Alloying effect on superconductivity in amorphous lanthanum-based alloys

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The effect of alloying on the superconducting properties of amorphous, liquid-quenched La-based alloys containing Al, Ge, and Au is studied. The transition temperature T_c of these superconductors depends largely on the La content and is not very sensitive to the second alloy constituent throughout the composition range investigated (~65–83-at.% La). From the data on T_c, the temperature dependence of the upper critical field $H_{c2}(T)$, and the residual-resistivity values, we estimate the coherence length $\xi(o)$, the density of states at Fermi level $N(E_F)$, and the electron-phonon coupling parameter λ as a function of alloy concentration. The implication of these results is that the electron-phonon interaction strength $\langle I^2 \rangle$ is essentially constant, suggesting that superconductivity in these alloys is of a localized nature.

INTRODUCTION

There has been considerable interest in Lanthanum and its compounds because of their unusual electronic and structural properties. Two allotropic forms of La exist: the dhcp ($T_c \simeq 4.9$ K) and the fcc ($T_c \simeq 6.1$ K) phases. Relative to its position in the periodic table, La has an anomalously high superconducting transition temperature (T_c) and, in fact, under high-pressure conditions (≥ 150 kbar), it has the highest observed T_c (≈ 12 K) for any elemental superconductor.[1] For polycrystalline La,[1,2] or stoichiometric La compounds like La_3Al, LaCu, and La_3Ga,[2] in which La was determined to play the dominant role in the superconducting properties, extremely large positive values of the pressure coefficient of T_c, $(\partial T_c/\partial P)_{P\approx 0}$, have been observed. From recent tunneling studies, it has been found that La is a moderately strong-coupled superconductor at normal pressure and that the coupling increase in strength under increasing pressure.[3] There is also some evidence of phonon softening as a result of high pressure.[3] Another interesting property of La is its anomalously low melting point as compared with those of other group-III-*B* elements with similar outer electronic configuration for the neutral atom (i.e., Sc, Y, and Lu).[4] Its negative thermal-expansion coefficient at low temperature is also unusual.[5]

It is now experimentally established that the T_c of pure La and some of its compounds depends largely on the La-La nearest-neighbor distance.[2,6] However, there is no general agreement on the type of electrons primarily responsible for the other unusual properties of La and its compounds. In some models, La is regarded as a pure *sd*-band transition metal,[7] while in others it is assumed that a narrow band of 4*f* electrons is present near the Fermi level.[4,8] Among the 4*f*-band models, there is a further split of opinion as to the importance of the 4*f* electrons in the observed superconducting properties of La and its compounds. For example, in order to explain the strong increase of T_c with pressure in La, Ratto *et al.*[8] claim that the 4*f* electrons at the Fermi level actually inhibit superconductivity. In their model, increasing pressure results in a reduction of the *f*-electron character at the Fermi level and therefore produces an increase in T_c. On the other hand, Wittig and co-workers[1,4] believe that the presence of 4*f* states close to the Fermi level enhances superconductivity in La. They assume a degeneracy of 4*f* states with conduction-electron states, resulting in a hybridization between them with the 4*f* electrons taking on conduction-electron character. High pressure is thought to increase this hybridization and therefore results in the T_c increase in La and other La-based materials. The occurrence of phonon softening in La under pressure, its low Debye temperature and low melting point have also been discussed by Wühl *et al.*[3] in terms of the enhancing effect of the 4*f* electrons.

One way to gain additional insight into the problem is to study the effects of other elements on the various properties over a significantly wide range of alloy concentration. However, most elements of interest have limited or vanishingly small solubility in La so that such a study is impossible. For this reason, previous efforts have, until recently, been concentrated on some stoichiometric compounds of La.[2] Because of their limited number, it is difficult to see any systematic trend in the correlation between the electronic structure and superconductivity. Amorphous alloys provide systems in which the same structure can persist over a large composition range. Recently, superconductivity in amorphous La-Au alloys has been reported by Johnson *et al.*[9] However, the composition range over which sharp superconducting transitions were obtained in these

alloys were relatively small. In this paper we report on superconductivity in two new La-based amorphous alloy systems La-Al and La-Ge, prepared by the liquid-quench technique. The La-Al system is particularly interesting since it is relatively free from the problem of rapid oxidation in air, unlike the La-Au alloys. Furthermore, the amorphous structure is found over a much larger range of concentration than other La-based systems reported previously. The observed changes in superconducting parameters of the alloys will be discussed in terms of current theoretical models.

