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Semiconductorlike transport in highly ordered Al-Cu-Ru quasicrystals

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The electrical conductivity and Hall effect of Al-Cu-Ru and Al-Cu-Fe quasicrystals have been studied in the temperature range 4.2–300 K. Through measurements on samples annealed at various temperatures we found that ordering of the quasicrystalline phase has a strong influence on electrical properties. The largest temperature variations of the Hall coefficient were observed in highly ordered Al-Cu-Ru samples, which also show the highest resistivities. The temperature dependence of the Hall coefficient implies that there exists a change in the carrier density. The electrical transport below 30 K is consistent with weak-localization and electron-electron-interaction theories. Conversely, at temperatures above 30 K, the observations can be consistently understood by recognizing that the increase of carrier density with increasing temperature overcomes the decrease of mobility. The characteristics of transport above 30 K are qualitatively similar to those of normal semiconductors.

The discovery[1,2] of stable quasicrystals (QC's) such as Al-Cu-Fe, Al-Cu-Ru, etc., without phason strain after annealing at high temperatures,[3] has made it possible to investigate the properties of QC's, unobscured by defects. Now it is well known that the stable QC's have extremely high resistivities[4,5] at low temperatures, compared with those of crystalline and amorphous solids. The better the quality of the quasicrystal, the higher the resistivity at low temperatures and the larger the negative temperature coefficient. It has been suggested that the temperature dependences of resistivity and magnetoresistivity in the low-temperature region are well described[6,7] by weak-localization[8] (WL) and electron-electron-interaction[9] (EEI) theories, which were originally developed for highly disordered conductors. The origin of the high resistivity of the stable QC's has been considered to be a combination of two effects: the existence of a pseudogap in the electron density of states at the Fermi level and the localization tendency of electrons near the Fermi level.[10] The former has also been considered to be the origin of the stability of QC's. Recently several authors have claimed that the electronic properties of QC's can be fully explained by the former band-structure effect alone.[11–13] Anomalous temperature dependences of the Hall coefficient and the thermoelectric power have also been reported.[4] However, they are not fully explained.

In this paper, we first describe the effect of ordering of QC phases on electrical properties. Then, we discuss our data on the temperature dependence of the carrier density in terms of WL and EEI theories.

We have investigated the formation of the icosahedral phase with various compositions in the Al-Cu-Ru and Al-Cu-Fe systems in previous papers.[14,15] Alloy ingots of more than 20 different compositions in each system were prepared by arc melting. To ensure complete mixing, each button was turned upside down and remelted four to six times. Thin ribbon samples with a thickness of ~ 20 μm, width of ~ 1 mm, and length of ≤ 10 mm were produced by melt spinning in an argon atmosphere. To obtain a single QC phase, each sample was annealed for 48 h at temperatures between 650 °C and 800 °C. The samples were wrapped in a Ta foil and sealed in a quartz tube with Ar gas. By changing the annealing temperature for each composition, we looked for the best annealing condition to reduce the phason strain. The quality of icosahedral phases was probed by x-ray diffraction. It has been reported[10] that in Al-Mn and Al-Li-Cu QC's the electrical conductivity is very susceptible to traces of second phases located at grain boundaries. Therefore detailed composition analyses were done to an accuracy of about ± 1 at. % by energy-dispersive analysis with x rays (EDX). The diameter of the electron beam is 15 nm. No composition differences between grains and grain boundaries were observed in our samples and no sign of oxide compounds was detected at the grain boundaries. The electrical resistivity and Hall coefficient were measured by a dc four-probe method in the range 4.2–300 K and by the van der Pauw method in the range 20–300 K. We note that the reproducibility of experimental data was confirmed more than ten times for the samples with the same composition and annealing condition.

