Band-Structure Gap and Electron Transport in Metallic Quasicrystals and Crystals

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Studies of icosahedral quasicrystals have revealed a conductivity pseudogap much narrower than the density-of-states pseudogap, resulting in a rapid suppression of electron diffusivity inside the latter. In contrast, measurements of the new metallic compound Al_2Ru show the formation of a semiconducting-like gap with localized gap states. The imminence of Anderson localization and absence of a real gap in quasicrystals are compared with current calculations of electronic properties on metallic quasiperiodic, as well as periodic, systems.

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Structurally ordered icosahedral (*i*) quasicrystals (AlCuRu [1], AlCuFe [2], and AlPdMn [3]) were seen to exhibit conductivity below Mott's minimum metallic value as well as anomalous variation of transport properties with temperature and composition [1–4]. It is now established that the Fermi-surface–Jones-zone interaction [4–6] and atomic potential scattering [7,8] are strong in these materials, giving rise to the distinct pseudogap ($\sim$0.1 Ry) [9] observed, which accounts for the small specific heat [1,2] measured and the interband absorption inferred from ac conductivity [10]. Earlier, it was pointed out [4] that the unusual electron transport might be explained in terms of fine features ($\leq$ 0.01 Ry) inside the pseudogap of crystal-analog phases known as approximants [5,11]. As will be shown later, this band-structure mechanism would require variations as large as an order of magnitude, within some fine features in the density of states $N(E)$. Meanwhile, in view of the order-of-magnitude smaller diffusivity $D \sim 0.2$ cm^2/s than in disordered metals [1,2], and strong potential scattering in the *i* phases, the validity of Boltzmann transport should be called into question. There have been suggestions that electronic states in a quasilattice may not be extended and can even become localized [5,12–14]. A proximity tunneling mechanism based on an internal structural model has also been proposed to explain the low conductivities in *i* phases [15]. Traditionally, the study of electron localization has focused on nonmetallic systems where the scarcity of mobile electrons provides a requisite for the said phenomenon. It would be of general interest to investigate electron localization in ordered systems based on good metals. Moreover, the study of quasicrystals could have implications for other complex crystalline materials such as the boron and fullerene compounds.

To shed light on the nature of electronic states in quasicrystals, a semiquantitative analysis of the conductivity spectrum $\sigma(E)$ inside the pseudogap is performed. $\sigma(E)$ is inferred from transport data and compared with experimental results on $N(E)$. A systematic study of the thermopower is also carried out to complement the analysis. Our study reveals a pseudogap of $\sim$0.01 Ry in the $\sigma(E)$ spectrum, an order of magnitude narrower than that in $N(E)$. To underscore the effects of a narrow $\sigma(E)$ pseudogap on transport properties, we have studied the semiconducting ordered crystalline compound Al_2Ru which has been predicted to have a direct gap of $\sim$0.1 Ry and an indirect gap of $\sim$0.01 Ry [16]. Since the nature of narrow gaps in the two ordered metallic systems is different, the comparison would shed light on the electronic structure in quasiperiodic systems.

Fresh ingots of AlCuFe and AlCuRu *i* alloys and Al_2Ru compound for the present study were made by melting together pure (> 99.95%) elements. In view of the large mismatch in the melting points of Al and Ru, special care was taken to ensure the homogeneity as well as composition of the $Al_{65}Cu_{20}Ru_{15}$ and Al_2Ru ingots. Samples cut from Al_2Ru were annealed in vacuum between 900 and 950 °C for 12 h and then water quenched. Samples of *i*-AlCuFe and AlCuRu were in ribbon form [4]. The phase purity of the samples was confirmed by powder x-ray diffraction. Transport and specific-heat measurements were performed as described elsewhere [4]. High-temperature conductivity data were taken while both heating and cooling the samples to ensure that no extrinsic effects were present. A major difference in the trend of conductivity $\sigma(T)$ of *i* phases and Al_2Ru is noted (Fig. 1). While the change in $\sigma(T)$ of *i* phases is gradual, that of Al_2Ru resembles a semiconductor, as manifested by the distinct break in the $\sigma(T)$ slope of the compound near 400 K. For Al_2Ru, depending on the annealing conditions, its value of σ(295 K) can vary by a factor of 3 while the ratio σ(295 K)/σ(4.2 K) can range from $\sim$1 to 12, the larger ratios being measured in samples with lower σ values. Figure 2 shows the resistivity $\rho(T)$ curve from the sample with the largest ρ(295 K). However, the activated form of $\sigma(T)$ is ubiquitous in all the samples measured, and the energy gap is determined to be 0.15–0.18 eV (Fig. 1). Thus, a real gap in quite good agreement with calculation is seen in this metallic crystal. We also note that our σ(4.2 K) values of $\sim$2 Ω^{-1} cm^{-1} are the lowest reported to date on Al_2Ru as well as Ga_2Ru [17]. Hall effect measurement has yielded an effective hole carrier concentration $p \sim (1-2) \times 10^{19}$ cm^{-3} from 4.2 to 295 K. Specific-heat data are shown in

