Dominant role of the electron–electron scattering in low-temperature electrical resistivity of organic metals

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The electrical resistivity of β-$(\mathrm{ET})_2X$ organic metals ($X = I_3$, AuI_2, I_2Br, IBr_2) has been measured at temperatures below 20 K. In this range of temperatures the resistivity of all the compounds obeys an expression with a term AT^2, where the coefficient A is independent of the residual resistivity and approximately the same for all the samples. The AT^2 contribution to the resistivity of organic metals is attributed to electron–electron collisions. In the case of the investigated compounds this electron scattering contribution is anomalously large because of the low values of the Fermi velocity and energy.

A characteristic feature of the behavior of organic metals belonging to the β-$(\mathrm{ET})_2X$ family [where ET stands for bis(ethylenedithiolo)tetrathiofulvalene and X is a linear anion of the type I_3, IBr_2, AuI_2, etc.] is a strong temperature dependence of the electrical resistivity at low temperatures. Typically, the resistivity falls by a factor of 2–3 between 15 and 4.2 K. This fall is superposed on a background of relatively small values of the ratio $R(300\ \mathrm{K})/R(4.2\ \mathrm{K})$, which are of the order of 300–1000. In ordinary metals with these values of the ratio $R(300\ \mathrm{K})/R(4.2\ \mathrm{K})$ the resistivity in practice ceases to vary at temperatures below 10–15 K.

We shall report experimental and theoretical investigations of the temperature dependence of the resistivity of metals belonging to the β-$(\mathrm{ET})_2X$ family, where $X = I_3$, AuI_2, IBr_2, and I_2Br. In the range $T < 20$ K the dependence $\rho(T)$ is given by

$$\rho(T)=\rho(0)+AT^2, \tag{1}$$

where the quadratic term is due to the contribution of electron–electron collisions and is anomalously large.

The experimental results are plotted in Fig. 1 in the form of the temperature dependence of the resistivity of metals using the coordinates ρ–T^2. In the case of β-$(\mathrm{ET})_2I_3$ this figure gives information on the behavior of both β_L and β_H phases characterized by low and high critical temperatures of the superconducting transition; the phase β_H was obtained in a cycle involving cooling of the crystal to 60 K under a pressure of 400 bar and subsequent removal of the pressure.[1] Figure 2 shows the form of $\rho(T^2)$ obtained for several β-$(\mathrm{ET})_2AuI_2$ crystals. We can see that the coefficient A in front of the quadratic term is practically the same for all the samples and equals $(6 \pm 0.2)\times 10^{-7}\ \Omega\cdot\mathrm{cm\ K}^{-2}$, whereas the residual resistivity $\rho(0)$ changes severalfold from sample to sample. The same conclusion that A is independent of $\rho(0)$ is obtained from a comparison of the behavior of two phases of β-$(\mathrm{ET})_2I_3$: the transition from β_L to β_H reduces $\rho(0)$ by a factor of about 20, whereas the value of $A = (2.5 \pm 0.2)\times 10^{-7}\ \Omega\ \mathrm{cm\ K}^{-2}$ remains constant within the limits of the experimental error.

There are two mechanisms that can generally give rise to a quadratic temperature dependence of the resistivity at low temperatures. The first is the electron–phonon scattering in a strongly disordered lattice, related to violation of the law of conservation of momentum[2] (see also Ref. 3 and the literature cited there). In this case we can expect the quadratic contribution to be proportional to the residual resistivity: $\rho(T) - \rho(0) \propto \rho(0)(T/T_D)^2$, where T_D is the Debye temperature. It follows from the results presented in Figs. 1 and 2 that in our case this relationship is not obeyed and the coefficient A is independent of $\rho(0)$.

The second mechanism that can give rise to a dependence of the $\rho(T) - \rho(0) \propto T^2$ type is the electron–electron scattering.[4] For normal metals the contribution of this mechanism to the resistivity is small, but it can increase considerably in the case of metals with low Fermi energies and velocities.

A detailed analysis of the electron–electron contribution to the resistivity of isotropic three-dimensional crystals can be found in Ref. 4. Similar calculations for the system with almost two-dimensional electron motion (which agrees well with calculations of the band structure) and experimental parameters of β-$(\mathrm{ET})_2X$ crystals yield the expression

$$\rho_{ee}(T)=KG(ck_F)\frac{e^2}{v_F E_F}\left(\frac{T}{E_F}\right)^2, \tag{2}$$

where K is a numerical coefficient; the factor G allows for the efficiency of the umklapp processes; c is the distance between the conducting layers; k_F, v_F, and E_F are the momentum, velocity, and energy of an electron on the Fermi surface. The factor G can be estimated from

$$G \approx \left[\int\limits_{V_m} n(\mathbf{r})e^{i\mathbf{g}\mathbf{r}}\,d\mathbf{r} \Big/ \int\limits_{V_m} n(\mathbf{r})\,d\mathbf{r}\right]^2, \tag{3}$$

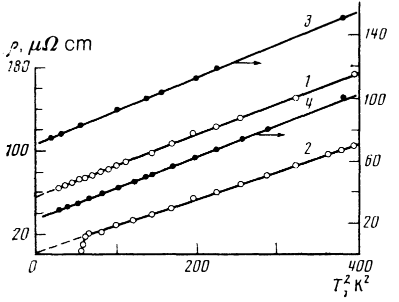

FIG. 1. Dependence $\rho(T^2)$; 1) β-$(\mathrm{ET})_2I_3$ in the β_L phase ($T_c = 1.5$ K); 2) β-$(\mathrm{ET})_2I_3$ in the β_H phase ($T_c = 7.5$ K); 3) β-$(\mathrm{ET})_2I_2Br$; 4) β-$(\mathrm{ET})_2IBr_2$.