Samples with quite high resistivity were obtained around the composition of $Al_{63}Cu_{25}Ru_{12}$, in which QC phases get well ordered and show sharp diffraction peaks with quite small full width at half maximum[16] (FWHM). For the samples of $Al_{63}Cu_{25}Ru_{12}$, the highest resistivity was obtained when annealed at 750 °C for 48 h as shown in Fig. 1(a). FWHM of x-ray diffraction peaks and the ratios of the integrated intensity of the (311111) order peak to that of the (222200) fundamental peak of these samples are listed in Table I. The FWHM of diffraction peaks shows that phason strain reduces with increasing annealing temperature. The resolution limit of the FWHM measurement is 0.0060 $Å^{-1}$. We see that there exists no phason strain in the 800 °C annealed sample. In contrast, the intensity of the (311111) order peak is quite large in the 750 °C annealed sample compared with the other two. The reason for the sample annealed at the intermediate temperature thus showing the largest intensity of the (311111) order peak is considered to be as follows. In general, the degree of order of as-quenched samples is fairly low and it is greatly improved when given sufficient annealing treatment. Moreover, the higher the annealing tempera-

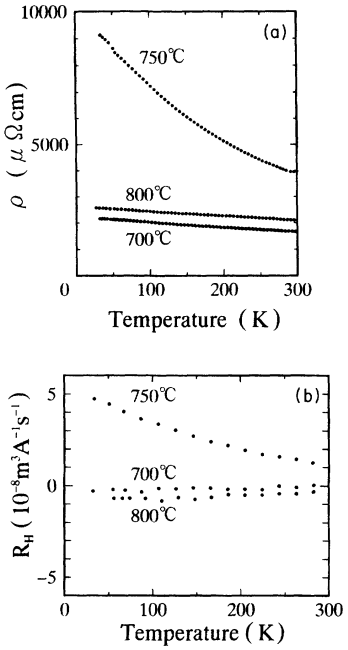

FIG. 1. Temperature dependences of (a) resistivities ρ and (b) Hall coefficient R_H of $Al_{63}Cu_{25}Ru_{12}$ with the annealing temperature of 700 °C, 750 °C, and 800 °C.

ture is, the lower the degree of order of the sample becomes in equilibrium. Therefore, it follows that the 750 °C and the 800 °C annealed samples are almost in equilibrium states, whereas the 700 °C annealed sample is not yet for the present annealing time.

As for the Hall coefficient, it is negative and exhibits a small temperature dependence in the 700 °C and the 800 °C annealed samples, while it is positive and shows a large temperature variation in the 750 °C annealed sample as shown in Fig. 1(b). It is known that the reduction of phason strain raises the resistivity of QC's.[10] One can see that these changes in the resistivity and the Hall coefficient were not only due to the phason strain but also to the ordering of the QC phase. We consider that the resistivity, the Hall coefficient, and the temperature variations in the present sample become larger as the ordering of the QC phase is developed. From this view the change in the sign and the temperature dependence of the Hall coefficient can be interpreted as the result of reformation of the Brillouin zone caused by the ordering of the QC structure.

The highly ordered 750 °C annealed samples of $Al_{63}Cu_{25}Ru_{12}$ are employed for further analyses. We note

TABLE I. FWHM of $Al_{63}Cu_{25}Ru_{12}$ annealed at 700 °C, 750 °C, 800 °C and the integrated intensity of the (311111) order peak normalized with that of the (222200) peak.

Annealing temperature		700 °C	750 °C	800 °C
FWHM ($Å^{-1}$)	(222 200)	0.0118	0.0077	0.0059
	(442 002)	0.0093	0.0077	0.0055
	(664 004)	0.0086	0.0081	0.0060
I_{311111}/I_{222200}		0.86	1.43	1.16

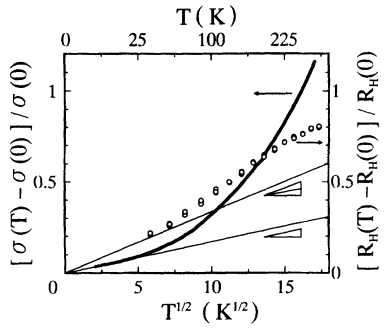

FIG. 2. Temperature dependences of $\{\sigma(T)-\sigma(0)\}/\sigma(0)$ (solid circles) and $\{R_H(T)-R_H(0)\}/R_H(0)$ (open circles) for $Al_{63}Cu_{25}Ru_{12}$. The triangles indicate that the upper solid line has a slope twice as large as that of the lower solid line which is fitted to $\{\sigma(T)-\sigma(0)\}/\sigma(0)$ below 30 K.

