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Electrical transport properties of the aluminum-ruthenium icosahedral phase

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We have measured the electrical resistivity of single-phase icosahedral aluminum-ruthenium thin films and of a primarily amorphous film at the same composition. The magnitude and temperature coefficient of resistivity between 4.2 K and room temperature are characteristic of disordered metals, and are nearly the same for both the primarily amorphous and icosahedral samples. We have examined icosahedral phase samples with grain sizes that differ by an order of magnitude, but see little difference in the electrical transport properties. We find that these results are consistent with recently proposed theories of electron transport in the icoshedral phase.

I. INTRODUCTION

The discovery[1] of a new phase of condensed matter displaying icosahedral point-group symmetry and quasiperiodic translational order has been met with a great deal of interest.[2] Most of this work has concentrated on the metallurgy and crystal structure of the new phase. Because the icosahedral point-group symmetry is novel and inconsistent with the concept of a periodic lattice, one might expect that some of the physical properties of this material will be significantly different from those of traditional metallic crystals and glasses. In a search for such novel properties, we have measured the temperature dependence of the electrical resistivity of one system of icosahedral-phase-forming alloys.

A number of studies of the electrical transport properties of multiple-phase icosahedral aluminum–transition-metal alloys have been performed.[3–6] All of the samples in these previous studies contained aluminum–transition-metal compounds or elemental aluminum in addition to the icosahedral phase. Single-phase icosahedral samples are needed to avoid the complications of measuring the electrical properties of coexisting crystalline or amorphous phases. We have successfully prepared single-phase aluminum–transition-metal icosahedral samples by surface modification of thin films. The aluminum-ruthenium system was chosen over the more carefully studied aluminum–3*d*-transition-metal systems (such as Al-Cr, Mn, Fe) in order to avoid magnetic effects on the transport properties at low temperatures and to take advantage of its relatively simple equilibrium phase diagram.[7]

II. SAMPLE PREPARATION AND CHARACTERIZATION

The melt-quenching technique usually employed to form icosahedral alloys did not produce single-phase material because the formation of $Al_{13}Ru_{14}$ could not be prevented.[8] Because of this difficulty, liquid-quenched samples were not used in this study. We have found that single-phase icosahedral Al-Ru samples are most readily produced by applying nonequilibrium solid-state processing techniques to thin films.[9] In particular, we have utilized the processes of ion-beam mixing at elevated temperatures and solid-state interdiffusion.

Several groups have independently observed that thin films of the icosahedral phase can be produced by reacting multiple thin layers of aluminum and certain transition metals[10,11] (including Al-Ru alloys[12,13]) at elevated temperatures under irradiation with a beam of energetic heavy ions. Interdiffusion of the two metals is enhanced by the secondary cascades produced by the incident ions, and also by production of mobile point defects. By ion mixing at appropriate temperatures, it is possible to produce a variety of stable and metastable phases in the surface film.

Surface alloys of icosahedral Al–16.5-at. % Ru, 50 nm thick, were produced by ion mixing six pairs of Al/Ru layers with 400-keV Xe to a total flux of 1×10^{16} Xe-ions/cm^2 at a temperature of 300 °C on an inert and electrically insulating sapphire substrate. The alloy composition was determined by Rutherford backscattering. Transmission-electron-microscopy (TEM) analysis of the reacted samples revealed single-phase icosahedral Al-Ru with grain sizes ranging from 30 to 50 nm (see Fig. 1). The dark-field image in Fig. 1(b) shows individual icosahedral grains against a dark background because the imaging aperture [dark circle in Fig. 1(a)] included only a small section of two icosahedral diffraction rings. The electron-diffraction pattern shows rings from only the icosahedral phase; no other phases were detected in the surface alloy.

