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Negative-temperature coefficients of electrical resistivity in amorphous La-based alloys

R. Mueller,* K. Agyeman,† and C. C. Tsuei
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
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A negative-temperature coefficient ($\alpha = \rho^{-1} d\rho/dT$) of electrical resistivity, $\rho(T)$, has been observed in many amorphous and disordered metallic conductors. The origin of this anomalous temperature dependence of resistivity is still unclear. To explain the negative-α anomaly, there are two theoretical approaches (i.e., the Ziman-type theory and the structural Kondo model) currently discussed in the literature. In an attempt to distinguish between these two approaches the resistivity of several liquid-quenched amorphous La-based alloy systems containing Al, Au, Ga, or Ge, has been analyzed as a function of composition and temperature. It is concluded that the resistivity data are inconsistent with the Ziman-type theory and are in favor of the structural Kondo-type model. This conclusion is based on the fact that (1) resistivity varies as $-\ln T$ ($T \gtrsim 100$ K) in alloys with negative α, and (2) the occurrence of negative α is independent of the valence of the La-based alloys.

I. INTRODUCTION

A negative-temperature coefficient ($\alpha = \rho^{-1} d\rho/dT$) of electrical resistivity, $\rho(T)$, has been observed in many crystalline,[1] amorphous[2] (solid), and liquid[3] metallic conductors. The origin of the anomalous temperature dependence of resistivity is a highly controversial topic. In the liquid state, both negative- and positive-temperature coefficients of $\rho(T)$ have been observed. These results have been rather successfully explained[3] in terms of the extended Ziman theory of electrical resistivity for liquid metals.[4] Owing to the liquidlike structure characteristic of amorphous metallic alloys, it is natural to apply Ziman's theory or its variants to explain the behavior of electron transport in the amorphous state. Although this approach is claimed to be consistent with the experimental results for several alloy systems;[5-7] its apparent success mostly depends on an assumption that the Ziman condition $2k_F \cong k_P$ is satisfied, where k_F is the Fermi wave vector and k_P the wave vector corresponding to the first peak in the structure factor $S(k)$. One should emphasize that this assumption has not been substantiated directly by any experiment. Recent results[8] of low-temperature specific-heat measurement of glassy metals are not consistent with the hypothesis of a minimum in the density of states at the Fermi level for easy glass formation. These results also indirectly cast doubts about the interpretation of the negative α in terms of the Ziman theory.

On the other hand, there are several alternative theoretical approaches to this problem. Of particular interest is the possibility that the origin of the negative α is an attractive exchange interaction between conduction electrons and the localized excitations associated with the structural indeterminacy in the atomic arrangement.[2] In essence, this is a structural analog of the Kondo effect. Recently, the thermoelectric power of an amorphous alloy of $Be_{40}Ti_{50}Zr_{10}$ has been measured up to the crystallization temperature (600 K).[9] The results are claimed to be incompatible with a Kondo model.

From the discussion above, it is clear that the dispute about the origin of the negative α centers around experiments of indirect nature such as the specific-heat and thermoelectric-power measurements. In this paper, we choose to deal with the temperature dependence of electrical resistivity, $\rho(T)$, directly, in an attempt to differentiate between the extended Ziman theory and the structural Kondo model. For this purpose, results of electrical resistivity measurements for several amorphous La-based alloy systems as a function of temperature will be presented and discussed in terms of the extended Ziman theory and the structural Kondo model.

II. EXPERIMENTAL PROCEDURES AND RESULTS

The amorphous state of the La-based alloys ($La_{1-x}M_x$, $M \equiv$ Al, Ge, or Au, $x \gtrsim 0.2$) was achieved by rapid cooling from the liquid state with the piston-and-anvil technique in a vacuum of $\sim 10^{-3}$ Torr. The details of alloy preparation have been reported elsewhere.[10] The resulting liquid-quenched samples were foils of irregular shape and approximately 2–3 cm in diameter and 40–50 μm in thickness. The structure of the samples was checked by x-ray diffraction which showed only broad peaks characteristic of a liquid structure. Since these amorphous alloys are also superconductors with transition temperatures $\lesssim 4$ K, the sharpness and the shape of the resistive superconductive transition were used as a supplementary criterion to eliminate samples containing small amounts of a second phase which could not be detected by x-ray diffraction.[10] Alloy compo-

