

# An absence of the Anderson transition in high-resistance alloys with a high electron density

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In three-dimensional electron systems with a high electron density it is not possible to reach the Anderson transition neither by increasing disorder nor by a combination of static disorder with a dynamic one (by high temperature), or by selecting a material with a large deformation potential and a large constant of electron-phonon interaction. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4775354>]

## 1. Introduction

According to a theory,<sup>1</sup> an increase of disorder in three-dimensional electron systems should lead to a quantum metal-insulator transition, which is called the Anderson transition. It occurs at a critical value of the parameter  $W/J$ , where  $W$  is an energy range of possible one-electron localized states,  $J$  is the overlapping integral between two adjacent such states. According to a scaling theory,<sup>2</sup> the transition is continuous, so that when approaching the transition from the metallic side at  $T=0$  the conductivity  $\sigma$  vanishes continuously.

The transition procedure is as follows. With increasing disorder, the mean free path of electrons  $l$  is reduced, as well as the conductivity  $\sigma = ne^2 l / \hbar k_F$ . Here,  $k_F$  is the wave vector of delocalized electrons at the Fermi level, and  $n \approx k_F^3$  is their concentration. Electronic functions of electrons are plane waves, and the free path  $l$  cannot be smaller than the wavelength,  $l \gtrsim k_F^{-1}$ . The resistance  $\rho$  reaches at  $l \sim k_F^{-1}$  the Mott limit

$$\rho_M = \sigma_M^{-1} = \frac{\hbar}{e^2} k_F^{-1}, \quad k_F l \approx 1. \quad (1)$$

According to modern concepts, upon approaching the Anderson transition the resistance of electron systems overcomes the Mott limit  $(\hbar/e^2)k_F^{-1}$  and keeps increasing. This is due to the fact that the electron wave functions become multifractal with singularities at each point.<sup>4,5</sup> At the transition point the resistance becomes infinite, and the conductivity goes to zero.

Both the original model of Anderson<sup>1</sup> and the scaling theory<sup>2</sup> operate on one-electron wave functions, and do not assume an electron-electron interaction. So, it is perhaps not surprising that experimental observations of the Anderson transition have been realized in the first place in doped semiconductors, where electron concentrations are relatively low (see in Fig. 1 the summary of experimental results from Ref. 3).

## 2. Low-temperature resistance of many pure metal alloys

Advances in understanding of the localization processes and a role of disorder in these processes overshadowed, generally speaking, the known fact that the Anderson transition is never observed in metals and alloys with a high carrier

concentration. Materials with a carrier concentration  $n$  of about one electron per atom,  $n \gtrsim a^{-3}$  ( $a$  is the interatomic distance) will be referred to as pure metal alloys or normal metals. They consist only metal atoms, which give easy their valence electrons in common use, but, as a rule, do not put extra electrons to their unfilled shells. Pure metal alloys do not contain as a component such elements as O, P, Ge, Si, Bi, etc.

By measuring the resistance  $\rho$  of many different pure metal alloys at low temperatures, in the presence of the Anderson transition, there would be observed all possible resistance values up to the highest, typical of insulators. It turned out that for any achievable level of disorder, these alloys are metallic with a resistivity of less than some characteristic value  $\rho^* \sim 300 \mu\Omega \cdot \text{cm}$ .

If an usual formula for resistance takes into account the fact that in the standard metals the Fermi wave vector  $k_F$  is of the order of the inverse interatomic distance  $a^{-1}$

$$\rho = \frac{\hbar k_F}{ne^2 l} \sim \frac{\hbar a^2}{e^2 l}, \quad (2)$$

then it appears that the resistivity  $\rho^*$  corresponds to the Mott limit  $k_F l \approx 1$ ,

$$\rho^* \sim \frac{\hbar}{e^2} a, \quad l \sim k_F^{-1} \sim a, \quad (3)$$

the Mott limit, in terms of energy, means that a frequency of electron scattering by static defects  $\hbar/\tau$  reaches the Fermi energy  $\varepsilon_F$ , and the dimensionless parameter

$$\alpha = \hbar/\tau\varepsilon_F \quad (4)$$

approaches unity from below.

