Stable Al-Cu-Ru Icosahedral Crystals: A New Class of Electronic Alloys

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Stable icosahedral $Al_{85-x}Cu_xRu_{15}$ ($15 < x < 20$) alloys of good metals are characterized by conductivities below the "minimum metallic value," and resistivity ratios $\rho(0.5\ K)/\rho(295\ K)$ as large as 4. Strong temperature dependences which lead to changes of sign in the Hall coefficient and thermopower are also observed. Electronic densities of states are found to vary rapidly with alloy composition. The unusual electronic properties of this new class of barely metallic systems are discussed in light of current theories on electronic structure and transport of icosahedral crystals.

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The discovery of icosahedral alloys[1] has spawned the search for unusual electronic properties in these new materials. On the theory front, exotic electronic states are being predicted for various models of the icosahedral quasicrystal.[2] While it is agreed that there are prominent structures due to Bragg-like diffraction,[3] detailed features of the electronic spectrum remain controversial.[4,5] Despite these theoretical efforts, the nature of electron transport in icosahedral (*i*) crystals continues to be not well understood.[6] Recent work by Kitaev[7] suggests that the electronic properties of perfect *i* crystals are fundamentally different from those of perfect crystals. However, in the limit of weak atomic potentials, *i* crystals and crystals could appear to have similar electronic properties. Indeed, transport and specific-heat studies of *i* phases with resistivity values below 100 $\mu\Omega$ cm indicate that they are similar to their corresponding crystalline phases.[8,9] A recent systematic study of Al-Cu-Mg and Ga-Mg-Zn *i* alloys shows distinct features in their electronic properties which are ascribed to the Fermi-surface–Jones-zone interaction,[10] confirming one of the theoretical predictions on electronic structure[3] and stability[11] of *i* phases. Meanwhile, it is realized that experiments with these intrinsically disordered *i* phases will not be able to reveal other novel properties. The discovery of stable Al-Cu-Ru *i* phases[12] and the later confirmation of their structural long-range order[13] have provided one of the best systems yet available for the investigation of unusual electronic properties in *i* crystals. Moreover, the strong *sp-d* hybridization in these systems provides a case study in the strong scattering regime. We report in this paper unusual electronic properties in Al-Cu-Ru *i* alloys. The barely metallic behavior of these alloys, which are based on good metals, is also unexpected. It is hoped that these new results on stable *i* phases will lead to further theoretical and experimental investigations of ordered quasicrystals.

Thin (~20-μm) ribbon samples of *i*-$Al_{85-x}Cu_xRu_{15}$ ($x=15$, 17, and 20) were prepared by melt spinning.[9] The ribbons were then annealed at 800 °C for 24 h to obtain single *i*-phase samples, and the structure was confirmed by x-ray diffraction using a Scintag XDS-2000 diffractometer. To eliminate any surface-impurity-phase problems, which are commonly present in melt-spun ribbons, both sides of the samples were ion milled using 1-keV argon ions, removing surface layers sufficiently thick (~1 μm) so that the results converge and are reproducible. The removal of surface impurity phases is essential for high-resistivity alloys such as the ones being studied. Transport and specific-heat measurements were performed as described elsewhere.[9,10]

Specific-heat results plotted in the form C/T vs T^2 are shown in Fig. 1. The linear electronic coefficient (γ) and the lattice contribution are separated from the total specific heat by fitting the data with the commonly used expression $C=\gamma T+\beta T^3+\delta T^5$ (Ref. 14). To ensure accuracy in the determination of γ, only the low-temperature ($1\ K < T < 3\ K$) data are used for the fit. Values of γ for the $x=20$, 17, and 15 samples are determined to be 0.11, 0.23, and 0.2 mJ/g-at.K^2, with their corresponding Debye temperatures being equal to 500, 527, and 500 K, respectively. The Debye temperatures obtained for these stable *i* phases are the largest observed so far in Al-based *i* phases,[8-10] with high Debye

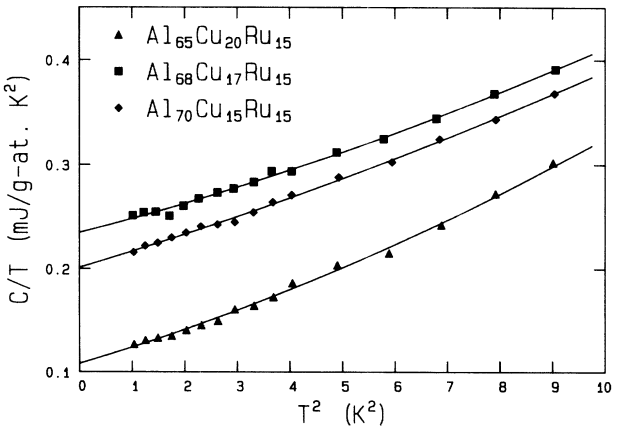

FIG. 1. Heat capacity of *i*-Al-Cu-Ru samples. Solid curves are fits by the expression $C=\gamma T+\beta T^3+\delta T^5$.