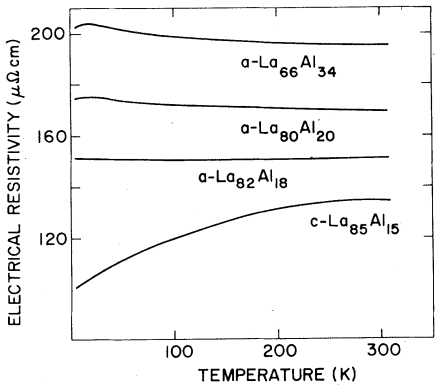

FIG. 1. Temperature dependence of electrical resistivity for several liquid-quenched La-Al alloys.

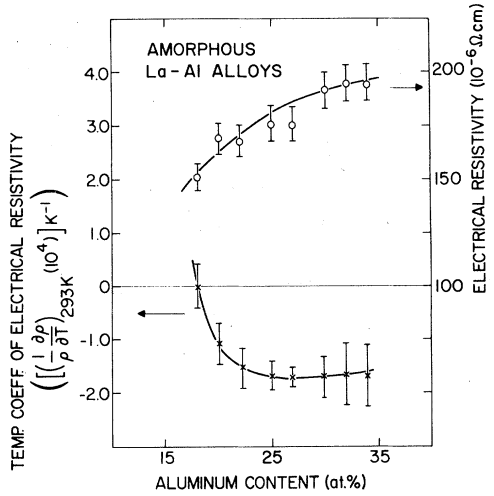

FIG. 2. Electrical resistivity and its temperature coefficient (at 293 K) for amorphous La-Al alloys obtained by liquid quenching.

sition was checked by electron-microprobe analysis and found to be within ± 1% of the nominal composition.

Resistivity measurements were made by a standard dc four-point method as a function of temperature in the range of 4.2 to 300 K. The absolute error in these resistivity measurements was estimated to be ± 10%, mainly due to the uncertainty in measuring the sample dimensions. The relative accuracy in resistivity was better than 0.1%. The temperature of the samples was measured with ~0.1 K accuracy by using a calibrated Ge resistance thermometer (4.2 to 100 K) and a copper-constant thermocouple (for 80 to 300 K).

In order to discuss the resistivity results in terms of the Ziman theory, k_P was determined from the x-ray diffraction pattern by using the following formula:

$$k_P = 4\pi \sin\theta_P/\lambda\,, \tag{1}$$

where $2\theta_P$ is the Bragg angle corresponding to the first peak in the structure factor $S(k)$. The electrical resistivity as a function of temperature for several La-Al alloys is shown in Fig. 1. It is interesting to note that all amorphous La-Al alloys exhibit relatively high resistivity and a zero- or negative-temperature coefficient (α). This is in contrast to the alloys containing relatively smaller amounts of Al (<18 at.%) which are crystalline after quenching. Only the positive-temperature coefficient of ρ was observed in these alloys. The value of electrical resistivity at 293 K increases with Al concentration as shown in Fig. 2. The sign of α is negative and essentially independent of Al content for $x > 22$ at.% Al (Fig. 2). We also have preliminary results on the resistivity of amorphous $La_{100-x}Au_x$ alloys. The results are similar to those found in amorphous La-Al alloys.

From the value of the ratio of resistances at $T = 300$ and 4.2 K, the sign of α in La-Au alloys is found to be negative for $x \gtrsim 20$ in good agreement with previous reports by Johnson *et al.*[11-13] A negative α has been also reported by Manning and Briscoe[14] for amorphous La-Au films ($\gtrsim 24$ at.% Au) obtained by vapor condensation at 4.2 K. The temperature dependence of resistivity of amorphous $La_{100-x}Ga_x$ alloys has been studied recently by Shull *et al.*[15] Their results again show that α is negative for all of the alloys studied with $x \geq 20$, but for alloys with $x = 16$ and 18, α is positive. Our results on amorphous $La_{100-x}Ge_x$ also indicate α is positive for $x = 16$ and 18. It appears that the negative-α anomaly is quite general in nature and has been observed in all amorphous $La_{100-x}M_x$ alloy systems studied so far, where $x \gtrsim 20$ and M can be Au, Al, or Ga.

