PHYSICAL REVIEW B VOLUME 18, NUMBER 7 1 OCTOBER 1978

Calorimetric and resistive measurements of amorphous "splat cooled" $La_{1-x}Ga_x$ foils

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(Received 23 March 1978)

The heat capacities, transition temperatures, electrical resistivities, and upper critical fields have been measured for a series of $La_{1-x}Ga_x$ alloys with $x = 0.16$–$x = 0.28$. Values of the Debye temperature, density of states, and electron-phonon coupling constant have been determined from these measurements. Superconductivity in this amorphous system is of the intermediate-coupling nature with $\lambda \simeq 0.8$ and the ratio of the non-phonon-renormalized density of states to that of the free-electron model is $N_\gamma(0)/(1+\lambda)\ N_{\mathrm{Fe}} \simeq 2.2$. Specific-heat data as a function of concentration suggest a change in short-range order for x between 0.22 and 0.26.

I. INTRODUCTION

Considerable progress has been made towards the understanding of amorphous superconducting metals since their discovery by Buckel and Hilsch.[1] However, most of the experiments on amorphous superconductors have been directed toward the simple (nontransition) metals. A survey of the available experimental data on the simple[2] amorphous metals leads one to the following conclusions: (i) they are strong-coupling superconductors with electron-phonon coupling constants as large as 2.4 values of $2\Delta_0/k_B T_c$ around 4.5; (ii) the electronic properties are well described by the simple free-electron model with the exception of the alloy systems of Bi and Pb which appear to be more complicated; and (iii) $\alpha^2(\omega)F(\omega)$ is enhanced at low frequencies as compared to the crystalline phase.

Amorphous transition metals (*a*-TM) have received much less attention than the simple metals. Recent experiments which are providing the first insight into the properties of *a*-TM suggest a much more complicated and interesting behavior than for simple amorphous metals. The systematic study of the effect of valence electrons per atom $\mathfrak{z}$ in 4*d* and 5*d* transition-metal alloy films by Collver and Hammond[3] shows a smooth variation in T_c except for a sharp triangular peak at a $\mathfrak{z}$ of 7. This behavior is markedly different from the crystalline behavior where T_c varies strongly with $\mathfrak{z}$. Specific-heat measurements by Shull and Naugle[4] showed amorphous $La_{x-1}Au_x$ alloys to be only intermediate coupling superconductors, and tunneling measurements by Tsuei *et al.*[5] indicated weak-coupling superconductivity in several *a*-TM alloys. These results are very interesting in light of the very general argument by Bergmann[6] to explain the universally strong-coupling behavior observed in simple amorphous metals in terms of additional phase space for electron-phonon scattering, resulting from elimination of the requirement to conserve crystalline momentum with the amorphous structure.

As a follow up to studies of the amorphous $La_{1-x}Au_x$ system,[4,7] measurements of the properties of a new but similar amorphous transition-metal alloy system $La_{1-x}Ga_x$ with $x = 0.16$ to $x = 0.28$ are presented. The "splat-cooled" foils were made at Cal Tech where resistive measurements of the superconducting transition temperature, temperature dependence of the electrical resistivity, and upper critical field were done. Similar samples were mailed to Texas A&M University, where the heat capacities of the foils were measured. X-ray studies at Cal. Tech. both prior to mailing and on returned samples after heat capacity measurements were completed, were used to establish the amorphous character of the bulk of the samples although traces of a crystalline phase were also observed. The heat-capacity measurements have been analyzed to extract values of the Debye temperature, electronic density of states, the jump in the specific heat at the transition temperature, and transition temperatures and relative abundances of the phases. The temperature dependence of the upper critical field and the value of the residual resistivity also have been used to calculate the electronic density of states. An estimate of the electron-phonon coupling constant has been extracted by use of the transition temperature and Debye temperature in the McMillan formula.[8] The results of these measurements are presented as a function of x and are compared to similar results for amorphous $La_{1-x}Au_x$ and crystalline La. Since efforts to crystallize these samples resulted in embrittlement and destruction of the sample, presumably due to oxidation even in the 10^{-6}-Torr vacuum, no comparison is offered with crystalline alloys of the same composition.

II. EXPERIMENTAL DETAILS

A. Sample preparation and resistive measurements

The samples used in these experiments were prepared by induction melting of the appropriate constituents on a silver boat under an argon atmosphere and quenching them from the liquid state using the "piston and anvil" splat-cooling technique.[9] The samples produced by this method are typically 1.5–3 cm in diameter and approximately 0.005 cm thick. The foils were scanned immediately after quenching with a General Electric diffractometer (Cu $K\alpha$ radiation). To insure that the samples did not oxidize or crystallize, they were sealed in evacuated tubes except during mounting in the experimental apparatus. These tubes were stored at 250 °K to prevent recrystallization.

