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Composition dependence of the electronic properties of Al-Cu-Fe and Al-Cu-Ru-Si semimetallic quasicrystals

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Electronic transport properties and specific heats of ordered icosahedral phase alloys in the Al-Cu-Ru-Si and Al-Cu-Fe systems are examined, and comparison with high-quality rhombohedral ($\frac{3}{2}$) approximant phase samples of Al-Cu-Fe is made. Strong temperature dependence and sensitivity to composition changes of these properties are observed. The similarity of transport properties between the icosahedral (i) and rhombohedral (r) phases of $Al_{62.5}Cu_{26.5}Fe_{11}$ is noted. The results can be qualitatively interpreted in terms of band structure. There appears to be sufficient evidence for a rapidly varying conductivity spectrum $\sigma(E)$ in the ordered i phases. However, important questions concerning the physics of these semimetallic quasicrystals remain to be answered.

I. INTRODUCTION

Since the discovery of the ordered icosahedral (i) phases, in the Al-Cu-Fe, Al-Cu-Ru,[1] and more recently Al-Mn-Pd (Ref. 2) systems, it has become possible to investigate the electronic properties of quasicrystalline materials unobscured by the effects of structural disorder.[3] The properties measured have shown unusual features; among them, low-dc conductivity, low electronic contribution to specific heat, and large and strongly temperature-dependent Hall coefficients and thermoelectric power. These properties are quite different from the metallic-glass-like behavior of the disordered quasicrystals.[3,4] In each of these materials,[5-9] the dc conductivity is comparable to or even less than the minimum metallic conductivity of 200 $\Omega^{-1}\,cm^{-1}$.[10] Because of the low conductivity and small carrier concentration, these materials can be classified as semimetals.[5,11] The proximity of these materials to a metal-insulator transition has also been suggested.[6] In addition, there is preliminary evidence that small variations in the composition of these structurally ordered phases can lead to significant changes in the conductivities.[3,5,6,9] Along with the temperature dependences of the Hall coefficients and thermopower observed, these results suggest that rapidly varying structures may exist in the density of states.[3,11] To provide a more quantitative basis for investigating the band-structure effects, i-phase alloys of $Al_{65-x}Cu_{20}Ru_{15}Si_x$ ($x=0,0.5,1.0$) are studied in an attempt to vary the Fermi energy on a fine energy scale. Since the chemical substitution is made only in the sp band, and the composition change is small, it is reasonable to assume that a shift in E_F results, but that the electronic structure remains unchanged. A similar study is also reported for the i-Al-Cu-Fe alloys (Table I) in which both Cu and Fe contents are varied. For these alloys, filling of the d band needs to be considered. We apply the free-electron model to estimate a variation in E_F of less than $\sim 0.1-0.3$ eV, for Al-Cu-Ru-Si and Al-Cu-Fe, respectively.

In addition to the band-structure mechanism, a proximity tunneling mechanism of conductivity, based on an internal structural model, is proposed to explain the low conductivities.[12] However, it is important to remark that any theory put forth to account for the behavior of the conductivity in these materials should also at the same

TABLE I. Electronic contribution to specific heat (γ), and Debye temperature (Θ_D), determined from specific-heat data fit to the expression $C=\gamma T+\beta T^3+\delta T^5$, with dc electrical conductivity (σ) at 4.2 K.

		γ (mJ/g atom K^2)	Θ_D (K)	$\sigma_{4.2\ K}$ ($\Omega^{-1}\,cm^{-1}$)
$Al_{62.5}Cu_{26.5}Fe_{11}$	i phase	0.32	560	270
	r phase	0.25	555	180
$Al_{63.5}Cu_{24.5}Fe_{12}$[a]		0.31	540	230
$Al_{62.5}Cu_{24.5}Fe_{13}$				150
$Al_{65}Cu_{20}Ru_{15}$[b]		0.11	500	75
$Al_{64.5}Cu_{20}Ru_{15}Si_{0.5}$		0.27	445	180
$Al_{64}Cu_{20}Ru_{15}Si_1$		0.21	485	280
$Al_{68}Cu_{17}Ru_{15}$[b]		0.23	530	180
$Al_{70}Cu_{15}Ru_{15}$[b]		0.20	500	100

[a] Reference 7.

[b] Reference 5. The $Al_{65}Cu_{20}Ru_{15}$ σ(4.2 K) cited here is obtained from one of the samples that did not achieve the lowest value reported earlier in Ref. 5.

