

Resistivity of metallic systems with a strong dynamic disorder

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Abstract. If the static disorder in a system is increased the conductivity and the electron mean free path decreases to the limit where it reaches the Ioffe-Regal criterion. In this paper experimental results are presented which show that dynamic disorder (produced by electron-phonon interaction) can produce similar effects as static disorder. In certain metallic glasses it has been found that when the resistivity as a function of temperature reaches a critical value (almost equal to the maximum metallic resistivity value) the TCR changes from positive to negative values.

Keywords. Resistivity; metallic systems; dynamic disorder.

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1. Introduction

In accordance with the known Ioffe-Regal criterion the electronic mean free path, l , cannot be shorter than the electron wavelength. When applied to the metals with the Fermi momentum K_F this means that

$$l > l_{\min} \approx \pi/K_F. \quad (1)$$

The metallic systems with l approximating l_{\min} are extensively being studied in the last few years due to the progress achieved in the technique of producing amorphous alloys. Mostly the small mean free path l is the consequence of the static disorder, i.e. random arrangement of atoms at low temperatures. On the other hand, the smallest possible l can also be obtained in some cases in a perfect crystal by increasing the temperature T , i.e. by introducing the dynamic disorder.

2. Comparison between static and dynamic disorders

Let us refer to the plane $(T, \hbar/\tau)$ with the Fermi energy ε_F on both the axes as a characteristic scale (figure 1). The condition of the degeneracy of the electron gas $T < \varepsilon_F$, along with the uncertainty relation

$$\Delta\varepsilon \approx \hbar/\tau \lesssim \varepsilon_F = \hbar^2 K_F^2/2m \quad (2)$$

which isolate a square in this plane (criteria (1) and (2) actually are equivalent, differing in the numerical factor $\pi/2$ only). The formula for the resistivity

$$\rho = m/ne^2\tau = \hbar K_F/ne^2l, \quad (3)$$

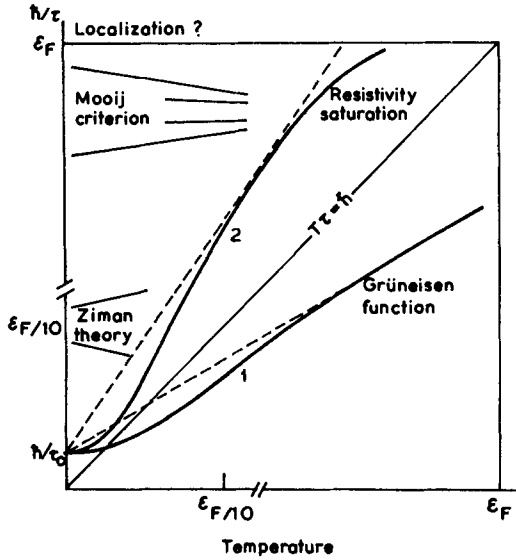


Figure 1. A diagram in $(T, \hbar/\tau)$ -plane illustrating applicability of the Boltzmann equation.

enables us to plot one more scale along the ordinate. Substituting into (3) the electron density $n = \nu a^{-3}$ (ν is the number of free electrons per atom, a is the mean interatomic distance) and $K_F = (3\pi^2 n)^{1/3}$ we obtain

$$\rho = (3\pi^2)^{-1/3} (\hbar/e^2) (a^2/\nu^{2/3} l). \quad (4)$$

Substituting the value of l_{\min} from (1) or (2) into (4), we get

$$\rho = (400 \div 600) \nu^{-1/3} \mu\Omega \cdot \text{cm}. \quad (5)$$

The dependence of ρ on ν being weak, we can assume $\nu = 1$ for all metals. Hence we obtain the resistivity scale shown in figure 1.