The samples mailed to Texas A&M University were at ambient temperature throughout the trip (a few days), but were maintained at 250 °K after their arrival until mounted for measurements. After completion of the heat-capacity measurements representative samples were returned to Cal Tech for further scanning. No noticeable deterioration of the samples was observed over periods of several months.

The electrical resistances of the samples were measured with a standard four-probe technique as a function of temperature in a variable-temperature cryostat surrounded by a superconducting solenoid with a maximum field capability of 8 T. At temperatures below 30 °K, the temperature was measured with a calibrated Ge resistance thermometer with an accuracy of ± 0.02 °K. At higher temperatures a Pt-PtRh thermocouple was used to measure the temperature of the sample. The upper critical field (H_{c2}) was determined from resistive transition curves with the field oriented transversely to the sample. The temperature for H_{c2} measurements was determined with a carbon resistor calibrated against a Lake Shore Cryotronics standard carbon-glass thermometer. The transition temperature was chosen as that temperature at which the resistance had decrease to half the residual resistance. Electrical resistivities were calculated using measured dimensions of the foil. The uncertainties in this value arise principally from the uncertainties in the measurement of the foil thickness, which was done with a micrometer. Mass densities ρ_m were measured by weighing the sample in air and then suspended in toluene.

B. Heat-capacity measurements

For the heat-capacity measurements, a piece of the foils about 0.5 in. in diameter with a weight of 10–30 mg was used. Due to the small heat capacities of these samples, the standard adiabatic technique is not adequate. Consequently, the ac technique of Sullivan and Seidel[10] and the relaxation method of Bachmann *et al.*[11] were employed in the measurement of the heat capacities. The ac technique was used to measure the background heat capacity which was as small as 8×10^{-8} J/K at the lowest temperatures. After the sample was added, the more reliable relaxation method was used. These techniques are now well known so only details peculiar to this particular calorimeter will be described.

The sample is mounted onto a 0.5-in. diameter, 0.008-in. thick sapphire substrate, with between 200 and 500 μg of UHU-Plus epoxy.[12] The working thermometer is a graphite film of DAG154[13] painted over the 0.007×0.1-in. gap between two silver contact pads evaporated onto the sapphire. This thermometer was calibrated each run against a calibrated Cryocal Ge resistance thermometer with an accuracy of ±0.007 K between 1.8 and 8 K, which is mounted in a copper constant-temperature reservoir. An evaporated Bi film provided the substrate heater. Four 0.001 25-in. Au–7-at.%-Cu leads were epoxied to the substrate and silver painted to the heater and thermometer contacts. The mass of the epoxy and silver paint are less than 200 μg. The other end of these leads is indium soldered to sapphire heat sinks, which in turn are indium soldered to the constant-temperature reservoir. These wires provide both electrical contact to the heater and thermometer and the thermal conductance to the bath; consequently, the accuracy of the measurements was reduced appreciably when this elaborate heat sinking was omitted.

Measurements of the sample heat capacity is a two-step process. First the background heat capacity of the substrate is measured with the ac technique. Then, the heat capacity with the sample epoxied to it is measured by the relaxation method. With $\Theta_D \approx 527$ K,[14] the sapphire substrate heat capacity was much less than the total heat capacity; consequently, it was necessary to use the less reliable ac technique to measure its heat capacity, particularly at the lower temperatures. At higher temperatures, the substrate heat capacity was also measured with the relaxation technique; good agreement between the two measurements was obtained. The heat capacity of several milligrams of UHU-Plus epoxy was measured in a separate experiment. These values were used to correct for the epoxy which held the sample to the substrate. It should be noted that the total addendum never contributed more than 10% of the sample heat capacity so that a 10% error in its determination results in at most a 1% error in the sample heat capacity.

