Electron transport in $La_{100-x}Al_x$ metallic glasses

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Values of the electrical resistivity, temperature coefficient of resistivity, thermopower, and super-conducting transition temperature for a series of $La_{100-x}Al_x$ metallic glasses prepared both as "splat-cooled" foils and "melt-spun" ribbons are reported. Differences between the two types of samples are discussed. We argue that the dominant contribution to the conductivity and thermopower is from La d states.

I. INTRODUCTION

Although considerable experimental and theoretical effort has been expended, several major gaps remain in the development of an understanding of electron transport in liquid and amorphous transition-metal alloys. The recent review article by Naugle[1] discusses the most popular scattering mechanisms which have been proposed to explain the systematic trends in the transport coefficients. Gallagher and Greig[2] had noted that the sign of the thermopower for a large number of amorphous transition metal alloys could be explained in terms of the Mott s-d model in which the sign of the thermopower should be the same as that of the energy derivative of the d-band density of states at the Fermi energy. A counterexample, however, is provided by amorphous La-Ga alloys which exhibit a negative thermopower[3] but which are expected to have a positive derivative of the d-band density of states at the Fermi energy. A similar counterexample is provided by the positive thermopower of amorphous Ca-Al alloys[4] which have a large d-band density-of-states contribution with a negative derivative at the Fermi surface. For the Ca-Al and Ca-Al-Ga amorphous alloys, Naugle *et al.*[5] (preceding paper) have proposed a simple model for these high-resistivity alloys which qualitatively explains the concentration dependence of resistivity and thermopower in terms of conduction by the Ca d states. In a similar vein, Gallagher and Hickey[6] have suggested that both thermopower and conductivity may be dominated by the d-band carriers in both Ca- and La-based amorphous alloys. Support for this idea is provided by theoretical calculations of the resistivity for liquid La by Ballentine and Hammerberg[7] who conclude that conduction is mainly by the d states.

La-based alloys may be readily quenched into the amorphous state, and many important properties have been measured as a function of solute concentration. Hall coefficients have been determined for both La-Ga (Ref. 8) and La-Al (Ref. 9). Densities of states are available from heat capacity measurements for the La-Ga alloys[10] and from critical-field measurements for the La-Al alloys.[11] Thermopower and resistivity measurements are available for the La-Ga alloys,[3] but the range of stability of the amorphous phase is much smaller than for the La-Al alloys. Only limited transport measurements[12] have been previously reported for amorphous $La_{100-x}Al_x$ samples. We present detailed measurements of the thermopower and resistivity for both "splat-cooled" and "melt-spun" samples at temperatures from 4 K to room temperature, covering the composition range $18 \leq x \leq 40$. The discussion of the low-temperature enhancement (knee) of the thermopower due to the electron-phonon interaction has been presented previously[13] and will not be addressed in this paper. Some preliminary results have been described earlier.[14]

II. EXPERIMENTAL

The La-Al metallic glass foils were prepared by the splat-cooling technique at the California Institute of Technology. The metallic glass ribbons were prepared by the melt-spinning technique at Northeastern University. Sections of the samples were examined by x-ray diffraction and differential scanning calorimetry to insure that they were amorphous prior to being sealed in evacuated Pyrex tubes and mailed to Texas A&M University where the transport measurements were made. The samples were then stored in the evacuated tubes at 255 K until they were mounted for the transport measurements. At the completion of these measurements they were again examined by x-ray diffraction to ensure that they remained amorphous.

The resistance was measured by a standard four-point technique from below the superconducting transition temperature to room temperature for a series of La-Al foils and ribbons covering values of Al concentration $18 \leq x \leq 40$. The superconducting transition temperatures were recorded, and the resistivities were determined from

the resistance and the geometry factor. The geometry factor was determined from measurements of the sample mass, length, and width, together with mass density. The mass densities were determined by measuring the weight loss of the samples on immersion in toluene. Thermopower measurements for the same samples were made from just above the superconducting transition temperature to room temperature using a conventional differential technique with a Pb foil as a reference element. At low temperatures (< 15 K) the Pb foil was calibrated against a Nb$_3$Sn foil. The absolute thermopower determined for this foil is in good agreement with that given by Roberts.[15] A detailed description of the apparatus and experimental techniques is given in the preceding paper.[5]

III. RESULTS

The normalized resistance $R(T)/R_0$ is plotted as a function of temperature for several of the foils and ribbons in Fig. 1. The temperature coefficient of resistance is negative for all samples and increases in magnitude as the Al concentration is increased. It is interesting to note that the temperature dependence of the normalized resistivity for the foils differs somewhat from that of the ribbons. This is most easily seen by comparison of the data points for the splat-cooled foil and the melt-spun ribbon of the same nominal composition, La$_{75}$Al$_{25}$. The ribbon has a room-temperature coefficient of resistance that is smaller in magnitude than that for the foil, and also its resistance appears to saturate at low temperatures; whereas the resistance of the foil is still increasing in this temperature range. Since both samples become superconducting, these differences cannot be examined at lower

temperatures. The room-temperature resistivities were determined to be 167 and 163 $\mu\Omega$ cm, and the superconducting transition temperatures 3.436 and 3.449 K, respectively, for the foil and the ribbon sample. The agreement between ρ and T_c, consequently, is well within the measurement accuracy, but there is a qualitatively different temperature dependence of ρ.

