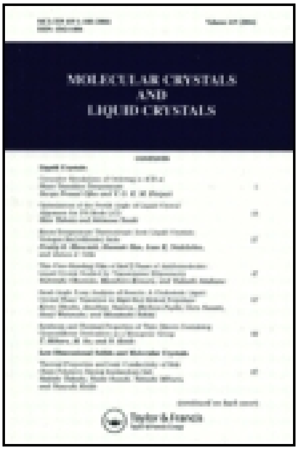

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Control of electronic properties of organic superconductors by uniaxial strain method

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Version of record first published: 18 Oct 2010

To cite this article: S. Kagoshima, R. Kondo, T. Shibata, H. Hirai, M. Maesato, H. Hoshino, T. Mori, H. Mori & S. Tanaka (2003): Control of electronic properties of organic superconductors by uniaxial strain method, Molecular Crystals and Liquid Crystals, 380:1, 77-84

To link to this article: http://dx.doi.org/10.1080/713738712

Mol. Cryst. Liq. Cryst., Vol. 380, pp. 77-84

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290101397

CONTROL OF ELECTRONIC PROPERTIES OF ORGANIC SUPERCONDUCTORS BY UNIAXIAL STRAIN METHOD

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We controlled the electronic properties of BEDT-TTF based organic conductors by using the uniaxial strain method. Electronic properties of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ were able to be controlled as suggested by the unified phase diagram proposed to this series of compounds. α-(BEDT-TTF)$_2$XHg(SCN)$_4$ (X = K, NH$_4$) showed essentially the same properties if their lattice parameters are appropriately controlled by the uniaxial strain method. Furthermore the reduction of the lattice parameter c enhanced the superconductivity suggesting that conventional discussions based on the volume effect is insufficient.

Keywords: organic superconductor; uniaxial strain; BEDT-TTF

1. INTRODUCTION

Possible mechanisms of the superconductivity of BEDT-TTF-based organic conductors have been discussed in relation to the effects of the unit cell

SK and RK acknowledge the financial support by the Grant-in-Aid for Specially Promoted Research (No.10102004) from the Ministry of Education, Science, Sports and Culture, Japan.

volume to the critical temperature. In developing high-T_c organic superconductors, compounds having a larger unit cell were expected to have the higher critical temperature T_c [1,2]. Experimentally, hydrostatic pressure application usually lowers T_c as typically observed in β- and κ-phases of BEDT-TTF superconductors [3]. An expansion of the unit cell in the conducting layer by a uniaxial ***stress*** application raised T_c in α-(BEDT-TTF)$_2$-NH$_4$Hg(SCN)$_4$ [4]. These volume effects have been ascribed to the electronic density-of-states at the Fermi level. Besides these, a novel idea has been also presented that the dihedral angle of neighbouring BEDT-TTF molecules dominates electronic states of θ-phase BEDT-TTF conductors [5]. Possible mechanisms of the superconductivity are also discussed in relation to the strong Coulomb correlation among conduction electrons [6]. A dimerized structure of BEDT-TTF is expected to be crucial for this possibility. It is because the electron density is one per a dimer in this class of compounds leading to an enhancement of magnetic fluctuations possibly responsible for the superconductivity.

We investigated electronic properties of θ- and α-phases of BEDT-TTF compounds to find the relation between the crystal structure and the electronic states, especially the superconducting state, by using the uniaxial ***strain*** method [7]. This method makes it possible to control the intermolecular distance along a desired direction without affecting those along perpendicular ones. The hydrostatic pressure application and the uniaxial stress method can control the unit cell volume but not the cell size along a desired direction. Furthermore, the uniaxial strain method possibly modifies the relative molecular arrangements such as the degree of dimerization and the dihedral angle because the rather large magnitude of uniaxial strain can be created.

In the present study, we found first that the uniaxial strain method can control the dihedral angle of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$. Second, we obtained two results in α-(BEDT-TTF)$_2$XHg(SCN)$_4$ (X = K, NH$_4$): (1) They have essentially the same electronic phase diagram although, under hydrostatic pressures, they appear to be quite different from each other, and (2) the superconducting T_c is raised by the factor of four by selectively control the unit cell size in the NH$_4$-compound.

2. EXPERIMENTAL

The basic idea to create the uniaxial strain is to encase a sample in some organic solid and, then, to put the composite of the sample and the organic solid in a hard cylinder. The composite is compressed uniaxially by applying an external force to a piston put on the composite. Any expansion due to Poisson's effect is suppressed because of the surrounding cylinder. One can expect the sample crystal be compressed uniaxially because its elastic properties are similar to those of the organic solid. Details of the experimental method have been described in our paper [7]. We used two kinds of organic solid: The first is epoxy resin, Stycast 1266. A crystal sample with four electrical leads was encased in the epoxy. The other is oil (for example, DEMNUM by Daikin Industries Ltd.) used for hydrostatic pressure studies. We first cooled down the pressure cell having the sample in the oil down to the range of 20 K. Then, we applied external forces to the sample-frozen oil composite through a long stainless-steel rod.