To test the accuracy of the specific-heat measurements, the heat capacities of pure Au and In samples were measured and compared to accepted values from the literature. The Au sample was a small piece of 0.05-in. wire which had been annealed at temperature near the melting point. The In sample was a foil rolled from indium wire and also annealed just below the melting point. The masses of these samples were adjusted to give a heat capacity comparable to those of the $La_{1-x}Ga_x$ foils. A fit of the Au data to $C=\gamma T+\beta T^3$ gives a value of $\Theta_D = 163.1$ °K and $\gamma = 0.79$ mJ/mole °K^2, which compared favorably with literature values of 164.6 and 0.79 by Corak *et al.*,[15] and 163.2 and 0.69 by Martin.[16] This represents an overall agreement within better than 3% with these previous measurements. The In data was compared to that of Clement and Quinnell[17] and Bryant and Keesom.[18] The overall agreement with the previous measurements was within 2.5% in this case. The measured value of the discontinuity at the superconducting transition is 9.8 mJ/mole °K^2 compared to 9.75 mJ/mole °K^2 reported in Ref. 17.

III. RESULTS

A typical x-ray diffraction scan is shown for a $La_{0.78}Ga_{0.22}$ alloy in Fig. 1. There is slight evidence for regions of crystallinity in the x-ray scans of those samples with Ga concentrations of $x < 0.20$ and >0.22, but crystalline inclusions appear to constitute a few percent of the sample for the other concentrations. The resulting values for the nearest-neighbor distance (nnd) and the effective microcrystal size μ from a Debye-Scherrer analysis of the x-ray data are given in Table I. The values of μ are typical of metallic glasses.

The temperature dependence of the electrical resistance of $La_{0.78}Ga_{0.22}$ is shown in Fig. 2. At low temperatures, the temperature coefficient of resistance $\alpha = R_0^{-1} dR/dT$ for this alloy is negative. A negative coefficient of resistance was observed for all of the alloy concentrations with $x \geqslant 0.20$ in the range of this study, but for $x = 0.16$ and 0.18, α was positive. Values of the electrical resistivity ρ of these alloys are also shown in Table I. The uncertainty in the determination of values of ρ is about 15% as a result of the difficulty in measuring the thicknesses of the foil samples. The crossover point for the sign of α corresponds to $\rho \simeq 150$ $\mu\Omega$ cm in agreement with the general trend observed in metallic glasses. At temperatures near 450 °K, the sample begins to crystallize. This exact temperature depends on the heating rate, which was 3 °K/min for the data of Fig. 2, where a precipitous drop in resistance indicative of crystallization occurs at $T \simeq 460$ °K.

The upper critical field H_{c2} as a function of temperature is shown in Fig. 3 for a $La_{0.78}Ga_{0.22}$ sample. As may be seen, H_{c2} depends linearly on temperature over the range accessible to this experiment. Measurements of $H_{c2}(T)$ were made only for samples with $x = 0.22$ and 0.20; consequently, only values of $(dH_{c2}/dT)_{T=T_c}$ for these two alloys are given in Table I. The resistive transitions from which these data were determined exhibited a dependence on the

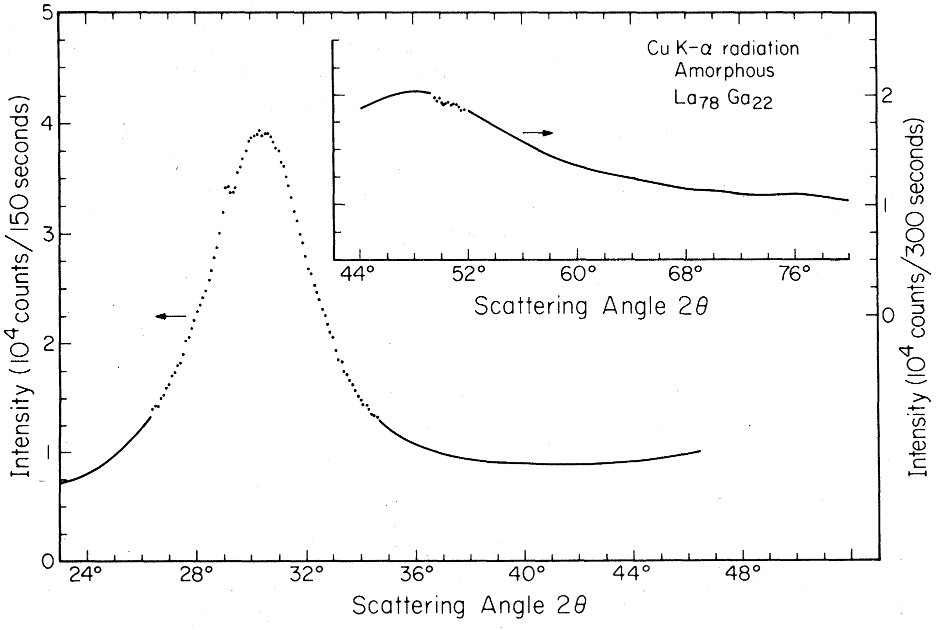

FIG. 1. Typical x-ray diffraction scan.