The negative of the thermopower is shown as a function of temperature for a series of splat-cooled foils with different Al concentrations in Fig. 2. The temperature dependence of $S(T)$ for the melt-spun ribbons is similar. The thermopower for all samples is negative over the entire temperature range, and its magnitude increases with increasing Al concentration over the entire concentration range, $18 \leq x \leq 40$. At high temperatures the thermopower is approximately linear in the temperature, and there is a "knee" in the neighborhood of 20 K. The low-temperature knee has been discussed recently in terms of electron-phonon renormalization effects.[13]

The thermopowers of the two samples, foil and ribbon, of the same nominal composition, La$_{75}$Al$_{25}$, are shown in Fig. 3. The temperature dependence of the thermopowers, in contrast to that of the resistances, for these two samples is essentially identical. The magnitude of the thermopower for the foil sample is about 10% greater than that of the ribbon. This is well outside of the precision of the thermopower measurements as seen in the following figure, but is not significant since the composition x of each may differ from the nominal by as much as ± 1. Consequently, thermopower provides no indication of the somewhat subtle differences in the temperature dependence of the resistance of these two samples produced by the two different quenching techniques.
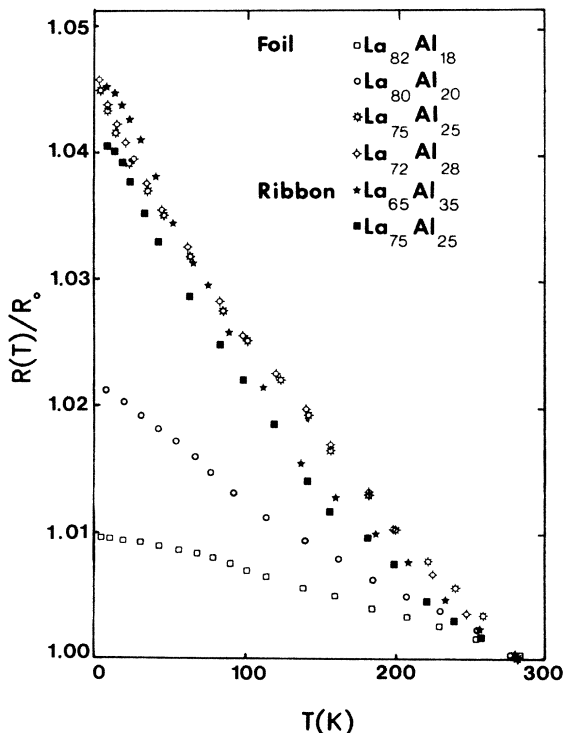

FIG. 1. Temperature dependence of the normalized resistance of a series of La$_{100-x}$Al$_x$ amorphous foils and ribbons.
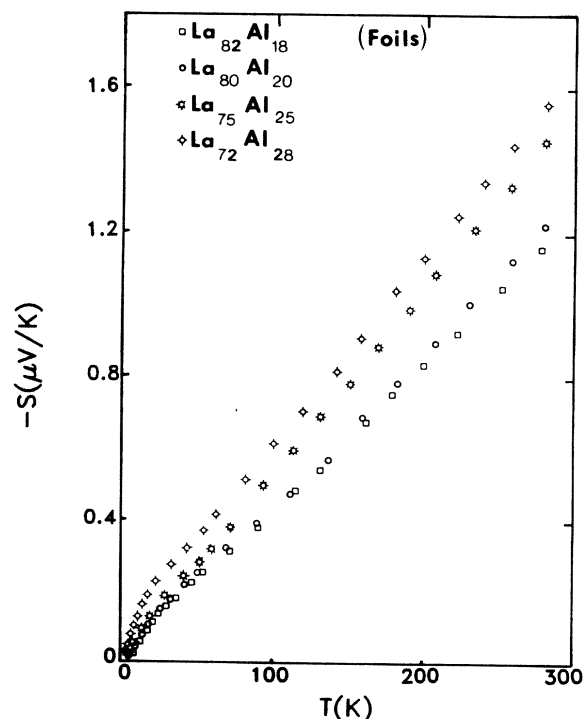