that these samples show the largest (311111) order peak of all our Al-Cu-Ru and Al-Cu-Fe samples, and that not even a trace of the second phase is observed at the grain boundaries by EDX. In addition, the samples of this composition exhibit the largest resistivity among all our samples. The conductivity of $Al_{63}Cu_{25}Ru_{12}$ increases nearly in proportion to $T^{1/2}$ below 30 K and roughly T above 30 K.[16] The $T^{1/2}$ dependence is consistent with the prediction of the EEI theory. The T behavior can be explained by the WL theory with the inelastic scattering time determined by electron-electron scattering. Such an explanation has been given in previous papers.[6,7]

According to EEI theory, the magnitude of the Hall coefficient varies as $AT^{1/2}$ at low temperatures, and the coefficient A is twice as large as that of the conductivity. On the other hand, no temperature variation of the Hall coefficient can be expected within the framework of the WL theory. Therefore, on the basis of both theories the temperature dependence of the Hall coefficient can be observed only at low temperatures. The temperature dependence of the Hall coefficient below 30 K is consistent with EEI theory as seen in Fig. 2, whereas it is inconsistent above 30 K. The temperature variation of the Hall coefficient shows an unexpected increase above 30 K. The disagreement between the experimental results and the theories can be simply interpreted as due to the temperature variation of carrier density. Such an interpretation has also been suggested for Al-Cu-Fe QC's.[17]

Here we make one free carrier analysis, the simplest one but applicable to both metals and semiconductors. The result is shown in Fig. 3. The magnitude of carrier density n is two or three orders smaller than that of normal metals, which reflects the situation that the Fermi level locates inside the deep pseudogap. The value of the Hall mobility μ_H is an order of magnitude smaller than normal metals, which is consistent with the weak-localization effect observed at low temperatures. In the high-temperature range above 30 K, n increases rapidly with increasing temperature while μ_H gradually decreases. The temperature dependence of conductivity is, therefore, dominated by that of n. The temperature dependence of the mobility is contrary to that expected from the WL theory and can be attributed to usual electron-phonon scattering. This situation is qualitatively the same as that of normal semiconductors. However, the temperature depen-

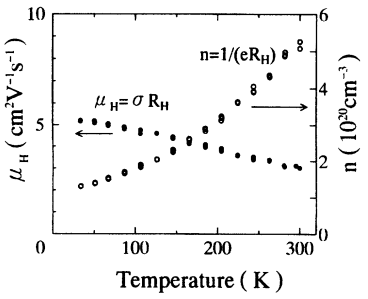

FIG. 3. Hall mobility μ_H and carrier density n as a function of temperature in $Al_{63}Cu_{25}Ru_{12}$.

dence of n is nearly AT^2 and is extremely weak compared to the thermal activation form, $\exp(-E/k_BT)$, of normal semiconductors having an energy gap at the Fermi level. We suggest a comparison of the present result with a previous report in which a direct comparison of the temperature dependence of conductivity of QC's with that of a normal semiconductor has been done.[18]