A film composed primarily of amorphous Al–16.5-at. % Ru was produced by mixing a similar set of bilayers at 30 °C with a total flux of 1×10^{16} ions/cm^2. Diffraction

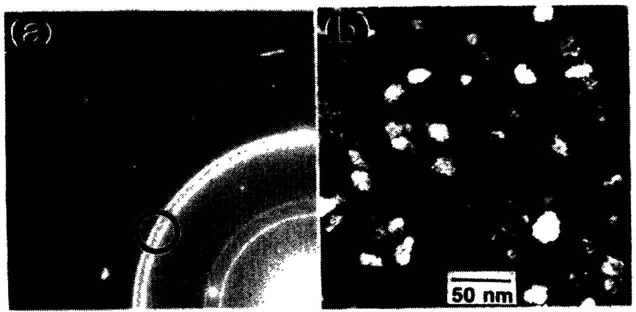

FIG. 1. Electron-diffraction pattern from icosahedral $Al_{83.5}Ru_{16.5}$ made by ion-beam mixing at 300 °C, and (b) dark-field TEM image of icosahedral grains obtained using the aperture position indicated in (a). The spots in (a) are from the sapphire substrate.

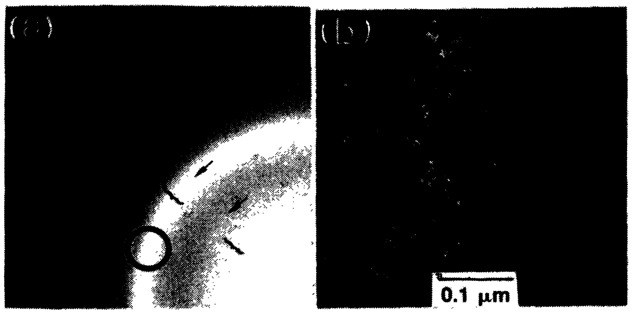

FIG. 2. (a) Electron-diffraction pattern showing four diffuse rings from amorphous $Al_{83.5}Ru_{16.5}$ (marked with curly braces) and three rings from Al-Ru (marked with arrows). (b) Dark-field TEM image using the aperture position indicated in (a) showing the Al-Ru phase particles (~10 nm) in the thinnest sample areas and very fine (≤1.2 nm) spots typical of amorphous material in thicker areas where the entire alloy layer is present.

patterns obtained by TEM analysis of this sample [see Fig.2(a)] show evidence of four diffuse bands (noted with curly braces) as well as several faint but relatively sharp rings. The outer three diffuse bands correspond to those readily observed in a similar alloy system, amorphous Al-Mn.[13] The innermost diffuse band is barely detectable in amorphous Al-Mn; it corresponds to a region of k space where two lines from the icosahedral phase are also found. Thus, the diffraction pattern of this amorphous material is like that of a very-fine-grained icosahedral phase with highly broadened features. (It has been suggested by Bendersky and Ridder that amorphous Al-Mn is actually a "microquasicrystalline" structure.[14]) The dark-field image of amorphous Al-Ru in Fig. 2(b) shows illuminated areas with dimensions less than 1.2 nm, characteristic of an amorphous material. The faint rings are due to the compound AlRu, which is present only near the surface of the sample and is seen in the thinnest part of the back-thinned sample [as seen on the left-hand of Fig. 2(b)]. Despite several attempts at different compositions, we were unable to produce a completely amorphous Al-Ru thin film by ion-beam mixing. For purposes of comparison, we also measured the resistivity of this primarily amorphous sample.

It has also been found that Al/Ru bilayers can be annealed at higher temperatures to produce the icosahedral phase without the assistance of ion-beam mixing. This solid-state interdiffusion reaction produces a very-fine-grained icosahedral material. An Al–20.3-at. % Ru bilayer sample was annealed at 450 °C for 30 min to produce a single-phase icosahedral layer with grain sizes ranging from 2 to 5 nm.[12]

III. RESULTS AND DISCUSSION

Resistivity measurements were performed using a standard four-point–probe technique[15] on the icosahedral phase and primarily amorphous thin films of Al-Ru, and the results are summarized in Table I. The resistivity of the icosahedral phase is approximately 40% larger than that of the primarily amorphous phase. Figure 3(a) is a plot of resistivity, $\rho(T)$, versus temperature for an Al–16.5-at. % Ru icosahedral-phase thin film produced by ion-beam mixing. Figure 3(b) shows the temperature dependence of resistivity for the primarily amorphous Al–16.5-at. % Ru thin film, also produced by ion-beam mixing. All of the samples exhibit a negative temperature coefficient of resistivity, $\alpha=(1/\rho)(\partial\rho/\partial T)$. We note that the measured temperature dependence of the resistivity of icosahedral Al-Ru is similar to that of primarily amorphous Al-Ru at the same composition, as seen from Fig. 3 and the resistivity ratios in Table I; the corresponding values of α vary from -4×10^{-4} to -9×10^{-4} K^{-1}.

