Transport Properties of $Al_{65}Cu_{15}Co_{20}$ and $Al_{70}Ni_{15}Co_{15}$ Decagonal Quasicrystals

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The temperature-dependent resistivity of the two-dimensional quasicrystals $Al_{65}Cu_{15}Co_{20}$ and $Al_{70}Ni_{15}Co_{15}$ is studied along the periodic direction (ρ_p) and in the quasiperiodic plane (ρ_q) from 4.2 to 600 K. A transport anisotropy of $\langle\rho_q/\rho_p\rangle \simeq 8$ is measured. In both materials ρ_p is metallic and can be described by a semiclassical electron-phonon scattering model. For ρ_q a nonmetallic behavior is found, suggesting a phonon-assisted tunneling mechanism.

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The discovery of quasicrystalline materials has prompted experimental studies of properties intrinsically related to the quasiperiodic nature of lattices [1,2]. Transport properties in particular are expected to be unique due to the lack of translational invariance [2–4]. The material first found with large quasicrystalline grains was the icosahedral compound AlLiCu, having quasiperiodic order over correlation lengths of several hundred angstroms. Experiments performed on this and related compounds showed several interesting features [5–7], such as suppressed density of states at the Fermi energy and magnetoresistance behavior consistent with weak localization. Recently, transport anomalies were found in the icosahedral AlCuFe [8] and AlCuRu [9,10], which were explained in terms of electronic band-structure effects by the authors. Phillips and Rabe [11] have also suggested an internal structural model for describing these anomalies.

To probe unique transport properties associated with the quasicrystallinity, measurements on quasicrystalline samples had to be compared with measurements on crystalline samples. Hence, the influence of disorder could not be well separated from the intrinsic properties. Since the recent discovery of stable two-dimensional (2D) decagonal quasicrystals [12], it has become possible to study the transport properties both in quasiperiodic and in periodic directions in the same samples. Structural studies of the decagonal $Al_{65}Cu_{15}Co_{20}$ by Chen *et al.* [13] showed spatial quasiperiodicity and evidence for an entropy stabilization mechanism. Resistivity measurements reported by Shu-yuan *et al.* [14] for $Al_{65-x}Si_xCu_{15}Co_{20}$, from 80 to 400 K, indicated metallic behavior along the periodic direction and nonmetallic behavior in the quasiperiodic plane. Measurements by Shibuya, Hashimoto, and Takeuchi [15] for $Al_{70}Ni_{15}Co_{15}$, from 4.2 to 300 K, showed a positive temperature coefficient in both periodic and quasiperiodic directions.

In an attempt to characterize unique features of anisotropic transport in quasicrystals, we have performed measurements from 4.2 to 600 K in the 2D decagonal compound $Al_{65}Cu_{15}Co_{20}$ (AlCuCo) and compared with data on the related compound $Al_{70}Ni_{15}Co_{15}$ (AlNiCo). An anisotropic resistivity between the quasiperiodic (ρ_q) and the periodic (ρ_p) directions was measured and found to vary from $\rho_q/\rho_p \simeq 10$ at 4.2 K to $\simeq 6$ at 600 K. The resistivity along the periodic direction is metallic over the entire temperature range, providing evidence for extended states and the absence of dominant impurity scattering. The ρ_p data are in quantitative agreement with the Bloch-Gruneisen model of transport in metals. In AlCuCo, ρ_q saturates below 100 K and decreases linearly with temperature above 100 K with a sharp change in slope at $\simeq 500$ K. In AlNiCo, ρ_q increases to a maximum at $\simeq 200$ K and subsequently shows nonmetallic behavior with a quadratic temperature dependence. The ρ_q data are in qualitative agreement with the model of phonon-assisted tunneling of carriers in extended states.