time address the strong temperature and composition dependences of the thermoelectric power and Hall coefficient reported in this paper. Meanwhile, further understanding of the i phases can also be advanced through studies of approximant phases. The electronic structures of several approximant phases are now known, both from band-structure calculations,[13,14] and x-ray spectroscopy measurements.[15–18] A recent study of the crystalline approximant α-AlMnSi phase shows electronic properties similar to those of the ordered i phase.[11] In this report, we also present a comparison study of i-Al-Cu-Fe with its approximant phase. Single-phase samples of the latter can now be obtained. The Al-Cu-Fe system is an excellent choice for further studies of this type, since, in a narrow range of composition, the icosahedral (i) phase and rhombohedral (r) phase (the $\frac{3}{2}$ crystalline approximant) can be formed at the same composition.[19] In a previous study of rational approximant structures in this system, the x-ray-diffraction pattern of the r phase shows broadened peaks at the same positions as those of the i phase.[20] Detailed studies of the phase diagram of the Al-Cu-Fe system in the i-phase region, have recently been performed.[19,21,22] These studies revealed a complex phase diagram with the thermodynamically stable i phase forming only in several narrow ranges of composition. A well-ordered i phase can be formed over a wider composition range, but some compositions transform when annealed at low temperature. The i phase studied in Ref. 7 was of this type. The transformed i phase corresponds to i phase with some phason disorder in which peak intensities were reduced by a Debye-Waller factor, and broadened by diffuse scattering around the peaks. The r phase can be formed at composition $Al_{62.5}Cu_{26.5}Fe_{11}$, and has sharp diffraction peaks grouped around the i-phase peak positions. A comparison of powder-diffraction patterns for i and r phase $Al_{62.5}Cu_{26.5}Fe_{11}$ is shown in Fig. 1.

II. EXPERIMENTAL PROCEDURE

Alloy ingots of nominal compositions $Al_{65-x}Cu_{20}Ru_{15}Si_x$ ($x=0,0.5,1.0$), $Al_{62.5}Cu_{26.5}Fe_{11}$, and $Al_{63.5}Cu_{24.5}Fe_{12}$ were produced by melting together pure ($\geq 99.95\%$) elements, under argon in an arc furnace. Ribbon samples of ~ 20 μm thickness were prepared by melt spinning, in an argon atmosphere. The samples were subsequently annealed in evacuated quartz tubes for up to 24 h, and then water quenched. Al-Cu-Ru-Si alloys were annealed from 800–860 °C, depending upon composition. Al-Cu-Fe alloys were annealed from 725–760 °C. The rhombohedral phase was formed by annealing quenched ribbon samples of composition $Al_{62.5}Cu_{26.5}Fe_{11}$ at 690 °C, for 210 h. Samples of the stable composition $Al_{62.5}Cu_{24.5}Fe_{13}$ were made by remelting an ingot with the correct average composition in an evacuated quartz tube, and then water quenching, to reduce compositional inhomogeneities. The ingot was then annealed at 830–850 °C for 24 h. The phase purity of the samples was confirmed by powder x-ray diffraction using either Cu $K\alpha$ or Co $K\alpha$ radiation.

Resistivity was measured from 0.5 to 295 K using the standard four-probe technique, with silver paint contacts.

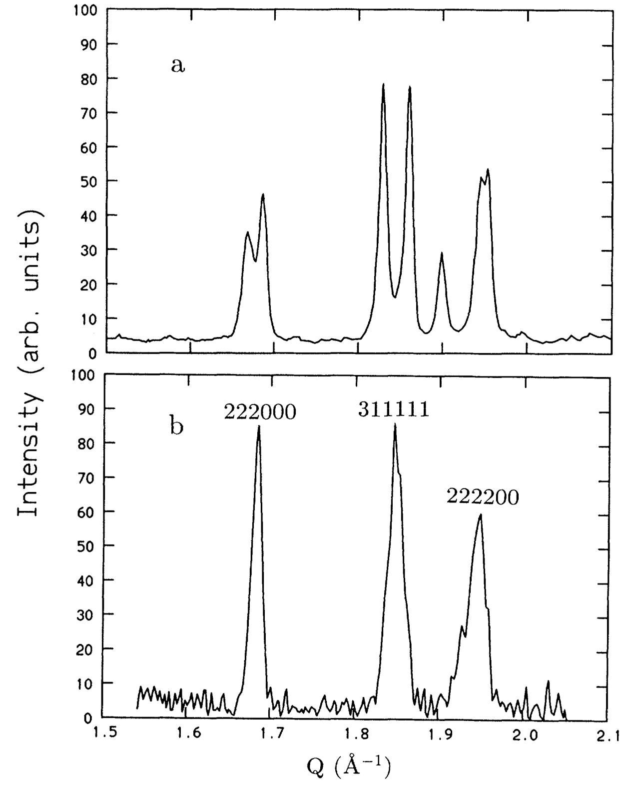

FIG. 1. X-ray-diffraction patterns for $Al_{62.5}Cu_{26.5}Fe_{11}$ r phase (a), and i phase (b).

Thermoelectric power was measured from 4.2 to 300 K, with respect to high-purity lead wires, using the differential technique. dc Hall effect measurements were performed using the six-lead method, in fields up to 4 T using a superconducting magnet. The Hall coefficient was measured at selected temperatures from 4.2 to 300 K. The leads were attached to the sample with silver paint. Due to the nature of the samples, it was very difficult for the small contacts necessary for the Hall leads to survive thermal cycling. This accounts for the scarcity of high-temperature data. Specific-heat measurements were performed using the thermal relaxation method at temperatures from 1 to 8 K as described elsewhere.[23]

III. RESULTS

Powder x-ray-diffraction patterns of i- and r-phase samples of $Al_{62.5}Cu_{26.5}Fe_{11}$ are compared in Fig. 1. All r-phase peaks correspond to those of the rhombohedral phase reported in Refs. 19 and 21 ($a=32.18$ Å and $\alpha=36°$).