Transport properties of metals with a sufficiently large electron mean free path l are accounted for by the noninteracting gas model based on the Boltzmann equation. This approach obviously is applicable inside the lower triangle in figure 1, where the electron energy uncertainty due to scattering is smaller than the temperature broadening of the Fermi distribution. However, this description is used sometimes in the upper triangle $T\tau < \hbar$. For example, shifting along the ordinate we reach a region, where the Ziman theory developed for the liquid metals is used. The wave functions in this theory are considered to be plane waves, and their scattering by a random potential is calculated in the Born approximation (Faber 1969). The success of the Ziman theory was conditioned, as a matter of fact, by a high electron density. The screening of the random potential of the ions is so strong that even in the absence of the long-range order the quantity l remains several times larger than the electron wavelength K_F^{-1} . That the quantity l can really be large in liquid follows from the values of the resistivity of pure liquid uni-, bi- and tri-valent metals (Faber 1969) that do not exceed $40 \mu\Omega \cdot \text{cm}$.

To the alloys with the resistivity of $\rho > 100/150 \mu\Omega \cdot \text{cm}$, Ziman's theory is not applicable. Then the empirical rule of Mooij (1973) should be used, the sign of the

temperature coefficient of the resistivity depends on the ρ value. It is to be emphasized that the applicability regions of the Ziman theory and the Mooij rule do not overlap. In particular, the negative sign of the temperature coefficient of resistivity of bivalent metals described by Ziman theory contravenes the Mooij rule.

If the resistivity of an alloy were $\rho \gtrsim 500 \mu\Omega \cdot \text{cm}$ at $\nu \approx 1$ ($n \approx 10^{21} - 10^{22} \text{ cm}^{-3}$) it would mean that $l < l_{\text{min}}$. Such an alloy would be expected to undergo the Anderson transition into the dielectric state. However, the amorphous alloys consisting of "metallic" atoms with weakly bound valence electrons never have the resistivity larger than $400 \mu\Omega \cdot \text{cm}$. On the other hand, there are no examples of the Anderson transition in metallic systems with $n \gtrsim 10^{20} \text{ cm}^{-3}$. Both facts seem to be the result of screening, that self-consistently decreases the amplitude of the random potential to a level which ensures the fulfilment of inequalities (1) and (2).

Thus, the problem of the Anderson transition near the upper side $\hbar/\tau = \varepsilon_F$ of the square in figure 1 proves to be closely connected with the screening, i.e., in the final analysis, with the electron-electron interaction. As for the latter, in the upper triangle $T\tau < \hbar$, it is affected by the elastic scattering; during the interaction time \hbar/T the electrons go through many collisions with scatterers (impurities or phonons) which determine the value of τ .

In principle, the upper side of the square in figure 1 can be approached by means of the electron-phonon interaction. The Grüneisen curve $\rho_{\text{id}}(T)$, describes in terms of the kinetic equation the resistivity caused by the phonon scattering. At temperatures above the Debye temperature θ it approaches the linear dependence

$$\rho = \alpha T \quad (T \gg \theta). \quad (6)$$

According to the order-of-magnitude estimate, for a typical metal with $K_F \approx a^{-1}$ and deformation potential $D \approx \varepsilon_F \approx e^2/a$ the asymptote is just the diagonal $\hbar/\tau = T$ of the square. Because of numerical coefficients, it may lie in reality either below (curve 1 in figure 1) or above the diagonal (curve 2). Curve 1 crosses the upper triangle only at low temperatures. In this domain l and τ are controlled by the elastic impurity scattering. It is known that under these conditions the behaviour of the electron-electron (Al'tshuler and Aronov 1979) and electron-phonon (Schmid 1973; Al'tshuler 1978) scatterings changes. At $T \gg \theta$ the scattering by phonons is quasielastic and in this sense resembles the scattering by impurities. Therefore the physical ideas forming the basis of the results of Al'tshuler and Aronov (1979), Schmid (1973) and Al'tshuler (1978) are also seemingly applicable for curve 2 at high temperatures. We mean here the change in the probability of the electron-electron scattering occurring because of the diffusion of one electron in the field of another, the appearance of a density of states extremum on the Fermi level (Al'tshuler and Aronov 1979) as well as the change in the probability of scattering by long wavelength phonons with the wave vectors $q \ll l^{-1}$ (Schmid 1973; Morton *et al* 1978).

