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ELECTRICAL AND MAGNETIC PROPERTIES

On Modified Mott ($T^{-1/4}$) Law in the Conductivity of Quasicrystals

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Abstract—In the conductivity of quasicrystals, modified with a metal additive, numerous cases of manifestation of the Mott $T^{-1/4}$ law have been found. In the icosahedral phases of the Al–Pd–Re system, this anomaly is observed not only in the limit of the marginal metallic conductivity, as was known until now, but long before this limit is reached. It is also shown that similar anomalies are characteristic of the Al–Cu–Fe system of quasicrystalline alloys, the level of metallic conductivity of which is two to three orders of magnitude higher than that in polycrystalline Al–Pd–Re materials. It is assumed that these anomalies are the manifestation of a wide distribution of two-level excitations of "chemically" localized electrons.

Keywords: quasicrystals, electrical properties, localization mechanism, two-level excitations

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INTRODUCTION

After thirty years of intensive research, variable range hopping (VRH) conductivity has become the focus of violent polemics about the intrinsic and non-intrinsic properties of quasicrystals [1–6]. This is not accidental.

All or the main components of quasicrystalline alloys are known to be good metals with a valence electron concentration of ~10^{23} cm^{-3}. Theoretical estimates show that, in metallic media of this type, the growth of disorder itself leads to neither Anderson localization nor a Mott–Anderson (MA) metal–insulator transition. If such a transition is observed, it means that there is a mechanism for preliminary reduction of the initial metallic conduction in the system. This may be the Heitler–London chemical localization (HL, covalent bonding) [7] or the granular morphology of materials due to the presence of oxides [8]. In any case, the parameter of the MA transition is not the mean free path, but rather the concentration of itinerant electrons.

On the other hand, VRH conductivity in disordered systems is characteristic of the insulator side of a Mott–Anderson metal–insulator transition. Accordingly, the $T^{-1/4}$ law is observed in the region of ultralow temperatures, bounded from above and not bounded from below up to $T = 0$ K, where, unambiguously, $\sigma(T) \equiv 0$. In quasicrystals of the Al–Pd–Re system, the only system where the $T^{-1/4}$ law has been observed so far, there is no such unambiguity. With rare exceptions, this law is observed in the range of ultralow temperatures bounded both from above and from below [9–12], so that the experimental curves $\sigma(T)$ in the range of low temperatures ($T \lesssim 1$ K) are approximated by Mott formula for VRH conductivity, modified by adding a metal-like contribution σ_0 in the form

$$\sigma(T) = \sigma_0 + A\exp\left(-B/T^{1/4}\right). \quad (1)$$

Here, σ_0 is an adjustable parameter; the rest notations are commonly accepted.

The paradox is that, directly in Mott model, expression (1) has no physical meaning. The presence of the first term means that the system is on the metal side of the MA transition. The presence of the second term means that the system is on the insulator side of this transition. Strictly speaking, this means that the modified Mott behavior of conductivity (MMBC anomaly) is observed in the absence of an MA transition. Therefore, the "activation" component in (1) cannot be VRH conductivity. Then, what does Mott $T^{-1/4}$ law mean?

We noticed that, if we abstract from the traditional content of the $T^{-1/4}$ law, then expression (1) can be understood as another manifestation of the additive conduction scheme. This phenomenon is well known in quasicrystals as the inverse Matthiessen's rule (IMR): an empirical regularity indicating that quasicrystals have autonomous conduction channels over current (σ_{ml}) and no-current (σ_{scl}) states in the form

$$\sigma(T) = \sigma_{ml} + \sigma_{scl}. \quad (2)$$

Here, σ_{ml} is a metal-like component associated with carriers, the concentration of which does not depend on temperature; σ_{scl} is a semiconductor-like (negative TRC) component, associated with thermally induced charge carriers [13].