All of the samples show a room-temperature resistivity greater than 150 $\mu\Omega$ cm and their temperature dependencies are thus consistent with the well-known Mooij correlation,[16] which states that when the room-temperature resistivity is greater than approximately 150 $\mu\Omega$ cm, the material will have a negative α below that temperature.

Despite an order-of-magnitude difference in their grain

TABLE I. Results of resistivity measurements on icosahedral and amorphous aluminum-ruthenium thin films between 4.2 and 300 K.

Sample	Synthesis technique	Grain size (nm)	$\rho_{4.2\ K}/\rho_{300\ K}$ ($\mu\Omega$ cm)
Icosahedral $Al_{79.7}Ru_{20.3}$	solid-state reacted at 450 °C	2–5	248/220=1.13
Icosahedral $Al_{83.5}Ru_{16.5}$	ion mixed at 300 °C	30–50	288/232=1.24
Icosahedral $Al_{83.5}Ru_{16.5}$	ion mixed at 300 °C	30–50	289/229=1.26
Amorphous $Al_{83.5}Ru_{16.5}$	ion mixed at 30 °C		196/164=1.20

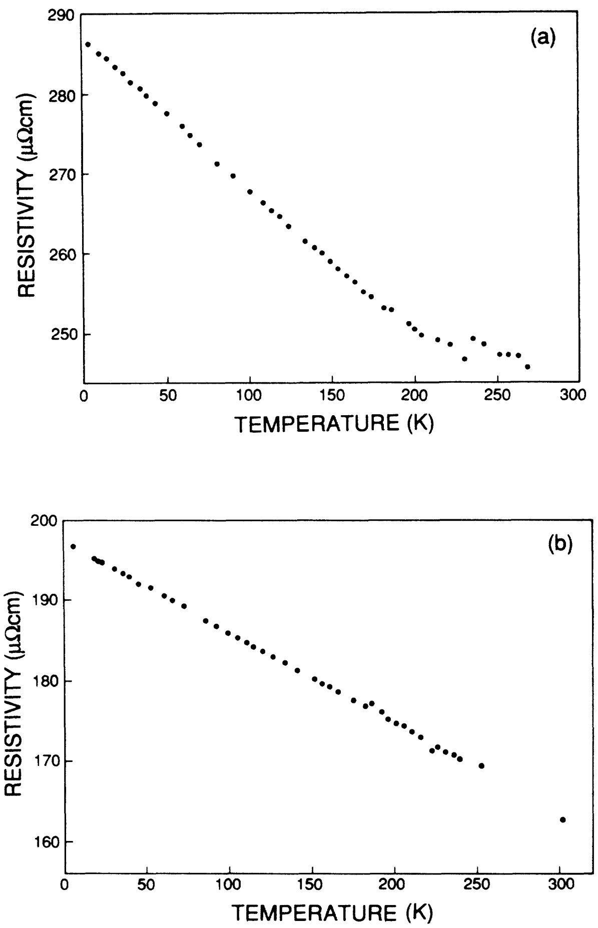

FIG. 3. (a) Plot of resistivity vs temperature (4.2 K to room temperature) for an Al–(16.5-at. %) Ru icosahedral-phase thin film produced by ion-beam mixing. (b) Plot of resistivity vs temperature for a primarily amorphous Al–16.5-at. % Ru thin film also produced by ion-beam mixing.

sizes, the ion-beam-mixed and solid-state-reacted icosahedral-phase samples have very similar electrical properties. This implies that the dominant electron-scattering mechanism is acting on a length scale less than or equal to the smaller grain sizes (2–5 nm). A high resistivity and negative α are commonly observed in disordered thin films[17] and bulk metallic glasses,[18] and are ascribed to a very short mean free path for conduction electrons in the material. Starting with the observed resistivity, the Drude theory of (scattering-dominated) conduction makes an estimate of the mean free path for the electron in these samples of about 2 Å. Since this estimated mean free path is much smaller than the grain size of the samples, it is not surprising that we fail to see an effect of grain size on the resistivity.