It is clear that if the curve $\rho(T)$ is situated in the upper triangle, the resistivity increase is to be limited with increasing temperature. This problem—designated as the problem of resistivity saturation—became the subject of numerous investigations after the publication of the paper by Fisk and Webb (1976) who connected for the first time the behaviour of the temperature dependence of the resistivity observed in Nb_3Sb and Nb_3Sn crystals with the Ioffe-Regel criterion. Since then a rather rich experimental

material has been gained (Sunandana 1979; Lawson 1985; Mori *et al* 1981; Nedellec *et al* 1985) which shows that the tendency to saturation is always present when the mean free path of carriers approaches to limit (1) (Gurvitch 1983).

Since the velocities of thermal motion of atoms are much lower than the electron velocities (static and dynamic disorders appear similar to an electron). However, when the disorder is dynamic the electron distribution function is broadened by the temperature.

3. Experimental approach to the dynamic disorder problem

The experimental study of the problem encounters some complications. Since the experiment is carried out at high temperatures and the electron structure of metals is complicated it may happen that the observed deviations of $\rho(T)$ from the linear dependence (6) are due to specific peculiarities of the electron spectrum of the material involved. One can imagine, for example, a simple semiconductor effect of the increase of the carrier density due to the excitation onto the Fermi level of electrons from a completely filled band. Along curve 2 it is the quantity \hbar/τ and not T that first becomes equal to the excitation energy. This also should affect the resistivity (Chakraborty and Allen 1979). As a matter of fact, the resistivity has to change, when T or \hbar/τ comes up to any characteristic energy describing the electron spectrum (such as the width of the peak in the density of states of A-15 superconductors (Cohen *et al* 1967); the energy of the s-d hybridization (Weger *et al* 1984 etc.).

It is difficult to consider these complications because we do not normally know the electron spectrum sufficiently well. This determines the strategy of the experimental studies of the resistivity saturation. On the one hand, this effect has to be searched for in various classes of materials and, on the other, one has to look for extra variables that could have influence on the limit value of the resistivity.

It is seen (Fisk and Webb 1976; Morton *et al* 1978; Sunandana 1979; Mori *et al* 1981; Gurvich 1983; Lawson 1985; Nedellec *et al* 1985) that resistivity saturation takes place in rather different materials. Particular attention should be drawn to the fact that the effect is observed in In_3Bi_3 (Mori *et al* 1981) containing no atoms with unfilled *d*-shells.

The present paper presents additional experimental data obtained on (i) Cu-Zr alloys in the crystalline state; for some compositions the $\rho(T)$ dependences exhibit not only saturation but even a maximum; (ii) on high quality WO_2 single crystals with a large anisotropy of ρ .

4. Alloys Cu-Zr (Gantmakher and Kulesko 1985)

The samples were produced by recrystallization of an amorphous ribbon (the accuracy in the composition determination was about 2–3%). Measurements were carried out on strips of dimensions $3.5 \times 25 \text{ mm}^2$ using d.c. method. The results of measurements are shown in figure 2 for three alloys of different compositions. Crosses stand for the values obtained before crystallization of the amorphous ribbon, circles after crystallization, the open and solid circles corresponding to different cycles of measurements.

All the known data on the electron structure of alloys of the system Cu-Zr (Ching *et al* 1984) give us no reasons to attribute the existence of a maximum in the two upper

