Dependence of the Electronic Properties of Quasicrystals on the Nonequilibrium Population of Two-Level Electron Traps

A. F. Prekul* and N. I. Shchegolikhina

* Mikheev Institute of Metal Physics, Ural Branch, Russian Academy of Sciences, Yekaterinburg, 620108 Russia
* e-mail: prekul@imp.uran.ru

Received December 2, 2021; revised December 2, 2021; accepted December 15, 2021

A new phenomenon is detected in quasicrystals: it is shown that the so-called “exotic” properties of real quasicrystalline materials are due to the presence of metastable electron traps with the nonequilibrium population of levels in the ground state of the system.

DOI: 10.1134/S0021364022030080

1. From the very beginning of studies of stable (ordered) icosahedral phases (I-phases), a phenomenon of a colossal-magnitude opposite-sign change in the residual conductivity \( \sigma(0) \) with growth of disorder has attracted great attention. The residual conductivity \( \sigma(0) \) can increase by two or three orders of magnitude. It is commonly accepted that optimally ordered I-phases are characterized by the conduction band with a large dip in the electron density of states (“pseudogap”) on the Fermi level. The existence and depth of the pseudogap directly depend on the degree of icosahedral long-range order. The higher the degree of icosahedral long-range order, the lower the residual conductivity \( \sigma(0) \) up to the metal–insulator transition in the limit where all wave vectors of the quasi-lattice are Bragg reflection vectors [1]. The colossal increase in the residual conductivity \( \sigma(0) \) with the growth of disorder was explained by the fact that disorder eliminates the pseudogap and recovers the structure of the conduction band of a typical metal. A quite consistent band paradigm of electronic phenomena, which is common for the entire isostructural family of ordered aluminum-based icosahedral phases, was developed on the basis of these concepts. In particular, the gradation of these phases into moderate-resistivity (Al–Li–Cu), high-resistivity (Al–Cu–Fe), and ultrahigh-resistivity (Al–Pd–Re) phases became clearer.

“Single-crystal” Al–Pd–Re materials are inconsistent with this paradigm. These materials appeared less insulating than polycrystalline Al–Pd–Re materials [2]. This property contradicts the above gradation of I-phases and makes it doubtful that the ultrahigh resistivity of polycrystals is an intrinsic property of the isostructural family [3–7]. A dilemma appeared: either the concept of the isostructural family or the band paradigm of the pseudogap should be rejected.

In this context, it is of interest to consider the variant of the pseudogap with the chemical localization of valence electrons by means of Heitler–London exchange (HL localization or covalent bonding) [1, 8].

2. Previously, we jointly studied the electronic heat capacity and local tunneling spectra within the Heitler–London theory of the pseudogap and experimentally justified the differential conductivity of quasicrystals in the form of the sum of elementary Schottky-like terms [9]:

\[
G(V) = \sum_i \mu_i n_i k_B (\delta V_i/V)^2 \exp(\delta V_i/V) / (1 + \exp(\delta V_i/V))^2. \tag{1}
\]

Here, \( \mu \) is the mobility of electrons, \( n_i \) is the number of electrons in individual types of traps, \( V \) is the bias voltage, \( k_B \) is the Boltzmann constant, and \( i \) is the multiplicity of covalent bonds. As a result, a “crystal-chemical” model of the electronic structure was developed; it implies the simple nonhybridized superposition of the continuous spectrum in the form of the conduction band with a wide pseudogap and the discrete spectrum in the form of the “Dirac comb” of doubly split local levels [10].

The integration of Eq. (1) with the equivalent replacement of \( V \) by \( T \) and taking into account the constant of integration \( \sigma_0 \) reproduces the total conductivity of the system in the form

\[
\sigma(T) = \sigma_0 + \sum_i \mu_i n_i k_B [1 + \exp(\delta E_i/k_BT)]. \tag{2}
\]

where \( \sigma_0 \) is the metallic conductivity through the conduction band and the second term on the right-hand side is the quantum conductivity \( \sigma_q(T) \) through excited levels of single-type traps.

At first glance, \( \sigma(0) \) and \( \sigma_0 \) are adequate parameters. It seems again possible to use the “band” mecha-
nism of the colossal increase in $\sigma(0)$ under the assumption that disorder in this case destroys traps and eliminates the pseudogap. However, traps are attributes of the icosahedral short-range order. They are local structures and the number of their types is strictly specified by the chemical composition and is limited by the saturaibility of covalent bonds. As a result, the fraction of covalently bonded electrons among the initial valence electrons of the alloy, $N_c/N_v$, is a structural invariant of the system, i.e., is independent of both the structure and perfectness of the system. Because of the charge conservation law, the fraction of residual free electrons, $N_{\text{free}}/N_v$, is also a structural invariant. Consequently, $\sigma_0$ in Eq. (2) can either decrease or at least remain constant with the growth of disorder. The system has no resources for an increase, the more so, for colossal increase in $\sigma_0$.