III. DISCUSSION

As mentioned in Sec. I, there are several theoretical models capable of explaining negative values for α. These models, however, represent fundamentally different approaches to electron transport in amorphous metals. In fact, these models predict different temperature dependence of resistivity at relatively high temperatures ($T \gtrsim \Theta_D$, Θ_D is the Debye temperature). This fact has been often neglected, in the literature, in discussing the resistivity data of metallic glasses. In the following, the resistivity data of various amorphous La-based alloys (especially the La-Al, La-Au alloy systems) will be discussed in terms

of the Ziman theory and the Kondo-like structural model in an attempt to distinguish between these two different approaches.

A. The Ziman-type approach

In view of the fact that the amorphous and liquid metals are similar in structure, order of magnitude of resistivity, and the temperature coefficient α, it is reasonable to extend the Ziman theory[4] which was originally developed for simple liquid metals to metallic glasses. Two major concerns about using the Ziman theory are (1) the theory may not be appropriate for strong scattering systems[16] of which most amorphous metals are; (2) the Ziman condition for negative α has never been established directly by any experiment. Usually k_f is calculated by assuming certain free-electron concentration. Unlikely valency such as 5 conduction electrons per phosphorous atom,[7] for example, was used in satisfying the Ziman criterion for amorphous Ni-P alloys. In the following discussion, it will be demonstrated that there is no self-consistency in using the Ziman-type theory to explain the negative-α anomaly observed in amorphous La-based alloys even when one is willing to discard the questionable aspects [points (1) and (2) mentioned above] of this approach. According to the extended Ziman theory for electron transport in liquid metals by Evans *et al.*,[17,18] the temperature dependence and the magnitude of electrical resistivity can be expressed by the following formula:

$$\rho(T)=\frac{3\pi\Omega}{4e^2\hbar V_F^2 k_F^2}\int_0^{2k_F} S(k,T)\,|V(k)|^2 k^3 dk\,, \qquad (2)$$

where Ω is the atomic volume, V_F the Fermi velocity, $S(k,T)$ the structure factor, and $V(k)$ the form factor (pseudopotential for simple metals, t-matrix element for transition metals).

To a good approximation, this formula is also useful for describing the resistivity of alloys with one element as the major constituent. The temperature dependence of resistivity is then dominated by that of the structure factor. The sign α will depend on whether the Ziman condition $k_P \sim 2k_F$ is satisfied or not. Although the value of k_P can be determined accurately by an x-ray diffraction experiment, k_F has to be calculated with a free-electron approximation. In analyzing our resistivity results, we assume that the numbers of conduction electrons for Al, Au, and La are 3, 1, and 0.5, respectively. The 0.5-valency value for La is based on a recent calculation by Duthie and Pettifor[19] and was first used in interpreting the resistivity data of liquid La by using the Ziman theory.[20] It should be pointed out that this assumption implies that

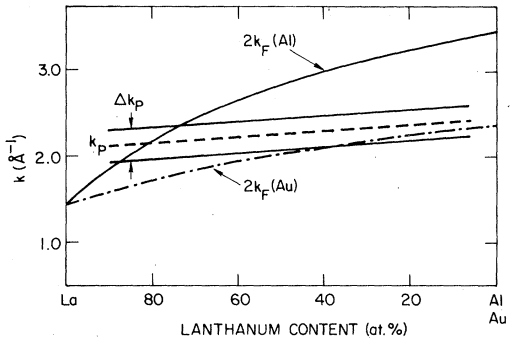

FIG. 3. k_P (as defined in the text), Δk_P, and $2k_F$ as a function of composition for amorphous La-Al, La-Au alloys. Δk_P indicates the maximum allowable range for k_P for yielding a negative α in terms of the Ziman theory.

