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Novel electronic states of organic conductors under uniaxial stress or uniaxial strain

S. Kagoshima*, M. Maesato, Y. Kaga, R. Kondo

Department of Basic Science, University of Tokyo, Komaba 3-8-1, Meguro, Tokyo 153-8902, Japan

Abstract

Uniaxial compression is expected to play a useful role in changing electronic properties of organic conductors because of the low-dimensional electronic structures. To control the intermolecular distance only along some specific axis, we developed the method of causing uniaxial strains along any direction. Novel electronic states were found in α-$(BEDT\text{-}TTF)_2KHg(SCN)_4$ and α-$(BEDT\text{-}TTF)_2I_3$ by controlling the direction of the uniaxial strain. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Uniaxial strain; High-pressure; Organic conductor; Electrical properties

1. Introduction

The pressure application plays an important role in the studies of organic conductors if they are soft enough to allow an appreciable strain in the crystalline lattice. The application of hydrostatic pressure has been playing dramatic roles in changing electronic states of organic conductors having low-dimensional electronic properties. An example is the metal–insulator transition induced by applying hydrostatic pressures to a quasi one-dimensional conductor $(DMeDCNQI)_2Cu$ [1,2]. Another example is the superconductivity under pressures in $(TMTSF)_2PF_6$ and its family, which show at ambient pressure, insulating properties with the presence of spin-density waves [3].

Fine controls of the lattice constant along a desirable direction, a uniaxial deformation, are useful for two purposes; a precise study of the electronic structure and a search for novel electronic states. The method of uniaxial stress application has been developed for such purposes. The uniaxial stresses were directly applied to the flat surfaces of single crystals of organic superconductors [4]. Also uniaxial tensile stresses were applied to some organic superconductors [5]. However, the uniaxial stress is not always applicable to samples because some samples may have growth-steps on the surface and they are too fragile to cut, polish and lap. Campos et al. innovated on the method of uniaxial stress application [6]. They developed the method of sample encasement in epoxy resin to overcome these difficulties. The key of their method is the similarity in elastic properties between the organic materials and the epoxy.

The uniaxial stress application necessarily causes so-called Poisson's effect that increases the lattice parameter of samples in the plane perpendicular to the direction of the stress application. For example, the uniaxial stress in the plane of a layered material increases both the interlayer distance and the lattice parameter along the in-plane direction that is perpendicular to the uniaxial stress. This makes it difficult to discriminate between the roles of the interlayer distance and the in-plane lattice parameter in dominating electronic properties.

We developed a uniaxial strain method that changes, in principle, only the lattice parameter parallel to the direction of external pressure application. Applying this method to the layered type of BEDT-TTF based organic conductors, we succeeded to create novel electronic states that have never been found in those materials.

In the following, we will describe the essential points of the design and operation of the apparatuses for the uniaxial strain application and show some examples of the novel electronic states discovered in the preliminary study.

2. Apparatus design and operation

The basic idea of the uniaxial strain application is to surround the side face of the sample-epoxy composite by a hard cylinder to suppress the expansion due to Poisson's effect. We developed two methods to realize this. In both

* Corresponding author. Tel.: +81-3-5454-6737; fax: +81-3-5454-4331.
E-mail address: kagosima@komaba.ecc.u-tokyo.ac.jp (S. Kagoshima).

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methods, we used a conventional type of clamp-cell designed for the application of ordinary hydrostatic pressures. A sample to be studied is embedded in epoxy or frozen oil that is filled in the cylinder of the pressure cell. An external force is applied to a piston, put on the frozen oil or the epoxy. The cell cylinder hinders the Poisson's effect when the cell is hard enough compared to the frozen oil or the epoxy.

In the frozen-oil method, a crystal sample with four electrical leads for resistance measurements is put in a Teflon cell filled with oil such as Demnum. A piston cylinder set on top of the Teflon cell can be pushed by a stainless steel rod whose other end is connected to a conventional load cell. The external force is applied to the piston after freezing the oil usually below about 20 K. Samples suffer no damage during measurements and can be used repeatedly in many experimental runs. However, it is difficult to change the geometrical arrangement of the pressure cell in the cryostat, which is necessary for measuring, for example, the directional effect of magnetic fields.

For the epoxy-crystal method, a crystal sample embedded in the epoxy is inserted in the pressure cell. A piston on the sample-epoxy assembly is pressed and clamped at room temperature as usually made in hydrostatic pressure application. We used the epoxy, Stycast #1266 and the catalyst B without heating, because the organic samples are easily damaged at elevated temperatures. In both methods the maximum pressure applied to the sample-head was 15 GPa (15 kbar). The lowest temperature reached was 0.5 K.

The epoxy-crystal method is feasible for the rotation of the sample in, for example, magnetic fields because of the absence of the force transmitting system from outside. It is also possible to make measurements even at room temperature. A drawback of this method is that the crystal samples embedded in the epoxy cannot be used again.