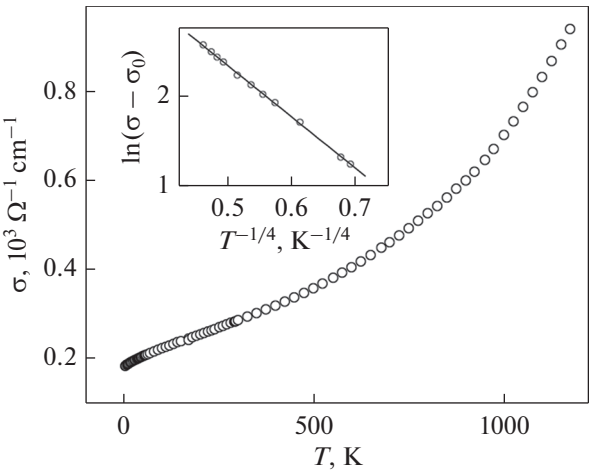

Fig. 1. Experimental dependence of the conductivity of the i-phase $Al_{70}Pd_{20}Re_{10}$ in the range 4.4–1200 K; (inset) the low-temperature part of the curve in coordinates $\ln(\sigma(T) - \sigma_0)$ vs. $T^{-1/4}$.

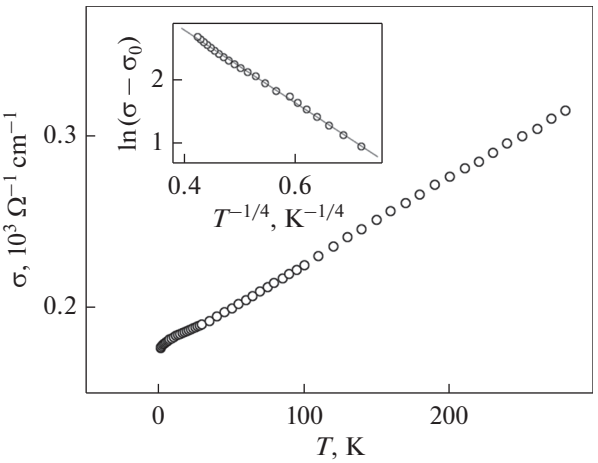

Fig. 2. Conductivity of the single-crystal i-phase $Al_{71.7}Pd_{19.4}Re_{8.9}$ [14]; (inset) the low-temperature part of the curve in coordinates $\ln(\sigma(T) - \sigma_0)$ vs. $T^{-1/4}$.

The attributes of the IMR are generally determined by the invariance of the σ_{scl} component with respect to the chemical composition, structure, and structural defects [13]. It is clear that, if MMBC and IMR are related regularities, then Mott $T^{-1/4}$ law, as well as IMR, must be observed in quasicrystalline materials of any type, regardless of the value of σ_0 or the chemical composition.

1. EXPERIMENTAL JUSTIFICATION

Until now, studies of the MMPP anomaly have been limited by polycrystalline Al–Pd–Re materials with a very small value of $\sigma_0 \le 1$ $(\Omega\ \text{cm})^{-1}$. In practice, Al–Pd–Re alloys can be ultrahigh-resistive, with $\sigma_0 \sim 1$ $(\Omega\ \text{cm})^{-1}$; highly resistive, with $\sigma_0 \sim 100$ $(\Omega\ \text{cm})^{-1}$; and moderately resistive, with $\sigma_0 \sim 1000$ $(\Omega\ \text{cm})^{-1}$ materials, depending on the composition, the perfection of the icosahedral long-range order (ILRO), and morphology.

First of all, it was interesting to find out whether the MMBC anomaly is observed in Al–Pd–Re materials with $\sigma_0 \gg 1$ $(\Omega\ \text{cm})^{-1}$, obviously far from the state of a marginal metal.

We have synthesized and investigated polycrystalline single-phase Al–Pd–Re materials with Re content of ~10 at % and $\sigma_0 \sim 200$ $(\Omega\ \text{cm})^{-1}$. The alloys were prepared from high-purity components no worse than 99.99% in an argon arc furnace. For homogenization, the ingots were turned over at least three times with an exposure of 1 min. At the last stage, quenching from the melt was carried out on a water-cooled furnace hearth using the hammer–anvil method. The flattened ingot was subjected to heat treatment at 920°C for 12 hours. After that, samples 1 × 1 × 15 mm in size were cut out by the electroerosion method for measuring the electrical resistance by the usual 4-contact method.

Figure 1 shows the curve of $\sigma(T)$ obtained by us in the temperature range 4.4–1200 K. Visually, the dependence is typical of polycrystalline Al–Pd–Re materials of high structural quality. The low-temperature part of this curve is shown in the inset in Fig. 1 in Mott coordinates $(\sigma(T) - \sigma_0)$ vs. $T^{-1/4}$. As it turned out, using σ_0 as an adjustable parameter, it is possible to achieve quite satisfactory linearization of the curve in the temperature range 4.4–22 K, so that $\sigma_0 \sim 180$ $(\Omega\ \text{cm})^{-1}$. Apparently, the MMBC anomaly has not disappeared, but only shifted to the region of higher temperatures.

