Vol. 34 (2003) *ACTA PHYSICA POLONICA B* No 2

ELASTIC ANOMALIES OF κ-$(ET)_2Cu[N(CN)_2]Br$ ASSOCIATED WITH THE INSULATOR-TO-METAL CROSSOVER*

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(Received July 10, 2002)

Longitudinal sound velocity has been measured for organic superconductors κ-$(ET)_2Cu[N(CN)_2]Br$ as a function of temperature. We measured the velocity of the sound propagating along both parallel and perpendicular to the two-dimensional conduction plane. The sound velocity of both directions shows a remarkable anisotropic behavior below T_M, in addition to the anomaly at $T_M = 37\,K$ associated with Insulator-to-Metal crossover.

PACS numbers: 74.25.Ld, 74.70.Kn

1. Introduction

Organic superconductors κ-$(ET)_2Cu(NCS)_2$ and κ-$(ET)_2Cu[N(CN)_2]Br$ show high-T_c superconductivity among organic materials at ambient pressure, where ET indicates BEDT-TTF: bis (ethylene di thio) tetra thia fulvalene. Temperature dependence of both compounds (hereafter abbreviated as NCS-salt and Br-salt, respectively) looks semiconducting at high temperatures, and metallic at low temperatures. They show an insulator-to-metal crossover behavior with a resistance maximum below 100 K [1,2].

Elastic properties of NCS-salt has been measured to investigate the superconducting properties, so far [3,4]. These measurements had been limited to the low temperature due to experimental difficulties. Recently, we have successfully extended our measurements to wide temperature up to 140 K, by using hand-made piezo-electric transducers, and we found a remarkable elastic softening and a minimum around 46 K, which corresponds to the Insulator-to-Metal crossover [5]. Similar behavior was reported by Frikach *et al.* for NCS- and Br-salts [6]. They showed that the temperature

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* Presented at the International Conference on Strongly Correlated Electron Systems, (SCES 02), Cracow, Poland, July 10–13, 2002.

of the velocity minimum shifted to higher temperatures by applying higher hydrostatic pressure. It is the same as the pressure dependence of the resistance maximum. This indicates that the high-temperature elastic anomaly correlates to the resistance maximum in these salts.

The ultrasonic experiments have been made only for the inter-plane direction in these previous reports. We will report the elastic properties and anisotropic characters in Br-salt.

2. Experiment

Longitudinal sound velocity of Br-salt has been measured by an ultrasonic measurement system with a phase comparison method. The propagation directions of the sound are both parallel and perpendicular to the two-dimensional conduction plane. The parallel and perpendicular directions to the conduction plane are abbreviated as In-plane and Inter-plane, respectively. The ultrasonic velocity has been measured by using devised piezo-electric transducers, which are made by thinning process of $LiNbO_3$ wafer by lapping [5]. The thickness of the transducer is 50 μm, and its resonance frequency is 96 MHz.

Single crystalline Br-salts were grown by electro-chemical oxidation method in 1,1,2-Trichroloethan. The precise condition for the single crystal growth is described elsewhere. In-plane axis of the single crystal was determined by the grazing-angle incident X-ray diffraction (GIXD) method (Rigaku Co. ATX-G).

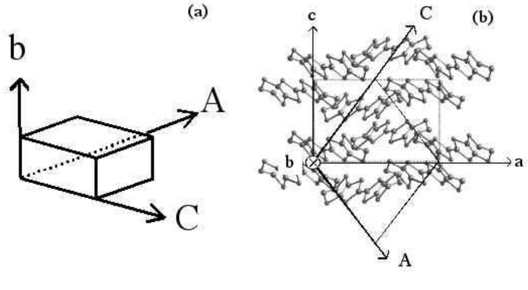

Fig. 1. (a) Crystal orientation of the sample measured in this work and (b) crystal structure of κ-$(ET)_2Cu[N(CN)_2]Br$.

Br-salt has orthorhombic symmetry. The size of the crystal is $A \times b \times C$ $= 2.17 \times 1.75 \times 2.17$ mm^3 for Br-salt, respectively, where b is Inter-plane axis. The axes a and c are crystallographic ones. The longitudinal sound velocity for Inter-plane direction corresponds to c_{33}. The propagation of the sound for the In-plane direction is perpendicular to (201) in crystallographic co-ordinates, which corresponds to C direction in Fig. 1.