temperatures expected for alloys with strong *sp-d* hybridization. Comparing their electronic γ values with the estimated free-electron values of ~ 1.1 mJ/g-at.K^2, these stable *i*-phase alloys are found to have a low electronic density of states at the Fermi level [$N(E_F)$]. Moreover, a rather rapid variation of $N(E_F)$ with Al-Cu content is noted. This suggests the presence of distinct features in the band structure of alloys in the narrow region of *i*-phase formation.

Conductivity as a function of temperature for the $x=20$, 17, and 15 samples is shown in Fig. 2(a). Room-temperature resistivities for the samples shown are $\simeq 6500$, 2800, and 4400 $\mu\Omega$ cm, respectively. The resistivity ratios $\rho(0.5\text{ K})/\rho(295\text{ K})$ range from 2 to 4, with the largest value being observed in the 20-at.% sample. Reproducibility of measurements was confirmed when the samples were thermally cycled; and also when samples from different batches were measured. Thus, low-temperature resistivities as large as 30000 $\mu\Omega$ cm are observed in stable *i* phases. These results have not been seen in bulk homogeneous metallic alloys composed mainly of good metals, including metallic glasses.[15] In fact, the room-temperature conductivities $\sigma(295\text{ K})$ are already near the "minimum metallic conductivity" $\simeq 200\ \Omega^{-1}\text{cm}^{-1}$ estimated for these alloys, indicating that these *i* phases are marginally metallic. Common features of $\sigma(T)$ behavior in these alloys are also noted. At low temperature ($0.5\text{ K} < T < 5$ K), $\sigma(T)$ is found to vary as $\sqrt{T}$, which is ascribed to electron-interaction effects.[16] At higher T, $\sigma(T) \propto T$ for $10\text{ K} < T < 30$ K, and it is found that localization effects play a dominant role in the variation of $\sigma(T)$. In this regime, the inelastic-scattering time τ_i due to electron-phonon interaction in high-resistivity metals is predicted to be proportional to T^{-2} (Ref. 16). The calculated variation of $\sigma(T)$ based on $\tau_i(T)$ determined from magnetoresistance data is also in reasonable agreement with measurement. The $\sigma(T)$ behavior discussed so far has been observed in disordered and amorphous metallic alloys.[15] However, at higher temperature ($T > 30$ K), unlike those reported previously, $\sigma(T)$ in the present alloys has a positive curvature which extends to room temperature. For metallic alloys, it was suggested, and was also experimentally observed,[17] that at high T, τ_i changes to become proportional to T^{-1}. Therefore, $\Delta\sigma(T) \propto T^p$ with $p \leq 1$ over the entire temperature range studied. In contrast, the activated form of $\sigma(T)$ at high temperature in stable *i* phases is reminiscent of those observed in the barely metallic regime of heavily doped semiconductors,[18] indicating the remnant of localized states in these phases.

Magnetoresistivity data $\Delta\rho/\rho$ vs H measured at different temperatures for the $x=20$ sample are shown in Fig. 3. Obtaining the electron diffusion constant $D \simeq 0.1$ cm^2/s ($k_F l \simeq 0.3$, where l is the mean free path) from the specific heat γ and the conductivity $\sigma(0)$, the various contributions to $\Delta\rho/\rho$ due to interaction and localization effects can be estimated. It is found that the localization

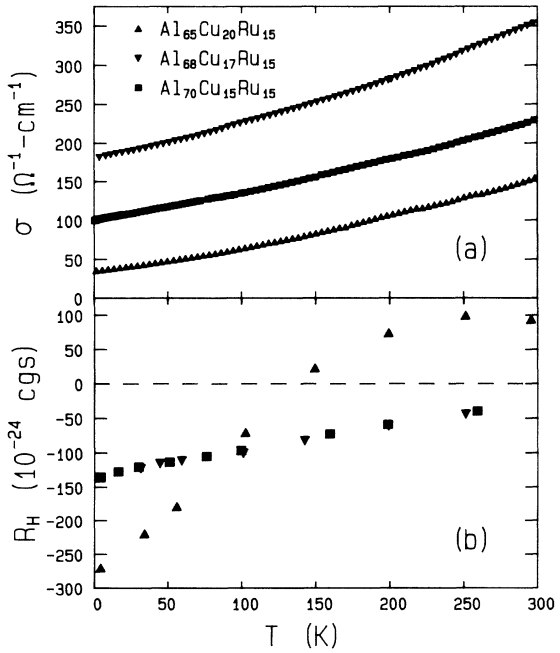

FIG. 2. (a) Conductivity and (b) Hall-effect results. Positive curvatures in $\sigma(T)$ for $T > 30$ K can be seen.

