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Anisotropic electrical conductivity, phase transition and thermal hysteresis of a charge-transfer salt dibutylammonium bis-7,7,8,8-tetracyanoquinodimethane DBA(TCNQ)$_2$*

Long Yun-Ze(龙云泽)[a)†], Chen Zhao-Jia(陈兆甲)[b)],
Peng Hai-Lin(彭海琳)[c)], and Liu Zhong-Fan(刘忠范)[c)]

[a)] *College of Physics Science, Qingdao University, Qingdao* 266071, *China*
[b)] *Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing* 100190, *China*
[c)] *Center for Nanoscale Science and Technology, College of Chemistry and Molecular Engineering, Peking University, Beijing* 100871, *China*

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This paper reports that a charge-transfer salt dibutylammonium bis-7,7,8,8-tetracyanoquinodimethane [DBA (TCNQ)$_2$] has been prepared. The temperature dependences of the DC electrical conductivity of the DBA (TCNQ)$_2$ single crystal measured along the crystallographic a, b, and c axes are reported. The crystal shows semiconducting behaviour and the room-temperature conductivities are highly anisotropic ($\sigma_a = 3.63\times10^{-4}$S/cm, $\sigma_b = 2.84\times10^{-6}$S/cm, and $\sigma_c = 1.82\times10^{-5}$S/cm). Particularly, a sharp semiconductor to semiconductor transition has been observed around 270 K on the resistivity curves measured under cooling and heating. In addition, thermal hysteresis phenomena on conductivity and differential scanning calorimetry curves are also reported.

Keywords: organic crystals, charge-transfer salt, conductivity, anisotropy
PACC: 7280L, 7360R

1. Introduction

Organic molecular conductors such as charge-transfer (CT) salts have drawn intensive interest due to their unique physical properties (for a review, see Ref.[1]) and widely potential applications in organic (nano) devices. For example, organic complexes with electrical switching effect are suitable for making nonvolatile memories.[2−4] The TCNQ salts can be used as ultrahigh density data storage via thermochemical hole burning using a scanning tunnelling microscope,[5,6] organic metal electrodes in ink-jet printing[7] and organic light-emitting devices.[8,9] High-performance low-cost organic field-effect (nano) transistors[10,11] and field emission devices[12] based on charge-transfer crystals of TTF-TCNQ, Cu-TCNQ, Ag-TCNQ were also investigated.

Some anion radical salts in a TCNQ system exhibit characteristic physical phenomena in a low-dimensional system such as anisotropy, electronic and structural instabilities. For instance, their conductivities and electron spin resonance spectra were highly anisotropic with respect to the crystal axis.[13−15] Metal-insulator transition was observed in many TCNQ salts such as TTF-TCNQ,[14] (NMe_3H)(I) (TCNQ),[15] (BEDT-TTF) (TCNQ),[16] $(BETS)_2$ (Br_2TCNQ)[17] and (CPDT-STF) (TCNQ).[18] Other phase transitions such as neutral-ionic phase transition in TTF-CA[19−22] and TMB-TCNQ,[20] semiconductor to semiconductor transition in (NMe_3H)(I)(TCNQ),[15] and spin-Peierls transition in MEM(TCNQ)$_2$[23] were also reported.

Although a lot of new CT complexes have been prepared and characterized in recent years, their physical properties need to be further investigated. Some physical questions such as enantiotropic solid-state phase transitions,[24] electronic and structural instabilities of mixed-stack organic CT salts[22] are still interesting and attractive. In this paper, we have

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†E-mail: yunze.long@163.com

prepared a new mixed-stack TCNQ salt dibutylammonium bis-7,7,8,8-tetracyanoquinodimethane [DBA $(TCNQ)_2$]. The temperature dependence of the DC electrical conductivity is semiconducting with markedly anisotropic room-temperature conductivities. In particular, an unusual phase transition occurs around 270 K, both the resistivity and activation energy decrease sharply, which is different from previous reported phase transitions. Thermal hysteresis phenomena were observed in conductivity and differential scanning calorimetry (DSC) measurements.