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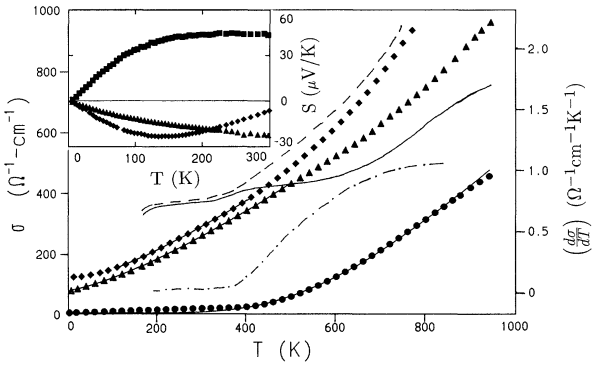

FIG. 1. σ vs T for ◆ i-$Al_{62.5}Cu_{25}Fe_{12.5}$, ▲ i-$Al_{65}Cu_{20}Ru_{15}$, and ● Al_2Ru compound. Solid lines are fits to conductivity models discussed in the text. The small upturn at $T<50$ K noted for the i-AlCuFe alloy is due to quantum correction effects [2(a)]. $d\sigma/dT$ vs T for --- i-AlCuRe, —— i-AlCuRu, and ·-·- Al_2Ru alloys. Inset: Thermopower vs temperature for ■ $Al_{62.5}Cu_{24.5}Fe_{13}$, ▲ $Al_{62.5}Cu_{26.5}Fe_{11}$, and ◆ $Al_{62.5}Cu_{25}Fe_{12.5}$ i phases. σ(4.2 K) values for them are 150, 270, and 120 $\Omega^{-1}\text{cm}^{-1}$, respectively. See text for discussion.

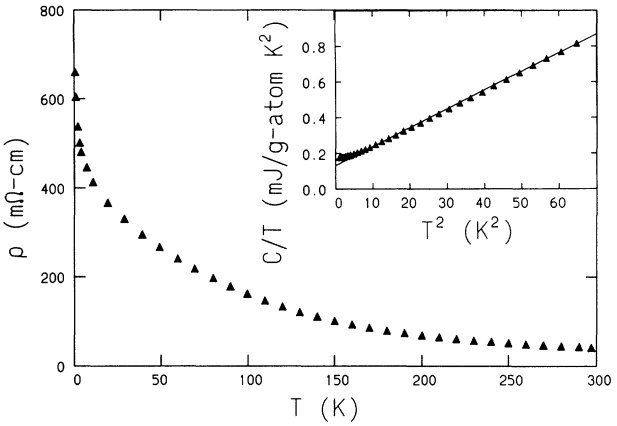

FIG. 2. ρ vs T for Al_2Ru. Inset: Specific-heat data plotted as C/T vs T^2. Solid line is a fit by $C=\gamma T+\beta T^3+\delta T^5$ where $\gamma=0.13$ mJ/g atom K^2, $\beta=0.011$ mJ/g atom K^4, and $\delta=-2.1\times10^{-6}$ mJ/g atom K^6.

the inset to Fig. 2. The electronic contribution γ is found to be 0.13 mJ/g atom K^2 and $\Theta_D=570$ K. The origin of a small anomaly seen below ~2 K is not known. It could be due to the presence of a minute trace of magnetic impurities in the starting materials. Both ρ and γ are significantly higher than inferred from band-structure calculations [16]. This apparent high density of gap states could be the result of impurity band effects due either to small nonstoichiometry (<0.5 at.%), despite our efforts to mitigate it, or to substitutional disorder in the high-temperature phase. The large $\rho(T)$ and its rapid upturn at low T suggest that the gap states are localized. Comparison with conduction models [18] awaits further purification of the samples.