Heat-capacity data, at temperatures in the range $1\leq T\leq 4$ K, were fit to the standard form $C=\gamma T+\beta T^3+\delta T^5$, including the T^5 term. Values of the electronic contribution γ and Θ_D are listed in Table I. Low-temperature specific-heat data for Al-Cu-Fe are shown in Fig. 2. Data for Al-Cu-Ru-Si are shown in Fig. 3. The electronic contribution γ, for each of the i-phase compositions, was significantly lower than the free-

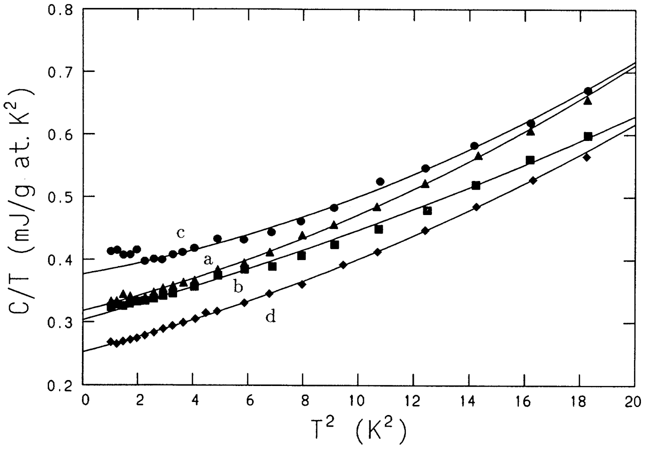

FIG. 2. Specific-heat data for *i*-phase $Al_{62.5}Cu_{26.5}Fe_{11}$ (a), *i*-phase $Al_{63.5}Cu_{24.5}Fe_{12}$ (b), *i*-phase $Al_{62.5}Cu_{24.5}Fe_{13}$ (c), and *r*-phase $Al_{62.5}Cu_{26.5}Fe_{11}$ (d). Solid curves are fits by the expression $C=\gamma T+\beta T^3+\delta T^5$.

electron value of ~ 1 mJ/g atom K^2. The variation of γ in Al-Cu-Ru-Si *i* alloys upon up to 1 at. % Si substitution for Al is significant; and it is as large as that seen in Al-Cu-Ru alloys, where up to 5 at. % Cu is substituted for Al.[5] The γ value for the *r* phase Al-Cu-Fe was lower than that of *i* phase of the same composition, which appears to correlate with the lower conductivity measured. Due to the upturn in the specific heat of $Al_{62.5}Cu_{24.5}Fe_{13}$ at decreasing temperature, reliable values for γ and Θ_D cannot be determined. The upturn could be accounted for by a trace amount of a magnetic phase, as small as a few ppm in the sample. Presence of a very minute amount of second phase is expected as the *i*-phase boundary is approached. The Debye temperature for this class of stable *i* phases, including those reported by us earlier,[5,7] are the highest observed in *i*-phase materials. To shed light on this, we have surveyed a large number of specific-heat and phonon spectrum data on various metallic systems in the literature. An empirical relationship $k_B\Theta_D \simeq 0.75-1.2\hbar\omega_M$ is noted, where $\hbar\omega_M$ is an approximate cutoff phonon energy in the phonon spectrum. Phonons in Al-Cu-Fe (Ref. 24) and Al-Pd-Mn (Ref. 25) *i* phases have recently been studied. From these results, one observes that $\hbar\omega_M \geq 55$ meV, which is higher than that of pure Al (~ 50 meV). The empirical relationship then indicates Θ_D to be at least ~ 480 K.

Electrical conductivity (σ) data for the Al-Cu-Fe samples are shown in Fig. 4. Conductivity increased as Al or Cu was substituted for Fe. The *r*-phase conductivity was less than that of the *i* phase of the same composition, with similar temperature dependence. The conductivity upturn, at low temperature, in the $Al_{62.5}Cu_{24.5}Fe_{13}$ samples has been seen previously in the Al-Cu-Fe system,[26] and is ascribed to strong electron-electron interaction in the weak localization regime. From the data shown for the Al-Cu-Ru-Si samples in Fig. 5, it can be seen that the conductivity increases with Si or Cu concentrations. There is a corresponding decrease in the ratio $\sigma(300\text{ K})/\sigma(4.2\text{ K})$ from ~ 3.4 for the $x=0$ sample, to ~ 1.4 for the $x=1$ sample. The conductivity of all samples measured in these two systems shows upward curvature above ~ 50 K. The positive curvature in σ as well as the larger than unity ratio $\sigma(300\text{ K})/\sigma(4.2\text{ K})/\sigma(4.2\text{ K})$ cannot be explained by weak localization theories.[27]

Thermoelectric power (S) data for Al-Cu-Fe samples are shown in Fig. 6 and that of Al-Cu-Ru-Si in Fig. 7. All have large values when compared to those of disordered metallic systems.[27] The temperature dependence of some of these alloys is also unlike that of metallic glasses where except for the small electron-phonon enhancement effect, observed at low temperatures, $S \propto T$. Sensitivity of $S(T)$ to small composition change is also noted. In particular, $S(T)$ changes sign upon small chemical changes in both systems.