2. Experimental

The new CT salt DBA $(TCNQ)_2$ was prepared from dibutylammonium iodide and TCNQ (Aldrich, 98%) in acetonitrile according to the method of Melby *et al.*[13] Dibutylammonium iodide was prepared by adding dibutylamine to hydrogen iodide solution. After filtering and drying at room temperature, a white crystal was obtained. A boiling solution of 0.2040 g (1.0 mmol) TCNQ in 25 mL acetonitrile was treated with a boiling solution of 0.1286 g (0.5 mmol) of dibutylammonium iodide in 7 mL of acetonitrile, and the mixture solution turned an intense green. The solution stood at room temperature for 30 min, then stood at 0°C for about 24 h. The black needles were collected on a filter and washed with ice-cold acetonitrile. Upon recrystallization from acetonitrile the product was obtained as fine black block single crystal with typical dimensions 5.0 mm×0.4 mm×1.8 mm.

The resulting DBA $(TCNQ)_2$ ($C_{32}H_{28}N_9$) has been characterized by elemental analysis (Elementar Vario EL analyser, Germany), x-ray powder diffraction (XRD), scanning tunnelling microscopy (STM, Nanoscope IIIA), and DSC. The cooling/heating rate in the DSC measurements is 10°C/min. The single crystal possesses a triclinic unit cell [a=6.6650(2)Å, b=14.259(3)Å, c=15.962(3)Å, α=83.25(3)°, β=79.37(3)°, γ=89.97(3)°, and V = 1480.2(5)Å^3 at 293 K]. Figure 1 exhibits the projection along the a-axis, b-axis and c-axis of the DBA $(TCNQ)_2$ crystal. The perspective views of the crystal structure is shown in Fig.2(a). Figure 2(b) is a molecular-resolution STM image of the ac plane, which shows well-ordered molecular arrangement on the crystal surface. The dimensions of the surface unit cell are a=6.3Å, c=15.6Å, and the angle between the a- and c-directions is 79.4°, which are in good agreement with the crystallographic data collected on an x-ray diffractometer.[25]

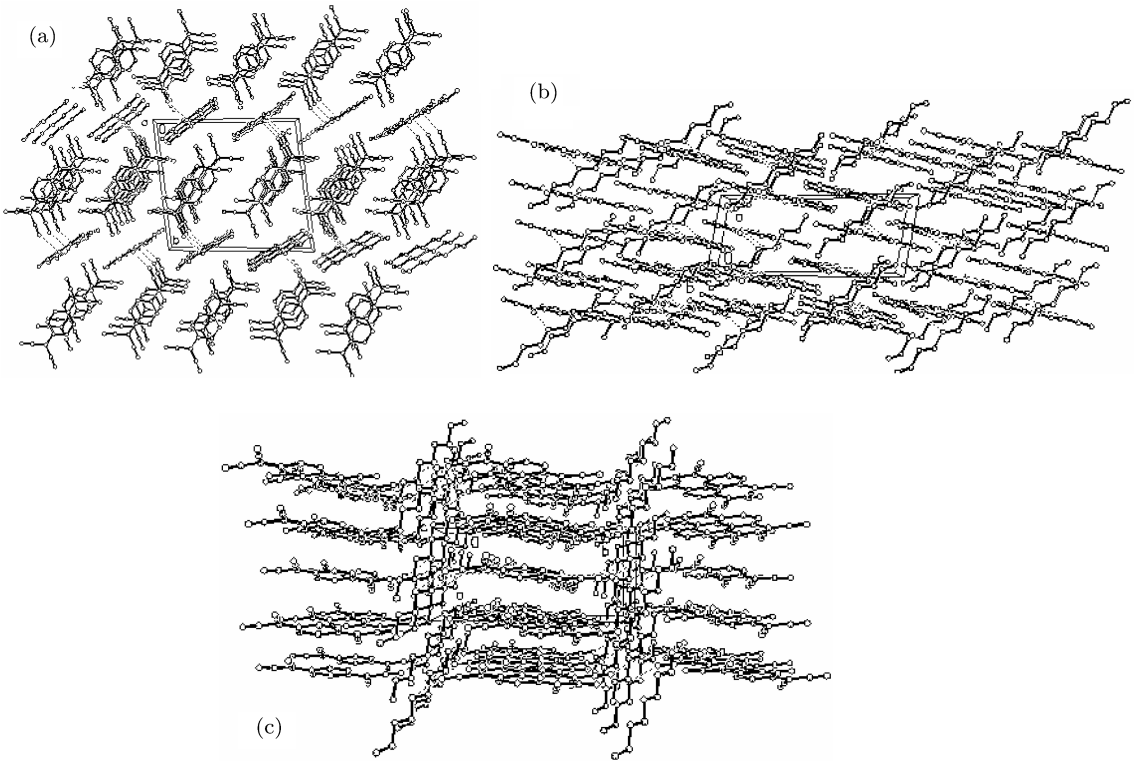


Fig.1. Projection along the (a) a-axis, (b) b-axis and (c) c-axis of the DBA $(TCNQ)_2$ crystal. Dashed lines show N-H$\cdots$N-C hydrogen bonds linking DBA cations and molecules TCNQ.