FIG. 2. Thermopower of the amorphous La$_{100-x}$Al$_x$ foils as a function of temperature.
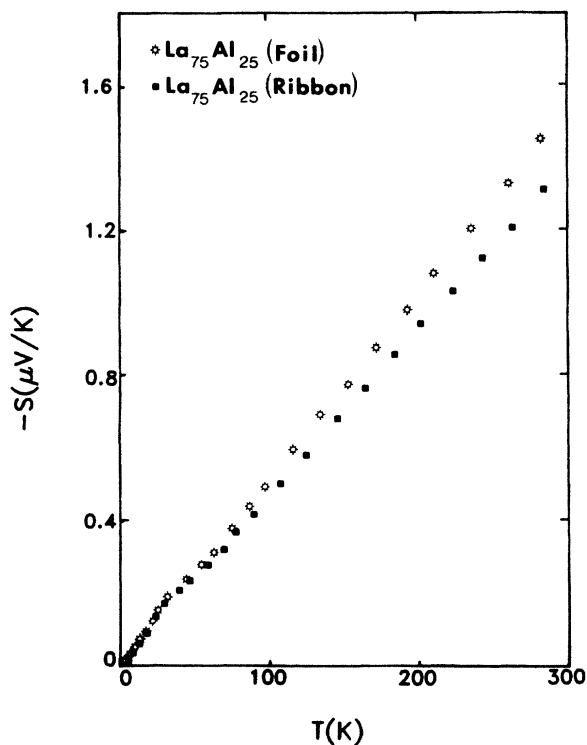
R. DELGADO *et al.*

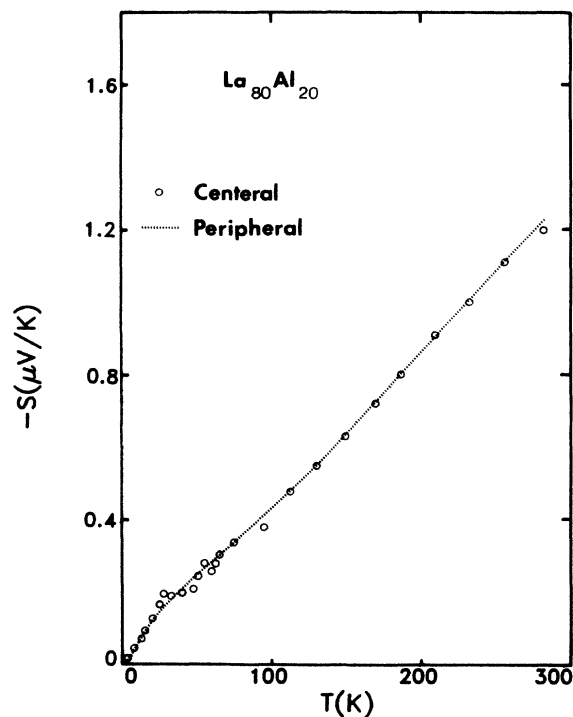FIG. 3. Comparison of the thermopower of a foil and a ribbon of the same nominal composition.

FIG. 4. Comparison of the thermopower of two pieces of the same $La_{80}Al_{20}$ amorphous foil, one from the peripheral portion ($\cdots$) and one from the central portion where traces of crystallinity are observed (O).

Figure 4 shows the thermopower for two pieces of the same $La_{80}Al_{20}$ foil. The data points are for a section taken from the center of the foil which is thought to have a small concentration of crystallites. The dashed line represents the data points for this alloy from Fig. 2. The scatter about this dashed line for the data points from Fig.

2 is much less than that of the data points from the piece from the center in the temperature range 30—70 K. In this temperature range the thermopower of the piece from the center shows a series of small peaks. X-ray diffraction scans indicated a very small concentration of crystalline material in this sample. Previous heat-capacity mea-

TABLE I. Selected values of room-temperature transport coefficients, mass densities, and superconducting transition temperatures for $La_{100-x}Al_x$ amorphous alloys.