TABLE I. Measured properties of splat-cooled amorphous $La_{1-x}Ga_x$ foils.

	X ray		Resistive measurements					Calorimetry measurements				
x	nnd[a] (Å)	μ[b] (Å)	T_c (°K)	ΔT_c[c] (°K)	ρ ($\mu\Omega$ cm)	$-dH_{c2}/dT$ (T/°K)	ρ_m (g/cm^3)	T_c (°K)	ΔT_c (°K)	ΔC (mJ/°K mole)	Θ_D (°K)	γ (mJ/°K^2 mole)
0.16	3.59	20	4.0	0.3	123	···	6.07 ± .05	3.94	0.24	31.9	109.6	5.91
0.18	3.57	19	3.9	0.1	···	···	6.24 ± .05	···	···	···	···	···
0.20	3.55	18	3.8	0.1	168	2.25	6.25 ± 0.5	3.84	0.13	46.1	109.6	6.10
0.22	3.54	18	3.7	0.1	200	2.25	6.28 ± .05	3.64	0.11	39.5	108.6	5.52
0.24	3.52	19	3.6	0.08	219	···	6.22 ± .05	3.62,3.52	0.19	34.8	115.3	6.72
								3.68,3.54[d]	0.26[d]	39.2[d]	111.6[d]	6.84[d]
0.26	3.51	19	3.5	0.2	···	···	6.28 ± .05	3.39,3.22	0.29	28.9	118.7	5.43
0.28	3.51	19	3.4	0.3	193	···	6.42 ± .05	3.09	0.16	22.6	117.8	4.11

[a] Nearest-neighbor distance.

[b] Effective microcrystal size from Scherrer formula.

[c] ΔT_c defined for 0.1–0.9 of normal-state resistance.

[d] Specific heats of samples from two different batches with this nominal concentration were measured.

measuring current as a result of flux flow. The data shown in Fig. 3 were determined in the limit of $I \rightarrow 0$. A detailed discussion of the flux flow regime will be published separately. Values of the mass density ρ_m, resistive transition width ΔT_c, and transition temperature T_c, in zero magnetic field are also included in Table I for the alloys.

The specific heat divided by absolute temperature is plotted in Fig. 4 as a function of the square of the absolute temperature for a sample with each of the alloy concentrations except $x = 0.18$. No specific-heat measurements were made at this concentration. The straight line represents the best fit above T_c to

$$C = \gamma T + \beta T^3 \ , \qquad (1)$$

subject to the condition that the entropy at T_c of the sample as calculated from the measurements of specific heat in the superconducting state is identical to that calculated using the extrapolation of this fit below T_c, i.e., that at T_c the entropy of the normal state and superconducting state is the same. With the assumption that the T^3 term can be explained by the Debye model for the low-temperature specific heat, the coefficient β may be expressed in terms of the Debye temperature Θ_D. Although the Debye model should not be expected to describe the phonon spectrum of amorphous metals, in the long-wave limit the discreteness of the lattice becomes unimportant. Thus disorder should not significantly effect the form of the spectrum. A jump in the specific heat ΔC at the superconducting temperature is readily observable. The principal results of these measurements are summarized in Table I by values of T_c, the width of the superconducting transition (ΔT_c), Θ_D, and γ. The uncertainties in the determination are approximately half of ΔT_c, 15%, 2%, and 10%, respectively.

It should be noted that two very closely spaced transition temperatures may be distinguished for the samples with $x = 0.24$ and $x = 0.26$. The transitions for

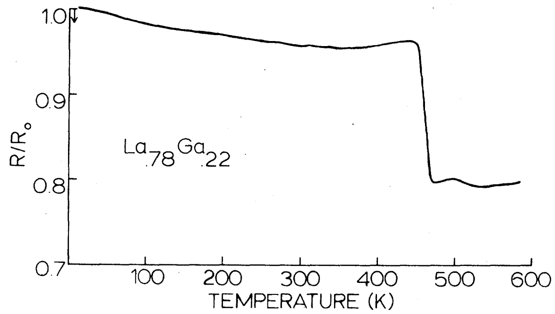

FIG. 2. Temperature dependence of normalized electrical resistance.