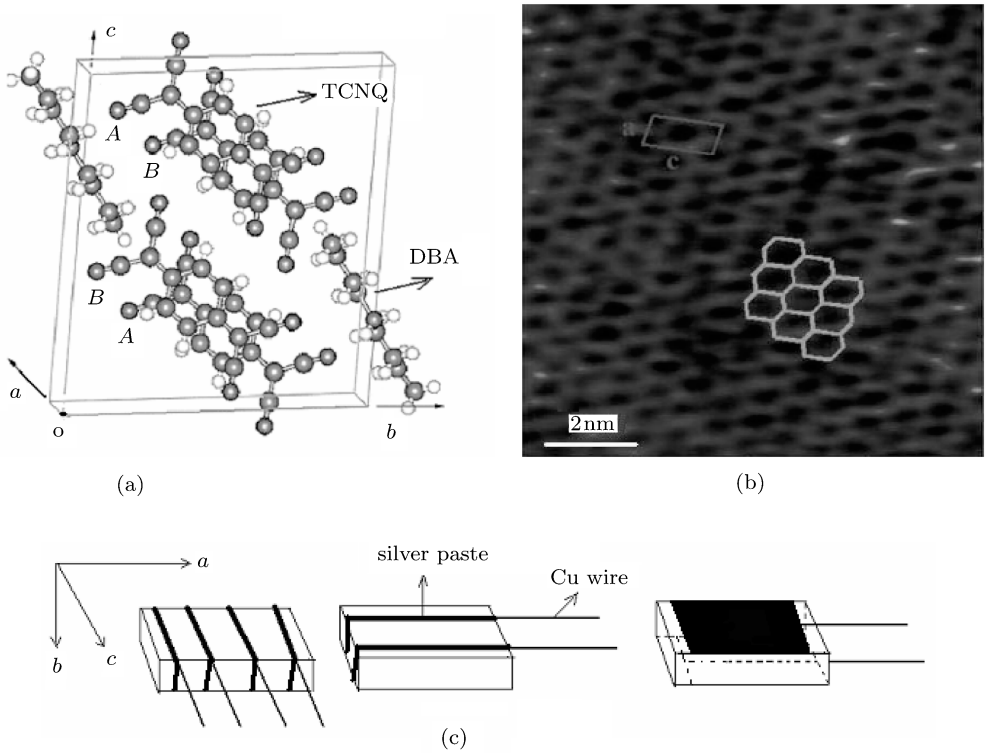


Fig.2. (a) Perspective views of the crystal of DBA $(TCNQ)_2$ ($C_{32}H_{28}N_9$). The single crystal possesses a triclinic unit cell [a=6.6650(2)Å, b=14.259(3)Å, c=15.962(3)Å, α=83.25(3)°, β=79.37(3)°, γ=89.97(3)°, and V=1480.2(5)Å^3 at 293 K]. It is noted that two types of planar TCNQ molecules (A and B) are stacked face to face along the a axis, with an AB repeated sequence. (b) STM image of the DBA $(TCNQ)_2$ crystal surface of the ac plane. (c) Configure of the Cu electrodes on the DBA $(TCNQ)_2$ single crystal.

DC electrical conductivities along the crystallographic a, b, and c axes were measured based on a standard four- or two-probe technique by using a Keithley 220-programmable current source and a Keithley 181-nanovoltmeter, which were autocontrolled by a computer. Figure 2(c) shows the configuration of Cu electrodes on three DBA $(TCNQ)_2$ crystals. For electrical contact, highly conductive silver paste was used. Here we note that the temperature dependent conductivities along b and c axes were measured by two-probe technique. The electrical conductivity data along the a-axis was measured in standard four-probe configuration. In addition, the contact resistance was measured in the order of $10^2\Omega$, which is quite smaller than the sample resistance ($> 10^5\Omega$).