Alloy	ρ ($\mu\Omega$ cm)	S/T (nV/K^2)	α (10^{-4}/K)	T_c (K)	ρ_m (g/cm^3)	R_H (10^{-11} Ω m/T)
$La_{82}Al_{18}(F)$	153	-4.2	-0.9	4.210	5.463	
	150[a]		-0.1[a]			
$La_{80}Al_{20}(F)$	158	-4.3	-1.0	3.904	5.379	3.74 (R)[b]
	170[a]	-4.5[c]	-1.0[a]	3.84[d]		
	163[e]			4.43[e]		
$La_{75}Al_{25}(F)$	167	-4.7	-1.4	3.436	5.257	
	175[a]		-1.7[a]			
	181[e]			3.98[e]		
$La_{75}Al_{25}(R)$	163	-4.6	-1.0	3.449	5.243	6.30[b]
$La_{72}Al_{28}(F)$	178	-5.5	-1.6	3.101	5.127	
	185[a]		-1.7[a]			
$La_{70}Al_{30}(R)$	178	-5.4		2.719		6.83[b]
$La_{65}Al_{35}(R)$	186	-5.9	-1.2	1.822	4.902	7.70[b]
$La_{60}Al_{40}(R)$	198	-7.0		1.356		8.71[b]

[a]Mueller *et al.*, Ref. 12.
[b]Tsai and Lu, Ref. 9.
[c]Schroder and Felsch, Ref. 16.
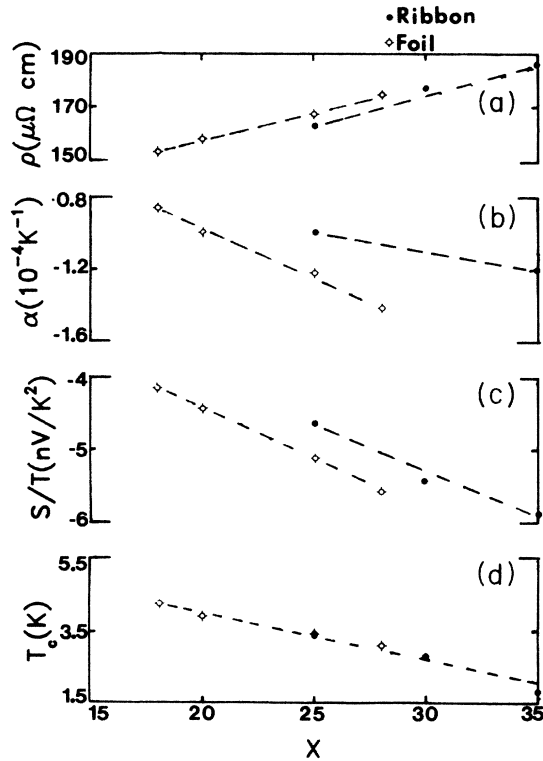[d]Bindilatti *et al.*, Ref. 17.
[e]Agyeman *et al.*, Ref. 11.

FIG. 5. Comparison of room-temperature values of transport coefficients and superconducting transition temperatures for La$_{100-x}$Al$_x$ ribbons and foils.

surements on similar La-Ga splat-cooled amorphous alloys[10] indicated the presence of a small amount of crystalline material in the center of the splat, too. These peaks in the thermopower appear to be associated with the small crystalline inclusions. Otherwise, the thermopowers of the two samples are identical. The close agreement reflects the precision and reproducibility of the thermopower measurements. For all other samples reported, care was taken to use only pieces from the peripheral portions of the splat-cooled foils. No evidence for crystallinity was observed for the melt-spun ribbons.

Room-temperature values for the transport coefficients, resistivity ρ, thermopower divided by temperature S/T, temperature coefficient of resistivity α, and Hall coefficient R_H, along with the mass density ρ_M and superconducting transition temperature T_c for La-Al alloys are tabulated in Table I. Values of the Hall coefficient are taken from Tsai and Lu.[9] Room-temperature values of $S/T = -5$ nV/K^2 for La$_{76}$Al$_{24}$ (Ref. 6) and $S/T = -4.5$ nV/K^2 for La$_{80}$Al$_{20}$ (Ref. 16) are in good agreement with measurements reported here. Values of the resistivity of La-Al amorphous alloys reported by Mueller et al.[12] and Agyeman et al.[11] are also in reasonable agreement with the values reported here, but the superconducting transition temperatures reported by Agyeman et al. are about 0.5 K higher than the present values. The value reported by Bindilatti et al.[17] for La$_{80}$Al$_{20}$ is about 0.1 K lower than the corresponding value reported here. The agreement between transition temperatures of the foil samples and the ribbon samples prepared in two different laboratories is, on the other hand, excellent. The trends with concentration of the superconducting-transition-temperature and room-temperature values of the transport coefficients for the films and foils of this study are illustrated in Fig. 5.