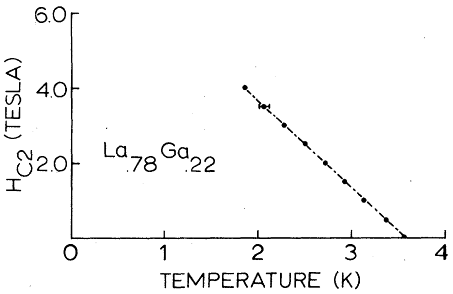

FIG. 3. Upper critical field H_{c2} as a function of temperature.

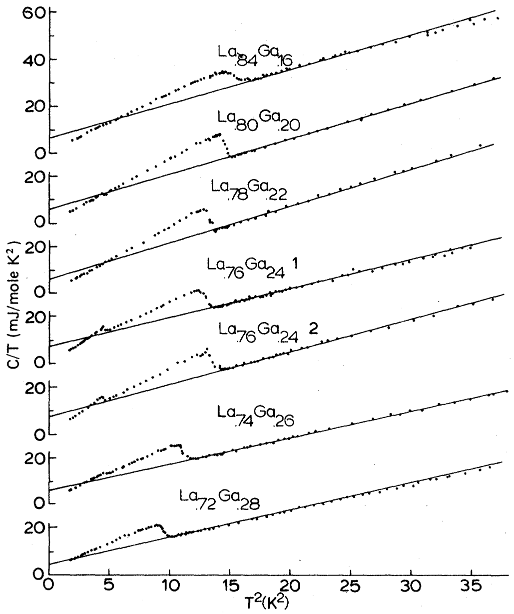

FIG. 4. Specific heats for amorphous $La_{1-x}Ga_x$ alloys.

$x = 0.20$ and 0.22 are very clean and sharp, whereas those for $x = 0.16$ and 0.28 are broader. Overall, the agreement between T_c determined by the calorimetric measurements and that determined by resistive measurements is excellent except for the sample with $x = 0.28$. For this sample, the calorimetric measurements indicate that the bulk of the sample transits about 0.3 °K lower than the resistive transition. A bump in the specific heat at 2.15 °K is evident for the samples with $x = 0.24$ and $x = 0.26$. A similar feature was observed for amorphous $La_{0.76}Au_{0.24}$ samples.[4] Surprisingly, x-ray scans of these particular samples indicated only small amounts of crystalline phase, not significantly in greater abundance than for the other concentrations of Ga where this feature is not detectable.

IV. INTERPRETATION AND DISCUSSION

The x-ray patterns indicate that these samples are rather homogeneous amorphous metals. Some crystalline inclusions of the order of a few percent are evident from x-ray studies in all of the samples. Only for the samples with concentrations near $x = 0.25$ is a superconducting transition readily observed (indicated by the small bump in C at $T = 2.15$ °K) that is definitely not associated with the amorphous phase. This phase cannot be identified by its superconducting transition temperature and constitutes at most 2%–5% of the sample. The bulk of the sample indeed transits into the superconducting state at T_c identified with the amorphous phase.

As in our earlier paper,[4] the decision to express the cubic term in the specific heat as a Θ_D rather than in terms of the coefficent β in Eq. (1) implicitly assumes the validity of the Debye model to describe the low-energy part of the vibrational spectrum in amorphous solids. In addition to the fact that there may be evidence for additional structural excitations in amorphous metals[19,20] which could lead to a larger value of β than would be expected from sound velocity measurements, it should be noted that the temperature range of these experiments is barely in the region where one might expect a true T^3 dependence of the vibrational contribution to the specific heat. A final determination of Θ_D will require very low-temperature specific-heat measurements which are just commencing at Texas A&M University. In spite of possible revisions in the value of Θ_D with the availability of very low-temperature heat-capacity measurements, it is instructive to examine the values of Θ_D as a function of x, and to use these with values of T_c to estimate the strength of the electron-phonon coupling constant λ in this alloy system.

A precise determination of λ for these alloys must await the availability of good tunneling data which is almost impossible to obtain with foil samples. Although derived using a particular model for the quantity $\alpha^2(\omega)F(\omega)$, the McMillan expression[8] for T_c of strong-coupling superconductors provides a way to estimate λ in the absence of detailed tunneling data. The values of λ determined from this expression with values of Θ_D and T_c from the specific-heat measurements and with $\mu^* = 0.1$ are listed in Table II. These values for λ lie between 0.7 and 0.9, close to those reported for $La_{0.80}Au_{0.20}$ and $La_{0.76}Au_{0.24}$ in Ref. 4, and significantly smaller than the values of $\lambda \sim 2$ observed for all simple (nontransition) amorphous superconductors.[2] Also listed in Table II are values of $\Delta C/\gamma T_c$ for these samples. These values vary from 1.37 to 1.97 with an uncertainty of approximately 20% due to the difficulty of determining both ΔC and γ within better than 10%. In general, the agreement with the BCS weak-coupling theoretical value for this quantity 1.43 is reasonably good.