The samples used in this study were extracted from premixed ternary alloys which were solidified at a 0.1°/h rate [16]. Single-grain crystals were oriented by x-ray diffraction, then cut and polished to samples with edge lengths of $\simeq 0.5$–5 mm. The preparation ensured that the surfaces were free of extrinsic conductive deposits often observed in crystals taken directly out of the melt. The x-ray studies showed diffraction peaks with instrumentation limited widths, indicating quasicrystalline order over correlation lengths of $\simeq 2000$ Å. Independent evidence of quasicrystallinity was provided by scanning tunneling microscopy where individual atoms were resolved in quasicrystalline order [17]. Contacts were made by using an Ag conducting paste and annealing at $\simeq 550$ K. Contact resistances were typically $\simeq 10^{-3}$ $\Omega\,\mathrm{cm}^2$. An ac current with amplitude 4 mA and frequency 11.5 Hz was applied and the voltage was measured using a lock-in technique. The errors in the resistivity measurements were typically less than 0.1%. The procedure used for deconvolving the resistance measurements along the periodic and quasiperiodic directions to obtain the respective resistivity components is based on the method introduced by Logan, Rice, and Wick [18] and is described in detail elsewhere [19]. Data above room temperature were taken with the samples placed in an oven through which a constant flow of dry nitrogen was maintained. Table I summarizes the sample geometries, values of the room-temperature resistivity, and anisotropy.

The resistivity anisotropy (Fig. 1) is very similar for

TABLE I. Dimensions and resistivities of the samples used in the study. For the slabs, L_p and L_q denote lengths along the periodic and quasiperiodic directions, respectively, and d the thickness. For the cylinders and disk, L_p and L_q denote the length along the cylinder axis and d the diameter. In samples A and B, resistances were measured along the L_p,L_q directions and the method by Logan, Rice, and Wick [18] (LRW) was used to obtain ρ_p,ρ_q [19].

Sample	Compound	Shape	L_p (mm)	L_q (mm)	d (mm)	ρ_p (300 K) ($\mu\Omega$ cm)	ρ_q (300 K) ($\mu\Omega$ cm)	ρ_q/ρ_p	Measurement
A(○)	AlCuCo	Slab	1	0.5	0.5	42	332	8	LRW
B(□)	AlNiCo	Slab	2.5	1.4	0.3	48	338	7	LRW
C(×)	AlCuCo	Cylinder	2	···	0.35	55	···	···	Four probe
D(+)	AlCuCo	Cylinder	···	1.4	0.3	···	260	···	Four probe
E(△)	AlCuCo	Disk	0.5	···	1	···	330	···	van der Pauw

AlCuCo (A,○) and AlNiCo (B,□). The mean value of ρ_q/ρ_p is a factor of 2 to 3 larger than that reported by Shu-yuan *et al.* [14] for $Al_{62}Si_3Cu_{20}Co_{15}$ and by Kimura *et al.* [6] for the resistivity ratio of the quasicrystalline to the crystalline phases of AlLiCu. Along the periodic direction the resistivity is metallic [Fig. 2(a)] with temperature coefficients $\alpha=(d\rho_p/dT)/\rho_{p0}^*=1.23\times10^{-3}$ K^{-1} for AlCuCo (A,○) and $\alpha=1.06\times10^{-3}$ K^{-1} for AlNiCo (B,□). The quantity ρ_{p0}^* was determined by linear extrapolation of the high-temperature resistivity to $T=0$. Comparable values of α were measured in the crystalline phase of AlLiCu [6]. However, metallic glasses with positive temperature coefficients and $\rho(300\text{ K})\simeq50$ $\mu\Omega$ cm have typically a factor of 5 smaller values of α. The relatively large α values found in AlCuCo and AlNiCo suggest that scattering by impurities along the periodic direction does not play a dominant role. The electronic mean free path can be estimated by $l_p=3/e^2\rho_{p0}^* v_F N_F$ which yields for low temperatures $l_p\simeq26$ Å, where we have inserted the free-electron values found in typical metals for the Fermi velocity $v_F=10^8$ cm/s and for the density of states at the Fermi level $N_F=0.33$ states/eV atom.

The temperature coefficient α and the mean free path l_p can be used to determine the electron-phonon coupling strength $\lambda=(1.22\times10^{-4})(\alpha v_F/l_p)\simeq0.8$, which is comparable with that found in strongly coupled metals [20].

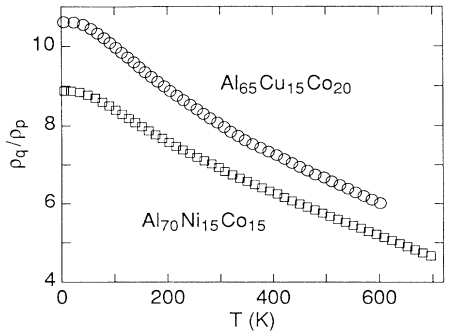

FIG. 1. Temperature dependence of the anisotropy between the resistivity in the quasiperiodic plane and the periodic direction.