Hall effect (R_H) results for Al-Cu-Fe alloys are shown in Fig. 8, and for Al-Cu-Ru-Si alloys in Fig. 9. The Hall coefficient (R_H) was field independent, in fields up to 4 T, for each of the alloys studied. In the Al-Cu-Fe system, the Hall coefficient was negative for each of the alloys except *i*-$Al_{62.5}Cu_{24.5}Fe_{13}$, which was large and positive, con-

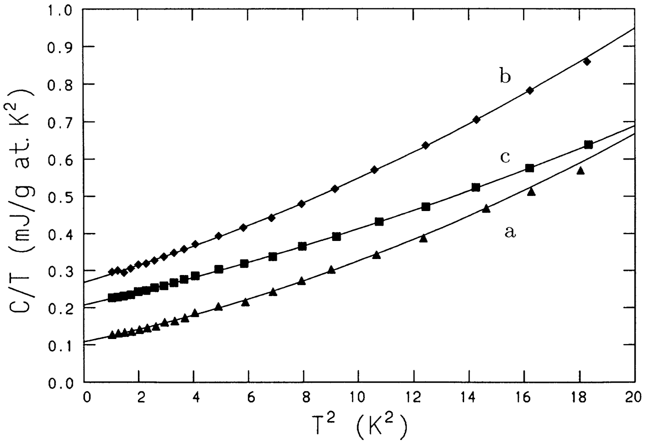

FIG. 3. Specific-heat data for *i*-phase $Al_{65}Cu_{20}Ru_{15}$ (a), $Al_{64.5}Cu_{20}Ru_{15}Si_{0.5}$ (b), and $Al_{64}Cu_{20}Ru_{15}Si_{1}$ (c). Solid curves are fits by the expression $C=\gamma T+\beta T^3+\delta T^5$.

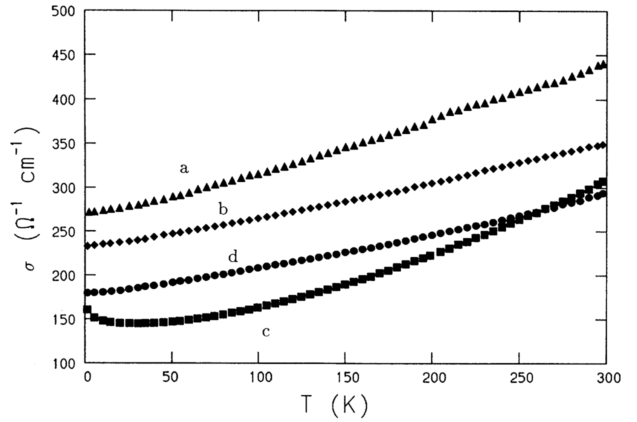

FIG. 4. Electrical conductivity data for *i*-phase $Al_{62.5}Cu_{26.5}Fe_{11}$ (a), *i*-phase $Al_{63.5}Cu_{24.5}Fe_{12}$ (b), *i*-phase $Al_{62.5}Cu_{24.5}Fe_{13}$ (c), and *r*-phase $Al_{62.5}Cu_{26.5}Fe_{11}$ (d).

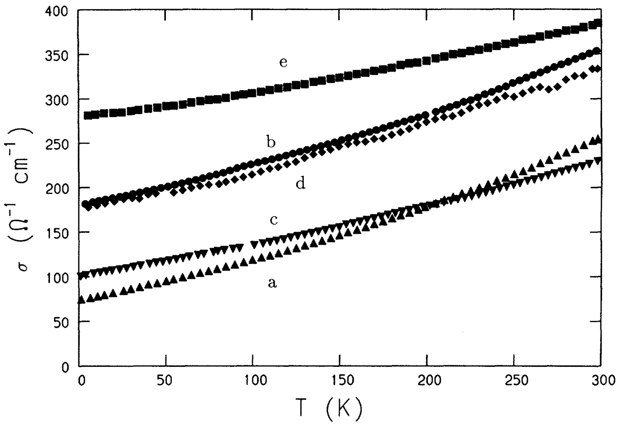

FIG. 5. Electrical conductivity data for i-phase $Al_{65}Cu_{20}Ru_{15}$ (a), $Al_{68}Cu_{17}Ru_{15}$ (b), $Al_{70}Cu_{15}Ru_{15}$ (c), $Al_{64.5}Cu_{20}Ru_{15}Si_{0.5}$ (d), and $Al_{64}Cu_{20}Ru_{15}Si_{1}$ (e).

sistent with the positive thermopower measured. The magnitude of R_H for the r phase was significantly larger than R_H of any of the i-Al-Cu-Fe samples measured. In the $Al_{65}Cu_{20}Ru_{15}$ sample, R_H had large temperature dependence, leading to a change in sign at ~150 K. As silicon was substituted for aluminum, the magnitude of R_H was reduced, as well as the temperature dependence. In both of these systems, the Hall coefficient is sensitive to small composition changes. It is clear that the trend of $R_H(T)$ is correlated to that of $S(T)$. As $S(T)$ becomes positive, $R_H(T)$ either becomes positive, or much less negative.