The external force was applied to the cross section of the epoxy rod at room temperature or the frozen-oil rod at 20 K. The pressure of 10 kbar applied to the cross section of the sample composite caused the uniaxial strain of the order of -10% in the epoxy method and of about -5% in the frozen oil method [7].

Sample crystals were prepared by conventional electrochemical method. To measure the electrical resistance, conventional dc four-lead method was employed using gold wires of 15 μmØ and carbon paste. In θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ the resistance was measured along the c-axis in the conducting plane, and in α-(BEDT-TTF)$_2$XHg(SCN)$_4$ along the b^*-axis perpendicular to the conducting plane.

3. CONTROL OF ELECTRONIC STATES OF θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$

θ(BEDT-TTF)$_2$CsZn(SCN)$_4$ has the layered structure consisting of conducting layers of BEDT-TTF molecule and insulating sheets of the anion. Electrical properties of these conductors are dominated by the arrangement of BEDT-TTF molecules in the conducting layers. Figure 1 schematically shows the molecular arrangements in the unit cell viewed perpendicular to the conducting plane. The electronic band structure calculation by the extended Hückel and the two-dimensional (2D) tight binding methods provides a cylindrical 2D Fermi surface whose cross section is elliptic [5].

A unified phase diagram has been proposed suggesting that the electronic states are dominated by the dihedral angle shown in Figure 1 between neighbouring molecules [5]. The dihedral angle is possibly related to the lattice parameter ratio a/c. The present sample is located on the phase diagram in a rather critical regime where the metal-insulator transition temperature rapidly changes as a function of the dihedral angle or a/c. Therefore, the sample is expected to show a dramatic change under the uniaxial strain parallel to the a- or c-axis.

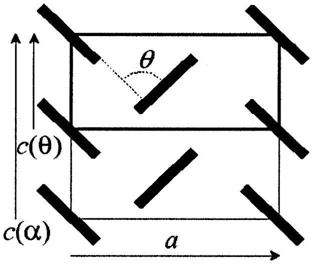

FIGURE 1 Schematic view of the molecular arrangements in the conducting plane of θ- and α-phases BEDT-TTF compounds. θ denotes the dihedral angle. $c(\theta)$ and $c(\alpha)$ denote the lattice parameter c of the θ- and the α-type BEDT-TTF compounds, respectively.

Figure 2(a) shows the temperature dependence of electrical resistivity of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ at various magnitudes of the uniaxial strain parallel to the a-axis. At the pressure of 15 kbar (uniaxial strain of about 12–13%) the insulating state is fully suppressed although no superconductivity was found down to the lowest temperature measured. Figure 2(b) shows the similar results obtained under the uniaxial strain parallel to the c-axis. The metal-insulator transition temperature increases with increasing the strain. These results are just what are expected from the unified phase diagram. The reduction in a reduces the dihedral angle leading to the stabilization of metallic state down to lower temperature range and that in c the opposite change. Thus we directly verified the

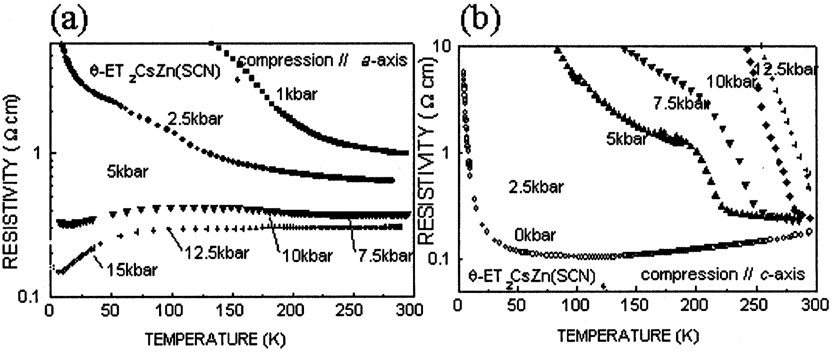

FIGURE 2 Temperature dependence of electrical resistance of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ measured parallel to the c-axis under the uniaxial strain along (a) the a-axis and (b) the c-axis. The pressures denote those applied to the cross section of the cylindrical composite of the sample and epoxy.

unified phase diagram, and the uniaxial strain method caused the expected change in the lattice.

4. CONTROL OF ELECTRONIC STATES OF α-(BEDT-TTF)$_2$KHg(SCN)$_4$ AND α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$

The α-phase BEDT-TTF compounds have the similar arrangements of BEDT-TTF in the unit cell to those of the θ-phase compounds. In the α-phase compounds, however, two molecules are contained in a unit cell along the *c*-axis as depicted in Figure 1 because of the absence of the inversion symmetry. This makes the first Brillouin zone half of that of the θ-phase compounds. The electronic band structure calculation provides a small size of cylindrical 2D Fermi surface and a pair of one-dimensional (1D) open Fermi surfaces [8]. It is because a basically cylindrical Fermi surface is cut by the Brillouin zone boundary and is reconstructed. However, the K-compound has quite different electronic states from the NH$_4$-compound under the ambient and hydrostatic pressures in spite of the structural similarity [9,10]. The K-compound has a density-wave state due to the nesting of the 1D part of the Fermi surface but has no superconducting state. The NH$_4$-compound has the superconducting state but no density-wave state. The expansion of the unit cell in the conducting plane caused by the uniaxial *stress* lead to the onset of the superconductivity in the K-compound [4]. However, it is uncertain whether it is due to the volume effect or to some others.