IV. DISCUSSION

A. Temperature dependence of conductivity

Howson[18] has recently considered the contribution of weak localization effects to the temperature dependence of the electrical conductivity for an amorphous transition-metal alloy over a wide temperature range. At very low temperatures, corrections to the Boltzmann equation from self-interference (localization effects) and electron interaction effects are expected to lead to a $T^{1/2}$ temperature dependence for σ. Such a temperature dependence has been reported by Tsai and Lu[9] for temperatures up to about 10 K for a series of melt-spun La-Al ribbons similar to those studied here. They also report that the temperature dependence for σ varies roughly as T from above 10 K to the highest temperatures of their studies, about 40 K. This is consistent with the predictions from Howson that, as the result of localization corrections, σ should then vary as T due to electron-phonon scattering up to a temperature of about $0.3\Theta_D$. This results from a T^{-2} dependence of the inelastic mean free path l_i, rather than the usual T^{-3} dependence, because the requirement for momentum conservation is relaxed in the amorphous metal. Above about $0.3\Theta_D$, l_i should vary as T^{-1} in the usual fashion with σ proportional to $T^{1/2}$. Howson gives the expression for the temperature-dependent part of the conductivity in this temperature range,

$$\sigma_T(T) = \frac{e^2}{\pi^2 \hbar L_i(T)} , \qquad (1)$$

where $L_i^2(T) = l_e l_i /2$, l_e is the elastic mean free path, and l_i is the inelastic scattering length. He notes that σ for several amorphous transition-metal alloys exhibits the sequence $T^{1/2}/T/T^{1/2}$ dependence characteristic of localization effects.

In Fig. 6 the electrical conductivity for both the melt-spun ribbon and splat-cooled foil of nominal concentration La$_{75}$Al$_{25}$ is plotted against $T^{1/2}$. The Debye temperature Θ_D for these alloys is estimated to vary from about 118 K at low Al concentrations to 145 K at the highest Al concentrations of these measurements based on the heat-capacity measurements for similar La-Ga alloys.[10] For La$_{75}$Al$_{25}$, $0.3\Theta_D = 38$ K. Above this temperature the contribution from localization to σ can be expected to vary as $T^{1/2}$. Indeed, σ for the melt-spun ribbon is linear in $T^{1/2}$ from $0.3\Theta_D$ to somewhat above $2\Theta_D$, the maximum temperature of these measurements. Although the data points are not spaced closely enough to accurately determine the regions where $\sigma(T)$ varies as T below $0.3\Theta_D$ and then as $T^{1/2}$ below 10 K, the data are consistent with those reported by Tsai and Lu[9] below 40 K for the ribbons with similar compositions, except that our absolute values for σ are as much as 25% larger than theirs. It has already been noted that our values of the
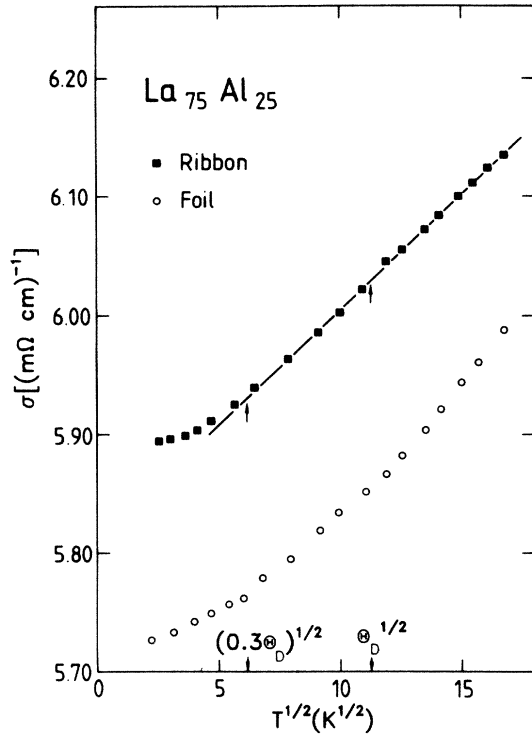
FIG. 6. Conductivity of a ribbon and foil of the same nominal composition as a function of $T^{1/2}$. Θ_D is the Debye temperature.

magnitude of σ as a function of composition are generally within 10% of those reported by other researchers[11,12] for both foil and ribbon samples. Under the assumption that the temperature dependence of σ for this ribbon is due to localization, as given by Eq. (1), we have estimated the inelastic mean free path for the $La_{75}Al_{25}$ ribbon to be

$$l_i(T) = \begin{cases} 4 \times 10^{-4} T^{-2}(m), & 10K < T < 0.3\Theta_D \\ 2 \times 10^{-6} T^{-1}(m), & T > 0.3\Theta_D \ . \end{cases}$$

From the data of Tsai and Lu for a $La_{78}Al_{22}$ ribbon, l_i in the temperature range $10\ K < T < 0.3\Theta_D$ would be estimated to be about a factor of 2 larger, but it must be emphasized that neither set of measurements provides a very accurate estimate of l_i in this temperature range. For the estimate of l_i we have assumed a value for $l_e = 3$ Å. This is approximately the nearest-neighbor distance. The free-electron model leads to an estimate of l_e less than the nearest-neighbor distance, but these are clearly not free-electron-like metals.

