c is taken at the midpoint of the transition.

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amorphous Al phase. Using the free-electron model, this gives an electronic mean free path of ~20 Å for an amorphous metallic element, which is significantly larger than those found in glassy alloys reported previously. The dependence of T_c vs x exhibits different trends for the two systems measured, but both indicate a T_c of >5 K for pure amorphous Al.

In the past, there have been reports of enhancements of T_c in disordered Al and granular Al-Al_2O_3 films[3] (up to ~3.3 K), in Al-Si eutectic alloys[4] (up to ~6.5 K), and in quench-condensed Al films implanted with Si (Ref. 5) (up to ~8.5 K), which greatly exceed that found in fcc Al (1.14 K). Various explanations have been proposed to account for the observed enhancements ranging from softening of phonon modes[6-8] induced by disorder, additional coupling via an exciton mechanism occurring at the metal-semiconductor interface,[4] and to pairing of electrons due to scattering off negative-U centers.[9] Results from the current study will allow us to directly address the effects of disorder on the enhancement of T_c.

McMillan[10] showed that softening of phonon modes could increase the electron-phonon coupling constant, leading to an enhanced T_c. The electron-phonon coupling constant is given by $\lambda=\eta/M\langle\omega^2\rangle$, where η is the Hopfield-McMillan parameter, M the ionic mass, and $\langle\omega^2\rangle$ the mean-square phonon energy defined by McMillan. Values of λ were derived from McMillan's T_c equation using specific-heat data and $\mu^*=0.10$ for amorphous metals,[11] and are listed in Table I. Taking $\langle\omega^2\rangle$ as proportional to the square of the Debye temperature Θ_D^2, one can assess the effects of disorder on values of $\langle\omega^2\rangle$ and η in glassy Al alloys. It is found that there is a 32–43% reduction in Θ_D and a ~50% decrease in the value of η as compared with fcc Al. Although it has been known that amorphicity reduces $\langle\omega^2\rangle$ and η,[11] the magnitude of the reductions observed here, particularly in glassy $Al_{92}La_8$, is unusually large. Indeed, the phonon softening is so large that the corresponding decrease in $\langle\omega^2\rangle$ actually overcompensates the adverse effect on λ due to a significant reduction in the atomic parameter η. An additional 15% reduction in Θ_D to ~210 K will produce $T_c\sim 8$ K, even when assuming η maintains an unfavorably low value. Our results show that softening of phonon modes is responsible for the enhanced superconductivity in the various forms of disordered Al and its alloys.[3-6] This mechanism of T_c enhancement is further supported by thermal stability studies of these alloys. The crystallization temperature decreases rapidly in going from the 87 at.% Al alloys (~570 K) to 93-at.% Al alloys (~410 K) (Refs. 1 and 2), consistent with the drastic decrease in Θ_D reported here. Meanwhile, the structural transformation temperatures of the high-T_c phases in metastable Al-Si (Refs. 4–6) are significantly lower than those observed in our alloys. Thus, the high-T_c metastable Al alloys are expected to have lower Θ_D than those studied here.

The following samples were selected for specific-heat and magnetic susceptibility measurements: $Al_{92}La_8$, $Al_{87}Ni_{8.7}Y_{4.3}$, $Al_{87}Fe_{8.7}La_{4.3}$, $Al_{87}Fe_{8.7}Gd_{4.3}$, and $Al_{87}Fe_{8.7}Ce_{4.3}$. The lanthanide-containing samples were chosen to investigate the magnetic properties of dilute moments in a simple metal matrix. From a structural viewpoint, these amorphous Al alloys are expected to have an advantage over amorphous alloys diluted with small amounts of magnetic species previously investigated.[12] This is because for solid-solution alloys in general, there is always a tendency for the solute atoms to cluster, even in the case of very dilute alloys. Glassy Al alloys are different in that a few at.% of rare-earth elements are essential to ensure formation of the amorphous phases,[1,2] thus clustering of rare-earth ions is not expected to be present. A fair comparison with theoretical predictions based on interactions between isolated spins can then be made.