In this connection, a question arose whether there is a limitation on the value of σ_0 and, accordingly, on the presence and degree of perfection of the ILRO for observing such an MMBC anomaly.

To resolve this issue, we used the data available in the literature for Al–Pd–Re materials, monocrystalline with $\sigma_0 \sim 176$ $(\Omega\ \text{cm})^{-1}$ [14] and amorphous with $\sigma_0 \sim 1470$ $(\Omega\ \text{cm})^{-1}$ [15], i.e., for dense materials morphologically different from polycrystals [1–5]. The corresponding curves are shown in Figs. 2 and 3. The insets in these figures show the low-temperature parts of the curves in Mott coordinates. As can be seen, quite satisfactory linearization is achieved in the temperature ranges 3.7–30 and 2–25 K, respectively.

Now, let us consider the role of chemical composition. We reanalyzed the conductivity, previously studied by us [16], of highly resistive and moderately resistive materials in quasicrystalline Al–Cu–Fe alloys with a Fe content of 12.5 at % and the values of $\sigma_0 \sim 200$ and ~1500 $(\Omega\ \text{cm})^{-1}$. As is known, it is not possi-

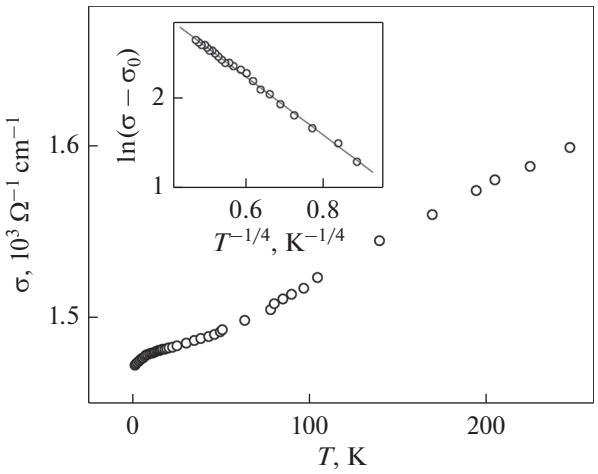

Fig. 3. Experimental dependence of the conductivity of amorphous material $Al_{72}Pd_{20}Re_8$ in the range 2–300 K [15]; (inset) the low-temperature part of the curve in coordinates $\ln(\sigma(T) - \sigma_0)$ vs. $T^{-1/4}$.

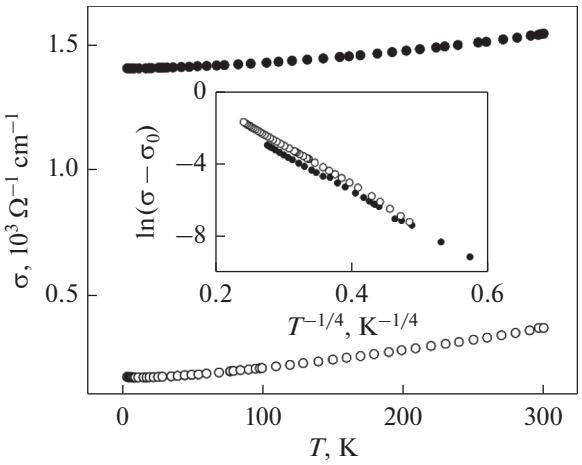

Fig. 4. Experimental dependences of conductivity for two $Al_{63}Cu_{25.5}Fe_{12.5}$ materials [16]; (inset) the low-temperature parts of these curves in coordinates $\ln(\sigma(T) - \sigma_0)$ vs. $T^{-1/4}$: (○) $\sigma_0 = 168$ (Ω cm)$^{-1}$ and (●) $\sigma_0 = 1408$ (Ω cm)$^{-1}$.

ble to obtain ultra-high resistive materials in this system. It seems incredible, but in both cases, the presence of the MMBC anomaly was confirmed. Figure 4 shows the $\sigma(T)$ curves, and the inset shows the approximation of the low-temperature parts of these curves in Mott coordinates. As can be seen, quite satisfactory linearization of the curves is achieved in the temperature range 18–290 K at $\sigma_0 = 168$ (Ω cm)$^{-1}$ and in the range 9–170 K at $\sigma_0 = 1408$ (Ω cm)$^{-1}$.