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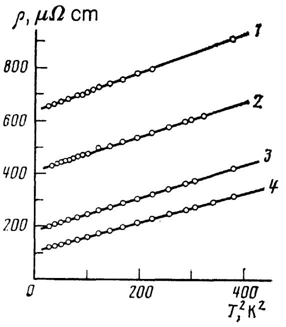

FIG. 2. Dependence, $\rho(T^2)$ for four samples of β-$(ET)_2AuI_2$ with different values of the residual resistivity.

where **g** is the reciprocal lattice vector and $n(\mathbf{r})$ is the distribution of the electron density in a unit cell; the integration is carried out over the unit cell volume. In the case of ordinary metals the function $n(\mathbf{r})$ does not change greatly within a unit cell because of the relatively weak potential of the ions which is screened strongly by conduction electrons. Therefore, in this case the factor G is small: $G \approx 0.1$–0.01. The energy band structure of organic metals is described well by the tight-binding model for which we have $G \approx 1$.

The following assumptions were made in the derivation of Eq. (2).

1. The umklapp processes are not limited by the law of conservation of momentum, i.e. $g < 2k_F$. This condition is satisfied for a closed Fermi surface lying quite close to the boundaries of the Brillouin zone, which is typical of β-$(ET)_2X$ compounds in which the band occupancy is 3/4 (Ref. 5).

2. The quantities k_F, g, and the reciprocal radius for the Debye screening are approximately equal.

3. The value of ρ_{ee} is calculated using the Born approximation which can overestimate the electron–electron contribution by almost one order of magnitude.

4. The real band structure is ignored.

Under these assumptions the value of K in Eq. (2) clearly lies within the interval 0.1–1. Bearing this in mind, we can estimate A with the aid of Eq. (2) but only to the nearest order of magnitude. The values $v_F \approx 10^7$ cm/s, $E_F \approx 0.1$ eV, and $ck_F \approx 5$ can be deduced from the experimental value of the plasma frequency ω_p (Ref. 6). In the model of noninteracting electrons under conditions of essentially two-dimensional motion we have $\omega_p \approx 4\pi ne^2/m$, $n = E_F m/2\pi c\hbar^2$, $v_F \approx (2E_F/m)^{1/2}$, and $k_F \approx mv_F/\hbar$, where n is the conduction electron density. Consequently, for $\omega_p \approx 0.7$ eV, we obtain $A \approx 2\times 10^{-7}\ \Omega\ \mathrm{cm}\ \mathrm{K}^{-2}$. The agreement between this A and the experimental value means that the electron–electron scattering mechanism can account for the T^2 dependence exhibited by the resistivity. This mechanism is supported also by the relatively small variation of A within the limits of the β-$(ET)_2X$ family with symmetric anions. The energy band structure is practically the same for the whole of this family.

Extrapolation of the dependence (1) from low to room temperatures gives $\rho(300\ \mathrm{K}) \approx 1.8\times 10^{-2}\ \Omega$ cm for β-$(ET)_2I_3$. This is in satisfactory agreement with the experimental value $\rho(300\ \mathrm{K}) \approx 3.6\cdot 10^{-2}\ \Omega$ cm, which can be reduced by a factor of 3–4 due to the constant-volume correction. We note that the thermal expansion due to heating from $T < 40$ K to 300 K increases the lattice parameters by about 1% (Refs. 7 and 8). This can be compensated by applying a pressure of about 2–3 kbar (Ref. 9) if the results of Ref. 10 are interpolated linearly to allow for changes in the parameters at pressures from 0 to 9.5 kbar.

The contribution of the electron–phonon scattering at temperatures $T \gg T_D$ can be estimated from the expression

$$\rho_{eph} \approx 8\pi^2 T\lambda/\hbar\omega_p^2, \qquad (4)$$

where λ is the dimensionless electron–phonon interaction constant. If $\lambda \approx 1$, we obtain $\rho(300\ \mathrm{K}) \approx 0.4\cdot 10^{-2}\ \Omega$ cm.

We can therefore see that the electron–electron scattering process makes a considerable contribution to the resistivity throughout the investigated temperature range.

In the case of organic metals belonging to the $(TMTSF)_2X$ family the low-temperature resistivity also includes a contribution proportional to T^2. In the compound with $X = PF_6$ above the transition to the insulating state (16–18 K) the resistivity can be described by Eq. (1) with $A = 2\times 10^{-8}\ \Omega\ \mathrm{cm}\ \mathrm{K}^{-2}$ (Ref. 11) right up to 80 K (at higher temperatures the thermal expansion is important). This contribution can also be explained by the electron–electron scattering.

For ordinary metals with one band the values of v_F and E_F are at least an order of magnitude higher than for organic metals and the factor G is one or two orders of magnitude less. Therefore, the coefficient A for ordinary metals is very small and the electron–electron contribution to the resistivity is observed only at very low temperatures when $\rho \propto T^5$. Organic metals are in this sense unique. They satisfy all the requirements necessary for the manifestation of the electron–electron scattering at all temperatures.

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