Transport properties of θ-$ET_2CsM(SCN)_4$ (M=Zn,Co) under ultra-high pressure

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Abstract

In order to investigate the electronic state of the organic conductors, θ-$ET_2CsM(SCN)_4$ (M=Zn,Co), under ultra-high pressure, we performed the resistivity measurements up to 8GPa with the cubic anvil press. The insulating states of these salts were suppressed in this pressure range but survived at low temperatures even at 7∼8GPa. The results were discussed in terms of anisotropic pressure dependence of the transfer integral.

Key words: metal-insulator transition ; organic conductor ; high pressure ; CDW

The electronic state of the organic conductor is well known to be sensitive to pressure. This is because this material is composed of the molecular assembly, which is weakly condensed almost only by the Van der Waals attraction, and the anion assembly. Indeed, in most of the major organic conductors, the physical properties have been investigated under pressure in a range of 0∼1.5GPa by means of the Be-Cu piston-cylinder or the helium gas pressure system. On the other hand, there is no study about the pressure dependence at far higher pressure except for a few experiments [1]. In this sense, many developments in this field, including the findings of new electronic phases, will be possibly achieved by the experiment in this pressure range that is scarcely opened up for the organics. In order to establish the experimental technique on the organic crystal under ultra-high pressure, we tried to measure the transport properties of the representative organics with the cubic anvil press.

We pick up θ-type BEDT-TTF-based layered conductors among many organic salts, because this series of the salts shows the metal-insulator transition at ambient pressure and the transition temperature increases depending on pressure up to 1GPa [2]. One will expect the emergence of the new electronic phase when an application of further high pressure suppresses such an insulating state. Then we tried to synthesize both high quality and small crystals of several θ-type salts and succeeded in the θ-$ET_2CsM(SCN)_4$ (M=Zn,Co) salts. This condition in the sample is crucial for the present study. In addition, these are in a shape of a slender parallelepiped, which is also advantageous for the present transport measurements. A typical size of the sample is $0.9\times0.2\times0.1$ mm^3.

In the present work, we studied transport properties of these salts under ultra-high pressure. The insulating states of both salts were suppressed in this pressure range but survived even at 7∼8GPa. This survival suggests that even an application of ultra-high pressure gives the anisotropic variation of the transfer integral rather than the lift of the dimensionality.

Single crystals of θ-$ET_2CsM(SCN)_4$ (M=Zn,Co) (hereafter abbreviated to CsZn and CsCo) were prepared by galvanostatic anodic oxidation of ET, using the CsSCN and $M(SCN)_2$ (M=Zn,Co) as electrolyte in 1,1,2-trichloroethane and 10% vol. of ethanol at a

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constant current of 1μA. The electrical resistance under ultra-high pressure was measured by the standard four-probe method with a dc current parallel to the conducting layer. Gold wires of 20μm in diameter were attached to a crystal with silver paste as electrodes. Then the sample was inserted to the Teflon cell with inner diameter of 1.5mm. In order to protect the sample and the weak contacts, we also fixed a small and thin paper in a shape of half column on the four wires near the sample. The ultra-high pressure in a range of 2∼8GPa was generated by the constant force during heat cycles from the cubic anvil press (ISSP).

Figure 1 and 2 show temperature dependence of the electrical resistance of the CsCo and the CsZn salts under several pressures, respectively. The resistance of both salts is successfully measured without any big resistive jumps that often appear in the resistivity measurement in many organics. This is somewhat surprising for us in considering the fragility of the present samples. All the data show the semiconducting behavior except for the metallic one in high temperature range of the CsZn salt. The value of the resistance of the CsCo salt around room temperature systematically decreases depending on the pressure but, around 100K, the resistance is elevated by the variation of the pressure from 2.0GPa to 4.0GPa. This fact may indicate that the electronic state of this salt passes through a turning point at such high pressure. This situation is more amplified in the CsZn salt. The semiconducting behavior is rather enhanced with pressure increased from 3.2GPa to 4.0GPa and then it is suppressed depending on the pressure. In addition, the temperature at which the metallic behavior changes into the semiconducting one shows a similar turning point around 4GPa, as shown in the inset.

Both of the CsCo and the CsZn salts show metal-insulator transition around 20K at ambient pressure. This insulating state is considered to originate from the charge ordering caused by the long-range Coulomb repulsion. The transition temperature is elevated by the application of pressure below 1GPa, as shown in the inset of Fig.2 (open circles). On the other hand, Watanabe et al. reported the emergence of the pressure-induced CDW at 1.07GPa for the CsCo salt [3]. They suggest that this is caused by the anisotropic pressure dependence of the transfer integral from the X-ray structural analysis. Through this fact, the present insulating state is very probably the CDW state. Then the turning point inevitably means the initiation of the suppression of it due to the lift of dimensionality.

In conclusion, we succeeded in the transport measurements of the θ-type BEDT-TTF-based organic conductor under ultra-high pressure. The technique acquired in the present work will be possibly applied to many organic conductors. The insulating states of

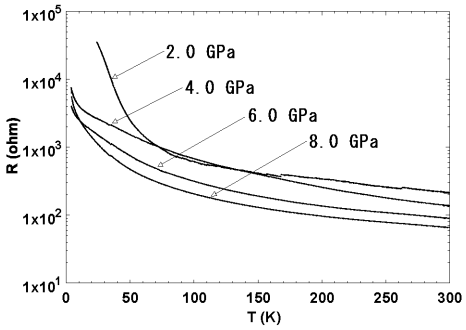

Fig. 1. Temperature dependence of the electric resistance of CsCo salt under pressure.

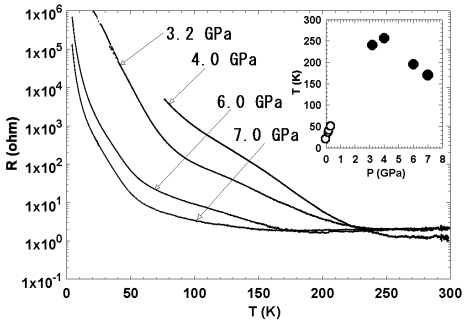

Fig. 2. Temperature dependence of the electric resistance of CsZn salt under pressure. Inset shows the metal-nonmetal transition temperature in the present work (closed circles) and the previous work [2] (open circles).

the CsCo salt and the CsZn salt were suppressed but stiffly survived even at 7∼8GPa. With the fact that the CDW state of the CsCo salt was induced by the pressure, we found that the anisotropic pressure dependence of the transfer integral of these salts is not so dominated by the lift of the dimensionality even under ultra-high pressure. This finding will become to be the important infomation when this method is applied to the other organic salts.

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