It is also easily noted in Fig. 6 that the temperature dependence of σ for the splat-cooled foil does not fit into the scheme outlined by Howson.[18] This is true for all of the foil samples, whereas the ribbon samples all show similar behavior to the ribbon in Fig. 6. This qualitative difference is not clearly understood, but perhaps it is related to the crystallinity detected in the center portions of the splat-cooled foil. Although these samples were taken from the peripheral regions of the foil and no significant differences in $S(T)$, T_c, or the magnitude of ρ were observed between them and the melt-spun ribbons, these small differences in conductivity which lead to a qualita-

tively different temperature dependence are perhaps the result of inhomogeneities in the foils. The temperature dependence of σ for these foils varies appreciably from foil to foil. It should be noted that the temperature dependence of σ for amorphous Ca-Al and Ca-Al-Ga melt-spun ribbons does not fit into the Howson scheme either. The electrical conductivity of a series of Ca-Al-Ga alloys exhibited a linear dependence on $T^{4/3}$ over a wide temperature range, $20\ K < T \le \Theta_D = 300$ K.[5] This temperature dependence for the Ca-based alloys is also not understood, but the consistent $T^{4/3}$ behavior of all those alloys, as opposed to the variation in the temperature dependence among the La-Al foils, suggests that inhomogeneiteies may not be responsible for the unusual temperature dependence in Ca-based amorphous metals. An alternative explanation for the different temperature dependence of foil and ribbon samples is that they represent different degrees of quenched in disorder, but no studies of annealing behavior have been made to pursue this possibility.

B. Resistivity and thermopower

In the explanation of systematic trends in the resistivity and thermopower it is common to consider first the influence of the scattering processes. Two of the most frequently cited mechanisms are Mott s-d scattering and the Ziman-Faber diffraction model. These and other scattering mechanisms are discussed in the recent review on electron transport in amorphous metals by Naugle.[1] In addition, "band-structure" effects, in particular conduction by d states, should be considered, as was shown in the preceding paper dealing with the compositional dependence of ρ and S and the sign of S in amorphous Ca-Al and Ca-Ga-Al alloys.[5] Independently, Gallagher and Hickey have suggested that d-band conduction may explain the sign of S for La-Al and Ca-Al alloys.[6]

Since partial structure factors are available for the amorphous La-Al alloys,[19] it is appropriate to calculate the resistivity and thermopower in the Ziman-Faber diffraction model for comparison with experiment. We have calculated the resistivity in this model using the following expression (see Naugle[1]):

$$\rho = \frac{30\pi^2 \hbar^3}{me^2 \Omega_0 k_F^2 \varepsilon_F} \sin^2[\eta_2(\varepsilon_F)]$$

$$\times \{C_{La}[S_{La\text{-}La}(2k_F)(1-C_{Al})+C_{Al}]\} \ , \tag{2}$$

where Ω_0 is the atomic volume, k_F the Fermi wave vector, ε_F the Fermi energy, η_2 the d phase shift, C_{La} the La concentration, C_{Al} the Al concentration, and $S_{La\text{-}La}$ the La-La partial structure value. The phase shift for liquid La calculated by Waseda *et al.*,[20] free-electron parameters for k_F and ε_F, and structure factors from Williams[19] were used with Eq. (2). The resistivity values calculated from this model are far too small and do not have the correct composition dependence.

The thermopower can also be calculated in this model from the Mott formula for S. It is given by

$$S = \frac{-\pi k_B^2 T}{3|e|} \frac{\partial \ln\sigma}{\partial \varepsilon} = \frac{\pi^2 k_B^2 T}{3|e|\,\varepsilon_F} \xi \ ,$$

where   (3)

$$\xi = \frac{q}{2} + \frac{r}{2} - 3 \ ,$$

with

$$q = a(2k_F)|t_{La}(2k_F)|^2/\langle a(Q)|t_{La}(Q)|^2\rangle \ , \tag{4}$$

$$r = \langle a(Q)k_F\partial\,|t_{La}(Q,\varepsilon_F)|^2/\partial k_F\rangle/\langle a(Q)|t_{La}(Q,\varepsilon_F)|^2\rangle \ , \tag{5}$$

and ε_F the Fermi energy, and k_F the Fermi wave number. Here $t_{La}(Q,\varepsilon_F)$ is the La T matrix, $a(Q)$ is the factor in brackets { } from (2), and $\langle\ \rangle$ indicates the average weighted to high Q (see, e.g., Naugle[1]). There are no reliable data for calculation of the term r which involves the derivative of the t matrix for La with respect to k_F. Thus it has been neglected, although for many metals it may provide the dominant term in S.[2] The average $\langle\ \rangle$ in (4) can be related directly to ρ. Values of the thermopower were calculated from (3) omitting the term r and adjusting $\langle\ \rangle$ to give the proper values of the resistance. The sign of the thermopower calculated in this fashion is incorrect. It is questionable whether inclusion of the term r could result in negative values of S.

