Band Structure Effects of Transport Properties in Icosahedral Quasicrystals

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Transport properties and optical conductivity are calculated for the crystalline approximant AlMn alloy. The number of electrons at the Fermi energy is very small and, based on the band structure, the anomalously small dc conductivity and temperature dependent thermoelectric power are explained. A model calculation for the two-dimensional Penrose lattice with random phason strain shows that it becomes more conductive than the perfect Penrose lattice. We propose the mechanism of the interband transition by phason randomness and inelastic scattering for the origin of the anomalous conductivity in real quasicrystals.

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The electronic density of states in quasicrystals has a pronounced pseudogap at the Fermi energy which stabilizes the quasiperiodic structure [1–3]. The calculated density of states shows very spiky structures in the whole energy range and the width of each peak is of order of 0.01–0.02 eV or less, which is another outcome of the quasiperiodicity [1,4].

Experimental results show very curious transport properties in quasicrystals. The absolute values of conductivity are anomalously small [5,6] and almost reach the values of doped semiconductors, e.g., 1 $(\Omega\,\mathrm{cm})^{-1}$ at 0.5 K in AlPdRe [7]. Generally higher qualified samples show lower conductivity. Amorphous systems of almost the same atomic compositions show the values of normal transition metal alloys [8]. The conductivity of these high qualified samples increases with increasing temperatures above 10 K. The temperature and magnetic-field dependence of the transport properties remind us the weak localization and, therefore, the transport properties have often been analyzed based on weak localization theory [8,9], though its applicability is questionable [10]. In fact, weak localization theory does not explain the small absolute values of the conductivity, because the short mean free path of the low conductivity contradicts weak localization. The conductivity in decagonal quasicrystals is very low and increases with increasing temperature within the quasiperiodic plane, and, on the other hand, that along the periodic axis is larger by more than a factor of 10 and decreases with temperature [11,12].

Many quasicrystals have associated crystalline compounds called crystalline approximants, whose local atomic structures are almost the same as those in the quasicrystals. In crystalline approximants such as AlMnSi [13,14] and AlCuFe [15,16], the transport properties and optical properties, both their absolute values and temperature dependence are quite similar to the quasicrystalline systems.

The crystalline approximant α-AlMnSi ($Al_{72.5}Mn_{17.4}Si_{10.1}$), the [1/1] approximant, is of simple cubic $Pm3$ symmetry and contains 138 atoms in a unit cell [17]. We use a model $Al_{114}Mn_{24}$ for α-AlMnSi, whose structure is a simple cubic aggregation of icosahedra of 54 atoms, called Mackay icosahedra with Al atoms substituted for all Si atoms. The electronic structure was calculated self-consistently by the linear muffin-tin orbital method in the atomic sphere approximation (LMTO-ASA) [18]. Both for Al and Mn atoms, s, p, and d states are included with 20 $\mathbf{k}$ points in the irreducible Brillouin zone for the self-consistent calculation and 35 $\mathbf{k}$ points for the final results of the density of states (DOS) and the conductivity elements [19]. It should be mentioned that the spiky structures in the DOS and conductivity are more pronounced by increasing the $\mathbf{k}$ points. The effects of Al d states are appreciable both below and above the Fermi energy. The Al d states near the Fermi energy push down the occupied Al p states due to the orthogonality within the same atomic sphere and narrow the occupied bandwidth. Based upon the resulting electronic band structure and the Boltzmann theory, the transport coefficients $\sigma_{\alpha\beta}$ and $\sigma_{\alpha\beta\gamma}$ can be calculated:

$$\sigma_{\alpha\beta} = e^2\tau\left(\frac{n}{m^*}\right)_{\alpha\beta} = \frac{e^2\tau}{\Omega_0}\sum_{n,\mathbf{k}} v_{n\alpha}(\mathbf{k})v_{n\beta}(\mathbf{k})\left(-\frac{\partial f}{\partial E_n(\mathbf{k})}\right), \tag{1}$$

$$\sigma_{\alpha\beta\gamma} = -\frac{e^3\tau^2}{\hbar\Omega_0}\sum_{n,\mathbf{k}} v_{n\alpha}(\mathbf{k})[\mathbf{v}_n(\mathbf{k})\times\nabla_{\mathbf{k}}]_\gamma v_{n\beta}(\mathbf{k})\left(-\frac{\partial f}{\partial E_n(\mathbf{k})}\right), \tag{2}$$

where $E_n(\mathbf{k})$, Ω_0, τ, T, and f are the energy of the band n at $\mathbf{k}$, the unit cell volume, the relaxation time, the temperature, and the Fermi-Dirac function, respectively, and $\mathbf{v}_n(\mathbf{k}) = \nabla_{\mathbf{k}}E_n(\mathbf{k})/\hbar$. The Hall coefficient and the thermoelectric power can be evaluated by