The fact that in any pure metal alloys the barrier (3) is not overcome, seems to mean that the high electron density prevents from appearing and developing the multifractal wave functions typical to the transition vicinity.

The continuity of the phase transition “metal-insulator” is experimentally proved only for doped semiconductors, and proved even in cases where a control parameter for the transition is the electron density.<sup>6</sup> With an increase of the electron density, the situation is changing. Fig. 2 shows

inhomogeneity in the electron system itself), which will not be discussed here (see Ref. 12, Ch. 7).

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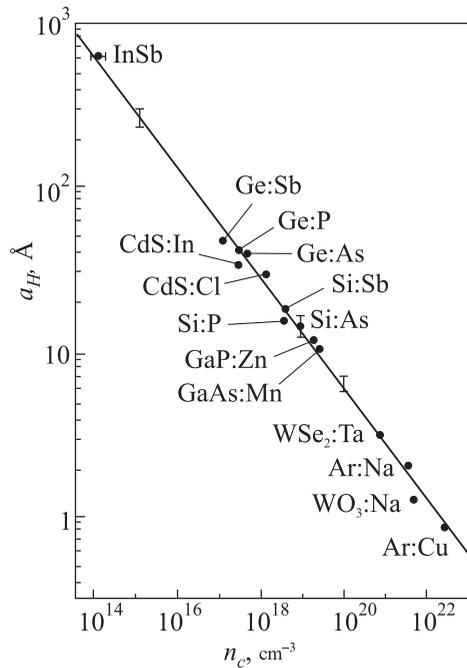


FIG. 1. Transitions metal-insulator in 15 different metals.<sup>3</sup>

results of experiments<sup>7</sup> on a disordered mixture of Ar and Cu atoms, obtained by simultaneous deposition of the atoms on a cold substrate. By changing the deposition time and the relative intensity of flow of the Cu and Ar atoms, it was possible to control a thickness of the film Ar:Cu and a relative concentration of Cu, and numerous calibration and measuring procedures allowed to determine these quantities with sufficient accuracy. In many films with a concentration of Cu close to critical one, the resistivity was found to be either about  $3 \cdot 10^{-2} \Omega \cdot \text{cm}$ , or at least by seven orders of magnitude higher, but never in between. That, and a similar result in a mixture Ar:Na, shown in Fig. 1, suggests that at concentrations  $n_c \geq 10^{21} \text{ cm}^{-3}$  the conductivity at the metal-insulator transition turns to zero abruptly. However, this should be checked on other systems with electron densities in the range  $10^{20} \text{ cm}^{-3} \lesssim n \lesssim 10^{22} \text{ cm}^{-3}$ .

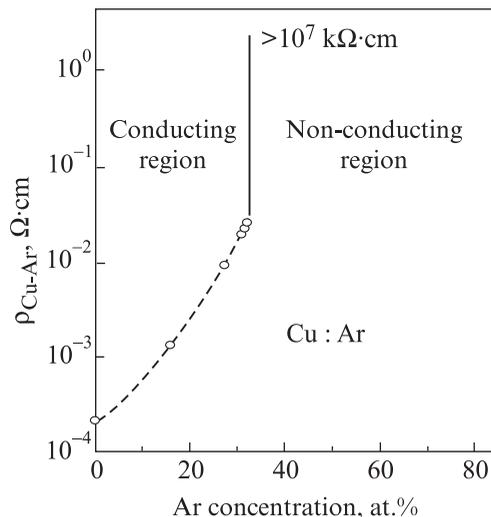


FIG. 2. The resistance at around 4 K of a mixture copper-argon, deposited on a cold substrate, depending on the composition of the mixture.<sup>7</sup>

Numerous low-temperature resistivity measurements in three-dimensional electron systems can be summarized as follows:

- for electron densities  $n \leq 10^{19} - 10^{20} \text{ cm}^{-3}$  the continuous phase metal-insulator transition takes place in accordance with the scaling theory<sup>2</sup> for non-interacting electrons under changes in both the level of disorder and electron concentration;
- with increasing the electron concentration in the region of  $10^{20} - 10^{21} \text{ cm}^{-3}$  at a very high level of disorder (amorphous matrix) there is a *jump-like* transition to a metallic state;<sup>7,8</sup>
- pure metal alloys with the electron concentration of  $n \geq 10^{21} \text{ cm}^{-3}$  remain in a metallic state at any level of disorder.