3. Results and discussion

As compared with ordinary conductors, a special and interesting feature of TCNQ salts or related compounds is that the π orbitals of the molecules are strongly directional and interact mainly along the stacks, leaving a relatively weak interaction in the perpendicular directions. Hence, the compounds usually exhibit very anisotropic conduction properties and behave as quasi-one-dimensional conductors. For the single crystal of DBA $(TCNQ)_2$, we found that the electrical conductivity values have been shown to be markedly anisotropic, differing by two orders of magnitude when measured along three major crystal axes. The highest room-temperature conductivity is $\sigma_a = 3.63\times10^{-4}$S/cm along the a-axis. The conductivity values along the other two crystal axes are 2.84×10^{-6} and 1.82×10^{-5}S/cm, respectively. The anisotropic conductivity ratio is $\sigma_a/\sigma_b \sim 128$ and $\sigma_a/\sigma_c \sim 20$. It has been reported that the conductivity anisotropy can reach ~400 for $(NMe_3H)(I)(TCNQ)$ crystal.[15] Here we note that the conductivity results are consistent with the molecular structure and arrangement of the DBA $(TCNQ)_2$ crystal. As shown in Fig. 2(a), two types of planar TCNQ molecules (A and B) are stacked face to face along the a-axis, with an AB repeat sequence. The a-axis is the long needle axis of the crystal.

Figures 3(a), 3(c) and 3(e) show the temperature dependences of electrical resistivity of the single crys-

tal along the a, b, and c axes, respectively. Qualitatively the data shows a semiconducting behaviour with clear hysteresis under cooling and heating (the cooling curve determined first). The resistivity increases as the temperature decreases below room temperature, but decreases abruptly at about 270 K, and then increases again, undergoing a sharp semiconductor to semiconductor transition.