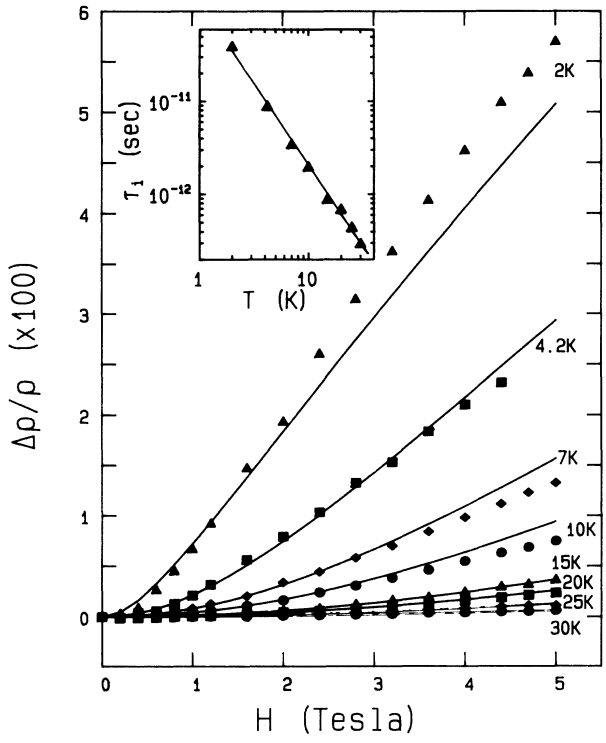

FIG. 3. Magnetoresistivity for $Al_{65}Cu_{20}Ru_{15}$ at the temperatures indicated. Solid curves are fits by the Fukuyama-Hoshino theory. Inset: Temperature dependence of inelastic-scattering time.

effect overwhelmingly dominates the magnetoresistivity. In fact, the positive and large magnetoresistivity measured and the trend of $\Delta\rho/\rho$ at increasing magnetic field and temperature are similar to those observed in metallic glasses with appreciable spin-orbit scattering.[15] The data are analyzed according to the Fukuyama-Hoshino expression for $\sigma(H,T)$ in the weak-localization regime.[19] Good agreement with measurement is obtained, resulting in a spin-orbit scattering time $\tau_{s.o.}=10^{-12}$ s, and an inelastic-scattering time $\tau_i=10^{-10}T^{-1.8}$ s. These values are within the range of those reported previously.[15,17] However, it must be admitted that the reason why weak-localization theory should still be applicable to these metallic i phases whose k_Fl values ($\simeq$0.3–0.5) are much less than unity is not known.

Now we proceed to discuss other striking features which also have not been seen in the transport properties of melt-spun metallic-glass and previously reported i-phase systems. First, large negative low-temperature Hall coefficients (R_H) were measured in the present i alloys, as shown in Fig. 2(b). The effective numbers of electron carriers (n) are 2.4×10^{20} cm^{-3} ($R_H\simeq-2.7\times10^{-22}$ cgs) for the $x=20$ samples, and 5×10^{20} cm^{-3} ($R_H\simeq-1.4\times10^{-22}$ cgs) for the $x=15$ and 17 samples. These numbers are of the same order of magnitude as those estimated using the free-electron relation $n\propto\gamma^3$. An additional unusual feature is that $R_H(T)$ shows a strong temperature dependence which has not been seen previously in high-resistivity metallic alloys, in which R_H varies by less than 10% over a similar temperature range.[15] There is even a sign change in R_H for the $x=20$ sample. One can examine if weak-localization effects on R_H can contribute to its temperature dependence. Considering the relationships $R_H=\sigma_{xy}/\sigma_{xx}^2H$ and $\Delta\sigma_{xy}/\sigma_{xy}=2\Delta\sigma_{xx}/\sigma_{xx}$ for weak localization,[16] the calculated changes in R_H are found to be much smaller than those measured. On the other hand, a theory of R_H for the marginally metallic regime ($k_Fl\lesssim1$) is not available for comparison. The latter statement also applies to our thermopower (S) results, which are shown in Fig. 4. The temperature dependence of S is unusual. For comparison, $S(T)$ of i phases of Al-Cu-Mg and Ti-Zr-Ni, which have metallic-glass-like resistivity values, have been measured and are also shown in Fig. 4. For metallic-glass systems, $S(T)$ is dominated by the electron diffusion contribution, which is proportional to the temperature. In addition, the electron diffusion term is enhanced by the electron-phonon renormalization factor $1+\lambda(T)$, where $\lambda(0)<1$ for most alloys, and $\lambda(T)$ is a decreasing function of T.[15] The shapes of $S(T)$ curves for Al-Cu-Mg and Ti-Zr-Ni i phases are similar to those observed in metallic glasses. For the latter systems, where $\lambda(T)$ is known, their $S(T)$ data have been successfully described by the aforementioned model. It is clear that the mechanism responsible for the unusual $S(T)$ behavior in the present alloys is fundamentally different from that of systems studied previously.