Three scattering mechanism have been proposed to explain the high resistivities observed in aluminum–transition-metal icosahedral-phase samples. The first possibility is that the perfect quasiperiodic electronic potential (e.g., of a quasicrystal) will produce enough elastic scattering to increase the resistivity. However, Sokoloff[19] has used perturbation theory to show that elastic scattering in a three-dimensional quasiperiodic potential will not produce the observed resistivities.

A second explanation for the short electronic mean free path in icosahedral Al-Ru is the scattering of aluminum conduction electrons from the empty ruthenium *d* states near the Fermi energy.[19] Scattering from *d* states has been observed before in a variety of dilute aluminum–transition-metal alloys,[20] and is likely to occur in aluminum-ruthenium alloys. In Friedel's model,[20] one considers the effect of placing dilute concentrations of transition-metal impurities into an aluminum matrix. Some of the empty ruthenium *d* states will have an energy which is nearly degenerate with that of aluminum conduction electrons at the Fermi level. The conduction electrons will be scattered into one of these localized *d* states and increase the resistivity. The length scale for these scattering events (the distance between ruthenium atoms) is consistent with our estimates of the mean free path for conduction electrons. It should also be mentioned that one can produce samples of icosahedral Al-Zn-Mg which do not contain transition metals. These materials have a room-temperature resistivity significantly lower than icosahedral Al-Ru, only 70–90 $\mu\Omega$ cm.[21,22]

A third scattering mechanism is that due to defects in the perfect quasicrystalline structure. Sokoloff[19] has shown that a high density of structural defects can produce resistivities and short mean free paths comparable to those reported here, and yet the diffraction peaks of the icosahedral phase would remain sharp. Because the samples studied here were produced under nonequilibrium conditions, structural defects may also contribute to the resistivities in Table I.

The icosahedral phase is likely to have considerable chemical disorder as well. We note from Table I that the ion-mixed icosahedral sample at 16.5 at. % Ru has a resistivity somewhat higher than the solid-state-reacted samples at 20.3 at. % Ru. Icosahedral grains in rapidly quenched Al-Ru alloys are found to have a composition of approximately 19 at. % Ru.[8] The metastable equilibrium phase diagram of Al-Ru shows that icosahedral Al-Ru is a compound and not a solid-solution phase.[8] Because the 16.5-at. % Ru icosahedral-phase samples are further off stoichiometry than the 20.3-at. % Ru sample, they should have greater chemical disorder, and hence, greater electrical resistivity, as we have observed.

IV. CONCLUSION

We have measured the temperature dependence of electrical resistivity of single-phase thin-film icosahedral Al-Ru and of primarily amorphous Al-Ru between 4.2 K and room temperature. The electrical transport properties of icosahedral Al-Ru are insensitive to grain sizes in the range of roughly 5–50 nm, are consistent with the Mooij correlation, and behave qualitatively like those of an amorphous metal. Our results are consistent with the effects of two proposed conduction-electron-scattering mechanisms: scattering from empty ruthenium *d* states and scattering from structural and chemical defects in the perfect quasicrystal.

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[1] D. Schechtman, I. A. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).

[2] See, for example, J. Phys. (Paris) Colloq. **47**, C3-1 (1986).

[3] K. Fukamichi, T. Masumoto, M. Oguchi, A. Inoue, T. Goto, T. Sakakibara, and S. Todo, J. Phys. F **16**, 1059 (1986).