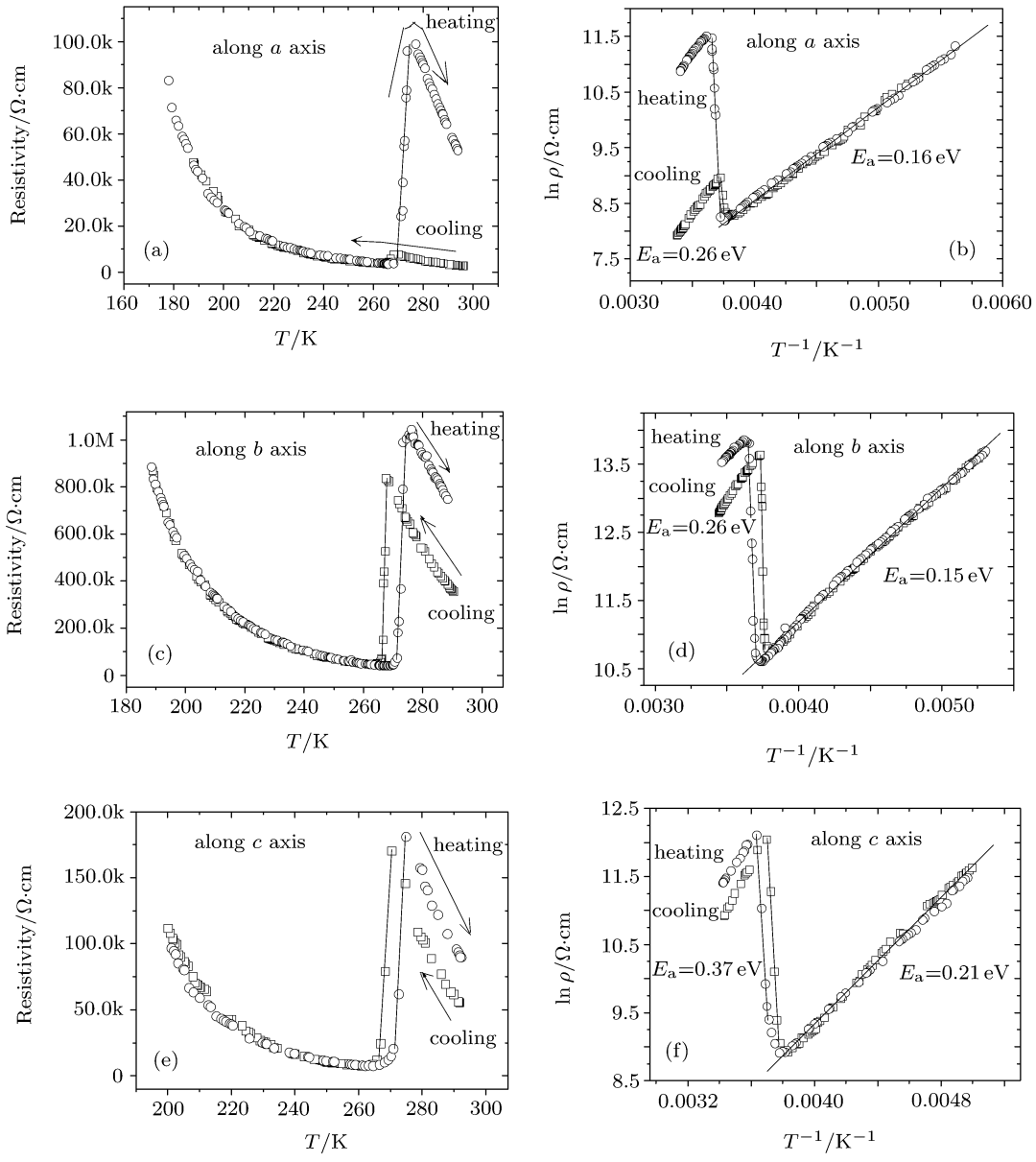


Fig.3. Temperature dependences of the DC resistivity of the DBA $(TCNQ)_2$ single crystal along the crystallographic a, b, and c axes, plotted as $\rho - T$ ((a), (c) and (e)) and $\ln\rho - T^{-1}$ ((b), (d) and (f)). Cooling curves determined first.

The temperature dependences of the resistivity can be interpreted by the thermal-activation model, which has been widely used to describe the conductivity data of some less conductive or mixed-stack CT salts and obtain their activation energies.[13,26,27] In this model, the resistivity increases exponentially with lowering temperature and follows the expression $\rho(T) = \rho_0 \exp(E_a/k_B T)$, where k_B is the Boltzmann constant, E_a is the activation energy. For intrinsic semiconductors, the relationship between E_a and the bandgap can be expressed as $E_g = 2E_a$. From the linear Arrhenius plots of $\ln\rho(T)$ versus T^{-1} in Figs.3(b), 3(d) and 3(f), we can determine the activation energy of the DBA $(TCNQ)_2$ crystal: E_a=0.26 eV

(before transition) and 0.16 eV (below 270 K) along the a-axis, E_a=0.26 eV/0.15 eV along the b-axis, and E_a=0.37 eV/0.21 eV along the c-axis, respectively. It should be noted that the activation energies decrease significantly after the semiconductor to semiconductor transition around 270 K (the highest conductivity values along the a, b, and c axes near the transition temperature are 2.8×10^{-4}, 2.5×10^{-5} and 1.3×10^{-4}S/cm, respectively). In addition, the transition temperature is 267 K under cooling and 272 K under reheating. We note that the phase transition in Fig.3 has been further evidenced by the DSC measurements (as shown in Fig.4). However, the transition temperature is 258 K for the cooling cycles and 264 K for the heating cycles, a bit lower than that determined by the resistivity measurements.

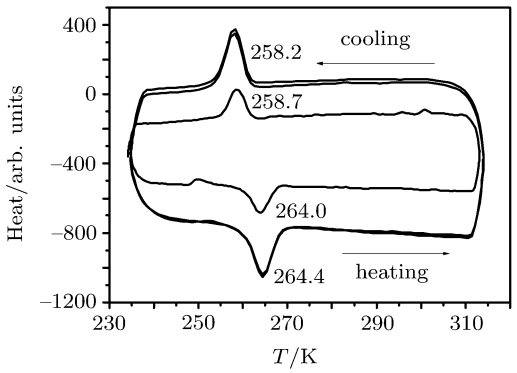


Fig.4. Differential scanning calorimetry traces of the DBA $(TCNQ)_2$ crystal for the cooling and heating cycles.

