Organic semiconductors with extremely narrow energy gap

K. Kajita\textsuperscript{a,}\textsuperscript{*}, N. Tajima\textsuperscript{b}, A. Ebina-Tajima\textsuperscript{a}, Y. Nishio\textsuperscript{a}

\textsuperscript{a}Department of Physics, Toho University, Miyama 2-2-1, Funabashi 274-8510, Japan
\textsuperscript{b}Molecular Materials Laboratory, RIKEN, Japan

Abstract

This paper describes the discovery and investigation of a group of organic conductors that behave as semiconductors with extremely narrow energy gaps when placed under high hydrostatic pressures. The most prominent character of them is that they have strongly temperature dependent carrier density and mobility and yet the resistance is constant over a wide temperature region. Up to now, we confirmed \( \alpha \)-type crystals of (BEDT-TTF)\textsubscript{2}I\textsubscript{3}, (BEDT-TSeF)\textsubscript{2}I\textsubscript{3}, (BEDT-STF)\textsubscript{2}I\textsubscript{3} and \( \beta \)-type crystal of (BEDT-TTF)\textsubscript{2}I\textsubscript{3} belong to this group. Among them, the typical one is \( \alpha \)-(BEDT-TTF)\textsubscript{2}I\textsubscript{3}. Under high-pressures, it is a semiconductor with the energy gap of about 1 meV. The carrier density decreases by about six orders of magnitude between 300 and 1 K. The carrier mobility, on the other hand, increases by six orders of magnitude in the same temperature region. These two effects just cancel out and give rise to the temperature independent resistance. At low temperatures, the mobility goes up to a value as high as \( 10^6 \) cm\textsuperscript{2}/(V s).

\#2002 Elsevier Science B.V. All rights reserved.

Keywords: Electrical transport; Hall effect; Magneto resistance; Narrow gap semiconductor; Pressure; (BEDT-TTF)\textsubscript{2}I\textsubscript{3}

1. Introduction

Some organic conductors are astonishingly pure despite being grown by rather simple procedures. Observation of de Haas-van Alphen (or Shubnikov-de Haas) effect\textsuperscript{[1]} or angular dependent magneto-resistance oscillation (AMRO)\textsuperscript{[2]} in many organic conductors evidences the existence of highly mobile carriers in them. Actually, the mobility of carriers in those crystals goes up to a value such as \( 10^6 \) cm\textsuperscript{2}/(V s) at low temperatures. Most of pure crystals of organic conductors so far studied, however, are metals with high carrier density. In this paper, we describe discovery and investigation of new types of non-metallic organic conductors that exhibit interesting transport phenomena\textsuperscript{[3]}. They are pure enough so that the carrier mobility depends strongly on temperature. They are either semiconductors with very narrow energy gaps or semimetals with very small band overlaps. The most interesting feature of them is that they have carrier systems with strongly temperature dependent mobility and density and that these two effects just cancel out giving rise to the constant resistance.

2. Experiment

We measured resistance, Hall resistance and magneto resistance using a conventional six probes method with dc current. Experimental results were used to derive the density and mobility of carriers as a function of temperature or magnetic field. Since samples we dealt with are either semiconductors or semimetals in which equal number of electrons and holes coexist, we should determine the characters of two types of carriers, separately. It was successfully done at temperatures below about 100 K where both the Hall effect and the magneto resistance were measured with enough accuracy. Combining data of these two measurements, we could determine the mobility of electrons and holes, together with the carrier density. In the analysis, we assumed that the density of electrons and holes is equal and the energy band is parabolic in the two dimensional plane. Experiment covered temperature between 300 and 0.5 K, magnetic field up to 15 T and pressure up to 20 kbar (we used clamp type pressure cells).

3. Results and discussions

As mentioned in Section 2, we determined the mobility of electrons and holes separately as well as their density. In most cases, the difference of their mobility was within a
factor of two. Therefore, in this paper, we present the data only of holes. In Figs. 1–4, we show the temperature dependences of the density and mobility of holes in three samples. Except for Fig. 2, the data in these figures are for samples under quasi-hydrostatic pressures where their resistance is independent of temperature.

3.1. \( \alpha-(BEDT-TTF)_2I_3 \)

The data in Fig. 1 is for \( \alpha-(BEDT-TTF)_2I_3 \). Under the ambient pressures, this sample is metallic above 135 K and insulating at low temperatures [4]. Under pressures above 15 kbar, resistance growth at low temperatures disappears and we observe the resistance almost independent of temperature all over the region from 300 to 1 K. Although, it looks like a dirty metal, our experimental results revealed that it is not the case. As shown in Fig. 1, the carrier mobility depends strongly on temperature and reaches to a value of \( 3 \times 10^5 \) cm²/(V s) at 1.5 K. Definitely, the sample is not dirty but very pure.