EXPERIMENTAL PROCEDURES

The alloys were prepared by inductive melting of the weighed constituents under argon. Samples were then prepared by the liquid-quenching technique,[10] in which the melted alloy is splat cooled between a "piston and anvil." The main improvements we introduced that seemed to insure a high yield of single-phase amorphous alloys included the following: (i) doing the quenching in a vacuum of better than 10^{-3} Torr (this probably helped to reduce the oxygen content in the samples) and (ii) the ability to remelt the alloy very quickly prior to quenching.

Several criteria were used to check for the amorphous structure in the samples. The structure was determined by x-ray diffraction which gave the intensity as a function of scattering angle (2θ). For a single-phase amorhphous sample, the x-ray (Cu $K\alpha$) pattern gave a prominent broadened peak centered at about $2\theta = 30.5°$. Samples that were relatively nonbrittle and had thicknesses less than 0.075 mm were usually found to be amorphous. In a few cases there were samples that exhibited amorphous characteristics, according to the above criteria, but still showed evidence of two phases in the superconducting transition. This took the form of a step in the resistance versus temperature curve. Only those samples with a single transition were used in the data reported in this work.

Transition temperatures were determined resistively by means of the standard four-point probe technique. Temperature measurements with an absolute accuracy of ±0.05 K were done with a calibrated Ge resistance thermometer. By definition, the point at which the resistance of the sample reducted to 50% of its normal-state value (R_0) was taken as T_c. The transition width ΔT was arbitrarily defined as the temperature interval between points corresponding to 0.1 R_0 and 0.9 R_0 of the transition curve.

Upper critical magnetic fields H_{c2} were determined as a function of temperature for a number of the La-Al alloys. This was done using a superconducting magnet capable of producing fields up to 30 kG. Temperatures during the H_{c2} measurements were obtained using a 100-Ω Allen-Bradley carbon resistor which had been calibrated in zero magnetic field with a Ge resistance thermometer. The critical fields were obtained by fixing the perpendicular magnetic field value at the sample and determining the corresponding transition temperature in the manner discussed above.

RESULTS AND DISCUSSION

The alloys reported here were of the form $La_{1-x}M_x$ ($M \equiv$ Al, Ge, or Au) with the following ranges of x: $0.18 \leq x \leq 0.34$ for Al, $0.17 \leq x \leq 0.22$ for Ge, and $0.18 \leq x \leq 0.25$ for Au. Of the three alloy systems, $La_{1-x}Al_x$ (with $x \geq 0.20$) was the least chemically reactive and, in fact, hardly showed any signs of oxidation even after several weeks of exposure to air. On the other hand, the La-Ge and the La-Au alloys oxidized so rapidly in air that it was necessary to cover them with a protective coating until ready for measurements. Under the same conditions, it was much easier to obtain the amorphous structure in the La-Al system than in the other two alloy systems.

In all three alloy systems the temperature coefficient of resistivity values were nearly zero for $x \leq 0.20$ and became progressively more negative with increasing values of x. Residual-resistivity values [$\rho(o)$] for all the amorphous alloys varied from about 120 $\mu\Omega$ cm for small x to about 200 $\mu\Omega$ cm for the large-x values. Details of the temperature-dependent resistivity measurements of these alloys and a discussion of the results in terms of current physical models on resistivity in amorphous materials will be presented elsewhere.

Over the whole range of compositions studied, the superconducting transitions were quite sharp, as shown for the case of the La-Al system in Fig. 1, which gives the normalized resistance as a function of temperature for several samples. A plot of T_c versus composition is given in Fig. 2. With the exception of the points for the La-Ge alloys, the transition widths ΔT were equal to or smaller than the symbols used to represent the data points in Fig. 2. T_c varies linearly with composition for the three alloy systems, though this is more obvious for the La-Al and La-Au alloys. It is interesting to note that the straight lines drawn through the three sets of data are parallel to each other, and that they extrapolate to approximately 6 K, which is roughly the T_c of β-La, the fcc phase of pure crystalline La.[2] The alloys con-