3. Results and discussion

We investigated strains induced by the external pressure to the frozen-oil or the epoxy by putting a commercially available strain gauge either parallel or perpendicular to the applied force. We verified that the uniaxial strain (contraction) of the order of 10^{-2} is caused by the pressure of about 0.5 GPa (5 kbar). It is difficult, however, to exactly evaluate the strain because, we used the strain gauge in an unusual way as embedding it in the epoxy or the frozen-oil.

We applied the uniaxial strain method to some α-(BEDT-TTF)$_2$X salts that have layered structures consisting of two-dimensional conducting sheets of BEDT-TTF molecules and insulating anions. Electronic properties of these conductors are dominated by the donor molecular arrangement within the conducting layer. We expect the uniaxial deformation along some in-plane directions will cause dramatic changes in electronic properties.

α-(BEDT-TTF)$_2$KHg(SCN)$_4$ and α-(BEDT-TTF)$_2$NH$_4$-Hg(SCN)$_4$ has a cylindrical two-dimensional (2D) Fermi surface and a pair of one-dimensional (1D) open Fermi surfaces [7]. Although these are isostructural and have almost the same lattice parameters at room temperature, only the NH$_4$-compound shows the superconductivity below about 1 K [8]. The K-compound shows a metal–insulator transition at about 10 K, caused by the nesting of the 1D part of the Fermi surface.

We measured the dc out-of-plane electrical resistance of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ under the uniaxial strain by the frozen-oil method. Fig. 1 shows temperature dependence of the resistance under the uniaxial strain along each of three crystallographic axes. The step-like anomaly observed at about 8 K at ambient pressure indicates the onset of the nesting. The uniaxial strain along the b-axis (out-of-plane direction) reduces the onset temperature of the nesting. No sign of resistance anomaly is found above about 7 kbar. We consider this, is due to the deterioration in the nesting of the 1D part of the Fermi surface. The decrease in the inter-planar lattice constant b, leads to two effects: the increase in the band width along the b-axis; and modification of the in-plane band structure. The latter is possible because the molecular long axis is not exactly vertical to the conducting layer. Either of these effects or both can cause the deterioration of the nesting of the Fermi surface.

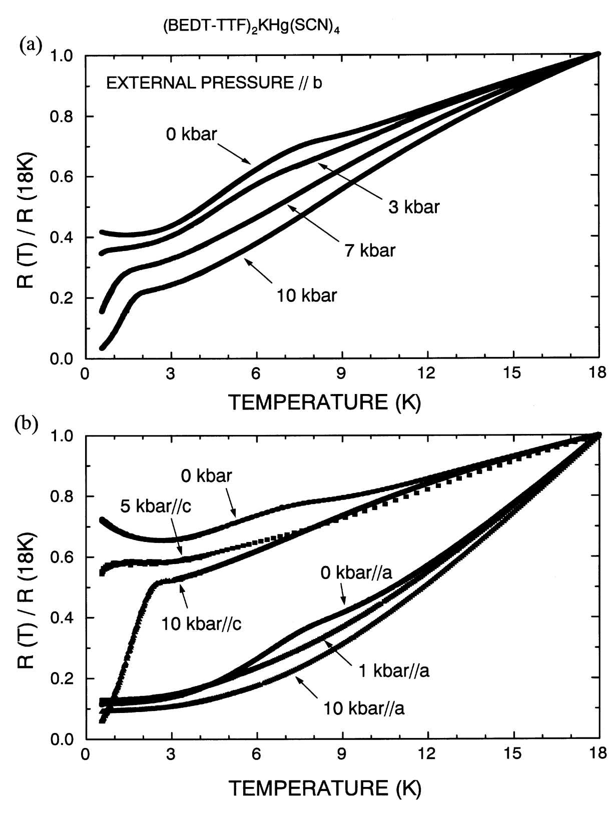

Fig. 1. Temperature dependence of the inter-plane resistance of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ under the uniaxial strain applied respective directions. The a- and c-axes are in the conducting layer.

At lower temperatures the resistance decreases rapidly with decreasing temperature under the uniaxial strain parallel to the *b*-axis. This is ascribed to the onset of superconductivity because a non-ohmic behavior is observed and the resistance is resurrected by applying weak magnetic fields. The onset temperature of the superconductivity increases with increasing the uniaxial strain. At the maximum external pressure of 10 kbar, the onset temperature was as high as 2 K. In preliminary measurements on NH_4 compound, we found the increase in the onset temperature of superconductivity by a factor of two under the uniaxial strain caused by the external pressure of 5 kbar. These results are consistent with those by Campos et al. under the *b*-axis uniaxial stress [9].