3. To solve the appearing contradiction, we note that the quantum conductivity $\sigma_q(T)$ in Eq. (2) at 1100–1200 K in optimally ordered I-phases is comparable with $\sigma(0)$ in extremely disordered materials. We hypothesized that disorder in quasicrystals does not destroy traps and does not eliminate the pseudogap. Traps become capable of the nonequilibrium of population of levels, i.e., of the holding of the high-temperature population state to extremely low temperatures. As a result, $\sigma(0) \equiv \sigma_0$ only if all traps are in the stable equilibrium state. Otherwise,

$$\sigma(0) = \sigma_0 + \sigma_{\text{mq}}(0),$$  \hspace{1cm} (3)

where $\sigma_{\text{mq}}(0)$ is the quantum (!!!) conductivity through metastable traps with a nonequilibrium population of levels.

To justify this concept, we searched for manifestations of the presence of metastable traps in the ground state of quasicrystalline materials and found the following.

(i) If the excited levels of metastable traps at $T = 0$ are filled, the thermal energy cannot be spent for their filling. Therefore, the colossal increase in $\sigma(0)$ owing to $\sigma_{\text{mq}}(0)$ cannot be accompanied by the corresponding increase in the Sommerfeld coefficient $\gamma$ in the linear heat capacity, unlike the pseudogap elimination mechanism. The “heat capacity deficit” effect is well known in experiments [11]. It is one of the so-called exotic properties of quasicrystals, which have not yet been explained.

(ii) Similarly, metastable Heitler–London pairs are “paramagnetic” centers by definition. The contribution $\sigma_{\text{mq}}(0)$ should be accompanied by a molecular Langevin (super-)paramagnetic term $\chi_{\text{sp}}$ in the magnetic susceptibility at low temperatures. Figure 1 shows the temperature dependences of the magnetic susceptibility in the (○) ordered and (●) disordered Al$_{63}$Cu$_{25}$Fe$_{12}$ alloy. This effect is apparently observed in all studied quasicrystal-forming systems and is explained by the presence of uncontrol magnet active impurities. It was only unclear why $\sigma(0)$ is almost proportional to the Curie constant in $\chi_{\text{sp}}$ [12]. The answer is obvious: both $\sigma_{\text{mq}}(0)$ and the Curie constant in $\chi_{\text{sp}}$ are determined by the nonequilibrium populations of the same traps.

(iii) The specificity of the quantum conductivity is that the mean free path of electrons is determined by the distance between equivalent traps rather than by the scattering by static defects as in $\sigma_0$. These distances are ~100 Å [13], which is equivalent to the carrier relaxation frequency $\Gamma \leq 10^{14}$ s$^{-1}$, which is characteristic of extremely pure metals. Consequently, the contribution $\sigma_{\text{mq}}(0)$ should be accompanied by the ultranarrow Drude-like maximum in $\sigma(\omega)$.

As known, the feature of $\sigma(\omega)$ in real quasicrystalline materials is the mysterious absence of the Drude maximum in the far infrared spectral range [14, 15]. This anomaly in optimally ordered quasicrystals is usually explained by the smallness of the Drude contribution compared to quantum absorption. This is really the case. Figure 2 shows experimental results [15] for $\sigma(\omega)$ in the optimally ordered Al$_{62.5}$Cu$_{25}$Fe$_{12.5}$ phase and the Drude contribution for $\sigma_{\text{dr}} = 250$ Ω$^{-1}$ cm$^{-1}$ at the relaxation frequency $\Gamma = 10^{15}$ s$^{-1}$, typical of disordered metals. Since the distribution of $\delta E_i$ is wide, it is clear that the reason is that the quantum absorption increases rapidly with almost zero energy [10, 14, 15] and masks the Drude maximum and not that the contribution is small. With an increase in $\sigma_{\text{stat}}$ at least by an order of magnitude under the same other conditions, i.e., at $\Gamma = 10^{15}$ s$^{-1}$, the Drude contribution will exceed an increase in the quantum absorption and will be observed in the entire infrared spectral range (see Fig. 2). Our experimental test in the disordered Al$_{62.5}$Cu$_{25}$Fe$_{12.5}$ phase with $\sigma_{\text{stat}} = 3500$ Ω$^{-1}$ cm$^{-1}$ shows that this is not the case. A fast increase in the quantum
absorption is still easily observed, which means that $\Gamma \ll 10^{15} \text{s}^{-1}$. Indeed, according to the condition that the Drude curve is to the left of the lowest energy in our experiment (0.08 eV), $\Gamma \leq 7 \times 10^{13} \text{s}^{-1}$. It is quite probable that the system allows two Drude contributions, one of which is related to $\sigma_0 \sim 250 \text{ } \Omega^{-1} \text{ } \text{cm}^{-1}$ and $\Gamma = 10^{15} \text{s}^{-1}$ and the other is related to $\sigma_{\text{msq}}(0) \sim 3300 \text{ } \Omega^{-1} \text{ } \text{cm}^{-1}$ and $\Gamma \leq 7 \times 10^{13} \text{s}^{-1}$ in complete agreement with Eq. (3).