The specific heat in the normal state is given by the sum of a linear electronic term, a cubic lattice term, plus a magnetic term if magnetic effects are present,

$$C=\gamma T+\beta T^3+C_m . \tag{1}$$

Below T_c, the linear electronic term is replaced with a function based on the BCS superconducting contribution to the specific heat. The renormalized density of states $N^*(0)$ is related to its "bare" value $N(0)$ via

$$N^*(0)=(1+\lambda)N(0)=0.422\gamma , \tag{2}$$

where γ is expressed in mJ/(g-at. K^2).

Susceptibility data were analyzed assuming Curie-Weiss behavior

$$\chi=\chi_0+C_{CW}/(T-\Theta_p) , \tag{3}$$

where χ_0 is the temperature-independent contribution, C_{CW} is the Curie-Weiss constant, and Θ_p is the paramagnetic temperature. The effective moment ($p_{\text{eff}}\mu_b$), related to C_{CW}, is derived in the high-temperature range (~150–300 K) where deviations from Curie-Weiss behavior are expected to be small.

In Table I, we list the results for the resistivity, specific heat, and dc susceptibility measurements with the data for

TABLE I. Resistivity, specific heat, and magnetic susceptibility for Al-rich, amorphous alloys measured.

Sample	ρ ($\mu\Omega$ cm)	$\frac{\rho_{4.2}}{\rho_{300}}$	γ (mJ/g-at. K^2)	Θ_D (K)	T_c (K)	$\frac{\Delta C}{\gamma T_c}$	λ	C (10^{-6} emu/g)	Θ_p (K)	p_{eff}
$Al_{92}La_8$	48	0.962	1.48	242±5	4.35	1.87	0.59			
$Al_{87}Ni_{8.7}Y_{4.3}$	53	0.997	1.07	293±5	2.71	1.85	0.55			
$Al_{87}Fe_{8.7}La_{4.3}$	145	1.009	1.35	291±5	0.90	1.40	0.44			
$Al_{87}Fe_{8.7}Gd_{4.3}$	110	1.013	~1.40	290±5				8966	−6.7	7.62
$Al_{87}Fe_{8.7}Ce_{4.3}$	119	0.975	4.65	292±5				255	−150	1.37

some samples shown in Figs. 2–4. The γ values (except for $Al_{87}Fe_{8.7}Ce_{4.3}$) are comparable to those of Al, and are, therefore, close to free-electron values. For $Al_{92}La_8$, the discontinuity in specific heat ($\Delta C/\gamma T_c = 1.87$) and the electron-phonon coupling constant ($\lambda = 0.59$) are typical of those found in intermediate- to weak-coupling superconductors. The $Al_{92}La_8$ low Debye temperature ($\Theta_D = 242$ K) reflects the reduced stability of this sample as compared with other samples measured. $Al_{87}Ni_{8.7}Y_{4.3}$, with $\rho = 53\ \mu\Omega$ cm and $T_c = 2.71$ K, is found to be comparable to those of the binary alloys measured with the equivalent Al content. With a Θ_D of 293 K, $Al_{87}Ni_{8.7}Y_{4.3}$ was found typical of binary alloys containing 87 at.% Al. For samples containing Fe, resistivities were found to be significantly higher, as in the case with $Al_{87}Fe_{8.7}La_{4.3}$ which has a resistivity of 145 $\mu\Omega$ cm. These values are at least a factor of 2 larger than for any Al-La alloy measured and are likely due to enhanced s-d scattering in the presence of Fe atoms. The superconducting temperature of $Al_{87}Fe_{8.7}La_{4.3}$ (0.9 K) is also significantly lower than those of alloys with similar Al content.

The dc and ac susceptibility for $Al_{87}Fe_{8.7}Gd_{4.3}$ is shown in Fig. 2(a). As can be seen from the plot of $1/(\chi-\chi_0)$, the susceptibility follows Curie-Weiss behavior over most of the temperature range measured with a small deviation below $\sim$20 K. The derived effective moment is $7.62\mu_B$ per Gd atom which is close to its ionic values of $7.94\mu_B$. The ac susceptibility exhibits a cusp at 1.9 K, indicating magnetic ordering. This cusp is suppressed when measurement is repeated with the superposition of a 100-Oe field, typical of spin-glass behavior. The specific heat of