only the s electrons contribute significantly to electrical conduction. This is, of course, unrealistic in view of the fact that the s and d bands of La are highly hybridized.[21] In the following, it can be shown that the resistivity data on various amorphous La-based alloys are not consistent with the Ziman theory, even under the most favorable condition as provided by this doubtful assumption of 0.5 electrons per La atom. In Fig. 3, k_P, and Δk_P (the width of the first peak in the structure factor at half maximum height) for amorphous La-Al and La-Au alloys are plotted as a function of La content. The x-ray diffraction patterns for all the amorphous La-based alloys studied are remarkably identical. The calculated values of $2k_F$ for the La-Al and La-Au alloys are also plotted in Fig. 3. From this figure, one can see that the Ziman condition for negative α can be satisfied in the concentration range of about 15–30 at.% Al which is roughly consistent with the experimental data obtained in this study (Sec. II). It should be mentioned that Delley *et al.*[20] have measured the $\rho(T)$ of liquid La-Sn alloys and found negative α of ρ between 30 and 65 at.% Sn in good agreement with the Ziman theory. On the other hand, as shown in Fig. 3, the line of $2k_F$ for La-Au alloys does not intersect with k_P except for alloys containing $\gtrsim$ 70 at.% Au. In terms of the Ziman theory, this would mean that negative α should not be observed in amorphous La-Au alloys with concentration in the experimental range. This is, of course, inconsistent with the experimental results of this investigation and those reported previously in the literature.[11-14] One could argue that the La-Au data simply reflect the possibility that the valency of La may depend upon the alloying constituent Al or Au. This is unlikely in view of the

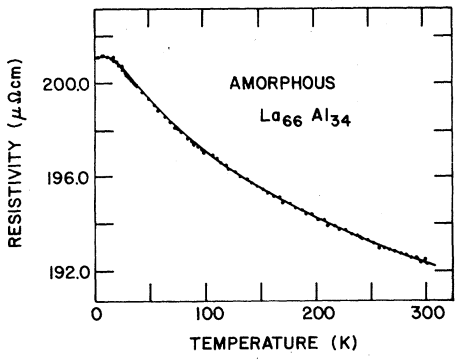

FIG. 4. Resistivity as a function of temperature for amorphous $La_{66}Al_{34}$.

highly localized nature of the electronic band structure of La[19] and the superconductivity[10] in a large number of amorphous *and* crystalline La-based alloys and compounds. It is also inconsistent with the fact that the occurrence of negative α in amorphous alloys $La_{100-x}M_x$ depends only on x (i.e., $x \gtrsim 20$) and *not* on M (M can be Al, Ga, Au, or Ge, and possibly Cu, Ag, or Ni).[11]

Besides the qualitative discussion of the Ziman criterion for negative α, one can gain some insight to the problem by analyzing the temperature dependence of resistivity for those alloys with a negative α.

Basically, the Ziman-type theory predicts that the resistivity of an amorphous metal as a function of temperature should follow directly the temperature dependence of the structure factor. For a negative-α metal, the resistivity can be expressed as follows:

$$\rho(T) \sim \rho_0 + AS(2k_F, T), \tag{3}$$

where A is a constant.

Based on a Debye approximation, Nagel[6] has predicted that the temperature dependence of $S(2k_F, T)$ should be $(C_1 - C_2T^2)$ for $T < \Theta_D$ and $(C_3 - C_4T)$ for $T \gtrsim \Theta_D$, where Θ_D is the Debye temperature and C_i $(i = 1-4)$ are constants. There are a number of measurements that have confirmed this prediction.[22] According to Eq. (3), the temperature-dependent part of the resistivity should vary as $(C_3 - C_4T)$ at relatively high temperature. In Fig. 4, results of very accurate measurements on the resistivity as a function of temperature for amorphous $La_{66}Al_{34}$ are presented. The Debye temperature of this alloy is about 100 K. From Fig. 4, one can see that the resistivity curve exhibits a nonlinear temperature dependence which apparently is not consistent with the Ziman-type theory. A detailed analysis of the resistivity data shown in Fig. 4 is deferred to a later discussion in conjunction with the structural Kondo mechanism for negative α.