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$$R^H_{xyz} = \sigma_{xyz}/\sigma_{xx}\sigma_{yy} \ , \tag{3}$$

$$S_{\alpha\alpha} = -\frac{k_B}{e}\int d\varepsilon\left(\frac{\varepsilon-\mu}{k_BT}\right)\sigma_{\alpha\alpha}(\varepsilon)\left(-\frac{\partial f}{\partial\varepsilon}\right)\Big/\int d\varepsilon\sigma_{\alpha\alpha}(\varepsilon)\left(-\frac{\partial f}{\partial\varepsilon}\right) . \tag{4}$$

The ac conductivity $\sigma^\alpha_{\rm IB}(\omega)$ is also given by

$$\sigma^\alpha_{\rm IB}(\omega) = \frac{2e^2}{i\omega m^2\Omega_0}\sum_{nn'}\sum_{\mathbf{k}}|P_{n\mathbf{k}:n'\mathbf{k}}{}^\alpha|^2 f(E_n(\mathbf{k}))[1-f(E_{n'}(\mathbf{k}))]\left(\frac{\hbar\omega}{E_n(\mathbf{k})-E_{n'}(\mathbf{k})}\right)^2$$
$$\times\left(\frac{1}{E_n(\mathbf{k})-E_{n'}(\mathbf{k})+\hbar(\omega+\frac{i}{\tau_{\rm IB}})}+\frac{1}{E_n(\mathbf{k})-E_{n'}(\mathbf{k})-\hbar(\omega+\frac{i}{\tau_{\rm IB}})}\right) . \tag{5}$$

Here $P_{n\mathbf{k}:n'\mathbf{k}}{}^\alpha$ is the transition matrix element of the momentum operator $P_\alpha = (\hbar/i)(\partial/\partial x_\alpha)$, and $\tau_{\rm IB}$ is the relaxation time for the interband transition.

The dc conductivity at $T = 0$ as a function of the Fermi energy is shown, together with the DOS, in Fig. 1, where the self-consistently determined Fermi energy is -0.0596 Ry and the pseudogap appears between -0.08 Ry and -0.02 Ry. The total number of bands is $(1s+3p+5d)\times 138 = 1242$ with spin degeneracy in the energy range of about 2 Ry wide, and the average DOS is about 1×10^3 states/(Ry unit cell). The calculated DOS is a very sensitively fluctuating function of energy; it actually varies between 1200 states/(Ry unit cell) and 70 states/(Ry unit cell) within a very small energy range of less than or equal to 0.01–0.02 eV. Once all bands are hybridized and repulsively interacting (anticrossing), the energy separation between two adjacent bands is just 2×10^{-3} Ry. Therefore, the DOS may fluctuate around the value of 1000 states/(Ry unit cell), which is really the case here. The effective value of "(electron number per unit cell)/(effective mass)" $(n/m^*)_{\alpha\alpha}$ is fluctuating around 0.5, between 0.1 and 1, or even less. The unit cell size of α-AlMnSi is $(1.268\ \text{nm})^3$. Assuming the typical value of the relaxation time τ for transition metal alloys, e.g., 10^{-15} s, then we can obtain a value $\sigma \simeq 13.8$–$138.0\ (\Omega\,\text{cm})^{-1}$, which explains the experimentally observed anomalously small conductivity. The reason for this small value is partly due to large effective masses, but mainly due to the small number density of electrons on the Fermi surface. Only a few bands intersect the Fermi surface with a small dispersion and several small electron and hole pockets appear. Most of the calculated effective masses of respective bands are between 2 and 10 near the Fermi energy. The spikiness of the DOS is actually the origin of the small value of $(n/m^*)_{\alpha\alpha}$. Furthermore, at several energies a small variation of the DOS causes a large variation of $(n/m^*)_{\alpha\alpha}$, and the character of wave functions is very important. The Fermi energy may not be pinned at the peak position of the DOS because of the associated structural instability. Any small variation in atomic compositions shifts the position of the Fermi level from a narrow valley to another and causes a large variation of conductivity at $T = 0$ K as reported experimentally [5,20,21].

