Strange Electric / Magnetic Behaviour of New (BEDT-TTF)(TCNQ)

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Abstract

Electric and magnetic properties for the third phase of (BEDT-TTF)(TCNQ) are investigated. The resistivity exhibits strange hysteresis in a wide range of temperature, with anomalies at 20 K, 80 K, and 175 K. The resistivity under pressure implies that the anomaly at 80 K originates from a kind of phase separation. The anomalies disappear when only 5% of F1-TCNQ is doped. The magnetic susceptibility measured by SQUID showed apparent change at 20 K and 175 K, but no significant change was observed at 80 K. The spin susceptibility measured by ESR, on the other hand, exhibited gradual increase at the temperature from 80 K down to 20 K.

Keywords: Single-crystal growth, Electron spin resonance, Magnetic measurements, Transport measurements

1. Introduction

Control of crystal structure is undoubtedly one of the most interesting current topics. Crystal engineering is one of the solutions for this problem in which case the constituent molecules are designed or modified so as to best interact each other in the crystal packing and achieve thermodynamic stability of the object [1]. The biological systems, on the other hand, sometimes utilize kinetic control of the nucleation processes. For example, construction of inorganic organisms made of calcium carbonate or phosphate in a controlled morphology is known as "biomineralization", and it is believed to be a result of regulated supersaturation / nucleation processes on biomacromolecules [2]. Because of this controlled morphology, biological systems can achieve necessary strength of their body.

During our study on crystal engineering using halogen bond of the iodine [3], we have accidentally met new morph of (BEDT-TTF)(TCNQ) of which crystal structure seems to be originate from the nucleation process controlled by tetraiodoethylene [4]. Despite the two morphs of (BEDT-TTF)(TCNQ) already reported are semiconductive below room temperature [5-8], the new salt exhibits metallic character down to the lowest temperature with anomalies at 175 K, 80K, and 20 K. To investigate the nature of the new salt more precisely, the authors have measured the resistivity under pressure, magnetic susceptibility, electron spin resonance, and the resistivity of the chemically doped salt.

2. Results and Discussion

Figure 1a shows temperature dependence of the resistivity for (BEDT-TTF)(TCNQ) at ambient pressure. The resistivity in heating process is slightly higher than that of cooling process. Though the resistivity at heating process approach that of cooling around 250 K, it never fits the original value even at or above room temperature.

The anomaly at 80 K becomes more apparent under pressure. As shown in Figure 1b, the resistivity around 80 K increases more sharply when hydrostatic pressure of 2 kbar is applied. In addition, it exhibits cooling rate dependence: when the sample is cooled slowly, the system goes high-resistivity state while its resistivity remains lower level when the sample is cooled rapidly. These phenomena can be explained by assuming that the anomaly at 80 K is a first-order transition accompanied by phase separation in which state two energetically equivalent phases coexist below 80 K. In this case, the second phase should be insulating and requires time for growing to achieve thermodynamic equilibrium. The anomalies at 20 K, 80 K, and 175 K disappear under pressure of 5 kbar, though the steep decrease of resistivity below 40 K looks like a trace of the 20 K anomaly.

The magnetic susceptibility shown in Figure 2 exhibits sharp drop at 20 K. The drop looks independent of the applied field direction. One of the two phases separated at 80 K probably goes to singlet state at this temperature. Absence of anomaly at 80 K in susceptibility measurement...
implies that the second insulating phase content of this material at ambient pressure is small.

Despite the 175 K anomaly isn’t very clear in the resistivity measurement, an apparent kink is observed in the susceptibility measurement. The slope is negative above 175 K, but it turns positive below this temperature. This isn’t behaviour of simple Pauli paramagnet and may be explained by the low-dimensional nature of this conductor as well as the effect of electron correlation, but we have no clear explanation at present.

Because the crystal structure of (BEDT-TTF)(F1-TCNQ) (F1-TCNQ = 2-fuлуoro tetracyanoquinodimethane) is very similar to this new (BEDT-TTF)(TCNQ) [9], we also tried doping of F1-TCNQ. The resistivity of 5% F1-TCNQ-doped sample is shown in Figure 1c [10]. In this salt we observed no apparent anomalies at 20 K and 80 K.

Figure 2b shows spin susceptibility obtained by ESR measurements. The increase from 80 K to 20 K is quite different from the behaviour of Figure 2a, which is an unusual phenomenon. By the analysis of g-tensor, the authors also calculated the contribution of BEDT-TTF and TCNQ. It is found that the fraction doesn’t change dramatically.

Summary

We have found the new phase of (BEDT-TTF)(TCNQ) by modifying its nucleation process. It exhibits strange but interesting physical properties. Because the intrinsic cause of the anomalies aren’t clear as yet, further experiments on magnetoresistance and specific heat are now under way.

References

[10] Though 20% of F1-TCNQ was doped in the preparation stage, we found only 5% of doping. The extent of doping was measured by mass spectroscopy.

Figure 1 a: Resistivity of (BEDT-TTF)(TCNQ) at ambient pressure. Though the anomaly at 175 K isn’t very clear at original graph, it can be seen as clear peak in the derivative graph (inset). b: Resistivity under hydrostatic pressure. c: Resistivity of (BEDT-TTF)(TCNQ) (0.8% F1-TCNQ) 105.

Figure 2 a: Magnetic susceptibility measured by SQUID. b: Spin susceptibility measured by ESR (ET = BEDT-TTF).