The value of the density of electron states at the Fermi level $N(0)$ can be determined from the coefficient γ of the linear term in the specific heat for a weak-coupling crystalline metal. Calculations by Bergmann *et al.*[21] indicate that a strong electron-phonon interaction may modify the temperature dependence of the electronic contribution to the specific heat so that this type of analysis would not be applicable. Although the calculation depends on the details of $\alpha^2(\omega)F(\omega)$, the fact that λ estimated above is not too large suggests that this effect is negligible for the present alloy system. Aside from the structural excitations for amorphous metals discussed above, there appears no obvious reason to expect that a similar analysis to determine $N(0)$ should not apply for amorphous metals. The heat-capacity measurements

TABLE II. Derived properties of amorphous $La_{1-x}Ga_x$ foils.

x	λ	$\Delta C/\gamma T_c$	$N_\gamma(0)$ (states/eV atom spin)	$N_{H_{c2}}(0)$ (states/eV atom spin)	$N_\gamma(0)/1+\lambda$ (states/eV atom spin)	$\frac{N_\gamma(0)}{(1+\lambda)N_{\mathrm{FE}}(0)}$
0.16	0.85	1.37	1.25	···	0.68	2.1
0.20	0.84	1.97	1.29	1.26	0.70	2.3
0.22	0.82	1.96	1.17	1.05	0.64	2.1
0.24	0.80	1.43	1.43	···	0.79	2.6
	0.82[a]	1.56[a]	1.45[a]	···	0.80[a]	2.7
0.26	0.77	1.57	1.15	···	0.65	2.2
0.28	0.75	1.78	0.87	···	0.50	1.7

[a] These values are from the second sample with the same nominal composition as listed in Table I.

of Ref. 20 indicate that the non-T^3 term associated with these excitations should have negligible effect on the value of γ determined at temperatures of these measurements. Values of $N_\gamma(0)$ determined with the values of γ from Table I are also listed in Table II. These values may be compared with the values for pure crystalline La[22] and amorphous $La_{0.80}Au_{0.20}$ and $La_{0.76}Au_{0.24}$ which are 2.1, 1.50, and 1.33 states/eV atom spin), respectively.

For an isotropic weak-coupling superconductor the density of states may be calculated from the slope of the upper critical field,[23]

$$N_{H_{c2}}(0) = \frac{\hbar\pi^2}{8\rho k_B e^2 \Phi_0} \left.\frac{dH_{c2}}{dT}\right|_{T=T_c} , \qquad (2)$$

where Φ_0 is the flux quantum and ρ the electrical resistivity. Strong-coupling corrections considered by Rainer and Bergmann[24] are probably negligible for these intermediate to weak-coupling superconductors but in any event could not be calculated without a detailed $\alpha^2(\omega)F(\omega)$ as determined from tunneling measurements. If $k_F L >> 1$, where L is the electron mean free path, one might expect this relation to hold for amorphous metals.[24] With values of ρ given in Table I it appears that these samples marginally meet this criteria. On this assumption, values of $N_{H_{c2}}(0)$ for the two samples for which dH_{c2}/dT have been measured are listed in Table II. These values are in excellent agreement with the values $N_\gamma(0)$ from the specific-heat measurements. The agreement is much better than the nearly 20% uncertainty expected for $N_{H_{c2}}(0)$ or even the 10% uncertainty in $N_\gamma(0)$. Such excellent agreement is fortuitous; nevertheless, the validity of Eq. (2) appears to be established in this instance. The poor agreement between $N_\gamma(0) = 1.33$ states/(eV atom spin) for $La_{0.76}Au_{0.24}$ and $N_{H_{c2}}(0) = 0.85$ states/(eV atom spin) noted in Ref. 4 is somewhat surprising in view of the agreement for the two $La_{1-x}Ga_x$ samples since $k_F L$ is not significantly different for these two different alloys.