### 3. Temperature dependence of resistance in high-resistance alloys

Because a velocity of thermal motion of ions,  $s$ , described by phonons, is much less than that of electrons  $v_F$ , the electrons do not distinguish the static disorder of lattice from defects and the dynamic disorder induced by phonons. Therefore, by increasing the temperature and adding dynamic disorder to static one, a random potential, in which electrons are placed can be affected. Hence, the idea is to take a material with very high residual resistance, i.e., with the parameter  $\alpha \leq 1$  close to unity, and to try, by raising the temperature, to obtain the resistance greater than  $\rho^*$ .

Within the framework of a classical theory of the metal resistance, this idea appears to be as follows. The scattering on disorder and phonons are considered as independent (Matthiessen's rule), so that the total resistance  $\rho_{cl} = \rho_0 + G(T)$ . The index "cl" indicates that the resistance does not take into account interference corrections caused by the wave nature of an electron. The temperature-dependent part of the resistance, called the Gruneisen function  $G(T)$ , can be expressed in terms of electron-phonon scattering  $\tau_{ph}$ , and can be written as

$$G(T) = \frac{m}{ne^2\tau_{ph}} = \frac{\hbar}{e^2} \frac{\alpha_{ph}(T)}{k_F}, \quad \alpha_{ph} = \hbar/\tau_{ph}\varepsilon_F, \quad (5)$$

so that

$$\rho_{cl}(T) = \rho_0 + G(T) = \frac{\hbar}{e^2} \frac{1}{k_F} (\alpha + \alpha_{ph}(T)) \equiv \rho^* (\alpha + \alpha_{ph}(T)). \quad (6)$$

At low temperatures  $T \rightarrow 0$  the function  $\alpha_{ph}(T) \propto T^5$ , and at  $T \geq T_D/3$  ( $T_D$  is the Debye temperature) it approaches the asymptote<sup>9</sup>

$$\alpha_{ph}(T) \rightarrow \gamma T/\varepsilon_F, \quad (7)$$

where the numerical coefficient  $\gamma$  depends on properties of a particular material.

Using a literal notation, in particular, putting the deformation potential  $D \simeq e^2/a$ , and setting the  $k_F$  equal to the reciprocal-lattice vector  $K$ , it turns out that the factor  $\gamma = 1$ .<sup>10</sup> In real metals, it usually remains of the order of unity,

although it can sometimes be either less or greater than one. Therefore, from Eq. (7) it is seen that at normal values of  $\gamma \lesssim 10$  and temperatures, below the melting point, the value of  $\alpha_{\text{ph}}$  does not exceed 0.1–0.01. The condition  $\gamma \gg 10$  indicates a strong electron-phonon coupling.

It seems as if Eqs. (6) and (7) admit the possibility that with increasing the temperature the resistance  $\rho$  may become higher than  $\rho^*$ . However, in high-resistance alloys  $\alpha \gtrsim 0.3$  – 0.4 relation (6) is violated in the sense that the static and dynamic part of the resistance are no longer independent. The part of the resistance, which depends on temperature, becomes much smaller and may even be of opposite sign. A number of experimental observations were summarized in Ref. 11 by Mooij, who formulated a rule of thumb. The sign of derivative of the resistivity  $d\rho/dT$  in high-resistance alloys correlates with a value of the resistance:  $d\rho/dT > 0$  in metallic alloys with the resistance lower than 100–150  $\mu\Omega \cdot \text{cm}$ , but  $d\rho/dT < 0$  in alloys with higher resistance:

$$\left. \begin{array}{l} d\rho/dT > 0 \text{ at } \rho < \\ d\rho/dT < 0 \text{ at } \rho > \end{array} \right\} 100\text{--}150 \mu\Omega \cdot \text{cm} \quad (8)$$

(see also Ref. 12, Ch. 1). This is in the case of relatively high temperatures, from 20 to 30 K to room temperature and even higher.