IV. DISCUSSION

The unusual electronic properties observed in the ordered i phases and related approximants raise questions

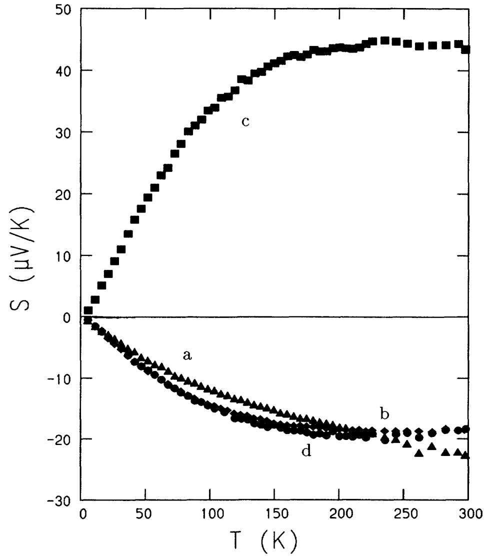

FIG. 6. Thermoelectric power data for i-phase $Al_{62.5}Cu_{26.5}Fe_{11}$ (a), i-phase $Al_{63.5}Cu_{24.5}Fe_{12}$ (b), i-phase $Al_{62.5}Cu_{24.5}Fe_{13}$ (c), and r-phase $Al_{62.5}Cu_{26.5}Fe_{11}$ (d).

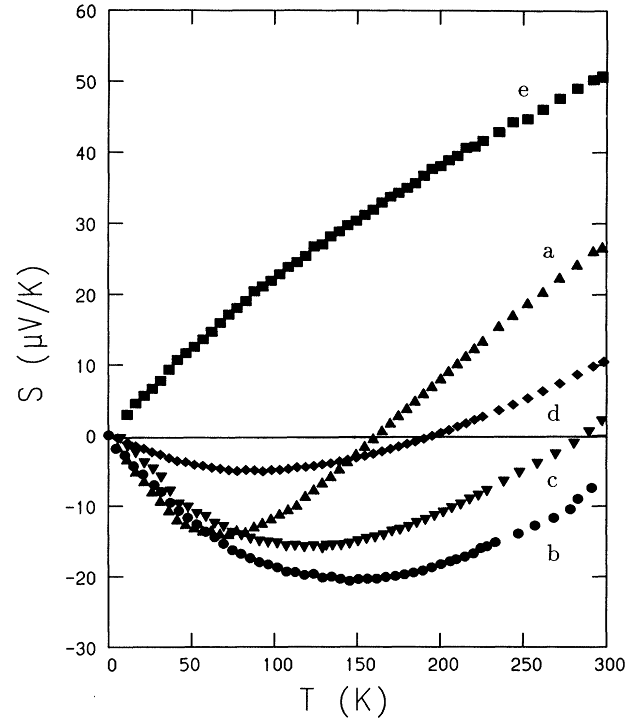

FIG. 7. Thermoelectric power data for i-phase $Al_{65}Cu_{20}Ru_{15}$ (a), $Al_{68}Cu_{17}Ru_{15}$ (b), $Al_{70}Cu_{15}Ru_{15}$ (c), $Al_{64.5}Cu_{20}Ru_{25}Si_{0.5}$ (d), and $Al_{64}Cu_{20}Ru_{15}Si_{1}$ (e).

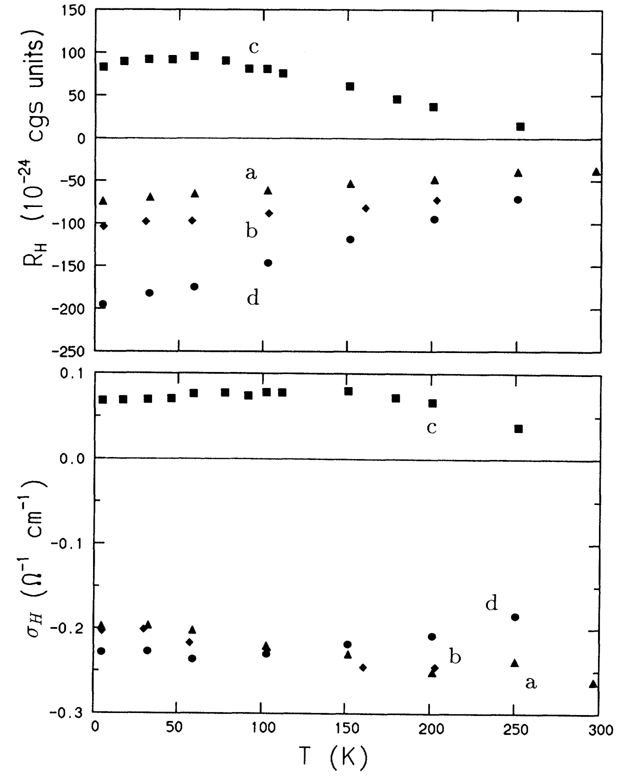

FIG. 8. Hall coefficient and Hall conductivity data at $H=4$ T for i-phase $Al_{62.5}Cu_{26.5}Fe_{11}$ (a), i-phase $Al_{63.5}Cu_{24.5}Fe_{12}$ (b), i-phase $Al_{62.5}Cu_{24.5}Fe_{13}$ (c), and r-phase $Al_{62.5}Cu_{26.5}Fe_{11}$ (d).