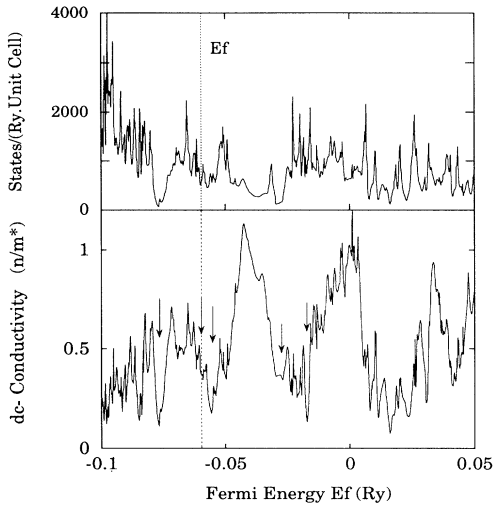

FIG. 1. The dc conductivity [actually the value of $(n/m^*)_{xx}$] and the density of states in α-AlMn as a function of the Fermi energy. The dashed line indicates the Fermi energy -0.0596 Ry determined by the self-consistent calculation. The arrows indicate the position of the Fermi energies for the thermoelectric power shown in Fig. 3.

The spikiness of the DOS is due to, in other words, folded bands in the superstructure of crystalline approximants and, therefore, if neglecting any elastic or inelastic scattering, the DOS in quasicrystals may become extremely singular. A small amount of disorder does not completely smear out the spikiness, because a few periods of the crystalline approximant with a small Fermi velocity may be enough to form the spiky structure of the DOS. However, the actual situation should be examined more carefully because the intrinsic chemical disorder is crucial.

The Hall conductivity (in cgs Gauss units) and the thermoelectric power are shown in Fig. 2 and Fig. 3, respectively. These are properties independent of the relaxation time τ, and the temperature dependence originates from the very fine structures of the DOS and the distribution function. The fluctuation of the Hall coefficient in Fig. 2 is more complicated because it depends sensitively

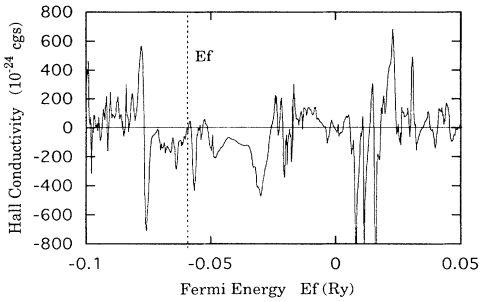

FIG. 2. The Hall conductivity in α-AlMn as a function of the Fermi energy. The Fermi energy by the self-consistent calculation is -0.0596 Ry, shown by the dashed line.

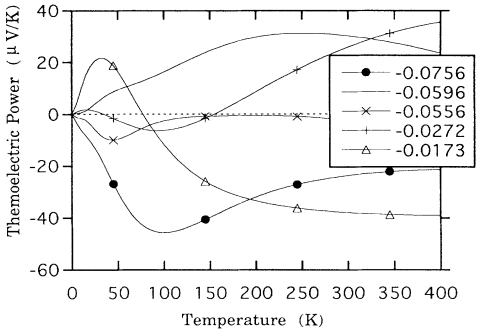

FIG. 3. The calculated thermoelectric power in the model α-AlMn. The assumed Fermi energies are -0.0756, -0.0596, -0.0556, -0.0272, and -0.0173 Ry, and also indicated in Fig. 1.

on whether the contribution comes from either an electron pocket or a hole pocket. The positions of valleys in the dc conductivity approximately correspond to the positions changing the sign of the Hall coefficient, which implies the crucial role of the band structure effects. Then the Hall coefficient is sensitive to the Fermi energy and possibly on the atomic composition as observed [5,20,21]. The thermoelectric power in Fig. 3 changes nonsystematically and very drastically with very little change of Fermi energy because of the fine spiky structure in the conductivity, and the peak value is determined by the energy derivative of the dc conductivity $\sigma(\varepsilon)$. An assumed Fermi energy of each curve is chosen to be at the bottom of the conductivity curve shown by an arrow in Fig. 1. All have a structure at 100 K and 300–400 K. These overall features of the thermoelectric power show a quite reasonable coincidence with the observed one with an appropriate Fermi energy [13,15].