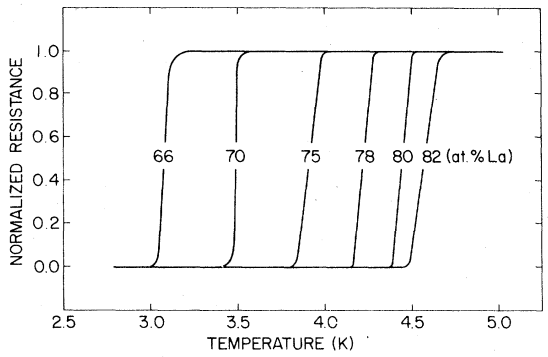

FIG. 1. Normalized resistance as a function of temperature for a series of amorphous La-Al alloys obtained by quenching from the liquid state.

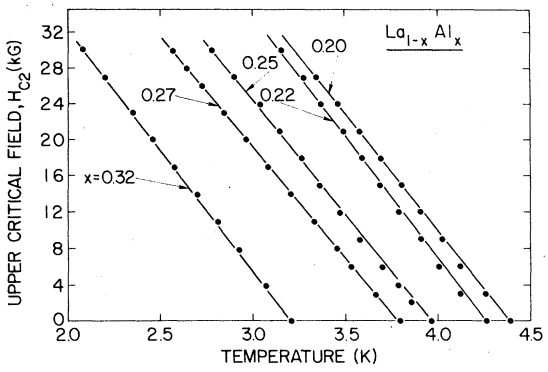

FIG. 3. Upper critical magnetic field H_{c2} as a function of temperature for a series of amorphous La-Al alloys.

taining Ge tended to have higher T_c's than other alloys with the same La content while the Au alloys generally had lower T_c's.

Results of critical field measurements are shown in Fig. 3 for a number of La-Al alloys. It can be seen that, within the temperature range available from the 30-kG magnet, the $H_{c2}(T)$ curves are linear and approximately parallel to each other. This linearity of $H_{c2}(T)$ over a temperature range large compared with the zero-field transition temperature T_{c0} has been observed for a number of amorphous superconductors.[9,11] The values of $(dH_{c2}/dT)_{T=T_{c0}}$ for the La-Al alloys are comparable to the La-Au values obtained by Johnson *et al.*[9] The average value of the initial slope for the five La-Al samples of Fig. 3 is 25.4 kG/K. From the definition of the upper critical magnetic field H_{c2}, the zero-temperature coherence length can be determined from the following expression:

$$\xi(0)=\left[\frac{\varphi_0}{2\pi T_{c0}}\left(\frac{dH_{c2}}{dT}\right)_{T_{c0}}^{-1}\right]^{1/2}, \tag{1}$$

where φ_0 is the flux quantum. The values of $\xi(0)$ calculated from Eq. (1) vary from 53.6 to 62.4 Å for the amorphous La-Al alloys. These short-coherence-length values are typical of superconductors in the extreme "dirty limit." This is to be expected[12] since amorphous materials are characterized by very short normal-state electronic mean free paths l (of the order of an atomic spacing), and extremely high Ginzburg-Landau parameters κ.

The density of states at the Fermi level $N(E_F)$ can be estimated from a knowledge of the initial slope of the upper critical field $(dH_{c2}/dT)_{T_{c0}}$ and the residual resistivity $\rho(0)$. The relevant expression is[11]

$$N(E_F)(1+\lambda)=\frac{-\pi h(dH_{c2}/dT)_{T_{c0}}}{16k_B e^2\varphi_0\rho(0)}, \tag{2}$$

where λ is the electron-phonon coupling and all the other quantities are expressed in Gaussian cgs units. Equation (2) was modified from Gor'kov's original expression[13] to give the conventional units of states eV^{-1} $atom^{-1}$ $spin^{-1}$ for the density of states. The results of this calculation are given in Table I. In Fig. 4, we see that, for the La-Al alloys, $N(E_F)(1+\lambda)$ decreases monotomically as the Al content increases.