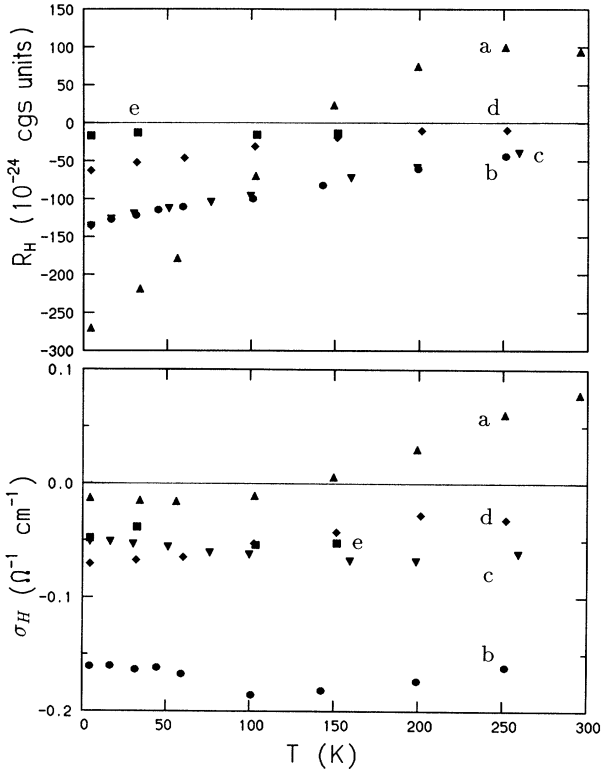

FIG. 9. Hall coefficient and Hall conductivity data at $H=4$ T for *i*-phase $Al_{65}Cu_{20}Ru_{15}$ (a), $Al_{68}Cu_{17}Ru_{15}$ (b), $Al_{70}Cu_{15}Ru_{15}$ (c), $Al_{64.5}Cu_{20}Ru_{15}Si_{0.5}$ (d), and $Al_{64}Cu_{20}Ru_{15}Si_1$ (e).

about their origin. It was proposed that the stability of a structure is enhanced by the interaction of the Fermi surface with a Brillouin- or Jones-zone boundary.[28] This interaction causes a minimum in the density of states, or the opening of a pseudogap, to occur when $2|\vec{k}_F|\simeq|\vec{G}|$, where $\vec{k}_F$ is the Fermi wave vector, and $\vec{G}$ is a reciprocal lattice vector. The electronic energy of the system can be reduced, enhancing the stability, if E_F lies in the pseudogap. Technically, in a quasiperiodic material the Jones zone does not exist, but a similar construction can be found using the planes, which are perpendicular bisectors of vectors, in reciprocal space corresponding to strong diffraction peaks. The pseudogap feature may be enhanced in the *i* phases, since the icosahedral symmetry leads to almost spherical Jones zones, which will interact with a large fraction of a spherical Fermi surface.[3,29] In the ordered *i* phases studied, this interaction is expected to be strong, due to the sharpness and intensity of the related diffraction peak (442 002),[3] and hybridization of the *sp* and *d* orbitals.[30,31] This is consistent with the observed values of γ, much reduced below the free-electron value of $\gamma_{FE}\sim 1$ mJ/g atom K^2. The presence of this pseudogap has been verified using x-ray emission and photoabsorption spectroscopies.[17,18,32] The pseudogap feature may also explain the optical measurements of *i*-Al-Cu-Fe,[33] according to a recent calculation.[34] The low-dc conductivity, due to the low density of states $N(E)$, means that the weak Drude part of the ac conductivity is overwhelmed by stronger interband absorption, resulting in a suppression of the Drude peak. While the reduced density of states can account for the low conductivity, a pseudogap width of $\sim 1-2$ eV is too wide to explain the temperature and composition dependences of σ, S, and R_H, as discussed below.

A. Band-structure effects on electron transport

Band-structure calculations performed for the (1/1) approximant α-Al-Mn-Si show a rapid variation in $N(E)$ superimposed on the pseudogap, from the large number of dispersionless bands.[13] The density of states is not known for the materials studied in this paper, but, since the *i* phase is ordered, with self-similar atomic arrangements, it is reasonable to expect that such structures may also exist for the higher-order approximant and *i*-phase structures in the Al-Cu-Fe and Al-Cu-Ru-Si systems. The existence of these structures can be used to provide a rather consistent description of the temperature and composition dependences of σ, S, and R_H. In the absence of band-structure information, only a qualitative account can be given.