For the i phases, it is clear that weak localization cannot explain the large increase in conductivity $[\sigma(T>290\text{ K})-\sigma(4.2\text{ K})]/\sigma(4.2\text{ K})\gg1$. Utilizing the scheme from the study of conduction near the mobility edge in disordered systems [18], one can in principle deconvolve the conductivity spectrum $\sigma(E)$ (defined as the conductivity as $T\rightarrow0$ with the Fermi level at energy E) from $\sigma(T)$ data via the expression $\sigma(T)=-\int\sigma(E)(\partial f/\partial E)dE$, where f is the Fermi function. However, in practice inversion programs of this kind are known to be very cumbersome and they may not even yield reliable results [19]. But as will be seen, our conclusions about the i phases actually do not depend on the exact functional form of $\sigma(E)$. Thus, a semiquantitative form of $\sigma(E)$ will suffice. We deduce *a priori* basic information about $\sigma(E)$ from transport data. Qualitative analysis of the strong dependence of thermopower and conductivity on temperature and composition indicate that the Fermi level is located near the minimum of a $\sigma(E)$ valley which is rapidly varying and slightly asymmetric [4]. The latter accounts for the sign change in the $S(T)$ curve of $Al_{65}Cu_{20}Ru_{15}$ [1]. Our analysis was based on the Cutler-Mott expressions [18] for $\sigma(T)$ and $S(T)$, where $S(T)=(k_B/e\sigma)\int\sigma(E)[(E-E_F)/k_BT](\partial f/\partial E)dE$. Thus, as E_F shifts from the region of positive $d\sigma/dE$ toward the bottom of a narrow $\sigma(E)$ valley upon varying the composition, the value of σ(4.2 K) decreases and the change of sign (from $-$ to $+$) in $S(T)$ becomes apparent below 295 K. A corollary to these findings is that alloys that show the lowest σ(4.2 K) values [i.e., E_F near $\sigma(E)$ minimum] should also exhibit among the strongest temperature dependences in the thermopowers, as was seen in i-AlCuRu [1] and now in i-AlCuFe (Fig. 1 inset). Thus, the study of i-$Al_{65}Cu_{20}Ru_{15}$ and i-$Al_{62.5}Cu_{25}Fe_{12.5}$ alloys that show the lowest σ(4.2 K) values and the strongest temperature dependences of $S(T)$ and $\sigma(T)$ in the two systems can yield a more characteristic trend of the conductivity spectrum near the pseudogap minimum than other alloys. However, further attempts to fine tune composition would be deemed unnecessary.

Based on the discussion presented, the width of the pseudogap in $\sigma(E)$ can now be estimated. From data and the Cutler-Mott expression for $\sigma(T)$, at $T\sim500$ K the relevant widths of $\sigma(E)$ are estimated to be ~0.1-0.2 eV for the two i phases. To obtain a more quantitative estimate, the data are least-squares fitted to the function $\sigma(E)=A+B|E-E_F|^\alpha$. This is done up to $T\sim400$-500 K (Fig. 1), near Θ_D of the i phases [2,4], in order to minimize the Debye-Waller-factor effect on the pseudogap [20]. In fact, the latter only comes into play above 600 K in the Knight shift for i-$Al_{65}Cu_{20}Ru_{15}$ [21]. Manifestation of this effect may be seen in the clear rise of $d\sigma/dT$ at ~380 and 600 K for the Al-Cu-Fe and Al-Cu-Ru i phases, respectively (Fig. 1). On the other hand, the almost 2 orders of magnitude larger rise of $d\sigma/dT$ for Al_2Ru over a similar temperature range can only be accounted for by a well-defined narrow gap. Meanwhile,