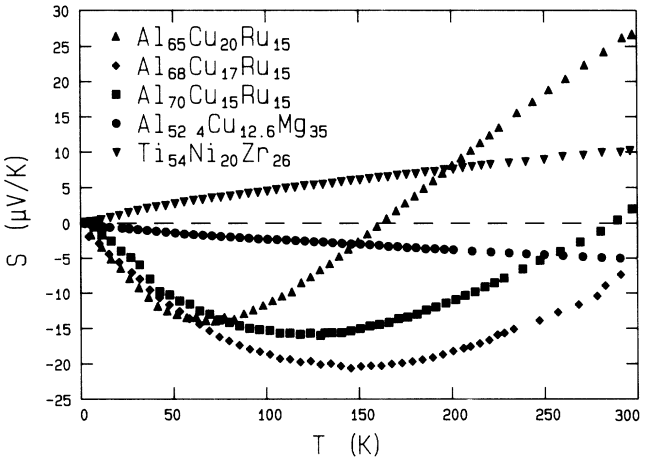

FIG. 4. Thermoelectric-power results.

Recognizing the marginally metallic nature of these alloys, however, it is plausible that an energy-dependent conductivity mechanism such as that proposed for noncrystalline materials with $E_F\gtrsim E_c$ (mobility edge) may explain the observed $S(T)$ behavior.[20]

In view of the wide range of transport data reported on stable i phases,[21] it is emphasized that the present results are established only after an extensive examination of the correlation of properties measured with phase purity. When the samples contain detectable but small ($<5\%$) traces of second phases (mostly Al_2Cu) due to either oxidation or improper heat treatment, both ρ and R_H are much reduced in magnitude. Moreover, they change by less than 30% from low temperature to room temperature. The shape of $S(T)$ is also very different from that observed in high-quality samples; namely, it resembles that seen in Al-Cu-Mg i phases. As the quality of samples improves, these properties converge to the ones reported here, with good reproducibility. Of course, one should study single-grained samples of these alloys, when they are available. However, it is expected that high-quality polycrystalline and single-grained samples should produce similar results, as is the case in Al-Cu-Li.[9,22]

Preliminary calculations of conductivity have demonstrated the breakdown of perturbation theory in perfect icosahedral crystals.[7] This suggests that unusual electronic properties can be expected, particularly in the strong-scattering regime. In fact, using the tight-binding approach, it is suggested that localized as well as critical states can exist in icosahedral crystals.[2] The understanding of activated conductivity at high temperature, and the unusual temperature dependences of the Hall effect and thermopower certainly require treatment beyond weak localization. Meanwhile, based on stability considerations, the rapid variation of γ with composition may be just a strong manifestation of the Fermi-surface–Jones-zone interaction in these perfect i phases.[3,5,10,11] This structural scattering mechanism, when applied to

interpret transport data, would require the existence of fine structures on the scale of ~ 0.02 eV in the electron band. Fujiwara[5] has computed the band structure of the crystal analog of the Al-Mn *i* phase, and a very spiky band structure is obtained for this relatively simple approximant. The situation for the quasiperiodic case is bound to be much more complex. However, in that case, consideration of the nature of electronic states should be of prime importance. Experimentally, it will be fruitful to compare the electronic properties of the various structural analogs of stable *i*-phase-forming systems. As for the low carrier concentration ($\sim 10^{-3}$ electrons per atom) observed, one needs to answer the question: Where are the electrons?

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