Conductivity can be written as[10]

$$\sigma(T)=\int\sigma(E)\left[-\frac{\partial f}{\partial E}\right]dE\ , \tag{1}$$

a weighted average of the conductivity spectrum $\sigma(E)$ over an energy range determined by the Fermi distribution. The increase of σ with temperature can be accounted for if E_F is located in a valley of $\sigma(E)$ that rises several fold above its minimum, within a width $\Delta E\sim 200$ meV. By considering the free energy carried by an electric current, the thermopower $S(T)$ can be written as[10]

$$S(T)=\frac{k_B}{e\sigma}\int\sigma(E)\left[\frac{E-E_F}{k_BT}\right]\left[\frac{\partial f}{\partial E}\right]dE\ . \tag{2}$$

The temperature dependence of S is more sensitive than $\sigma(T)$ to the variation in $\sigma(E)$ near E_F due to the odd function about E_F: $(E-E_F)(\partial f/\partial E)$ in the integrand. Thus, $S(T)$ imposes an added constraint on the variation of $\sigma(E)$. However, except for its shape, the width of $\sigma(E)$ is similar to that inferred from $\sigma(T)$, according to our numerical finding. The unusual temperature dependence and change of sign, observed in the $Al_{65}Cu_{20}Ru_{15}$ sample, can be explained if the Fermi level lies near the bottom of the $\sigma(E)$ valley, but with $\sigma(E)$ being asymmetric (Fig. 10). After all, $N(E)$ appears to be minimized at this composition (Table I); the suggested asymmetry in $\sigma(E)$ may reflect that of $N(E)$ found in band-structure results.[13] As aluminum is substituted for copper to increase the electron density, E_F increases, and moves toward the region where $d\sigma/dE$ is more positive, causing S to become more negative, according to Eq. (2). Meanwhile, σ(4.2 K) should increase several fold, in agreement with experiment. Also, since $(-\partial f/\partial E)$ in Eq. (1) is an even function about E_F, the temperature dependence of σ is expected to decrease as E_F moves further away from the bottom of the $\sigma(E)$ valley. This prediction is also realized in the data. Based on this line of argument, one would be surprised by the fact that when Si, which has

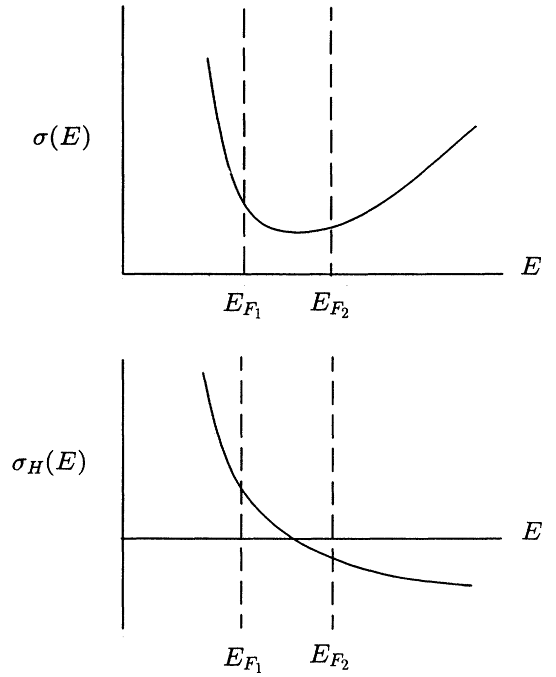

FIG. 10. Schematics of $\sigma(E)$ and $\sigma_H(E)$ consistent with the observed $S(T)$ and $R_H(T)$ in the i-Al-Cu-Ru-(Si) and Al-Cu-Fe systems. The values of E_{F_1} and E_{F_2} shown are suggested Fermi energies for i-$Al_{65}Cu_{20}Ru_{15}$ and i-$Al_{62.5}Cu_{24.5}Fe_{13}$, respectively.

one more valence electron than Al, is substituted for Al, S actually becomes more positive. This apparent paradox can be easily resolved by knowing the nature of electronic states of Si in Al-TM (TM= transition metal) compounds. It was shown earlier, from soft x-ray emission study, that although a "metallic" model may be more appropriate for describing Si in an icosahedral phase of Al-Mn-Si, its s-like states lie deep inside the valence band, just like in covalently bonded Si.[15] In other words, the s states do not contribute at the Fermi level, only the p states do. As a result, there is a depletion in the average electron density as Si is substituted for Al, and E_F decreases. As E_F moves toward the region where $d\sigma/dE$ is more negative, $\sigma(4.2\text{ K})$ should increase, while S should become more positive, which are observed. The typical width of the $\sigma(E)$ valley (~ 0.2 eV) utilized in the discussion is of the same order as the estimated shift in the Fermi level due to the composition variation.

For the Al-Cu-Fe system with varying Fe content, one should consider the status of d-band filling[30,31] in addition to the change in electron density due to the 1–2 at. % variation in Al and Cu discussed above. Adopting the valence of -2.4 found for Fe in the Al_7Cu_2Fe compound,[31] the fractional increase in average valence from 13 at. % to 11 at. % Fe (Table I) of i-Al-Cu-Fe is estimated to be $\sim 0.066/1.9$ resulting in a shift in E_F of $\sim +0.23$ eV. Since $Al_{62.5}Cu_{24.5}Fe_{13}$ has the lowest σ among those studied by us, it is reasonable to assume its Fermi level lies near the bottom of the $\sigma(E)$ valley, as shown in Fig. 10. Similar to the discussion on Al-Cu-Ru-Si, the position of E_F is chosen for the purpose of setting the initial condition. For comparison, the lowest $\sigma(4.2\text{ K})$ value ($\sim 100\ \Omega^{-1}\text{cm}^{-1}$) was reported for i-$Al_{62.5}Cu_{25}Fe_{12.5}$,[6] whose Fermi level is shifted $\sim +0.06$ eV with respect to that of i-$Al_{62.5}Cu_{24.5}Fe_{13}$, consistent with the trend in $\sigma(E)$ shown in Fig. 10. At this point, the discussion on Al-Cu-Ru-Si can be applied, leading to the trend in $\sigma(4.2\text{ K})$ observed, and a change of sign of S from positive to negative, as the Fe content increases.