The first attempt to explain the Mooij rule theoretically was made in Ref. 13 using the scaling theory<sup>2</sup> of the quantum metal–insulator transition. However, the problem is that in these systems the transition is just not observed, so the assumption that we are in its vicinity, is not very convincing. Of more interest is the note in the book Ref. 14 (section 2.5.3) that the Mooij rule may be due to weak localization, which results in a negative temperature coefficient of resistance. In the development of this notice in the present paper, the possibility of explaining the empirical laws (8) is studied by considering an effect of weak localization in a simple model.

We are interested in highly disordered alloys with values of  $\alpha$  in the range of  $0.2 \lesssim \alpha \leq 1$ . As can be seen from Eq. (7), for these alloys up to room and even higher temperatures, the inequality is fulfilled

$$\alpha \gg \alpha_{\text{ph}}(T). \quad (9)$$

The dimensionless frequency of electron-electron collisions  $\alpha_{ee} = \hbar/\tau_{ee}\varepsilon_F = (T/\varepsilon_F)^2$ , which also lead to the loss of phase coherence, is far less than  $\alpha_{\text{ph}}$ . This means that due to the large  $\alpha$  in these alloys up to room temperatures there remains a coherent diffusion mode, in which there should take place the diffraction of an electron wave on a random potential field of impurities. For  $\alpha \ll 1$ , when the electron wave function is a long wave train and for calculation, one can restrict to the first approximation of perturbation theory, the result of diffraction is weak localization.<sup>15–17</sup> The effect is an appearance of the quantum correction  $\delta\sigma$  to the conductivity, expressed through the diffusion length  $L_\varphi$ , determined by scattering on phonons:

$$\delta\sigma = \frac{e^2}{\hbar} \frac{1}{L_\varphi} = \frac{e^2}{\hbar} k_F (\alpha\alpha_{\text{ph}})^{1/2}, \quad L_\varphi = l\sqrt{\tau_{\text{ph}}/\tau}. \quad (10)$$

Strictly speaking, in the region of interest  $\alpha \sim 1$ , it is not allowed to restrict to the first approximation and to use the

formulas of weak localization.<sup>16,17</sup> However it is very instructive to see how a relative contribution of this first approximation changes with increasing  $\alpha$ .

It should be noted that this, not quite correct extension of applicability of quantum corrections to finding the qualitative features of transport properties is used quite often. For example, by doing so, one can determine a form of the temperature dependence of conductivity in the critical region near the metal-insulator transition or a position of the crossover from the logarithmic temperature dependence of two-dimensional electron systems to exponential one.

By adding to the classical expression for conductivity of three-dimensional medium  $\sigma_{\text{cl}} = 1/\rho_{\text{cl}}$  the expression for the quantum correction (10), we obtain

$$\sigma = \sigma_{\text{cl}} + \delta\sigma = \frac{e^2}{\hbar} k_F \left[ \frac{1}{\alpha + \alpha_{\text{ph}}} + (\alpha\alpha_{\text{ph}})^{1/2} \right]. \quad (11)$$

In expression (11) for the conductivity, the monotonically increasing with temperature value of  $\alpha_{\text{ph}}$  in the first of the two terms is included in the denominator, and in the second in the numerator. Equating to zero the derivative  $\partial\sigma/\partial\alpha_{\text{ph}}$ , we obtain the equation

$$\alpha + \alpha_{\text{ph}} = \sqrt{2}(\alpha_{\text{ph}}/\alpha)^{1/4} \quad (12)$$

for a line along which this derivative changes the sign (see Fig. 3). Above this line, the derivative  $\partial\sigma/\partial\alpha_{\text{ph}}$  and, as consequence, the derivative  $\partial\sigma/\partial T$  are positive, below they are negative. Specifically, it appears that for  $\alpha > 0.7$  at all physically relevant temperatures (room and lower) an increase in the temperature leads to a decrease in the resistance.