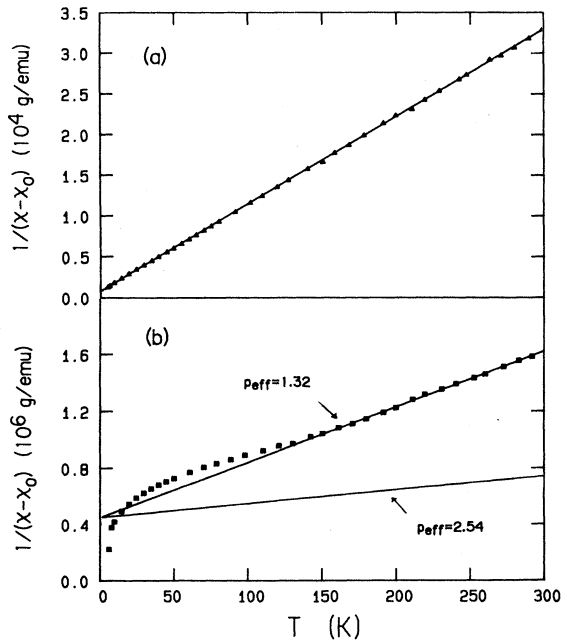

FIG. 2. Temperature dependence of the dc susceptibility plotted as $1/(\chi-\chi_0)$ vs T for (a) $Al_{87}Fe_{8.7}Gd_{4.3}$ ($\chi_0 = 4.75\times10^{-6}$ emu/g) and (b) $Al_{87}Fe_{8.7}Ce_{4.3}$ ($\chi_0 = 1.07\times10^{-6}$ emu/g), the line labeled $p_{\text{eff}} = 2.54$ (corresponding to full ionic moment of Ce^{3+}) is shown for comparison.

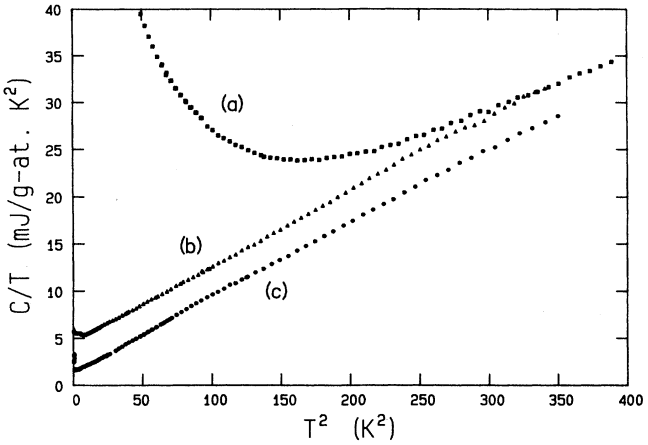

FIG. 3. C/T vs T^2 for (a) $Al_{87}Fe_{8.7}Gd_{4.3}$, (b) $Al_{87}Fe_{8.7}Ce_{4.3}$, and (c) $Al_{87}Fe_{8.7}La_{4.3}$.

$Al_{87}Fe_{8.7}Gd_{4.3}$ is partially shown in Fig. 3 along with that of $Al_{87}Fe_{8.7}La_{4.3}$ and $Al_{87}Fe_{8.7}Ce_{4.3}$ for comparison. As can be seen, its specific heat is dominated by a large magnetic contribution which peaks at 4.4 K and gradually tails off at higher temperatures (Fig. 4). For $Al_{87}Fe_{8.7}$-$La_{4.3}$, which according to susceptibility measurements is nonmagnetic, the simple Debye law (linear dependence of C/T vs T^2) is followed for temperatures below $\sim$10 K with deviations occurring at higher temperatures. The lattice heat capacity of $Al_{87}Fe_{8.7}Gd_{4.3}$ can be approximated as that of $Al_{87}Fe_{8.7}La_{4.3}$ over the temperature range measured, since it is not expected to change upon substitution of few at.% Gd for La. The electronic and magnetic contributions can then be determined with the constraint that the magnetic entropy (per mole Gd) $S_m = \int (C_m/T)dT$ be less than the maximum entropy available, $R(\ln(8))$. This condition is satisfied for $\gamma = 1.4 \pm 0.4$ mJ/(g-at.K^2), which is comparable to $Al_{87}Fe_{8.7}La_{4.3}$. C_m and S_m are shown in Fig. 4 and inset, respectively. At T_f (defined by the cusp in susceptibility),