From specific-heat data Wagner *et al.* [5] obtained $\lambda\simeq0.33$–0.45 in AlLiCu and AlCuMg. The large value estimated for λ in AlCuCo and AlNiCo implies that the materials undergo a superconducting transition at a few degrees. However, we found no evidence of superconductivity down to 0.6 K in AlCuCo and 4.2 K in AlNiCo. The overestimate of λ suggests that the assumption of the density of states being equal to the free-electron value

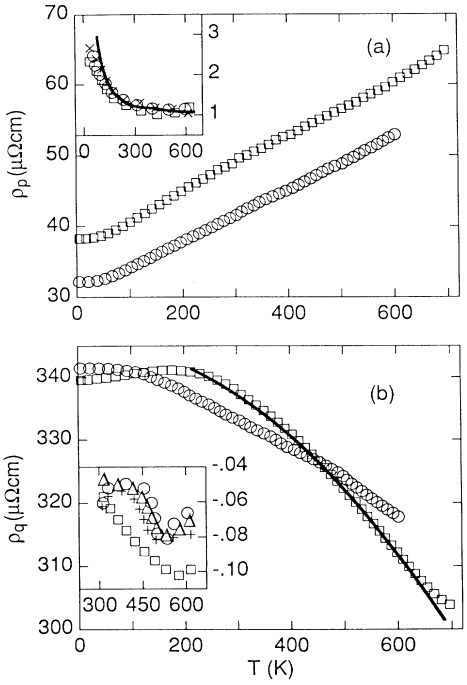

FIG. 2. (a) Temperature dependence of the resistivity along the periodic direction in $Al_{65}Cu_{15}Co_{20}$ (A,○) and $Al_{70}Ni_{15}Co_{15}$ (B,□). Inset (a): Temperature dependence of $d\ln(\rho_p-\rho_{p0})/d\ln T$ for $Al_{65}Cu_{15}Co_{20}$ (A,○;C,×) and $Al_{70}Ni_{15}Co_{15}$ (B,□). The solid line is a fit to Bloch-Gruneisen theory with $\Theta_D^*=400$ K. (b) Temperature dependence of the resistivity in the quasiperiodic plane in $Al_{65}Cu_{15}Co_{20}$ (A,○) and $Al_{70}Ni_{15}Co_{15}$ (B,□). Inset (b): Temperature dependence of $d\rho_q/dT$ plotted in the region where a change in slope is observed in $Al_{65}Cu_{15}Co_{20}$ (A,○;D,+;E,△). No such feature is evident in $Al_{70}Ni_{15}Co_{15}$ (B,□).

may not be valid. A suppressed density of states at the Fermi level is feasible as observed in the icosahedral compounds [5–7], implying a larger value for l_p than the above estimate. A possible mechanism for the suppression has been proposed by Nagel and Tauc [21] for metallic glasses. The authors suggested that the stability of metallic glasses is the result of a reduced density of states at the Fermi level, an argument which could be applied also to quasicrystals [11,22].

Assuming that electron-phonon normal processes dominate the scattering, the semiclassical Bloch-Gruneisen (BG) model [23] yields

$$\rho_{\mathrm{BG}} = mv_F/ne^2l \propto (T^5/\Theta_D^{*3})F(\Theta_D^*/T)\,,$$

where m is the mass of the carriers, e the charge, n the carrier density, and l the mean free path. The transport Debye temperature Θ_D^* determines the onset of small angle scattering. Θ_D^* is generally smaller or on the order of the thermodynamic Debye temperature Θ_D. The function F is an integral over the Fermi surface taking into account the randomization of the carrier momentum due to phonon scattering. The integral is constant for $T \ll \Theta_D^*$ leading to $\rho_{\mathrm{BG}} \propto T^5$, and is proportional to $(\Theta_D^*/T)^4$ for $T > \Theta_D^*$ leading to $\rho_{\mathrm{BG}} \propto T$. In the inset of Fig. 2(a) we plot the temperature dependence of the logarithmic derivative $d\ln(\rho_p - \rho_{p0})/d\ln T$ obtained from the data (A,○;B,□;C,×) and compare with that calculated from Bloch-Gruneisen theory (solid line). Good agreement is found from 150 to 600 K for both materials using $\Theta_D^* = 400$ K. Deviations are obvious for temperatures below 100 K possibly due to processes neglected in the simple BG model, such as umklapp processes.