Thus, the experimental temperature dependencies of resistance of high-resistance alloys can be described using quantum corrections obtained in the first order perturbation theory. The localization remains weak, but thanks to a very small elastic mean free path  $l \sim k_F^{-1}$ , persists up to high temperatures, leading to the Mooij rule.

#### 4. Materials with a large constant of electron-phonon interaction

If in a pure metallic material the electron-phonon interaction is strong, the coefficient  $\gamma$  in Eq. (7) can appear to be

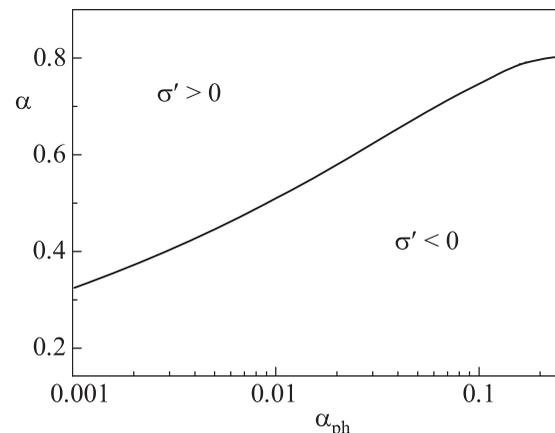


FIG. 3. A sign of the derivative  $\partial\sigma/\partial T$  depending on values of the parameters  $\alpha$  and  $\alpha_{\text{ph}}$ .

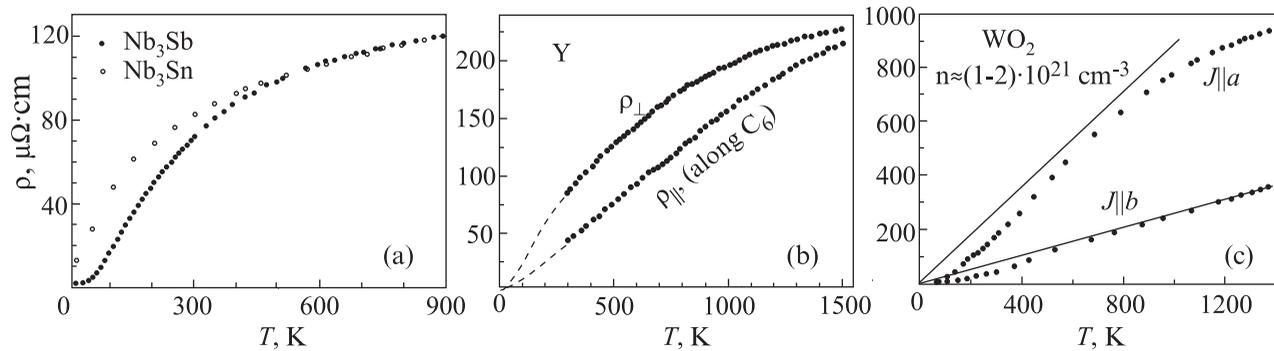


FIG. 4. The saturation of the resistance in materials with strong electron-phonon interaction: alloys Nb<sub>3</sub>Sb and Nb<sub>3</sub>Sn (Ref. 18) (a); a single crystal of Y with an anisotropic resistance (Ref. 19) (b); a single crystal of WO<sub>2</sub> with an anisotropic resistance and a somewhat smaller electron density (Ref. 20) (c).

$\gamma \geq 20$ . Suppose, for example,  $\gamma \sim 25$ , and the Fermi energy  $\varepsilon_F \sim 10^4$  K. Then, at about 400 K, the dimensionless frequency of electron-phonon collisions,  $\alpha_{\text{ph}}$ , according to Eqs. (5) and (7), will be of order unity. Therefore, even for a small residual resistance,  $\alpha \ll 1$ , the total resistance can reach  $\rho^*$ .

However, an experiment does not support this assumption. As can be seen in Fig. 4, where the curves  $\rho(T)$  for several materials are shown, when approaching  $\rho^*$  the resistance stops following the Grüneisen function and instead of a linear growth there is a tendency to saturation. In single crystals with anisotropic resistance this tendency manifests first for the current directions, corresponding to a rapid increase in resistance with temperature (Figs. 4(b) and 4(c)), so that when temperature increases an isotropization of the resistance takes place.