Recent tunneling experiments on La under high pressure[3] have shown that its electron-phonon coupling parameter λ increases with pressure. The opposite effect on λ is observed on alloying as the La content is decreased. For example, in the La-Al alloys, we estimate that λ changes from 0.81 to 0.68 when La is lowered from 80 to

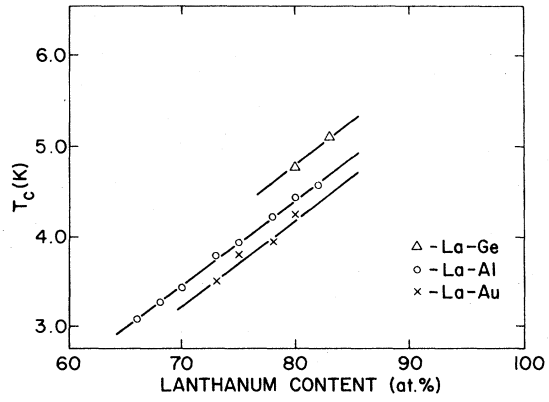

FIG. 2. Superconducting transition temperature T_c as a function of composition for amorphous La-Ge, La-Al, and La-Au alloys.

TABLE I. Properties of the amorphous La-Al alloys.

at. % Al	$\rho\,(o)$ ($\mu\Omega$ cm)	T_{co} (K)	$\left(\frac{dH_{c2}}{dT}\right)_{T_{co}}$ (kG K^{-1})	$\xi\,(o)$ (Å)	$N(E_F)(1+\lambda)$ (states eV^{-1} atom^{-1} spin^{-1})
20	163	4.43	-25.4	54.1	1.37
22	172	4.30	-26.7	53.6	1.24
25	181	3.98	-25.0	57.4	1.13
27	185	3.82	-23.9	60.1	1.09
32	194	3.23	-26.2	62.4	1.05

68 at. %. These λ values were obtained from McMillan's equation,[13] which gives T_c in terms of λ, the Debye temperature θ_D, and the electron-electron Coulomb pseudopotential μ^*. Debye temperatures were estimated from recent specific-heat measurements on similar alloys.[14] In accordance with normal practice, and in the absence of tunneling data, we used a fixed value of 0.1 for μ^*.

As discussed by McMillan,[15] the electron-phonon coupling parameter can be expressed

$$\lambda = N(E_F)\langle I^2\rangle / M\langle\omega^2\rangle\,, \tag{3}$$

where $\langle I^2\rangle$ is the squared average electron-phonon interaction, M is the atomic mass, and $\langle\omega^2\rangle$ is the squared average phonon frequency, which is related to Θ_D^2 through a proportionality constant.[16] From the estimated change in Θ_D when the Al content is increased from 20 at. % to 32 at. % and the calculated values of λ and $N(E_F)$, it is found that $\langle I^2\rangle$ remains fairly constant over the composition range for the La-Al alloys studied, changing by only 5%. The value of $\langle I^2\rangle/M\langle\omega^2\rangle$ is found to be even more constant (see Table II). In fact, the ratio of this quantity at the two extremes of composition for the amorphous La-Al alloys, for example, is nearly 1.0. Since the last observation implies that λ is directly proportional to $N(E_F)$, it can be concluded that the observed change in λ, and therefore in T_c results directly from variation in $N(E_F)$.

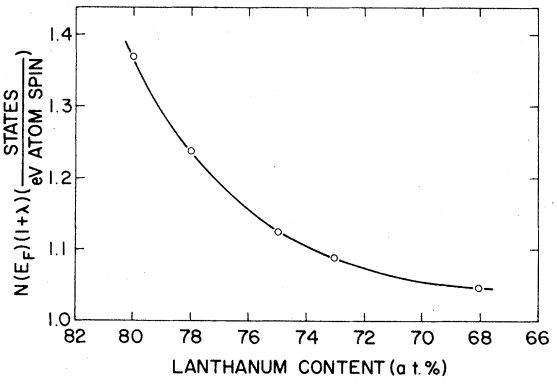

FIG. 4. Plot of the unrenormalized electronic density of states near the Fermi surface, $N(E_F)\,(1+\lambda)$ vs lanthanum content for the La-Al alloys.