On the other hand, carrier density also depends on temperature. At room temperatures, the carrier (hole) density is about \( 10^{21} \) cm³. It decreases with decreasing temperature to a value of about \( 10^{15} \) cm³ at 1.5 K.

The behavior of the carrier density at low temperatures gives additional information about the carrier system. As shown in the figure, the carrier density decreases with decreasing temperature even at the lowest temperature region we measured. It indicates that the system is a semiconductor. From the temperature dependence of carrier density at the lowest temperature region, we can estimate the energy gap and also the mass of the carrier. The band gap is about 1 meV and the mass is about 0.02\( m_0 \).

Strong temperature dependence of the mobility and the density shown in Fig. 1 is the most prominent feature of this carrier system. Both of them change by about six orders of magnitude from 300 to 1 K. It should be noted that the effects of the change in the carrier density and that of mobility just cancel out and gives rise to the constant resistance. We can hardly believe that such an astonishing phenomenon occurred accidentally in this sample. Therefore, we claim that there must be some mechanisms that give
rise to the correlated temperature dependence of the carrier density and the mobility.

3.2. \(\theta-(BEDT-TTF)\_2I_3\)

The second member of this group is \(\theta-(BEDT-TTF)\_2I_3\). Under the ambient pressure, this sample is a two-dimensional metal with a large Fermi surface. Holes with the density of about \(10^{21}\) cm\(^{-3}\) carry electric current as shown in Fig. 2. (A small drop in \(n_{\text{eff}}\) that occurs between 30 and 10 K is ascribed to the characteristic structure of the Fermi surface of this sample.) With the change in the mobility of carriers, the resistance decreases by two or three orders of magnitude between 300 and 1.5 K [5].

When we apply pressures, this sample undergoes a phase transition at about 5 kbar. Entering into the high-pressure phase, the character of the carrier system varies drastically as is clearly demonstrated in Fig. 3. The carrier density is no more constant. It decreases by several orders of magnitude from 300 to 1.5 K. The mobility, on the other hand, increases with decreasing temperature. Here again, we find an example in which changes in the carrier density and the mobility occur in such a way so that the resistance remains constant.

3.3. \(\alpha-(BEDT-TSeF)\_2I_3\)

Fig. 4 gives the data for another member of the group; \(\alpha-(BEDT-TSeF)\_2I_3\). The feature of the temperature dependence of the resistance of this sample resembles to that of \(\alpha-(BEDT-TTF)\_2I_3\). It is metallic above about 60 K and changes to an insulator there. When we apply pressures above 6 kbar, insulating behavior at low temperature disappears and we again find temperature independent resistance. The mobility and the density of carriers in the high-pressure region are shown in Fig. 4.

Above 20 K, the behavior of carriers is qualitatively the same with other two samples. For example, the hole density at 300 K (about \(10^{21}\) cm\(^{-3}\)) is close to those of other samples. The reduction of carrier density with decreasing temperature is also common to all three samples. Below 20 K, however, the behavior of the carrier system is different. In other two samples, the carrier density continues to decrease at lower temperatures. In \(\alpha-(BETSeF)\_2I_3\), on the other hand, the hole density is almost constant below 20 K. This indicates this sample is not a semiconductor but a semimetal.

An important fact we should note in Fig. 4 is that below 20 K where the carrier density is constant, the carrier mobility is also constant. The change of the density and the mobility looks to be correlated. This fact strongly suggests that the mechanism that determines the temperature dependence of the density and the mobility is identical. If the temperature dependence of carrier density and the mobility is determined by different mechanisms, they should behave independently and we may observe temperature dependent resistance in this region.

So far, we demonstrated the discovery of new types of transport phenomena exemplifying three organic conductors. Recently, we found a new member of this group, \(\alpha-(BEDT-STF)\_2I_3\). Transport property of this sample under high-pressures is similar to those we described in this paper.

4. Conclusion

We found a group of organic conductors that exhibit new types of transport phenomena. The most prominent characteristic is that they have carrier systems with temperature dependent density and mobility and yet their resistance is almost independent of temperature. As stated in [3], no other materials are known that behave like them. The mechanism that gives rise to this peculiar behavior of transport phenomena is not clarified yet. So far, our investigation covers only crystals composed of the cation of BEDT-TTF family and the anion I\(_3\). A wider survey is necessary to clarify the mechanism of the phenomena.

Acknowledgements

This work was partially supported by a Grant-In-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan and carried out as a part of “Research for the Future” Projects supported by Japan Society for Promotion of Science.

References