The observed optical conductivity is also unusual, showing a linear energy dependence in a wide energy range and no Drude peak [14,16]. The absence of the Drude peak is due to the small density of conduction electrons at the Fermi energy and the short relaxation time for intraband scattering [14,16]. The optical conductivity due to the interband transition is shown in Fig. 4, with several different relaxation times τ_{IB}. The linearity and the peak position are reasonably reproduced in the calculation. The linearity is due to the absence of the Drude term and the presence of the pseudogap at the Fermi energy. The peak at 0.25 Ry is the contribution of the interband transition.

In order to understand the effect of randomness at $T = 0$ K, the conductance of the two-dimensional Penrose lattice with random phason strain is calculated in the tight-binding nearest neighbor model with a constant hopping integral t as a function of the Fermi energy and the random phason density [22]. We can see that at some Fermi energy, the conductance reduces with increasing the density of the random phason. The static random phason destroys the quasiperiodicity of the systems and the states are localized in a two-dimensional "random" system. However, the conductance increases with increasing static random phason density at other energies (e.g., $E/t = 0.1$) for a finite system size, as shown in Fig. 5. To introduce the phason strain, we shift the grid lines from their ideal positions for the perfect Penrose lattice while constructing the lattice by the grid method. The parameters shown in the figure specify the width of the random distribution of this shift normalized by the average grid-line spacing. Presumably this energy $E/t = 0.1$ locates in a very small energy gap of the perfect two-dimensional Penrose lattice. With increasing density of the random phason strain, the dense and very small energy gaps are smeared out. Then the DOS increases or is smeared out and the channels of the electronic transport open out. In other words, the interband transition due to elastic scattering by the random phason strain increases the conductivity in the two-dimensional Penrose lattice. The spiky structure exists in the three-dimensional quasicrystals, though it is not the actual energy gap, and the phason assisted conduction is presumably the case also in three-dimensional quasicrystals.

To understand the temperature dependence of the dc conductivity, the effects of the random phason strain can be replaced with the effects of interband transition due to electron-phonon or electron-electron inelastic scatter-

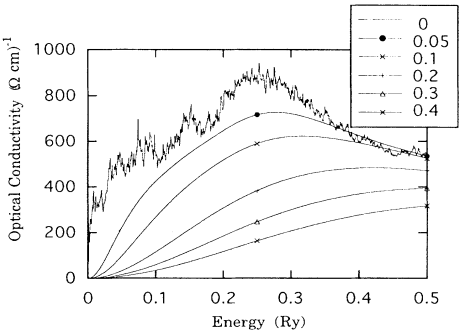

FIG. 4. The optical conductivity in the model α-AlMn, for $\hbar/\tau_{\mathrm{IB}} = 0$, 0.05, 0.1, 0.2, 0.3, and 0.4 Ry.

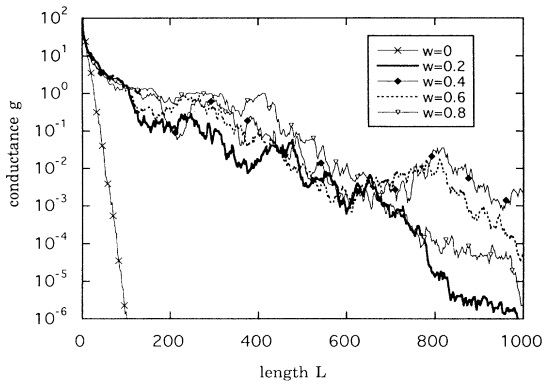

FIG. 5. Length dependence of the conductance in the two-dimensional Penrose lattices of the width $M = 178$ with random phason strain at the energy $E/t = 0.1$. Parameters specified are the strength of the randomness of phason strain or the density of random phason strain.

ing. These inelastic scattering mechanisms enhance the electron transport at elevated temperatures. A static magnetic field also induces interband transitions and this may explain the abnormal magnetoresistance. The wave functions in crystalline approximants and quasicrystals are not uniform but a percolated "stain" connecting several specific atoms of atomic clusters. This feature is one aspect of the power law decaying wave functions. Some of the power law decaying wave functions found in the two-dimensional Penrose lattice are actually this type. We believe that, in three-dimensional quasicrystals, this is really a possible form of wave functions which show the very spiky structure in the DOS, because a certain spiky peak originates mainly from some particular atoms while others originate from other atoms. Therefore, the above interband transitions are the local hopping mechanisms between states separated infinitesimally in energy. The interband transition mechanism was also proposed very recently by Mayou *et al.* [23], but we should emphasize that the spiky structure of the DOS separated by about 0.01 eV is essentially important to this mechanism.