The absence of the dependence of the MMBC anomaly on the chemical composition is also confirmed by the consideration of the Al–Li–Cu and Al–Mn–Si systems. Due to the complete similarity of the pictures, we do not present them here.

2. DISCUSSION

The results presented above allow one to consider that MMBC and IMR are the same phenomenon, and this is very important. The point is that, earlier, by joint studies of elementary electronic excitations by the methods of heat capacity and local tunneling spectra in a model Al–Cu–Fe12 alloy, we showed that the source of σ_{scl} in the IMR is two-level electron traps or systems (TLS) with a wide distribution of the level-splitting energies δE_i from $\lesssim$5 meV to $\gtrsim$1 eV [17]. On the one hand, this served as a basis for a "crystal-chemical" model of the electronic structure, which assumes a hybridization-free superposition of two types of spectrum: continuous, in the form of a conduction band with a wide pseudo-gap, and discrete, in the form of a "Dirac comb" of doubly split local levels [18]. On the other hand, an empirical justification of the differential conductivity of quasicrystals appeared in the form of the sum of elementary Schottky-like terms:

$$G(V) = \sum_i G_{Vi}(V) = \sum_i \mu_e n_i k_B \frac{(\delta V_i/V)^2 \exp(\delta V_i/V)}{(1+\exp(\delta V_i/V))^2}. \quad (3)$$

Here, μ_e is the electron mobility, n_i is the number of electrons associated with a particular type of a trap, V is the bias voltage, and k_B is the Boltzmann constant.

Integration of expression (3) with an equivalent replacement of V by T and taking into account the constant of integration C reproduces the additive conductivity schemes (1) and (2) in the form

$$\sigma(T) = C + \sum_i \mu_e n_i \kappa_B / [1 + \exp(\delta E_i / k_B T)]. \quad (4)$$

In contrast to (1), the component of thermalized conductivity in (4) is similar not to Mott formalism, but rather to the Landauer formalism [19] generalized for a mesoscopic system with two contacts and a large number of autonomous quantum conduction channels over excited levels equivalent to TLS [18].

It is easy to notice a certain similarity between the crystal-chemical and Mott models. With a change in temperature, there is a change in the modes of thermal activation of carriers: discrete in one case and continuous in the other [20]. It is not ruled out that the patterns of discrete and continuous changes in the thermal activation modes are difficult to distinguish in the experiment. Let us see what simple modeling gives.

Figure 5 reproduces the experimental curve $\sigma(T)$ for the phase of Al–Cu–Fe_{12} from [18] and its decomposition into elementary terms in the temperature

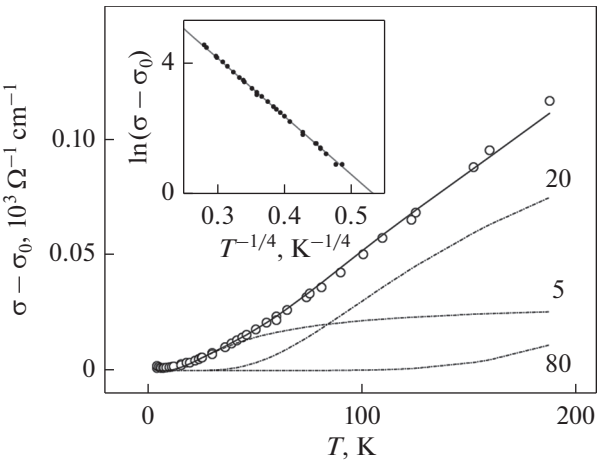

Fig. 5. (○) Temperature-dependent part of the $\sigma(T)$ curve for $\sigma(T)$ $Al_{63}Cu_{25}Fe_{12}$ (○) and (solid line) its description by terms of (dash-dotted lines) 5, 20, and 80 meV; (inset) this curve in coordinates $\ln(\sigma(T)-\sigma_0)$ vs. $T^{-1/4}$.