The values of the density of states determined from specific-heat measurements and/or critical-field measurements are enhanced by the electron-phonon interaction. For comparison with calculations of the density of states which do not include the electron-phonon renormalization, those should be divided by $1+\lambda$. Values of $N_\gamma(0)/(1+\lambda)$, the non-phonon-renormalized (NPR) density of states, are given in Table II. The NPR density of states for many of the amorphous simple (nontransition) metals is predicted accurately by the free-electron model. This model is not expected to apply to the amorphous transition metals with large d-band contributions. Values of $m_t^*/m_0 = N(0)/(1+\lambda)N_{\mathrm{FE}}$ where N_{FE} is the free-electron value of the density of states are listed in Table II. The values of N_{FE} were calculated with the densities from Table I and under the assumption that La and Ga each contribute three free electrons.

Values of four of the important parameters, Θ_D, λ, $N(0)$, and T_c which have been determined, are displayed as a function of alloy concentration x for amorphous $La_{1-x}Ga_x$ and $La_{1-x}Au_x$ alloys in Fig. 5. The behavior of these properties as a function of x appears to be similar for the two different second constituents, and the magnitude of the parameters are generally the same within about 10%–15%. There is a relatively smooth behavior of the properties as a function of concentration except for Θ_D. One perhaps can visualize a rather constant density of states to about $x = 0.25$ and then a rather sharp drop with increasing x. The break appears more dramatic for Θ_D, however, where a constant value of $\Theta_D \simeq 109\,°K$ is observed for Ga concentrations up to $x = 0.22$, which suddenly increases to $\Theta_D \simeq 118\,°K$ over a narrow concentration range between $x = 0.22$ and $x = 0.26$. It is in this same narrow concentration range that two distinct, very closely spaced transition temperatures can be resolved in the specific-heat data for both the Ga and the Au alloys. This is very close to the composition with $x = 0.2$ at which the Bernal holes in the Bernal model for random packed structures[25] would just be filled with one Au or Ga impurity atom on the average. It can be conjectured that additional impurities

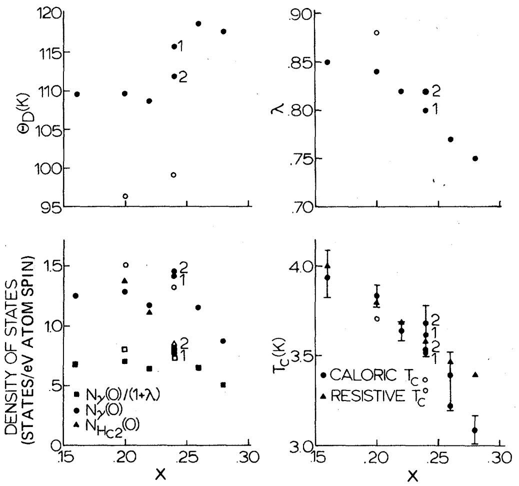

FIG. 5. Properties of amorphous $La_{1-x}Ga_x$ and $La_{1-x}Au_x$ as a function of Ga or Au concentration. The solid symbols represent data for $La_{1-x}Ga_x$ from this work. The open symbols are for $La_{1-x}Au_x$ taken from Ref. 4. The numbers beside data points at 24% correspond to the order in which data for the two samples at that concentration are listed in Table I. Error bars on the T_c plot represent ΔT_c from calorimetric measurements.

added above this concentration may result in a modification of the short-range ordering at the La sites and produce the observed changes in properties.

The ratio of the Θ_D values for the Ga alloy and the Au alloys at the same concentration are within about 5% of the inverse ratio of the square root of their densities, well within experimental accuracy ($\rho_m = 9.4$ g/cm^3 for $La_{0.76}Au_{0.24}$ and $\rho_m = 8.9$ g/cm^3 for $La_{0.8}Au_{0.2}$). Since the low-temperature specific heat is determined by the low-frequency acoustical modes, this implies that the elastic moduli do not depend strongly on the choice of these two impurities.

V. SUMMARY AND CONCLUSIONS

A systematic study of a large number of properties of well-characterized $La_{1-x}Ga_x$ alloy samples over the full range of concentrations for which splat cooling yields the amorphous phase has been presented. The amorphous samples exhibit bulk superconductivity and are weak- to intermediate-coupling superconductors with $\lambda \simeq 0.8$ in contrast to the amorphous simple (nontransition) metals which characteristically have $\lambda > 2$. For these samples which have $k_F L > 1$, the calorimetric determination of $N(0)$ is identical within experimental accuracy to the determination from critical-field measurements. Within the limitations of trying to describe a band structure for amorphous metals, the d electrons result in a non-phonon-renormalized density of states $N_\gamma(0)/(1+\lambda)$, about twice the free-electron value. The Debye temperature for these alloys is approximately 110 °K. The relative magnitudes of Θ_D for the alloys with Au and with Ga are consistent with the measured changes in density for the two alloys.