In Fig. 2(b) the temperature-dependent resistivity in the quasiperiodic plane is plotted. Note that the behavior of ρ_q is different in both materials. In AlCuCo we find a linear decrease above 100 K with a sharp change in slope at 500 K. In the inset of Fig. 2(b) this anomalous high-temperature behavior is illustrated for samples A(○), D(+), and E(△) as an expanded plot of $d\rho_q/dT$ vs T. In all three samples we note a sharp jump of the derivative with midpoints at 450 K (D), 470 K (E), and 490 K (A). The reduced slopes change from $\alpha \simeq -1.48\times10^{-4}$ K^{-1} to $\alpha \simeq -2.36\times10^{-4}$ K^{-1} within a temperature interval of 80°. As the measurements were performed in three different contact arrangements, we rule out the possibility of errors in the deconvolution procedures causing the anomalous feature. Differential scanning calorimetry measurements on AlCuCo samples could not verify the occurrence of any first-order phase transition around 500 K [24].

Although the saturation behavior of ρ_q below 100 K is qualitatively similar to that measured in metallic glasses, the temperature coefficients of the latter are typically 3 times larger in magnitude at comparable resistivities [25]. Hence, the behavior of ρ_q deviates from that expected from the Mooij correlation between α and ρ for metallic glasses near the metal-insulator transition. Furthermore, we measured ρ_q in AlCuCo below 4.2 K and found that the saturation essentially persists down to $\simeq$0.6 K, providing no evidence for localization behavior. To check for the possibility of magnetic scattering, susceptibility measurements were performed in AlCuCo crystals [26], which showed a temperature-independent diamagnetic behavior ($|\chi| \simeq 10^{-7}$ emu/g) from 10 to 300 K. According to a classification scheme of metallic glasses in terms of their magnetic states [27], this suggests that AlCuCo is similar to nonmagnetic metallic glasses in which the Fermi level is in the sp band.

Figure 2(b) also shows the data obtained on AlNiCo (B,□) where ρ_q initially increases with T and above 200 K decreases with a quadratic dependence. The data are in good agreement with $\rho_q = \rho_{q\max} - \beta T^2$ for $\beta = 10^{-4}$ $\mu\Omega$ cm/K^2 over a temperature range of 200 to 700 K [solid line in Fig. 2(b)]. The lack of any sharp feature at 500 K, as seen in AlCuCo, is evident from the plot of $d\rho_q/dT$ vs T in the inset of Fig. 2(b) (B,□). Previous measurements of a negative T^2 behavior in metallic glasses have been accounted for by multiphonon scattering processes [25]. This is treated within the framework of the Faber-Ziman theory where the resistivity depends on the Debye-Waller factor [23]. At low temperatures ($T < \Theta_D$) the Debye-Waller factor can be expanded in powers of T resulting in $\rho = \rho_0 - \beta T^2$. However, the T^2 dependence measured up to 700 K in AlNiCo is inconsistent with the Faber-Ziman model, since Θ_D is likely to be on the order of $\Theta_D^* = 400$ K [Θ_D(AlLiCu) = 340 K, Ref. [6]].

Besides models based on the Boltzmann transport theory for explaining negative temperature coefficients [28], a mechanism based on localization theory was proposed by Jonson and Girvin [29] for random metal alloys. The authors showed that even in the regime of extended states prior to localization, a breakdown in the adiabatic phonon approximation leads to an enhanced mobility with increasing temperature via phonon-assisted tunneling. The dynamics of the electron-phonon interaction determines the negative temperature coefficient of the resistivity. The data on AlCuCo and AlNiCo indicate the existence of extended states along the periodic direction without dominant impurity scattering. The lack of evidence for localization behavior in the quasiperiodic plane further supports the notion that the materials are in the regime of extended states. The measured negative temperature coefficients for ρ_q could be accounted for by phonon-assisted tunneling where the carriers are able to hop between states of different energies owing to a dynamic energy exchange with the phonons. The change in slope at 500 K in AlCuCo possibly arises from the excitation of high-energy phonons [22]. The linear and quadratic temperature dependences of ρ_q in AlCuCo and AlNiCo, respectively, depend on the details of the dynamics of the electron-phonon interaction. The initial increase of

ρ_q with T in AlNiCo can be attributed to conventional electron-phonon scattering. In Ref. [11] it was supposed that real tunneling through domain walls with low N_F, a kind of inhomogeneous Nagel-Tauc model, occurs in high-resistivity quasicrystals. At present the nature of the domains is not clear and remains to be investigated in further experiments.