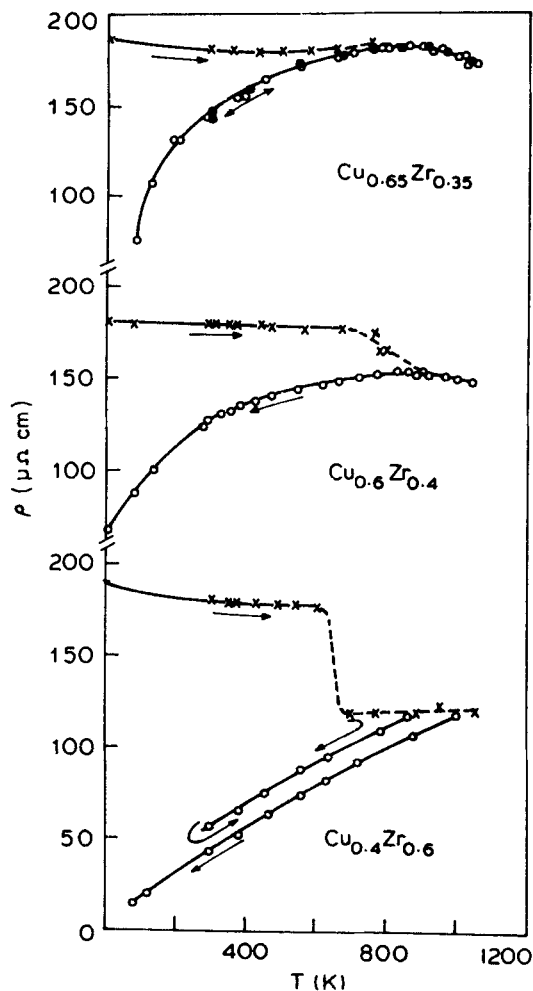


Figure 2. Resistivity of three Cu-Zr samples with different Cu content.

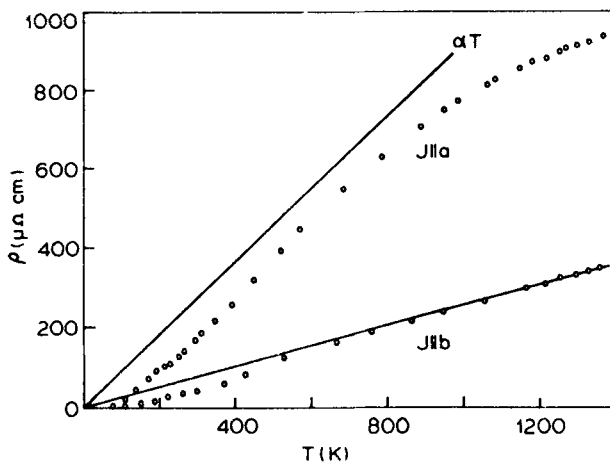


Figure 3. Temperature dependence of resistivity of WO_2 samples of different orientation.

curves to any peculiarity of the dispersion law in copper-rich alloys. At the same time we see correlation between the existence of a maximum and the change of ρ during crystallization. The maximum is observed only when ρ falls down during crystallization insignificantly, i.e. when the dynamic disorder is as effective as the static one.

In the above section we have affirmed that the amplitude of the scattering potential decreases self-consistently thus preventing localization. In our opinion, it is possible to pass over this affirmation using the two-band model of electron spectrum. The carriers in one of the bands may become localized whereas in the second band they may remain delocalized thus securing the conservation of metallic conductivity. Then the existence of the maximum could be explained reasonably well. Let both s- and d-electrons be present in the alloy. Starting with room temperatures the d-electrons are in a "limiting regime" $l \approx a$. If the source of scattering were static disorder, the decrease of resistivity with the temperature increase could be interpreted in terms of thermally activated hops of localized carriers. A variant of these speculations is believed to be valid also for localization induced by dynamic disorder. Then we have to admit that phonons strengthen localization at low temperatures and weaken it at high temperatures.

The proposed explanation implies coexistence of localized and delocalized state at the Fermi level. This contradicts Mott's postulate (Mott and Davis 1979).

5. Oxide WO_2 (Gantmakher *et al* 1986)

Samples in the form of sticks were cut from single crystals grown by the vapour transport. They were about 2–4 mm long and $0.3 \times 0.4 \text{ mm}^2$ across. The crystal orientation was determined using the x-ray technique. The residual resistance did not exceed 1–2% of the room resistance and could be neglected. The resistivity of WO_2 is anisotropic. The diagonal components of the resistivity tensor written down in the main axes at room temperatures are $\rho_1 = 50 \mu\Omega \cdot \text{cm}$; $\rho_2 = 60 \mu\Omega \cdot \text{cm}$; $\rho_3 = 180 \mu\Omega \cdot \text{cm}$. The temperature measurements have shown that in some directions resistivity of WO_2 exhibits a tendency to saturation while in others it does not. This is illustrated in figure 3. The experimental curves $\rho(T)$ are plotted for the directions where ρ_{room} has its maximum and minimum values.