Phenomenologically, the experimentally observed curves  $\rho(T)$  can be described<sup>18</sup> with the concept of shunt resistance  $\rho_{\text{sh}}$ , assuming that

$$\rho(T) = [\rho_{\text{cl}}(T)^{-1} + \rho_{\text{sh}}^{-1}]^{-1}. \quad (13)$$

Equation (13), corresponding to a scheme of two parallel resistances, is typical for electronic systems with several groups of carriers. In systems with a single group of carriers, a contribution of different scattering processes is usually described by the scheme of series resistances. However, in such systems, one can come to formula (13) by introducing some correlations of scattering events. For example, suppose that between scattering events there must pass the minimum time  $\tau_0$ , then all restrictions are removed and everything proceeds as usual.<sup>21</sup> If the moment of the first scattering event is  $t = 0$ , then the probability of the next event is assumed to be

$$p = \begin{cases} 0, & t < \tau_0, \\ 1/\tau, & t > \tau_0. \end{cases}$$

Then, in the standard formula for the conductivity  $\sigma = ne^2\tau/m$ , written through  $\tau$  and the effective mass  $m$ , instead of  $\tau$  as the average time between collisions there will be  $\tau + \tau_0$ . Hence, expression (13) is obtained with

$$\rho_{\text{sh}} \simeq \frac{\hbar}{e^2} \frac{\alpha_0(T)}{k_F}, \quad \alpha_0 = \frac{\hbar}{\tau_0} \varepsilon_F. \quad (14)$$

The assumption of the existence of time  $\tau_0$ , as applied to scattering by phonons, means the finiteness of the time of

emission or absorption of a phonon by an electron, which would limit the frequency  $\hbar/\tau_{\text{ph}}$  from above by the value  $\hbar/\tau_0$ . To estimate qualitatively a possible value of  $\tau_0$  it should be assumed that this is the time during which the electron and phonon are shifted with respect to each other by the phonon wavelength  $\lambda$ . Assuming  $\lambda \sim a$ , we obtain the estimate

$$\tau_0 \sim a/v_F \sim \hbar/\varepsilon_F, \quad (15)$$

so that

$$\alpha_0 \sim 1 \quad \text{and} \quad \rho_{\text{sh}} \sim \rho^*. \quad (16)$$

We emphasize that the assumption that the time of interaction between an electron and a phonon is purely qualitative, and Eqs. (15) and (16) do not have a rigorous theoretical basis.

## 5. Conclusion

Results of the performed analysis are convenient to formulate using the right side of Eq. (6). In the first section of the article it is talked about trying to find a pure metal alloy, in which the static disorder would make the resistance  $\rho > \rho^*$ , i.e.  $\alpha > 1$ . However, none of the systems with high electron density could be transformed by disorder into a state with multifractal wave functions. In Sec. 3 there are discussed efforts to achieve the same effect by increasing the sum  $\alpha + \alpha_{\text{ph}}$  due to the mutual effect of disorder and temperature. The way appeared to be blocked by an effect of weak localization (the Mooij rule). Finally, in the described in Sec. 4 experiments with materials with a large constant of electron-phonon interaction it was revealed that with increasing temperature, there occur a deviation from the Gruneisen functions and a saturation of the function  $\alpha_{\text{ph}} \rightarrow 1$ .

All this does not apply to quasicrystalline alloys, which are also purely metallic, but behave quite peculiar. In a maximally disordered amorphous state their residual resistance is less than  $\rho^*$ ; after settling the quasicrystalline symmetry the resistance grows and becomes larger than  $\rho^*$  (in quasicrystals Al<sub>70</sub>Pd<sub>22.5</sub>Re<sub>7.5</sub> with proper heat treatment the conductivity even turns to zero, i.e. there is the Anderson transition observed<sup>22</sup>), and then after the crystallization and the onset of the translational symmetry the resistance falls again and sets at a level much lower than  $\rho^*$ . However, such a behavior can be explained by special factors (the appearance of