At concentrations slightly above $x = 0.22$ an abrupt change of about 10% in Θ_D, a change in the concentration dependence of $N(0)$ and the appearance of two closely spaced transition temperatures are observed. It is conjectured that these observations may reflect a qualitative change in the short-range order of the La atoms when the impurity atoms have just filled the Bernal holes in the dense random packed structure. Other measurements such as photoemission, Hall effect, and thermopower may be more sensitive to such a change.

It is hoped that further studies of this type incorporating as many different measurements as possible on a single system and extending to other amorphous transition-metal systems will lead to as complete a picture of the nature of the amorphous transition metals as has been developed for the amorphous simple metals.

ACKNOWLEDGMENTS

The authors, particularly S.J.P. and W.L.J., are grateful to Professor P. Duwez for many stimulating discussions and encouragement. Density measurements of these alloys were made by A. Drehman. One of the authors (W.H.S.) gratefully acknowledges a predoctorial fellowship from the Robert A. Welch Foundation during much of the period of these experiments. Research supported in part by the NSF Grant No. DMR-75-04364, the Robert A. Welch Foundation, Houston, Texas, and the Energy Research and Development Agency.

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[1] W. Buckel and R. Hilsch, Z. Phys. 138, 109 (1954).

[2] See G. Bergmann, Phys. Rep. C 27, 159 (1976) for a thorough survey.

[3] M. M. Collver and R. H. Hammond, Phys. Rev. Lett. 30, 92 (1973).

[4] W. H. Shull and D. G. Naugle, Phys. Rev. Lett. 39, 1580 (1977).

[5] C. C. Tsuei, W. L. Johnson, R. B. Laibowitz, and J. M. Viggiano, Solid State Commun. 24, 615 (1977).

[6] G. Bergmann, Phys. Rev. B 3, 3797 (1971).

[7] W. L. Johnson, S. J. Poon, and P. Duwez, Phys. Rev. B 11, 150 (1975).

[8] W. L. McMillan, Phys. Rev. 167, 331 (1968).

[9] P. Duwez, R. H. Willens, and R. C. Crewdson, J. Appl. Phys. 36, 2267 (1965).

[10] P. F. Sullivan and G. Seidel, Phys. Rev. 173, 679 (1968).

[11] R. Bachmann, F. J. DiSalvo, Jr., T. H. Geballe, R. L. Greene, R. E. Howard, C. N. King, H. C. Kirsch, K. N. Lee, R. E. Schwall, H.-U. Thomas, and R. B. Zubeck, Rev. Sci. Instrum. 43, 205 (1972).

[12] UHU-Plus is a two-component epoxy manufactured by H. and M. Fischer GmbH, West Germany.

[13] Dag 154 is graphite in isopropyl alcohol made by Acheson Colloids Co., Port Auron, Mich.

[14] G. Krauss and W. Buckel, Z. Phys. B 20, 147 (1975).

[15] W. S. Corak, M. P. Garfunkel, C. B. Satterthwaite, and A. Wexter, Phys. Rev. 98, 1969 (1955).

[16] D. L. Martin, Phys. Rev. 170, 650 (1968).

[17] J. R. Clement and E. H. Quinnel, Phys. Rev. 92, 258 (1953).

[18] C. A. Bryant and P. H. Keesom, Phys. Rev. 123, 491 (1961).

[19] H. v. Löhneysen and F. Steglich, Phys. Rev. Lett. 39, 1205, 1372(E) (1977).

[20] J. E. Graebner, B. Golding, R. J. Schutz, F. S. L. Hsu, and H. S. Chen, Phys. Rev. Lett. 39, 1480 (1977).

[21] G. Bergmann, W. Kolar, and H. Werner, Z. Phys. 247, 252 (1971).

[22] A. Berman, M. W. Zemansky, and H. A. Boorse, Phys. Rev. 109, 70 (1958).

[23] L. P. Gor'kov, Zh. Eskp. Teor. Fiz. 37, 1407 (1959) [Sov. Phys. JETP] 10, 998 (1960).

[24] See, for example, N. F. Mott and E. A. Davis, *Electronic Processes in Noncrystalline Solids,* (Oxford University, London, 1971), p. 79.

[25] J. D. Bernal, Proc. Roy. Soc. Lond. A 280, 299 (1964).