Figure 2 shows temperature dependence of the sound velocity change for Br- and NCS-salts below 140 K. Both salts show remarkable anomalies at low temperatures. The result of NCS-salt was shown in the same figure for comparison. The anomaly caused by the superconductivity is found at 8.9 K and 11.8 K for NCS- and Br-salts, respectively. For the Br-salt, the velocity change for the sound propagating along In-plane direction is almost the same as that for Inter-plane direction.

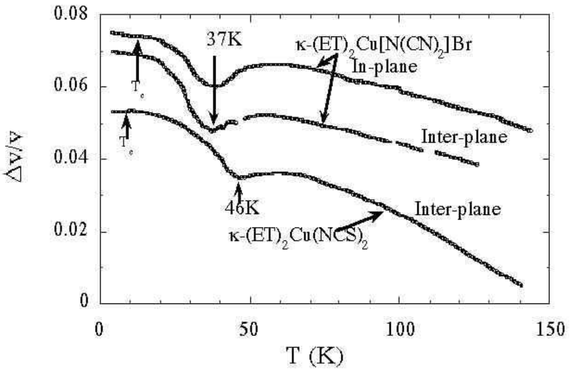

Fig. 2. Temperature dependence of longitudinal sound velocity in κ-(ET)$_2$Cu(NCS)$_2$ and κ-(ET)$_2$Cu[N(CN)$_2$]Br.

An anomaly has been observed around T_M = 46 K and 37 K for NCS- and Br-salts, respectively. For NCS-salt, the amount of the anomaly at 46 K is 7.5×10^{-3}. On the other hand, the anomaly in Br-salt is 11×10^{-3} and 8.0×10^{-3} for the sound velocity along in-plane and inter-plane directions, respectively. Temperature dependence of the sound velocity looks very similar for both salts, except the characteristic temperatures T_M. The amount of anomaly above T_M of the In-plane direction is slightly larger than the Inter-plane one. But, the difference between them becomes remarkable in the temperature range below T_M. The sound velocity of the Inter-plane direction increases more steeply below T_M. In general, the elastic constant in the insulating region is larger than in the metallic region. The increase of the elastic constant was observed at the metal-insulator transition in some organic salts. If this argument is applicable for the anisotropic behavior in Br-salt, this may be related to the anisotropic charge state.

The observed sound velocity minimum in our measurements is smaller than the report by Frikach *et al.* [6] We consider, it is ascribed to the difference of the experimental configuration. They utilized the sound wave delay to measure thin specimens. We did not use that. We think that the experimental configuration without delay is simple and better, if the short sound pulse would be available.

3. Discussion

Merino and McKenzie have suggested that strong electron-phonon interaction leads a phonon softening near the coherence temperature T^* that is the border of fermi liquid to *badmetal* for the triangular Hubbard-Holstein Hamiltonian with half filling [7]. According to their calculation, the phonon anomaly appears at $T^* = 0.1\ t$ when $U = 5.5\ t$, where U and t are the Coulomb repulsion and the hopping integral. This condition gives the mass enhancement of 3.8, which may correspond to the case of κ-type ET-salts. If t is chosen to be 1000 K, $T^* = 100$ K. This is consistent with the observation. It would be needed to clarify the mechanism of the sound velocity minimum in their picture.

Recently, Sasaki *et al.* have discussed the charge aspect of these salts [8]. They focused their attention on the fact that anisotropic behaviors develop below $T_M = 37$–38 K and 46–50 K for Br- and NCS-salts, respectively. These temperatures correspond to the sound velocity minimum. Therefore, It would be thought that the anisotropic behavior in the sound velocity is related to the change of charge state of this salt. We will make further investigations on the origin of the sound velocity minimum both experimentally and theoretically.

The authors thank K. Kanoda, M. Lang and T. Sasaki for valuable discussions, and M. Nakamura for his help in low temperature experiments. The experiments were carried out in the Cryogenic Division of Center for Instrumental Analysis Iwate University. This work was supported by a Grant-in-Aid for Scientific Research from Ministry of Education, Culture, Sports, Science and Technology.

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