We measured the dc out-of-plane electrical resistance of both compounds under the uniaxial strain. Figure 3(a) shows the temperature dependence of resistance of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ under the uniaxial strain along the *c*-axis. We employed the frozen-oil method. The step-like anomaly at about 8 K at ambient pressure indicates the onset of the density waves. It is suppressed by the uniaxial strain along the *c*-axis. The superconductivity appears above about 5 kbar (strain of about −2.5%). On the other hand, the *a*-axis compression suppressed the density-wave state followed by the stabilization of the metallic state. The reduction in *c* is considered to be crucial for the superconductivity.

This interpretation is reinforced by similar measurements of the NH$_4$-compound as shown in Figure 3(b). We used again the frozen-oil method. The uniaxial strain parallel to the *c*-axis raised the superconducting critical temperature T_c up to about 6 K. The estimated strain there is about −3%. Further strains lowered T_c. When we made the uniaxial strain parallel to the *a*-axis, the superconductivity was suppressed and the metallic state is stabilized.

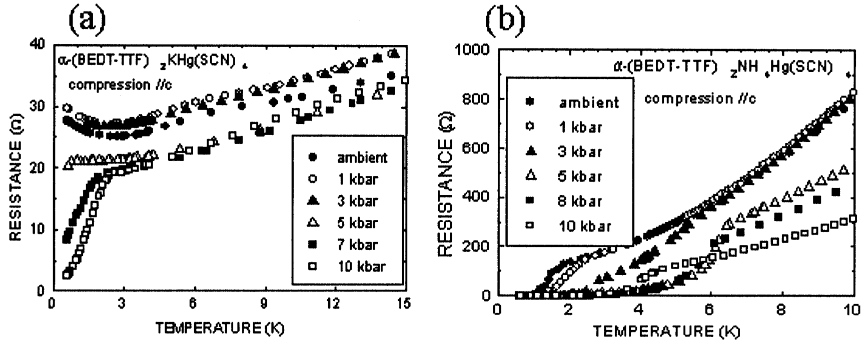

FIGURE 3 Temperature dependence of electrical resistance of (a) α-(BEDT-TTF)$_2$KHg(SCN)$_4$ and (b) α(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ measured parallel to the b^*-axis under the uniaxial strain along the c-axis. The pressures denote those applied to the cross section of the cylindrical composite of the sample and frozen-oil.

It is to be noted in Figure 3(b) that, at 4.5 kbar, a resistance anomaly is found at about 9 K reminiscent of the onset of the density waves. By angle dependent magnetoresistance measurements, we found that the topology of the Fermi surface in this state was essentially the same as that of the K-compound in the density-wave state [11]. At 6 kbar or higher, we verified that the original Fermi surface was resurrected.

These results suggest the unified phase diagram for the K- and NH$_4$-compounds as shown in Figure 4. The superconducting state is realized when we reduce the lattice parametern c, which is ascribed either to the

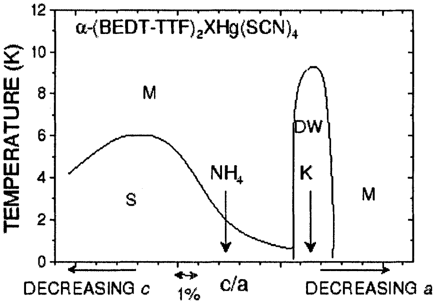

FIGURE 4 The obtained phase diagram of α-(BEDT-TTF)$_2$XHg(SCN)$_4$. The symbols M, S and DW denote the metallic, superconducting and the density-wave states, respectively. The arrows denote the location of the K- and the NH$_4$-compounds at ambient pressure.

reduction in the intermolecular distance along the c-axis, or to the increase in the dihedral angle between BEDT-TTF, or both. The density wave state is induced by controlling a in the limited range.

We conjecture that a change in the electronic dimensionality accounts for the above phase diagram. The Fermi surface of the present compounds in the normal metallic state consists of a sheet-like surface suggesting the 1D nature parallel to the a-axis and a cylindrical one responsible for the 2D properties in the ac plane. Naively speaking, the reduction in a makes the system more one-dimensional and that in c more two-dimensional. The former is consistent with the density wave state caused by the reduction in a in the NH_4-compound.

The present results suggest that the conventional discussion on the superconducting critical temperature T_c based on the volume effect is insufficient. In the K- and the NH_4-compounds, the reduction in the lattice parameter c, with no change in other parameters, enchanced the superconductivity. This suggests that the future discussions on the superconductivity must be made based on not only the volume effect but also the band structure along each direction and the relative molecular arrangements such as the dimer formation.

5. CONCLUSION

Using the uniaxial strain method we revealed that θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ suffers the changes in electronic properties expected from the conventional phase diagram for this series of compounds. The electronic properties of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ are essentially same with α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ and the lattice parameters a and c dominated the change in the electronic states.

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