The uniaxial strain in the conducting plane causes novel effects on the electronic properties: the anomaly due to the nesting is easily suppressed by the uniaxial strain under the external pressure of about 1 kbar along the *a*-axis (inter-columnar direction). Normal metallic behaviors are observed down to 0.56 K. The hydrostatic pressure also suppresses the nesting under the pressure of about 5 kbar, above which the normal metallic state is realized. We consider that the hydrostatic pressure effectively compresses the sample along the *a*-axis, the highest conducting axis.

In contrast to this, the effect of the uniaxial strain parallel to the *c*-axis (intra-columnar direction) is similar to that of the strain parallel to the *b*-axis. The superconductivity appears at low temperatures. Recently, the temperature dependence of lattice parameters of this family of compounds have been measured down to 11 K by Endo et al. [10]. They found that only the superconducting compound shows a significant decrease in the ratio of the in-plane axes *c*/*a*, below about 200 K. In our uniaxial strain study, the *c*/*a* was directly controlled at low temperatures. We found, in accordance with Endo et al.'s results, the superconductivity was realized by reducing this parameter *c*/*a*.

α-(BEDT-TTF)$_2$I$_3$ undergoes a metal–insulator transition at 135 K at ambient pressure [11]. The insulating phase is nonmagnetic [12] and no superlattice is formed at the transition. In spite of experimental and theoretical studies, the origin of this transition is still unclear. To obtain further insight into this transition and search for novel electronic states, we made the uniaxial strain studies on α-(BEDT-TTF)$_2$I$_3$, where the epoxy-crystal method was employed.

Fig. 2 shows temperature dependence of the in-plane (//*a*-axis) resistance under the uniaxial strain. The *a*-axis (intra-columnar direction) strain gradually suppresses the metal–insulator transition. However, the transition is not fully suppresses at the maximum external pressure of 15 kbar and the resistance increases with decreasing temperature at low temperatures. This *a*-axis strain effect is rather small, but is similar to the behavior under hydrostatic pressures, where the transition is fully suppressed at 15 kbar [13].

The metal–insulator transition also tends to be suppressed by the uniaxial strain along the *b*-axis, the inter-columnar direction, and the *c*-axis, the out-of-plane direction. We found a significant decrease in the resistance well below the metal–insulator transition temperature, suggesting a dramatic change in the electronic state. This contrasts with the effect of the hydrostatic pressure, where the transition is monotonically suppressed with increasing pressure and no such decrease in the resistance is observed [14]. It is to be noted that the metal–insulator transition is fully suppressed by the maximum external pressure of 15 kbar along the *b*-axis. The ratio of the room temperature resistance to the helium temperature one reaches four in the condition of the *b*-axis uniaxial strain although it is about two under hydrostatic pressures of 15 kbar. It implies that the *b*-axis contraction induces another metallic phase. Further studies such as magnetoresistance studies are necessary to clarify the nature of this novel metallic state.

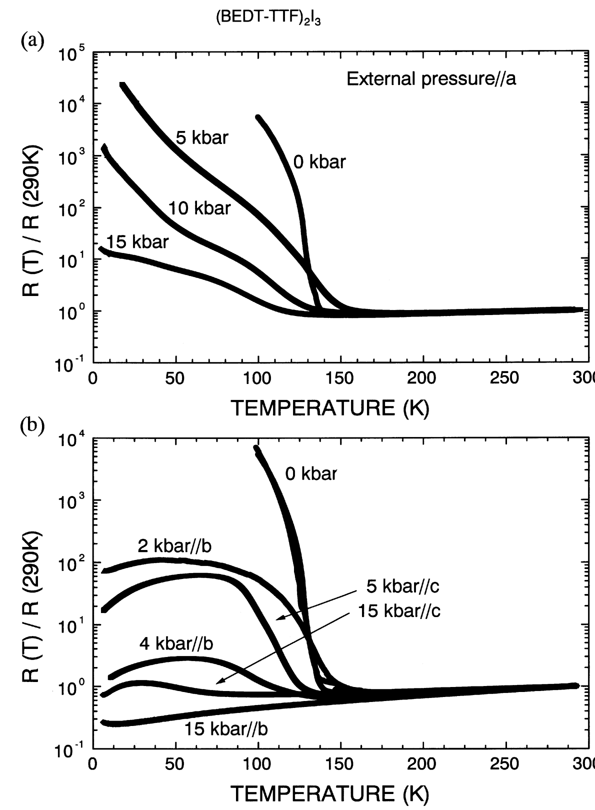

Fig. 2. Temperature dependence of the in-plane (//*a*) resistance of α-(BEDT-TTF)$_2$I$_3$ under the uniaxial strain along respective directions. The *a*- and *b*-axes are in the conducting layer.

The present study suggests that the uniaxial strain method provide another tool for condensed matter physics to artificially control materials structures. For quantitative studies, however, we have to find the exact arrangement of atoms or molecules under the uniaxial strain. We are preparing an X-ray diffraction apparatus for this purpose.

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