Crystal and band structures of organic superconductor under the uniaxial strain

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Abstract

In order to investigate the relationships between electronic properties and crystal structures, a structure analysis of the organic superconductor, α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$, was performed using the observed 700–1300 Bragg reflections under the uniaxial strain along the each crystal axis of 1.5–2.0 kbar piston pressure. It was found that the calculated Fermi surfaces in the two dimensional conducting layer are shrunk along the *c*-axis and swallowed along the *a*-axis under the b^*- and *c*-axial strain, while shrunk along the *a*-axis and swallowed along the *c*-axis under the *a*-axial strain. The changes in the density-of-states at the Fermi level calculated from the obtained structures are qualitatively consistent with the observed change of the $T_{S.C.}$.

Key words: Organic superconductor; Uniaxial Compression; X-ray diffraction; Crystal structure

The application of the hydrostatic pressure has played important roles to bring out novel electronic properties of organic conductors. In such organic crystal, molecules are connected with weak van der Waals's force, and the pressure can easily change the distance between molecules, inducing a dramatic change in the macroscopic electronic properties.

Recently, we developed the uniaxial strain method, which changes only the lattice parameter parallel to an external force.[1] In reality, the superconductivity was induced or the superconducting transition temperature ($T_{S.C.}$) was enhanced in some organic superconductors under the uniaxial strain. [2]

We applied the above uni-axial strain method to the organic superconductor, α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$, whose transition temperature is 1.5 K at ambient pressure, and found the enhancement of the $T_{S.C.}$ under the b^*- and *c*-axial strain. Especially the *c*-axial strain realized that at 6 K, which is about 4 times as high as that at ambient pressure. On the other hand, under the *a*-axial strain the superconductivity was promptly suppressed.[3]

In this paper we report the changes in the crystal structure of α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ under the uniaxial strain in order to investigate the interrelation between the crystal and electronic structures and the enhancement of the $T_{S.C.}$.

We developed a unique type of X-ray diffractometer for the above purpose. A conventional sealed type X-ray tube of Mo K_α and a typical X-ray detector are independently moved on the upper-hemisphere, at the center of which the measured sample is mounted with no rotational freedom. This arrangement has the same basic function as the ordinary four-circle X-ray diffractometer.

A pressure cell for this X-ray study was also developed. The sample was encased in an epoxy resin cylinder. The cylinder is set in a Beryllium pipe to suppress Poisson's effects and ensure the high transmission of Mo K_α X-ray.

The lattice parameters were precisely determined based on 50 - 60 stronger Bragg spots in the range

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between 20 and 30 degree of so-called 2θ. We verified that only the length of the crystal axis along the external force is reduced by about 1 % under the piston pressure of 1.5–2.0 kbar while other parameters change within $\pm$ 0.2 %.[4] It indicates that "the uniaxial strain method" really creates the uniaxial strain accompanied with little Poisson's effects. The determinations of the crystal structure were performed using Crystal Structure Analysis Package of teXsan by Molecular Science, based on 700 - 1300 observed Bragg reflections whose intensities are calibrated considering the length of X-ray path in the Beryllium and the epoxy resin. The R-factors and Rw-factors of all the final structures were obtained below 10 %.[5]

Figure 1 shows the schematic view of the molecular arrangements in the conducting layer and geometry of the Fermi surfaces. We found a clear difference in the molecular arrangements between the b^*- and c-axial strain increasing the $T_{S.C.}$ and the a-axial strain decreasing that; the dihedral angle between AI (AII) and B (C) increases by 1–2 degree and the distance between molecules along the c-axis decreases under the b^*- and c-axial strain, while the angle slightly decreases and the distance along the a-axis decreases under the a-axial strain.

These changes in the molecular arrangements make the Fermi surface in the two-dimensional conducting layer shrunk along the c-axis and swallowed along the a-axis under the b^*- and c-axial strain (Figure 1(b)), and shrunk along the a-axis and swallowed along the c-axis under the a-axial strain. These results indicates that the bandwidth along k_a decreases and that along k_c increases under the b^*- and c-axial strain, and the opposite phenomena occurs under the a-axial strain.

These changes in the bandwidths influence the density-of-states at the Fermi level (DOS), since the length of the Fermi surface almost perpendicular to k_a (one-dimensional part) is about twice as long as that to k_c (small two-dimensional part), as shown in the Fig. 1(b). The DOS's are calculated as -5 % for the a-axial strain, +7 % for the b^*-axial strain and +24 % for the c-axial strain, respectively. Comparing with the observed behaviors of $T_{S.C.}$, these results are qualitatively consistent in the BCS expression for the relation between $T_{S.C.}$ and DOS, although the superconductivity is too promptly suppressed under the a-axial strain.

We investigated the crystal structure of the organic superconductor, α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$, under the uniaxial strain. The molecular arrangements in the conducting layer are controlled as expected from the direction of the external force, and the DOS calculated from the obtained structures are also varied; the DOS increased under the b^*- and c-axial strain enhancing the superconductivity, and decreased under the a-axial strain suppressing that. These changes are qualitatively consistent with the observed change of the superconducting transition temperature.

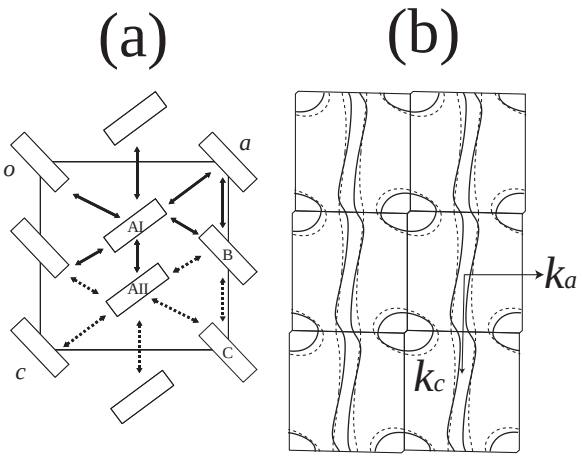

Fig. 1. Schematic view of the molecular arrangement viewed along the molecular long axis in the conducting layer (a), and that of the geometry of Fermi surface under the c-axial strain by the piston pressure of 1.5 kbar (b). In (a) AI and AII are interrelated by an inversion operation and B is on the inversion center. In (b) the solid line and the dotted line denote the Fermi surfaces under the uniaxial strain and at ambient pressure, respectively. The size of the first Brillouin zone under the uniaxial strain is normalized to that at ambient pressure.

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[5] R-factor (Rw-factor), the number of used spots for the crystal structure analysis; 9.2 %(6.5 %), 693 spots for the a-axial strain of 2.0 kbar, 8.7 % (5.9 %), 936 spots for the b-axial strain of 1.0 kbar, and 9.2 % (8.1 %), 1316 spots for the c-axial strain of 1.5 kbar.