(iv) The quantum conductivity $\sigma_q(T)$ in Eq. (2) is the sum of numerous autonomous discrete terms [10]. Consequently, the addition $\sigma_{\text{msq}}(0)$ should be manifested in the picture of a stepwise change in the conductivity in the process of relaxation of the strongly nonequilibrium state. We use the results obtained in [10] and numerically simulate change in $\sigma(T)$ in the Al$_{63}$Cu$_{25}$Fe$_{12}$ phase by the successive “freezing” of high-energy terms. Figure 3 shows the equilibrium curves $\sigma(T)$ including all six terms $\delta E_i = 5, 20, 80, 250, 400$, and $1500 \text{ } \text{meV}$ (line VI), terms $\delta E_i = 5, 20, 80, 250$, and $400 \text{ } \text{meV}$ (line V), terms $\delta E_i = 5, 20, 80$, and $250 \text{ } \text{meV}$ (line IV), terms $\delta E_i = 5, 20, 80$ meV (line III), terms $\delta E_i = 5$ and $20 \text{ } \text{meV}$ (line II), and the term $\delta E_i = 5 \text{ } \text{meV}$ (line I), which is assumed to be equilibrium.

In the above procedure, $\sigma_{\text{msq}}(0)$ increases from 0 to $\sim 3300 \text{ } \Omega^{-1} \text{ } \text{cm}^{-1}$. If this strongly nonequilibrium material is heated from 0 K, the increase in the conductivity owing to the term $\delta E = 5 \text{ } \text{meV}$ will be observed only below the deblocking temperature of the term $\delta E = 20 \text{ } \text{meV}$, etc. A further evolution is seen in the figure.

A characteristic multistep picture of variation of $\sigma(T)$ is observed. The number of steps, as well as the number of quantum conductivity terms in Eq. (2), is determined by the multiplicity of covalent bonds.

The vertical dashed line in Fig. 3 indicates a boundary between temperatures below and above room temperature to which materials were usually quenched. To the left of this boundary, parallel lines...
clearly indicate the picture of the well-known empirical inverse Matthiessen rule [13], which has not yet been explained. The empirical inverse Matthiessen rule at $T \leq 300$ K is a part of the model diagram in Fig. 3. Figure 4 shows the total diagram reconstructed from the experimental data reported in [15, 16] for the Al–Cu–Fe alloy with the nominal Fe content of ~12.5 at%.

The model and experimental picture are in qualitatively excellent agreement with each other. The oscillatory character of the envelopes of all partial hysteresis loops is particularly expressive. It appeared that such diagrams were observed when studying the conductivity of Al–Cu–Fe and Al–Pd–Re quasicrystal-forming systems in different stages of the structural relaxation from "amorphous" to "optimally ordered" states [17, 18], but the physical meaning of these diagrams, as well as the inverse Matthiessen rule, could not be understood. The comparison of Figs. 3 and 4 with Fig. 1b in [17] and Fig. 2a in [18] indicates good numerical coincidence of the number of steps with the number of elementary terms of the quantum conductivity. All these facts unambiguously prove that features of the electron transport in real quasicrystals are determined by the presence of the metallic, $\sigma_0$, and quantum, $\sigma_q$, conductivities. Moreover, the quantum conductivity manifests itself in two ways. Equilibrium traps ensure the thermally induced increase in the conductivity at finite temperatures, whereas nonequilibrium traps ensure the increase in $\sigma(0)$, thus creating the illusion of the colossal increase in the metallic conductivity. It is clear that the inverse Matthiessen rule is due to the joint action of these two factors.