In conclusion, we presented the electron transport properties in a crystalline approximant based on the band structure and the conductance in two-dimensional Penrose lattices with random phason strain to discuss the abnormal electronic transport in quasicrystals. The elastic scattering due to the random phason, and the inelastic scattering by electron-phonon and electron-electron interactions are crucial, and are responsible for the anomaly of the transport in quasicrystals. The pseudogap and spiky structures in the DOS are also the key to the interband transition affecting the electron transport.

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[1] T. Fujiwara and T. Yokokawa, Phys. Rev. Lett. **63**, 333 (1991).
[2] E. Belin and A. Traverse, J. Phys. Condens. Matter **3**, 2157 (1991); M. Mori, S. Matuo, T. Ishimasa, T. Matuura, K. Kamiya, H. Inokuchi, and T. Matsukata, J. Phys. Condens. Matter **3**, 767 (1991).
[3] J. Friedel, Helv. Phys. Acta **61**, 538 (1988); A. P. Smith and N. W. Ashcroft, Phys. Rev. Lett. **59**, 1365 (1987).
[4] T. Fujiwara, J. Non-Cryst. Solids **156/157**, 865 (1993).
[5] B. D. Biggs, S. J. Poon, and N. R. Munirathnam, Phys. Rev. Lett. **65**, 2700 (1990).
[6] T. Klein, C. Berger, D. Mayou, and F. Cyrot-Lackmann, Phys. Rev. Lett. **66**, 2907 (1991).
[7] F. S. Pierce, S. J. Poon, and Q. Guo, Science **261**, 737 (1993).
[8] K. Kimura and S. Takeuchi, *Quasicrystals: The States of the Art*, edited by D. P. DiVincenxo and P. J. Steinhardt (World Scientific, Singapore, 1991).
[9] K. Kimura, H. Iwahashi, T. Hashimoto, S. Takeuchi, U. Mizutani, S. Ohashi, and G. Itoh, J. Phys. Soc. Jpn. **58**, 2472 (1989).
[10] A. Sahnoune, J. O. Ström-Olsen, and A. Zluska, Phys. Rev. B **46**, 10629 (1992).
[11] S-y. Lin, X-m. Wang, L. Lu, D-l. Zhang, L. X. He, and K. X. Kuo, Phys. Rev. B **41**, 9625 (1990).
[12] S. Martin, A. F. Hebard, A. R. Kortan, and F. A. Thiel, Phys. Rev. Lett. **67**, 719 (1991).
[13] B. D. Biggs, F. S. Pierce, and S. J. Poon, Europhys. Lett. **19**, 415 (1992).
[14] X. Wu, C. C. Homes, S. E. Burkov, T. Timusk, F. S. Pierce, S. J. Poon, S. L. Cooper, and M. A. Karlow, J. Phys. Condens. Matter **5**, 5975 (1993).
[15] B. D. Biggs, Y. Li, and S. J. Poon, Phys. Rev. B **43**, 8747 (1991).
[16] C. C. Homes, T. Timusk, X. Wu, Z. Altounian, A. Sahnoune, and J. O. Ström-Olsen, Phys. Rev. Lett. **67**, 2694 (1991); S. E. Burkov, T. Timusk, and N. W. Ashcroft, J. Phys. Condens. Matter **4**, 9447 (1992).
[17] V. Elser and C. L. Henley, Phys. Rev. Lett. **55**, 2883 (1985); P. Guyot and M. Audier, Philos. Mag. B **51**, L15 (1985); M. Cooper and K. Robinson, Acta Crystallogr. **20**, 614 (1966).
[18] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).
[19] T. Fujiwara, Phys. Rev. B **40**, 942 (1989); In this reference, Al *d* states were not included in the calculation. The number of electrons within each atomic sphere and the position of the bottom of the conduction bands do not change. Proceedings of the 8th International Conference on Rapidly Quenched and Metastable Materials, Sendai, 1993 [Mater. Sci. Eng. A (to be published)].
[20] F. S. Pierce, P. A. Bancel, B. D. Biggs, Q. Guo, and S. J. Poon, Phys. Rev. B **47**, 5670 (1993).
[21] P. Lindqvist, C. Berger, T. Klein, P. Lanco, F. Cyrot-Lackmann, and Y. Calvayrac, Phys. Rev. B **48**, 630 (1993).
[22] S. Yamamoto and T. Fujiwara (unpublished).
[23] D. Mayou, C. Berger, F. Cyrot-Lackmann, T. Klein, and P. Lanco, Phys. Rev. Lett. **70**, 3915 (1993)