It is worthy of note that the observed phase transition is similar but a bit different from previous reported transitions in the CT compounds.[14−23] Usually the conductivity of the CT salts changes (or decreases) near the metal–insulator transition[14−16,18] or semiconductor–semiconductor transition,[15] or even shows a possible devil's staircase behaviour in TTF-CA at the neutral–ionic transition.[19] In the present case, with lowering temperature both the resistivity and activation energy decrease sharply after the phase transition. In addition, the resistivity along the a-axis increases more than one order of magnitude after reheating to 280 K (Fig.3(a)), whereas the resistivity in the perpendicular directions changes only a little (Figs.3(c) and 3(e)). Such transition is some kind of first-order structural transition in molecular systems[24] and related with the hydrogen bonding network. As shown in Fig.5, two half-populated alternating hydrogen bonds (2.10(3)Å and 2.17(3)Å) link DBA cations and molecules TCNQ(A), which give rise to a 'zig-zag' distortion of TCNQ stacks. The degrees of CT from a donor (DBA) to TCNQ(A) and TCNQ(B) are –0.82(5) and –0.21(5), respectively, which are estimated from the mean bond lengths of TCNQ, a widely used method suggested by Kistenmacher *et al.*[28] The electronic (valence) and structural (Peierls) instabilities occurring either separately or together in organic CT crystals with mixed stacks of donors and acceptors have been intensively reported.[19−22] For example, it has been reported that with lowering temperature at ambient pressure the hydrogen bonding network may result in the inequality and redistribution of the formal charge transfer, and thus a so-called neutral-to-ionic (N-I) phase transition or Peierls transition may occur.[21,22]

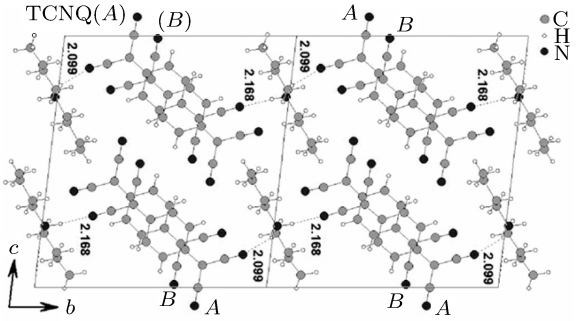


Fig.5. The two-dimensional structure of the DBA $(TCNQ)_2$ crystal. Dashed lines indicate the two half-populated alternating N–H···N–C hydrogen bonds (2.10(3)Å and 2.17(3)Å).

In addition, thermal hysteresis phenomena were observed in both resistivity curves (Fig.3) and DSC curves (Fig.4). The transition temperature determined from the heating curves is about 5–6 K higher than that determined from the cooling curves, namely, the hysteresis loop across about 5–6 K. Thermal hysteresis phenomena around the metal-insulator transition of TCNQ salts in conductivity measurements[14,18] and around the N-I phase transition of TTF-CA and TMB-TCNQ in neutron scattering and specific heat measurements have also been observed.[20] It should be noted that hysteresis around the equilibrium temperature is a general property of a solid-solid phase transition in molecular systems (for a review, see Ref.[24]), the heating transition occurs at a higher temperature than the equilibrium temperature and the cooling transition at a lower temperature. By now, Mnyukh's nucleation-and-growth model,[24] and Ubbelohde's 'hybrid crystals' and 'smeared transitions',[24] have been proposed for the mechanism. For mixed-stack CT complexes

such as TTF-CA and TMB-TCNQ,[20] temperature-induced N-I phase transition accompanying with ionicity jump and/or structural changes is a key issue. For the present case, the resistivity values in Fig.3 are not reproducible across the phase transition, which indicates the possible formation of charge traps (or ionic phase) and structural relaxation in the mixed-stack DBA $(TCNQ)_2$ crystal. The alternating hydrogen bonds are expected to produce ionic transport with different relaxation time constants. However, further studies are needed to clarify the possible N-I phase transition in this crystal.

4. Conclusion

In summary, a quasi-one-dimensional CT single crystal of DBA $(TCNQ)_2$ with mixed stacks of donors and acceptors has been prepared and characterized. The semiconducting crystal shows anisotropic electrical conductivity with σ_a=3.63×10^{-4}S/cm along the long needle axis at room temperature and anisotropic ratio σ_a/σ_b ∼128. The temperature dependences of the DC resistivity measured along the a, b, and c axes under cooling and reheating indicate that the crystal undergoes a semiconductor-semiconductor transition around 270 K possibly due to the instability of the hydrogen bonding network.

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