We decompose $1/\mu_H$ into the temperature-dependent component $1/\mu_i(T)$ and the independent one $1/\mu_e$: $1/\mu_H = 1/\mu_i + 1/\mu_e$. μ_i and μ_e are defined as $1/\mu_i = m/e\tau_i$ and $1/\mu_e = m/e\tau_e$, where τ_i and τ_e are the inelastic and the elastic scattering times, respectively. The temperature dependence of $1/\mu_i$ and $1/\mu_e$ for $Al_{63}Cu_{25}Ru_{12}$ annealed at 750 °C is shown in Fig. 4. The inelastic scattering rate $1/\tau_i$ is not negligible at temperatures above 100 K and becomes comparable with the elastic one $1/\tau_e$ at 300 K. This result is significant because it implies that the constructive interference effect of multiple scattering vanishes at temperatures higher than ~200 K. The frequent occurrence of an inelastic event will destroy the constructive interference responsible for weak-localization effects in this temperature range. We note that this situation is consistent with the initial free electron approximation assumed to calculate n and μ_H. It has been reported that in Al-Cu-Fe and Al-Pd-Mn QC's the weakly localized state is destroyed above 100–200 K.[19] As mentioned above the $1/\mu_i$ was found to increase with increasing temperature and to vary as AT^2, which is consequently followed by $1/\tau_i \propto T^2$. This temperature dependence of the inelastic scattering rate can be attributed to electron-phonon scattering.

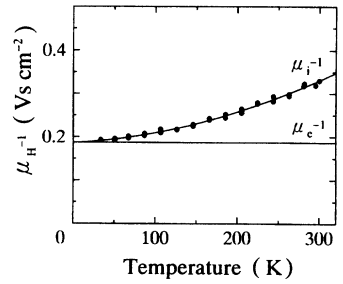

FIG. 4. Temperature dependence of the inverse of Hall mobility $1/\mu_H$ for $Al_{63}Cu_{25}Ru_{12}$, which is decomposed into the temperature-dependent component $1/\mu_i$ and the independent one $1/\mu_e$.

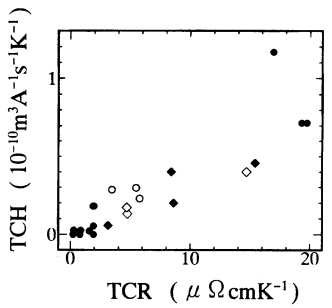

FIG. 5. Plots of TCH vs TCR for Al-Cu-Ru (●, present work; ◆, Ref. 20) and for Al-Cu-Fe (○, present work; ◇, Ref. 20).

The same analysis as carried out here is also possible for samples with other composition and annealing conditions. Of course, a more complicated analysis is required in the strict sense. In particular, it is necessary to take into account two kinds of carriers in case the Hall coefficient changes sign with temperature.[4,11] Though the formula we used for calculating the carrier density seems inadequate for the system, which has both kinds of carriers, one should note that there exists an obvious correlation between the temperature variation of the Hall coefficient and that of resistivity as seen in Fig. 5. Here, the temperature coefficient of Hall coefficient (TCH) and the temperature coefficient of resistivity (TCR) are defined by $|R_{H,300\,K} - R_{H,100\,K}|/(300-100\ K)$ and $|\rho_{300\,K} - \rho_{100\,K}|/(300-100\ K)$, respectively. The data measured by Pierce *et al.*[20] are also included in Fig. 5. The figure shows that the temperature variation of the effective carrier density dominates that of resistivity. Similar correlation between R_H and ρ has been observed recently in Al-Pd-Mn QC.[21] Therefore, we conclude that in the high-temperature region the temperature variation of the effective carrier density is the main origin of the dependences of resistivity and the Hall coefficient.

Recently, theoretical calculations on approximant phases have shown that the electrical conductivity increases with increasing temperature and the Hall coefficient can have a large temperature variation.[11] These results are considered to be caused by the mechanism of the interband transition which takes place between neighboring spiky bands with an energy difference of about $100k_B$. A large increase in the carrier density with increasing temperature can be also explained within this picture.[4,11]

In summary, the ordering of QC structure is found to be responsible for drastic changes of resistivity, Hall coefficient, and their temperature variations. The temperature dependences of resistivity and the Hall coefficient of highly ordered Al-Cu-Ru QC are not consistent with the WL and the EEI theories at temperatures above 30 K. The disagreement with the theories is considered to be due to temperature variation of the carrier density, which is not taken into account in the theories, whereas the mobility decreases with increasing temperature as a result of electron-phonon scattering. These results indicate that the electronic transport of QC's with high resistivity is considered to be qualitatively similar to that of normal semiconductors.

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