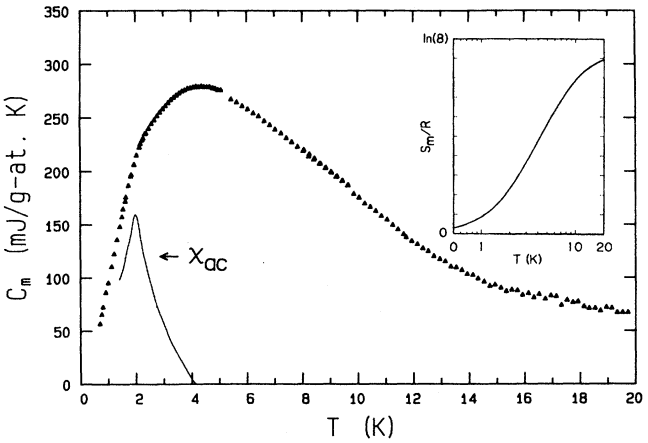

FIG. 4. Magnetic specific-heat contribution C_m and ac susceptibility χ_{ac} (arbitrary unit) vs T for $Al_{87}Fe_{8.7}Gd_{4.3}$. In the inset is shown the corresponding magnetic entropy vs T.

only 20% of the maximum entropy has been developed and full entropy is not reached until ~30 K.

For canonical spin glasses (three-dimensional magnetic solutes dissolved in noble metals hosts), a broad maximum in the specific heat is usually seen at a temperature ~20 to 30% higher than T_f (Ref. 13). $Al_{87}Fe_{8.7}Gd_{4.3}$ is unusual in that the peak in specific heat (4.4 K) is found at a temperature more than twice T_f (1.9 K). The absence of a cusp in the specific heat and the position of the observed maximum relative to T_f (defined by magnetic measurements) have posed a challenge for theoretical description. Soukoulis and Levin[14] have proposed a cluster mean-field approach, which accounts reasonably well for both of these behaviors in canonical spin glasses based on interaction among magnetic clusters of spins. The main contribution to C_m in this model comes from intracluster interaction while the interaction determining the behavior of the susceptibility is the intercluster exchange. However, since typical canonical spin glasses are more likely to have clustering effects than our alloy, the observed peak in C_m exceeding T_f by more than a factor of 2 in $Al_{87}Fe_{8.7}Gd_{4.3}$ is unexpected on the basis of the cluster model. Clearly, more experimental and theoretical work is needed to yield a more coherent picture of spin-glass behavior in the present alloys.

The dc susceptibility for $Al_{87}Fe_{8.7}Ce_{4.3}$ is shown in Fig. 2(b). The high-temperature part exhibits simple Curie-Weiss behavior above 150 K with an effective moment of $1.32\mu_B$. This moment is intermediate between that of the trivalent moment ($2.54\mu_B$) and the tetravalent moment (0) of Ce. Ce is well known to form homogeneous mixed-valent compounds due to its spatially extended $4f$ orbital and, consequently, nearly degenerate $4f^1$ and $4f^0$ valence states. Ce in our glassy alloy exhibits significant valence instability at low temperature as evident from the susceptibility data where the slope of $1/(\chi-\chi_0)$ (proportional to $1/p_{\text{eff}}^2$) tends to diverge corresponding to the Ce gradually freezing into its nonmagnetic $4f^0$ ground state. The effective moment at 5 K is $\sim 0.25\mu_B$. Such a significant mixed-valence behavior has never been observed, to our knowledge, in amorphous metals containing magnetic rare-earth elements.[12] The specific heat, shown in Fig. 3, shows no magnetic contribution down to ~3 K. The origin of a small upturn below 3 K is unknown at present. The lattice contribution is found to be identical, within experimental error, to that of the other samples containing 87 at.% Al measured, with a Θ_D of 292 K. The electronic contribution to the specific heat for $Al_{87}Fe_{8.7}Ce_{4.3}$ is enhanced over that observed in other samples with $\gamma=4.65$ mJ/(g-at.K^2). This enhancement [80 mJ/(mol-CeK^2)] is not uncommon in other Ce-containing mixed valence compounds[15] and is consistent with x-ray photoemission spectroscopy measurements on $Al_{84}Ce_{16}$ which show the broadened $4f$ band of Ce positioned just 0.3 eV below the Fermi level.[16] Further investigations of the mixed-valence behavior of Ce in conjunction with structural studies in these Al-based alloys are underway.

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