Brown et al.[21] have used a muffin-tin model to obtain an expression for the resistivity due to Mott s-d scattering,

$$\rho = \frac{12\pi^4 k_F \hbar \Gamma}{e^2 K_0^5} N_d(\varepsilon_F) \ , \tag{6}$$

which by the Mott formula gives the result (3) for the thermopower with

$$\xi = \tfrac{1}{2} + [\partial \ln N_d(\varepsilon)/\partial \ln\varepsilon]_{\varepsilon=\varepsilon_F} \tag{7}$$

and N_d the d-band density of states at the Fermi energy. The parameters Γ and $E_0 = \hbar^2 K_0^2/2m$ which give the width and energy of the d resonance are not available, but the sign of the thermopower predicted in this model can be determined from (7). Since La is an early transition metal, we expect that $dN_d/d\varepsilon$ will be positive in these alloys. Thus Mott s-d scattering under the assumption that $dN_d/d\varepsilon$ is positive would also predict a positive thermopower for the La-based alloys, whereas for both the La-Al alloys of this study and La-Ga alloys[3] the measured thermopowers are negative.

On the other hand, if we assume, as in the preceding paper,[5] that the d states dominate the conductivity in the two-band model and that the contribution S_d from the d band is at least as large as S_s, then the negative thermopower may be explained with the Mott formula for S_d. This would require that

$$\frac{1}{\sigma_d}\frac{\partial\sigma_d}{\partial\varepsilon}\bigg|_{\varepsilon=\varepsilon_F} = \left[\frac{1}{N_d}\frac{\partial N_d}{\partial\varepsilon} + \frac{1}{v_{Fd}}\frac{\partial v_{Fd}}{\partial\varepsilon} + \frac{1}{l_d}\frac{\partial l_d}{\partial\varepsilon}\right]_{\varepsilon=\varepsilon_F}$$

$$= \left[\frac{2}{k_{Fd}v_{Fd}} + \frac{1}{l_d}\frac{\partial l_d}{\partial\varepsilon}\right]_{\varepsilon=\varepsilon_F} \tag{8}$$

be greater than zero. We would expect the d-band Fermi velocity v_{Fd} and mean free path l_d to be small and relatively energy independent in these high-resistivity amorphous metals. The sign of $\partial\sigma_d/\partial\varepsilon$ would be principally determined by that of $\partial N_d/\partial\varepsilon$ which is expected to be positive. Also, the resistivity of these alloys as a function of composition may be expected to vary roughly as N_d^{-1} since they appear to be very close to the Ioffe-Regel limit where l is already close to a lattice spacing and thus should not vary appreciably. The trend in $\rho(x)$ is in general agreement with the trend in $N(0)^{-1}$ for both the band density of states and the dressed density of states as estimated from critical-field measurements for a similar series of amorphous La-Al alloys,[11] although the ratio of $N(0)^{-1}$ as a function of concentration x to that at $x=20$ rises at first more sharply than $\rho(x)/\rho(20)$ but appears to approach the value of $\rho(40)/\rho(20)$ as x approaches 40. Support for a major contribution by d-band conduction is provided by recent calculations by Ballentine and Hammerberg[7] who conclude that the d states dominate electrical conduction in liquid La.

One problem still remains, however. The sign of the Hall coefficient is positive for La-based glassy metals,[8,9] but also the thermopower is negative. In the two-band model discussed in the preceding paper the expression for the conductivity is given by

$$\sigma = \sum_j \frac{e^2 l_j}{4\pi^2\hbar} k_{Fj}^2 \ , \tag{9}$$

where $j=s$ or d for the two bands. In terms of the Mott formula for S_d, a negative thermopower contribution for S_d would imply a positive Fermi velocity, i.e., $d\varepsilon/dk > 0$. This should result in a negative value of the d-band contribution to R_H according to some recent theoretical explanations offered for the positive Hall effect observed for so many amorphous transition-metal alloys.[22-24] Clearly, the Hall coefficient in amorphous and liquid metals is not a well understood quantity and the interpretation of its sign in terms of the sign of $\partial\varepsilon/\partial k$ still remains controversial. Nevertheless, in the admittedly simplified analysis of the thermopower and conductivity described above, this theory of R_H implies that the contribution to R_H from the d band which dominates the electrical conductivity is negative. In the two-band model the Hall coefficient is given by

$$R_H = \sum_j \sigma_j^2 R_j \bigg/ \left[\sum_j \sigma_j\right]^2 \ , \tag{10}$$

where R_j is the contribution from the particular band. In this model the contribution from the s band would have to be positive and far larger in magnitude than that of the d band.