[4] K. V. Rao, N. Karpe, R. Malmhäll, H. U. Åström, and H. S. Chen, in *Rapidly Solidified Alloys and Their Mechanical and Magnetic Properties,* edited by B. C. Giessen, D. E. Polk, and A. I. Taub (Materials Research Society, Pittsburgh, 1986), p. 229.

[5] C. Berger, D. Pavuna, and F. Cyrot-Lackmann, J. Phys. (Paris) Colloq. **47**, C3-489 (1986).

[6] D. Pavuna, C. Berger, F. Cyrot-Lackman, P. Germi, and A. Pasturel, Solid State Commun. **59**, 11·(1986).

[7] S. M. Anlage, P. Nash, R. Ramachandran, and R. B. Schwarz, J. Less-Common. Met. **136**, 237 (1988).

[8] S. M. Anlage, B. Fultz, and K. M. Krishnan, J. Mater. Res. **3**, 421 (1988).

[9] W. L. Johnson, Prog. Mater. Sci. **30**, 81 (1986).

[10] D. Lilienfeld, M. Nastasi, H. Johnson, D. Ast, and J. Mayer, Phys. Rev. Lett. **55**, 1587 (1985).

[11] J. A. Knapp and D. M. Follstaedt, Phys. Rev. Lett. **55**, 1591 (1985).

[12] D. M. Follstaedt and J. A. Knapp, J. Mater. Sci. **90**, 1 (1987).

[13] D. M. Follstaedt and J. A. Knapp, Nucl. Instrum. Methods B **24/25**, 542 (1987).

[14] L. A. Bendersky and S. D. Ridder, J. Mater. Res. **1**, 405 (1986).

[15] L. J. van der Pauw, Philips Res. Rep. **13**, 1 (1958).

[16] J. H. Mooij, Phys. Status Solid A **17**, 521 (1973).

[17] L. I. Maissel, in *Handbook of Thin Film Technology,* edited by L. I. Maissel and R. Glang (McGraw-Hill, New York 1970), p. 13-1.

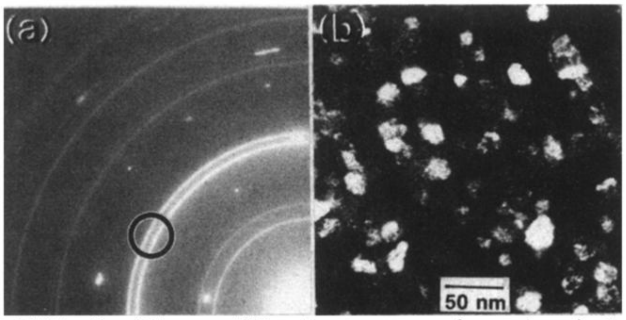
[18] P. J. Cote and L. V. Meisel, in *Glassy Metals I,* edited by H. J. Güntherodt and H. Beck (Springer-Verlag, Berlin, 1981), p. 141.

[19] J. B. Sokoloff, Phys. Rev. Lett. **57**, 2223 (1986); Phys. Rev. B **36**, 6361 (1987).

[20] J. Friedel, in *Metallic Solid Solutions,* edited by J. Friedel and A. Guinier (Benjamin, New York, 1963), p. XIX-1.

[21] K. M. Wong, E. Lopdrup, J. L. Wagner, Y. Shen, and S. J. Poon, Phys. Rev. B **35**, 2494 (1987).

[22] D. V. Baxter, R. Richter, and J. O. Strom-Olsen, Phys. Rev. B **35**, 4819 (1987).



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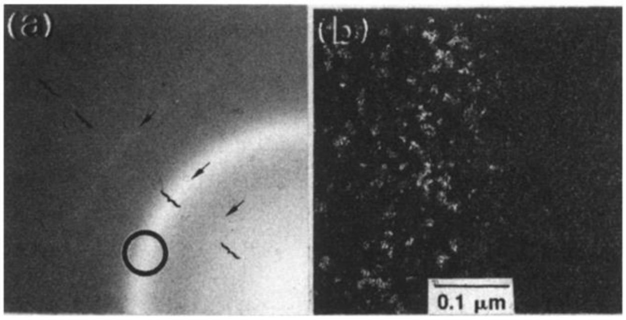

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