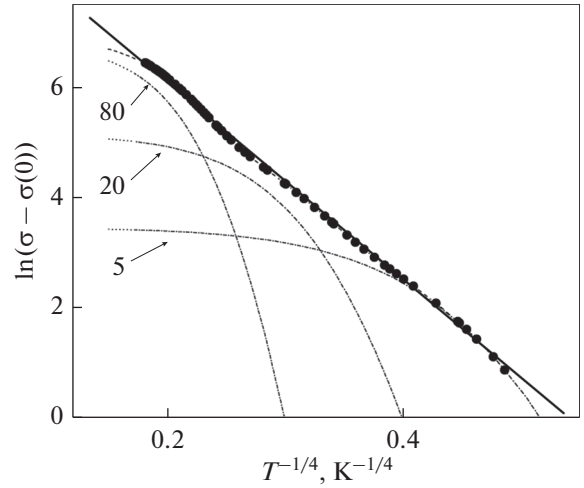

Fig. 6. (Dash-dotted lines) Diagram illustrating the behavior of separate terms with δE_i = 5, 20, and 80 meV and (solid points) the sum of these terms in Mott coordinates; (solid line) Mott law.

range 4–200 K. By analogy with Fig. 4, we might expect linearization of the low-temperature part of this curve in Mott coordinates. And just so it happened.

The result is shown in the inset. This linearization interval is approximated in (4) by the sum of three elementary terms of quantum conductivity with δE_i = 5, 20, and 80 meV. How these terms look in Mott coordinates is shown in Fig. 6. As can be seen from the figure, they do not have linearized sections. Another thing is their sum. It is shown with solid dots. For comparison, the solid line shows the ideal Mott law. Note that these dependencies are really hardly to distinguish.

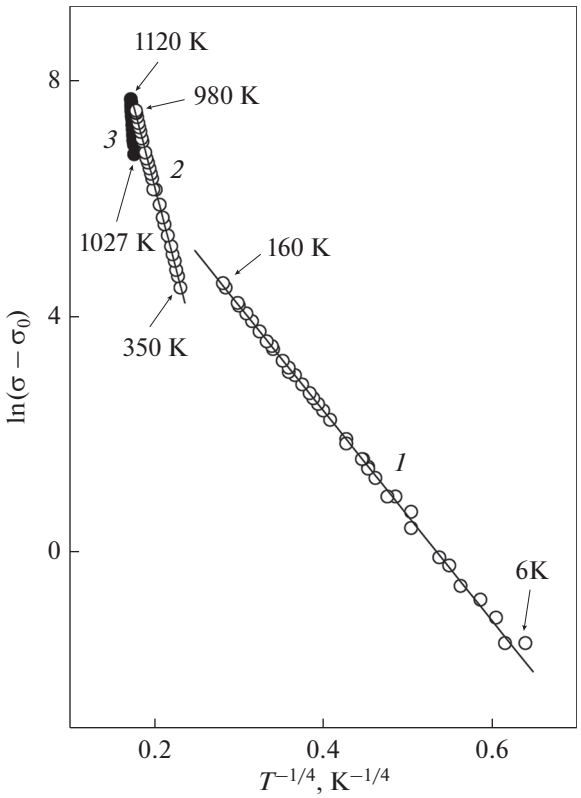

Fig. 7. Piecewise-linear approximation of the $\sigma(T)$ curve in the $Al_{63}Cu_{25}Fe_{12}$ phase in the range 4–1200 K: σ_{01} = 249, σ_{02} = 430, and σ_{03} = 1500 $(\Omega\,\text{cm})^{-1}$.

It should be noted that, in Mott coordinates, it is not the elementary terms of quantum conductivity that are linearized separately, but rather the sum of two or three terms. This provides a fairly simple way to make sure that, of the two indistinguishable descriptions, it is the description by Mott law that is formal. In the $Al_{63}Cu_{25}Fe_{12}$ phase in the temperature range 4–1200 K, up to seven elementary terms are observed [18], which is two to three times more than necessary for one MMBC anomaly. Accordingly, in the range 4–1200 K, by varying σ_0, it is possible to obtain a specific piecewise-linear approximation by several MMBC anomalies. The aforesaid is illustrated by Fig. 7.

Of course, it is hardly worth arguing that the patterns of piecewise linear approximation mean a sequence of several MA transitions. The procedure for expanding the experimental curve in Fig. 7 in Mott coordinates is pretty simple. With an increase in temperature, higher-lying GL-terms, identical to low-lying terms, come into play. In this case, low-lying terms, due to the impossibility of an inverted TLS population (depletion effect), flatten out and play the role of new temperature-independent contributions σ_{01}, σ_{02}, and σ_{03}.

