

Electronic and structural properties of organic superconductor κ -(BEDT-TTF)₂Cu[N(CN)₂]I

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Abstract

Thermopower and x-ray diffuse scattering were measured in single crystals of κ -(BEDT-TTF)₂Cu[N(CN)₂]I. A two stage superstructural transformation was found and characterized by diffuse x-ray scattering. Thermopower measurements show its close relation to the formation of the insulating state at ambient pressure. Formation of the superconducting state was studied by resistance measurements under the uniaxial compression.

Key words: organic superconductor; thermopower; superstructure; uniaxial compression

1. Introduction

Among the members of the family of κ -(BEDT-TTF)₂Cu[N(CN)₂]X (X=Cl, Br and I) organic superconductors, the salt with X=I salt is least studied, mostly because of the difficulty of crystals growth. According to the expectation based on ionic radii of halogen atoms, the compound should occupy a place at the high-pressure side of the universal phase diagram for the κ -phases [1], implying metallic state at ambient pressure transforming with pressure into an insulator. In reality, the salt shows insulating properties below 100 K at ambient pressure and no sign of superconductivity was originally found under hydrostatic pressure up to 5.2 kbar [2]. The formation of the insulating state in the salt at ambient pressure was reasonably described in terms of low temperature structural transformation [3]. Recently, superconductivity with T_c up to about 8 K was found in high

quality single crystals of the X=I salt under a hydrostatic pressure above 1.2 kbar [4]. To understand the origin of so different behavior of the old and the new samples and to correlate the electronic properties with lattice transformations, we have undertaken the study of temperature dependence of x-ray diffuse scattering and of the thermopower, as well as resistivity under uniaxial compression.

2. Results and Discussion

The crystals of κ -(BEDT-TTF)₂Cu[N(CN)₂]I were synthesized by electrochemical oxidation of BEDT-TTF in a 1,1,2-trichloroethane medium [4]. Thermopower measurements were made using alternating gradient technique [5] for two directions of heat flow along the principal directions within conductive plane. X-ray diffuse scattering measurements were made using the fixed-sample, fixed-film monochromatic Laue method [6]. An imaging plate was used to obtain quan-

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titative characterization of superstructure reflexes.

The x-ray Lauegrams show superstructural transformations at around 200 K and 100 to 130 K for both old and new samples. The superstructure formed at about 200 K is commensurate and has the same wave vector $c^*/2$ for both types of the samples. The second transformation gives a difference between the samples [7], namely (1) in the wave vector of the superstructure ($c^*/3$ in old versus $0.38c^*$ in new samples), (2) in the completeness of the superstructural transformation (well defined spots in new samples contrary to diffuse spots in old ones), (3) in the temperature of transformation, decreasing from ~ 130 K in new to 100 K in old samples.

With these results it is natural to assume the old and the new crystals have different compressibility of the lattice, caused by the presence of superstructure. This determines different behavior of the samples under hydrostatic pressure. The formation of $0.38c^*$ incommensurate superstructure in presence of $c^*/2$ commensurate superstructure gives complicated reconstruction of the Fermi surface [3], which should influence transport properties of the crystal. In Fig.1 we show on the same graph the temperature dependence of thermopower and of intensity of superstructural reflexes. At room temperature the thermopower shows metallic behavior which is consistent with the band structure calculation [8]. A low-temperature transformation at ~ 150 K leads to nonmetallic behavior of $S(T)$, which is especially evident in sign change of thermopower for a -direction where hole pockets of the Fermi surface are dominating. At the same temperature the resistivity shows smooth transition from metallic to insulating behavior being evidence of real gap formation on the Fermi surface.

Since the formation of the insulating ground state at low temperatures is correlated with low-temperature superstructural transformation [3], it can be expected that under pressure the $0.38c^*$ superstructure is suppressed at the metal-insulator boundary. This is indeed seen in unusual pressure dependence of low temperature resistivity and of superconducting T_c , when compression was applied along selected axis of the crystal, a and c . T_c increases from about 5 K up to 7 K when compression applied along a -axis increases from 1.5 to 8 kbar. At the same time resistivity relaxation is observed as the evidence of a structural transformation involved. It is logically to assume that a superconducting phase with higher T_c appears while superstructural phase with low T_c is suppressed. It is interesting to note that the effect of compression along c -axis is quite different.

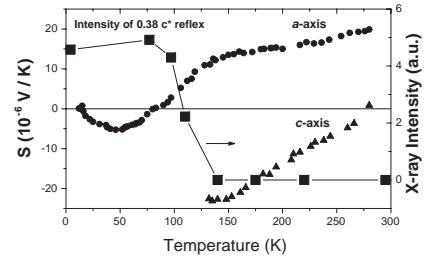


Fig. 1. The temperature dependencies of thermopower for a - and c -directions and intensity of $0.38c^*$ superstructural reflex on x-ray Lauegram

3. Conclusion

The correlation between the temperature dependence of Seebeck coefficient and the intensity of superstructural reflexes gives a clue to the understanding of the insulating state formation in the κ -(BEDT-TTF)₂Cu[N(CN)₂]I salt. It indicates that the superstructural effects are of importance for description of these compounds.

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