Harris[25] has recently proposed a different approach to explain the frequent observation of a positive Hall coefficient in transition-metal glasses. He relates both the thermopower and Hall coefficient to the energy derivative of the relaxation time at the Fermi energy $\partial\tau/d\varepsilon$. A large negative value of $\partial\tau/d\varepsilon$ would produce both a positive thermopower and a positive value of R_H. Consequently, this theory would lead to the same correlation between the sign of the thermopower and R_H as that based on the sign

of $\partial\varepsilon/\partial k$ and this also would require that R_H be determined principally by the s band for the Ca- and La-based alloys discussed in these companion papers.

It is perhaps worthwhile to note a different correlation for the sign of R_H in amorphous alloys with d bands near the Fermi surface. In the two alloy systems considered in these companion papers (Ca-based[5] and La-based) the sign of R_H is the same as that of the energy derivative of the d-band density of states at the Fermi surface, $dN_d/d\varepsilon$. Although the available data on R_H are limited to only a few amorphous alloy systems with d bands, the correlation between the sign of R_H and the sign of $\partial N_d/\partial\varepsilon$ of the dominant d band seems to be well satisfied. (See Bandyopadhyay *et al.*[26] and references therein). This correlation is consistent with domination of R_H by s states with the sign determined by that of $\partial\tau/\partial\varepsilon$ at the Fermi energy since $\partial\tau/\partial\varepsilon$ should be large and negative when the Fermi energy lies below the d resonances, but it is not obvious how such a correlation would result from the suggestion by Weir *et al.*[22,23] that the sign of R_H is determined by $\partial\varepsilon/\partial k$ of the s band. Realistic calculations of the contribution to R_H from each band in a liquid transition metal such as La where the thermopower is negative and R_H is positive should be very helpful in resolving these problems.

V. SUMMARY AND CONCLUSIONS

The electron transport properties of amorphous $La_{100-x}Al_x$ alloys for $18 \leq x \leq 40$ may be summarized as follows.

(i) The room temperature values of electrical resistivity are large (> 150 $\mu\Omega$ cm) and increase with increasing Al content.

(ii) The temperature coefficients of resistivity are negative and their magnitudes increase with increasing Al content.

(iii) The thermopower is negative and its magnitude increases with increasing Al content. The low-temperature anomaly (knee) in the thermopower has previously been explained in terms of electron-phonon renormalization effects.[13]

(iv) The transition temperature T_c was found to decrease with increasing Al content in agreement with previous reports,[11] but the values of T_c measured in this work are somewhat lower.

With the exception of the temperature dependence of the electrical resistance, the transport properties of splat-cooled and melt-spun samples are very similar. Neither the Ziman-Faber model nor the Mott s-d model appears

to describe electron transport in the amorphous La-Al alloys. The sign of the thermopower and the concentration dependence of the resistivity are consistent with a major contribution to the electrical conductivity in these alloys from the La d-state electrons. This is consistent with recent calculations by Ballentine and Hammerberg[7] which suggest that the La d states dominate electrical conduction in liquid La. Recent measurements of the electron transport properties of amorphous Ca-Al and Ca-Al-Ga alloys[5] have also been interpreted in terms of a major contribution to the electrical conductivity by the Ca d band in the preceding paper. It is interesting to note that these two alloy systems, one usually considered to be composed of simple metals, are the only two amorphous-metal alloy systems for which d-state conduction appears to be important. For both the Ca- and the La-based alloys the sign of the Hall coefficient is opposite to that of the thermopower. This suggests, at least in the simplest models of the sign of the Hall coefficient, that the Hall transport must be dominated by s states in both of these alloy systems.

There is a linear dependence of the electrical conductivity on $T^{1/2}$ from about $0.3\Theta_D$ to above $2\Theta_D$ for the melt-spun ribbons that is in excellent agreement with the predictions of Howson[18] for electron-phonon scattering in amorphous metals. The temperature dependence of the splat-cooled foils is not, however, consistent with this expected behavior. Furthermore, the functional form of the temperature dependence does not appear to be consistent from foil to foil. Although it cannot be conclusively established, we think that the unusual temperature dependence of the conductivity of the foils may be the result of very small crystalline inclusions or similar inhomogeneities.

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