The above results have several interesting implications: First, the constancy of $\langle I^2\rangle/M\langle\omega^2\rangle$ is in agreement with a recent work of Varma and Dynes.[17] They found that this quantity is approximately constant for a given class of similar materials which are characterized by a dominant orbital of the same nature near the Fermi surface. Second, though the observations agree with the claim that superconductivity in the amorphous state is largely determined by the parameter $\eta \approx N(E_F)\,\langle I^2\rangle$, it is further noted that, for those La-based alloys, variation in η is determined by $N(E_F)$. Originally taken to be a *purely* local atomic parameter,[16] η is now considered to represent an overlap integral among the atoms.[18] Third, all the observations suggest that, in the La-based alloys, the mechanism responsible for superconductivity is localized at the La atom, and that variation in T_c is largely dependent on the La-La nearest-neighbor distance. The last point is confirmed in Fig. 2, where T_c is shown to be relatively insensitive to the second constituent, and also demonstrated in several experiments.[2,6]

Wittig *et al.*[1,4] have developed a model of superconductivity in La in which the dominant orbitals near the Fermi surface are f orbitals. In order to explain the strong increase in T_c with pressure for La, Wittig[4] argues that the band structure of La is of the form $(sd)^{3-\epsilon}4f^{\epsilon}$ and that the degeneracy of the $4f$ states with the conduction electrons could lead to an appreciable hybridization. In this model, the effect of pressure or in our case, alloying with nonmagnetic elements, is simply to change ϵ, the fraction of a conduction electron bound in a $4f$ scattering resonance. Pressure increases ϵ and therefore increase T_c, while alloying presumably decreases ϵ, resulting in the

TABLE II. Properties of the amorphous La-Al alloys.

at. % Al	Estimated Θ_D (K)	λ	$N(E_F)$ (states eV^{-1} $atom^{-1}$ $spin^{-1}$)	$\lambda/N(E_F)$
20	112	0.81	0.75	1.08
22	113	0.79	0.70	1.13
25	116	0.76	0.64	1.17
27	117	0.74	0.63	1.17
32	121	0.68	0.62	1.10

observed systematic T_c decrease in Fig. 2.

The possible relation between this kind of hybridization and λ [or $N(E_F)$] is provided by the recent microscopic theory of Hanke *et al.*[19] which seeks to explain the interdependence of phonon softening and high T_c in some transition-metal compounds. Hybridization between localized d states and extended p states at the Fermi level is shown to result in anomalously high nonlocal dielectric function (i.e., an increase in the screening). This increased screening accounts for the observed phonon anomalies or soft modes and a consequent increase in T_c due to an enhancement of λ. Future theoretical work extending the concepts of Hanke *et al.* to La is desirable since it could shed some light on the still baffling topic of the electrons responsible for superconductivity in La. Encouraging signs that the theory can be applied to La include its high T_c, the observation of phonon softening under pressure, and the moderately strong-coupling character of La even at normal pressure [$2\Delta(0)/k_B T_c = 3.75$].[3]

In a recent paper, Butler[20] has also shown the crucial part that f-like electron states at the Fermi surface can play in the superconductivity of transition metals. His detailed calculations are for $4d$ transition metals for which he shows that the most important contributions to λ result from processes involving scattering between d and f states. For the early rare earths and actinides, Butler speculates that the effects of d-f (and possibly f-g) scattering could be even more important in producing high T_c due to the more advantageous positioning of the atomic f orbitals. However, in his view, achievement of high T_c may not be possible for these materials because of exchange effects. For La, in which such exchange effects are not expected, we believe that the unusually high T_c is consistent with Butler's theory.

In conclusion, we have found that changes in T_c of La-band amorphous alloy of Al, Ge, and Au result mainly from changes in $N(E_F)$. From the observed near constancy of $\langle I^2\rangle/M\langle\omega^2\rangle$ and $\langle I^2\rangle$ over a large concentration range it can be inferred that localized electronic states play a prominent role in the superconductivity mechanism. As far as superconductivity in these amorphous alloys is concerned, the added elements, Al, Ge, and Au appear to act as diluting agents, merely varying the La-La nearest-neighbor distance which affects the overlap integral η among the atoms. Aside from the convenience provided by working with these amorphous materials, especially the possibility of a systematic change in properties, we note that structure is not a fundamental consideration. This is demonstrated by the recent high-pressure work[21] on amorphous $La_{78}Au_{22}$ for which the T_c behavior under pressure was qualitatively the same as the behavior of polycrystalline La,[1,2] and stoichiometric compounds like La_3Al, La_3Ga, and LaCu.[2] Because of the rather attractive oxidation properties of the La-Al system, a tunneling study on it will be useful in providing more definitive information on the electron-phonon coupling strength in these alloys.

ACKNOWLEDGMENTS

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