In conclusion, we find a large temperature-dependent transport anisotropy in $Al_{65}Cu_{15}Co_{20}$ and $Al_{70}Ni_{15}Co_{15}$ crystals. The resistivity in the periodic direction is quantitatively accounted for by the semiclassical Bloch-Gruneisen theory of electron-phonon scattering. The resistivity in the quasiperiodic plane can be described qualitatively by a model of phonon-assisted tunneling in the regime of extended states.

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[1] D. Shechtman *et al.*, Phys. Rev. Lett. **53**, 1951 (1984).
[2] For a review, see *Physics of Quasicrystals,* edited by P. J. Steinhardt and S. Ostlund (World Scientific, Singapore, 1987).
[3] K. Ueda and H. Tsunetsugu, Phys. Rev. Lett. **58**, 1272 (1987).
[4] M. Goda, J. Phys. Soc. Jpn. **56**, 1924 (1987).
[5] J. L. Wagner *et al.*, Phys. Rev. B **38**, 7436 (1988).
[6] K. Kimura *et al.*, J. Phys. Soc. Jpn. **58**, 2472 (1989).
[7] J. L. Wagner, B. D. Biggs, and S. J. Poon, Phys. Rev. Lett. **65**, 203 (1990).
[8] B. D. Biggs, Y. Li, and S. J. Poon, Phys. Rev. B **43**, 8747 (1991).
[9] B. D. Biggs, S. J. Poon, and N. R. Munirathnam, Phys. Rev. Lett. **65**, 2700 (1990).
[10] T. Klein *et al.*, Europhys. Lett. **13**, 129 (1990).
[11] J. C. Phillips and K. M. Rabe, Phys. Rev. Lett. **66**, 923 (1991).
[12] L. X. He, Y. K. Wu, and K. H. Kuo, J. Mater. Sci. Lett. **7**, 1284 (1987); A. P. Tsai, A. Inoue, and T. Masumoto, Mater. Trans. **30**, 300 (1989).
[13] H. Chen *et al.*, Phys. Rev. Lett. **65**, 72 (1990).
[14] L. Shu-yuan *et al.*, Phys. Rev. B **41**, 9625 (1990).
[15] T. Shibuya, T. Hashimoto, and S. Takeuchi, J. Phys. Soc. Jpn. **59**, 1917 (1990).
[16] A. R. Kortan *et al.*, Phys. Rev. B **40**, 9397 (1989).
[17] A. R. Kortan *et al.*, Phys. Rev. Lett. **64**, 200 (1990).
[18] B. F. Logan, S. O. Rice, and R. F. Wick, J. Appl. Phys. **42**, 2975 (1971).
[19] S. Martin *et al.*, Phys. Rev. Lett. **60**, 2194 (1988).
[20] P. B. Allen, Phys. Rev. B **36**, 2920 (1987); M. Gurvitch, Physica (Amsterdam) **135B**, 276 (1985).
[21] S. R. Nagel and J. Tauc, Phys. Rev. Lett. **35**, 380 (1975).
[22] J. C. Phillips (private communication).
[23] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge Univ. Press, Cambridge, 1972), p. 225.
[24] H. S. Chen (unpublished).
[25] M. A. Howson and B. L. Gallagher, Phys. Rep. **170**, 265 (1988).
[26] B. Batlogg (unpublished).
[27] U. Mizutani, Prog. Mater. Sci. **28**, 97 (1983); Mater. Sci. Eng. **99**, 165 (1988).
[28] For a review, see D. G. Naugle, J. Phys. Chem. Solids **45**, 367 (1984).
[29] M. Jonson and S. M. Girvin, Phys. Rev. Lett. **43**, 1447 (1979).