4. To summarize, the colossal increase in $\sigma(0)$ is the decisive but not single effect of metastable traps in the ground state of the system. The strong dependence of the electric, magnetic, thermal, and optical properties of real quasicrystalline materials on the existence of nonequilibrium populated traps is detected. The brightest manifestation of this dependence should obviously be the violation of the classification of I-phases in terms of the degree of perfectness of the icosahedral long-range order. The fact that Al–Pd–Re single-crystal materials are not ultrahigh-resistive materials means that these materials are far from the stable equilibrium state. The direct experimental proof of this fact would be the detection of the above manifestations of the nonequilibrium populations in initial single-crystal materials and the disappearance of these manifestations in the process of additional thermal treatments. However, such systematic studies have not yet been performed. For this reason, we consider only the effects that acquired the status of empirical regularities. These are the colossal increase in $\sigma(0)$ at the heat capacity deficit of free electrons, the molecular (super)paramagnetism at low temperatures, the ultranarrow optical Drude maximum, the multistep character of relaxation processes, and the inverse Matthiessen rule in the electron transport. This is obviously sufficient for the general conclusion that the tendency to nonequilibrium population is a fundamental feature of quasicrystal-forming alloys. This property has not yet taken into account in experiments and theories. Meanwhile, as seen, it is responsible for a number of effects that complicate the understanding of the properties of truly equilibrium quasicrystalline structures.

ACKNOWLEDGMENTS

We are grateful to S.M. Podgornykh for assistance in the magnetic experiments and stimulating discussions.

FUNDING

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (contract no. AAAA-A18-118020290104-2, theme Spin).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.
REFERENCES
1. C. Janot, Quasicrystals, 2nd ed. (Oxford Science, Oxford, 1994), p. 324.
2. J. Q. Guo, T. J. Sato, E. Abe, H. Takakura, and A. P. Tsai, Philos. Mag. Lett. 80, 495 (2000).
3. I. R. Fisher, X. P. Xie, I. Tudora, C. W. Gao, C. Song, P. C. Canfield, K. Dennis, D. Abanoz, and M. J. Kramer, Philos. Mag. B 82, 1089 (2002).
4. J. Dolinsek, P. J. McGuinness, M. Klanjišek, I. Smiljanić, A. Smontara, E. S. Zijlstra, S. K. Bose, I. R. Fisher, M. J. Kramer, and P. C. Canfield, Phys. Rev. B 74, 134201 (2006).
5. S. J. Poon and Ö. Rapp, Phys. Rev. B 76, 216201 (2007).
6. J. Delahaye and C. Berger, Eur. Phys. J. B 88, 102 (2015).
7. Yu. Kh. Vekilov, M. A. Chernikov, and Ya. Dolinchek, Phys. Met. Metalloved. 117, 16 (2016).
8. V. F. Gantmakher, Phys. Usp. 45, 1165 (2002).
9. A. F. Prekul and N. I. Shchegolikhina, JETP Lett. 103, 603 (2016).
10. A. F. Prekul and N. I. Shchegolikhina, Crystals 6 (9), 119 (2016).
11. T. Klein, C. Berger, D. Mayou, and F. Cyrot-Lackmann, Phys. Rev. Lett. 66, 2907 (1991).
12. J. J. Prejean, C. Berger, A. Sulpice, and Y. Calvayrac, Phys. Rev. B 65, 140203 (2002).
13. D. Mayou, C. Berger, F. Cyrot-Lackmann, T. Klein, and P. Lanco, Phys. Rev. Lett. 70, 3915 (1993).
14. C. C. Homes, T. Timusk, X. Wu, Z. Antounian, A. Sahnoune, and J. O. Strom-Olsen, Phys. Rev. Lett. 67, 2694 (1991).
15. A. F. Prekul, L. V. Numerovannaya, A. B. Rol’shchikov, N. I. Shchegolikhina, and S. V. Yartsev, Fiz. Met. Metalloved. 82, 75 (1996).
16. A. F. Prekul and N. I. Shchegolikhina, Crystallogr. Rep. 52, 996 (2007).
17. R. Haberkern, C. Roth, R. Knofle, F. Zavaliche, and P. Haussler, in Proceedings of the 6th International Conference on Quasicrystals (World Scientific, Singapore, 1998), p. 643.
18. R. Haberkern, K. Khedhri, C. Madel, and P. Häussler, Mater. Sci. Eng. A 294–296, 475 (2000).

Translated by R. Tyapaev