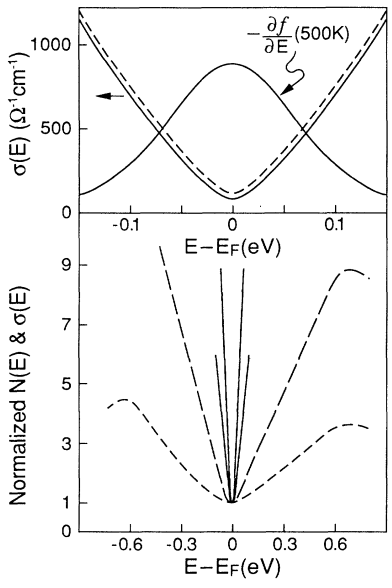

FIG. 3. Upper part: $\sigma(E)$ vs $E-E_F$ for --- i-AlCuFe and —— i-AlCuRu alloys. Also shown is df/dE plotted in an arbitrary but linear scale for $T=500$ K to show consistency of the T and E ranges covered. $\sigma(E)$ for Al_2Ru, if plotted for $|E-E_F|<0.1$ eV, would be too close to the abscissa to be seen since $\sigma(T<300\ \text{K})<20\ \Omega^{-1}\text{cm}^{-1}$. Lower part: --- $N(E)/N(E_F)$ for i-AlCuRu (inner plot) and i-AlCuFe (outer plot); —— $\sigma(E)/\sigma(E_F)$ for i-AlCuRu (inner plot) and i-AlCuFe (outer plot). The slight asymmetries in $N(E)/N(E_F)$ are introduced to resemble calculated results [5].

we have also obtained $\sigma(E)$ for the rhombohedral (R) AlCuFe approximant, using the data from Ref. [4]. The result for this crystalline phase is almost the same as for the i phase, but one should note that this R phase has large unit cells of $\sim$1400 atoms and can thus be considered quasicrystal-like as far as electronic properties are concerned. Attempts are made to fit $S(T)$ data for the group of i phases discussed here, but the results are arbitrary, since the exact location of E_F is not known. However, the analysis of $S(T)$ even when the small asymmetry in $\sigma(E)$ is included [4] does not alter our final conclusion. $\sigma(E)$ can now be compared to the schematic plots of $N(E)$ (Fig. 3) which can be inferred from experiments and calculations. X-ray spectroscopy measurements fix the width ($\sim$0.1 Ry) of the pseudogap in $N(E)$ [9]. $N(E)$ at the pseudogap width is inferred from the approximants [5,11] which are found to have similar $N(E)$ to the i phases [22]. $N(E_F)$ is deduced from specific heat γ [2,4]; $\gamma=0.15$ mJ/g atom K^2 and $\Theta_D=500$ K for i-$Al_{65}Cu_{20}Ru_{15}$ studied here. The widths of $\sigma(E)$ for i-$Al_{62.5}Cu_{25}Fe_{12.5}$ and i-$Al_{65}Cu_{20}Ru_{15}$ are clearly much narrower than the i phase pseudogaps (Fig. 3, lower part). Clearly, applying the standard conductivity equation based on Boltzmann transport would lead to an anomalous behavior of the diffusivity $D\sim\sigma(E)/N(E)$. The latter would decrease rapidly from a metallic-glass-like to an anomalous value as the minimum of the pseudogap is approached. Should any quantitative relation between $\sigma(E)$ and $N(E)$ be taken seriously, in view of the sketchy $N(E)$, one finds that $\sigma(E)\sim N^{\alpha}(E)$ with $\alpha>3$. This transport behavior suggests that Anderson localization is imminent [18].

The formation of a pseudogap is prominent in the approximants [5,11,22]. A recent electronic structure calculation based on icosahedrally arranged plane-wave components and moderately strong pseudopotential results in the formation of a real gap in i crystals but not in regular crystals [23]. Of course, these studies are made within the framework of crystalline solids. On the other hand, Kitaev [14] has shown that electron momentum is not a good quantum number in a quasicrystal and that localization may be imminent. More exact treatments have been carried out on several 1D quasiperiodic models with different forms of atomic potential [5,12,13]. For sufficiently strong potential, recent models indeed show Anderson localization [12,13] with the localized region being bordered by two mobility edges [13]. The present findings of imminent electron localization and the absence of a real gap in high-resistivity ($\sim10^2$ higher than metallic glasses) quasicrystals bear some resemblances to the predictions of these theories. But in view of the observation of a well-defined gap in ordered metallic crystals, the question of whether the absence of a real gap in ordered metallic quasicrystals is the result of quasiperiodicity needs further investigation. Stated more generally, further studies of band-gap formation in ordered metallic systems are in order.

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