The Hall conductivity σ_H can be obtained from the Hall coefficient R_H via the expression $\sigma_H = R_H\sigma^2$. Thus we can plot $\sigma_H(T)$ for the i-phase alloys, as shown in Figs. 8 and 9. The trend in $\sigma_H(T)$ can be obtained once $\sigma_H(E)$ is known, since these two quantities are related via an expression similar to Eq. (1). Previously, the positive Hall coefficients observed in some metallic glasses with free-electron-like $|R_H|$ were poorly understood.[27] Explanations given for this behavior were based primarily on the introduction of a negative effective mass m^*, which requires the existence of a well-defined dispersion relation $E(\vec{k})$. The existence of such a well-defined $E(\vec{k})$ is not at all certain in a disordered metallic glass, since $\vec{k}$ is not a good quantum number. Recently, a different approach to this problem was put forth, based on numerical calculations for σ_H, which do not rely on $E(\vec{k})$.[35] The result of these calculations is that an approximate correlation of the sign of σ_H and the derivative of $N(E)$ is obtained:

$$\sigma_H(E) \sim -\frac{dN(E)}{dE} \sim -\frac{d\sigma(E)}{dE} . \tag{3}$$

We have extended the correlation to include $\sigma(E)$ in (3) based on the observed trend in γ and σ, although the scaling relationship between the latter is unknown for the i phases. This correlation can now be utilized to formulate a consistent qualitative explanation for the behavior of $\sigma_H(T)$ in terms of the energy derivative of σ. A schematic plot of $\sigma_H(E)$ based on relation (3) is shown in Fig. 10. Of course, the position of E at which $\sigma_H(E)$ changes sign can only be approximate. Based on the schematics of $\sigma(E)$ and $\sigma_H(E)$, the trend in $\sigma_H(T)$ and its correlation with $S(T)$ for the two i-phase systems upon composition variation are clear. The stronger temperature dependence of σ_H in the i-$Al_{65}Cu_{20}Ru_{15}$ and i-$Al_{62.5}Cu_{24.5}Fe_{13}$ is consistent with the fact that their Fermi levels are closer to the $\sigma(E)$ minimum, and consequently the region where $\sigma_H(E)$ changes sign. It will be of interest to study the $S(T)$ and $\sigma_H(T)$ of i-$Al_{62.5}Cu_{25}Fe_{12.5}$ with the lowest $\sigma(4.2\text{ K})$ value[6] in the i-Al-Cu-Fe system.

B. Unanswered questions

Despite our success in explaining qualitatively the unusual electron-transport behavior observed in ordered i phases, important questions remain in understanding the physics of this class of ordered phases. First, one would be puzzled by the rapid variation of $\sigma(E)$ if it were proportional to $N(E)$. Recent calculations of $\sigma(E)$ based on the band structure of α-AlMn indicate fine structure in $\sigma(E)$ [assuming $\sigma(E) \sim N(E)$] of ~ 0.1–0.2 eV,[36] comparable to that obtained in this work. This finding should be characteristic of the approximant phases, including the r phase of Al-Cu-Fe. Our measurements show that the temperature dependences of the transport properties of i- and r-Al-Cu-Fe are similar, and their σ and γ values are of the same order of magnitude. Therefore, rapid variation in $\sigma(E)$ is expected to exist in a quasicrystal, as obtained here. However, for systems with chemical disorder, such as those studied experimentally, it is doubtful that the fine structures in $N(E)$ alluded to can exist. As a result of the disorder, the electron's scattering time is comparable to that in amorphous metals.[3] This also leads to the question of whether this type of disorder would mitigate the quasiperiodic effects on electronic states. Therefore, the rapid variation in $\sigma(E)$ cannot be explained solely on the basis of band-structure calculations. The nature of electron states inside the pseudogap should be investigated further. Such investigation has just begun.[37]

Finally, one should address the implications of a narrow effective bandwidth on transport properties. At low temperatures, expression (2) can be approximated by

$$S/T \sim (k_B/eE_F)(d\ln\sigma/d\ln E)_{E_F} .$$

With $d\ln\sigma/d\ln E$ being of the order unity, E_F is estimated from measurement of S/T to be ~ 0.1 eV. This order of magnitude of E_F is comparable to that estimated from carrier density inferred from Hall measurement; and it is of the same order as the Debye energy derived from specific-heat results. Thus, the effects of strong electron-phonon renormalization on electron transport should also be considered.

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