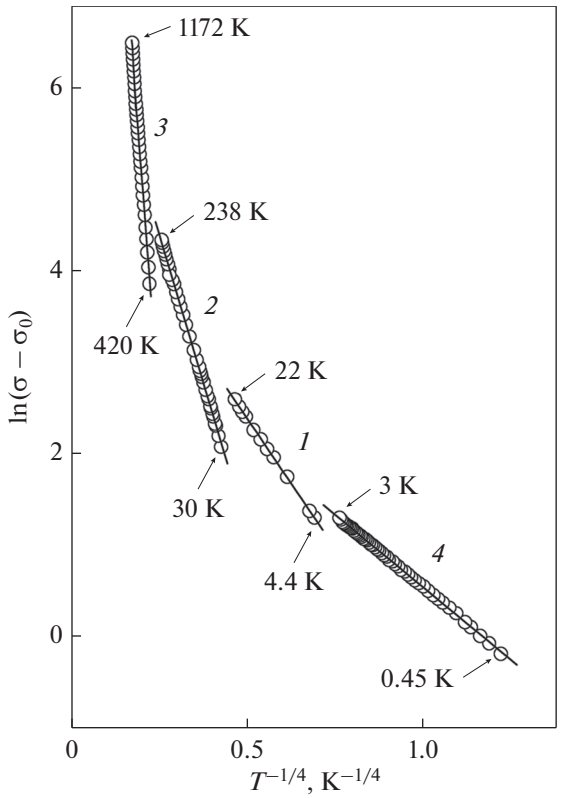

Fig. 8. Piecewise-linear approximation of the $\sigma(T)$ curve in the $Al_{70}Pd_{20}Re_{10}$ phase in the range 4–1200 K: (*1*) $\sigma_{01} = 179.5$; (*2*) $\sigma_{02} = 189$; and (*3*) $\sigma_{03} = 280$ $(\Omega\,\text{cm})^{-1}$. Additional section (*4*) in the range 0.45–3 K was constructed according to [21], $\sigma_{04} = 0.7$ $(\Omega\,\text{cm})^{-1}$.

Such processing can be interesting and useful methodologically as an express method for detecting a change in thermal activation modes. We applied it to the $\sigma(T)$ curve shown in Fig. 1 for the Al_{70} $Pd_{20}Re_{10}$ phase in the entire temperature range 4–1200 K. The result of the analysis of these data is shown in Fig. 8 in the form of linear segments 1, 2, and 3. Indirectly, this means that the Al–Pd–Re system has an equally wide spectrum of two-level excitations as the Al–Cu–Fe system.

However, in the Al–Pd–Re system, this picture can be extended to the region of lower temperatures using the corresponding data [21]. A very rich picture of piecewise-linear approximation arises, showing that, in polycrystalline Al–Pd–Re materials, the spectrum of two-level excitations covers the far and very far infrared regions and that the multiplicity of covalent bonds can be ~10. Probably, this is the essential difference between the Al–Pd–Re phases and the phases in other icosahedral systems.

CONCLUSIONS

With this work, we essentially continue the development of the idea of Gantmakher two-step electron localization [7], according to which the MA transition in quasicrystalline alloys, if any, is preceded by chemical localization and strong reduction of the initial metallic bond. This case, apparently, includes those rare exceptions when the experiment is described by expression (1) without the adjustable parameter σ_0.

However, practice has shown that chemical localization gives rise not only to deep electron traps. It gives rise to a wide distribution of trap types and a wide discrete spectrum of two-level excitations. As a result, the quantum conductivity over the excited levels of equivalent traps becomes a significant factor in the entire temperature range, from ultralow to the melting point [17, 18].

To understand what Mott $T^{-1/4}$ law means in combination with the adjustable term σ_0, we postulated the identity of this combination as a whole with the inverse Matthiessen's rule. It turned out that this combination is observed in the absence of an MA transition and is associated with the stage of preliminary reduction of the metallic bond. It also turned out that Mott formalism and the Landauer formalism are difficult to distinguish experimentally. As a result, the effects of chemical GL localization can easily be mistaken for the effects of Anderson localization, which, in our opinion, was the case in practice.

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