B. The Kondo-type approach

The Kondo-type approach to anomalous electrical conduction in amorphous metals was first suggested by Cochrane *et al.*[23] to explain the low-temperature ($T \gtrsim 10$ K) resistance minima observed in many glassy metals. The origin of the resistivity-minimum phenomena is still not clear at the present time. There are, however, increasing amounts of evidence[24-27] to suggest that they are related to the *bona fide* Kondo effect which is due to the exchange interaction between magnetic impurities and conduction electrons. The structural Kondo approach can be extended to understand the negative-α anomaly observed in many disordered and amorphous metals at relatively high temperatures. In such an extension, it is important to realize that a quantum-mechanical tunneling between the two configurational levels is *not* essential. As pointed out before,[2] any localized internal degree of freedom (such as local phonons) which gives rise to excitations that are degenerate on the scale of k_BT $(T \gtrsim \Theta_D)$ can lead to a negative α through this structural Kondo mechanism. The orthogonality condition as defined in Ref. 23 is essential to assure that the structural Kondo Hamiltonian as originally proposed by Cochrane *et al.* is valid. This condition is probably satisfied in amorphous metals with resistivity $\gtrsim 100$ $\mu\Omega$cm which corresponds to an electronic mean free path of the order of interatomic distance. In this regard, we note that the resistivity of amorphous La-based alloys are of the order or larger than 100 $\mu\Omega$cm. In terms of the Kondo-type approach, resistivity as a function of temperature can be expressed by the following equation:

$$\rho(T) = a + c\ln(T^2 + T_\Delta^2). \tag{4}$$

A fitting of this equation with the experimental data for amorphous $La_{66}Al_{34}$ is demonstrated in Fig. 4 [the solid curve represents Eq. (4) with the fitting parameter $a = 219.08$ $\mu\Omega$cm, $c = -2.34$, and $T_\Delta = 45.4$ K]. The theory and experimental results are replotted on a logarithmic temperature scale in Fig. 5. to illustrate the Kondo-type temperature dependence of resistivity in this amorphous alloy. It is quite clear from this figure that the experimental data do show a $-\ln T$ dependence suggested by the Kondo-type model as opposed to the $(C_3 - C_4T)$ behavior predicted by Ziman-type theory.

There is one more experimental result one can use to differentiate between the Ziman-type and

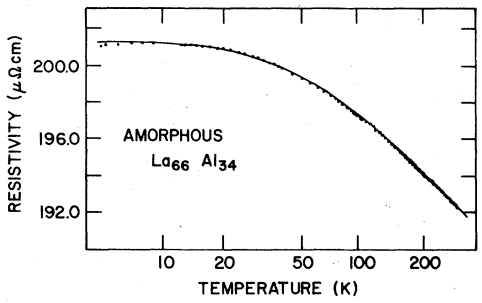

FIG. 5. The same data shown in Fig. 4 except on a $\ln T$ scale, the solid curve represents $\rho(T)=a+c\ln(T^2+T_\Delta^2)$ with $a=219.08$ $\mu\Omega$ cm. $c=-2.34$, $T_\Delta=45.4$ K.

Kondo-type approaches. That is the fact that negative α has been observed in amorphous $La_{100-x}M_x$ alloys only with $x\gtrsim 20$, and $M=$ Al, Ga, or Au. This observation suggests that the negative-α anomaly is not related to the valency of the second element in the alloy. This is inconsistent with the $k_p\sim 2k_F$ condition for negative α (k_p is found experimentally to be a constant for all these La-based alloy systems) and lends further evidence against the Ziman-type approach. On the other hand, it has been pointed out that amorphous alloys such as the La-based alloys with $x\gtrsim 20$ contain certain structural defects which could be the source of the structural internal degrees of freedom for the Kondo-type scattering.[2]

In summary, we have systematically studied the electrical resistivity of several liquid-quenched amorphous La-based alloy systems as a function of temperature and composition. The results are used to distinguish between the Ziman-type and the Kondo-type models for the negative-temperature coefficient of resistivity. The following facts are inconsistent with the Ziman-type theory and are in favor of the structural Kondo-type model: (a) Resistivity varies as $-\ln T$ in alloys with negative α. (2) The occurrence of negative α is independent of the valency of the alloys.

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*Present address: Brown Boveri & Company, Research Center, 5405 Dättwil/Baden, Switzerland.
†Present address: Department of Physics, University of Ghana, Legon, Ghana.

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