For quantitative interpretation of results we tried, as usual, to extract from the function $\rho(T)$ an "ideal" part described by the Boltzmann equation. The difficulty is that even for this ideal part the analytical expression for an arbitrary electron and phonon spectra exists only in the asymptotical form, while the analytical expressions for high-temperature corrections, which are of interest for us, are not known at all. Let us consider in detail the quantity ρ_{id} . In the isotropic model with the spherical Fermi surface and Debye phonon spectrum the dependence $\rho_{\text{id}}(T)$ is described by the Grüneisen function. Note that at $T = \theta$ the value of this function is still 6% smaller than that of the asymptote (6). So the latter can only be used beginning with $T \gtrsim (1.5 \text{ to } 2)\theta$. For the isotropic model $\rho_{\text{id}}(T)$ is really known within the whole temperature range. However, if the Fermi surface consists of several isolated closed sheets and the phonon spectrum has optical branches the Grüneisen function becomes very complicated. In both cases a specific temperature θ_0 appears at which new processes start: transitions between sheets or scattering by optical phonons. At $T \gg \theta$, θ_0 asymptote (6) is still valid, but at low temperatures it is impossible to calculate $\rho_{\text{id}}(T)$ without a detailed knowledge of the spectra. In WO_2 the dependence $\rho_{\text{id}}(T)$ is certainly more complicated

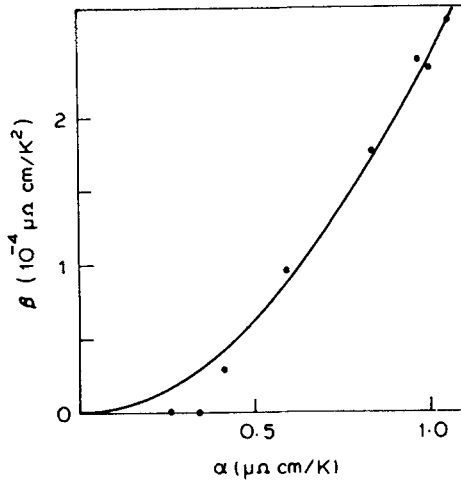


Figure 4. Correlation between coefficients α and β in the expression $\rho = \alpha T + \beta T^l$ which describes the WO_2 experimental results.

than in the isotropic model. It is difficult to say whether the complications are caused by the optical phonon scattering or by interband transitions—in all likelihood both factors are responsible. However, it became clear that the Grüneisen curve could not be used for description of $\rho_{\text{id}}(T)$ in WO_2 . Therefore in the analysis of the curves we have only used the data for temperatures $T \gtrsim 700$ K assuming that in this region $\rho_{\text{id}} \sim T$. Note that the residual resistance of our samples at these temperatures was always smaller than 1% of the total and obviously could be neglected.

In all our experiments the high-temperature deviations of $\rho_{\text{id}}(T)$ from a straight line were comparatively small. Therefore it might be worthwhile assuming that the correction $\rho - \rho_{\text{id}}(T)$ is small to write it in the form

$$\rho - \rho_{\text{id}} = \beta T^l, \quad l > 1. \quad (7)$$

In principle the curves $\rho(T)$ for various directions of the current with respect to the crystal axes could be similar differing only in the scale along the ρ -axis, i.e. $\beta \sim \alpha$. This would be the case, for example, if the deviation of ρ from ρ_{id} were the result of increase of carrier density. Our measurements show, however, that in WO_2 an “enhanced anisotropy” is realized: the anisotropy of the correction (7) is larger than the anisotropy of ρ_{id} itself (see figure 4). Since the sign of the high-temperature correction is negative, the “enhanced anisotropy” of the correction means a decrease in the anisotropy of ρ with increasing T . It is known that something like this is also observed in other materials. For example, yttrium is an anisotropic metal with high absolute value of the resistivity. At high temperatures its resistivity saturates and the anisotropy of the resistivity vanishes (Zinovev *et al* 1975). This gives us reasons to believe that the phenomenon observed in WO_2 is a rather common one.

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