

Short Notes

Thermal expansion of organic superconductor α -(BEDT-TTF)₂ NH₄Hg(SCN)₄

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The temperature dependence of the linear thermal expansion coefficients (LTEC) of a single crystal of α -(BEDT-TTF)₂NH₄Hg(SCN)₄ where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene was studied by the method of precision capacitive dilatometry in the temperature range 2–250 K along the crystallographic direction *b* (perpendicular to the crystal layers). Negative values of LTEC were found below 4 K. Probably it is due to charge fluctuations as the temperature approaches the temperature of transition to the superconducting state *T_c*. It has been suggested that the bends on temperature dependence of LTEC observed in the temperature range 25–45 K are related to order-disorder arrangement of NH₄⁺ ions. Weak maximum of the LTEC, detected at a temperature of about 200–220 K, can be caused by the processes of charge redistribution and the associated intermolecular interaction fluctuations.

Keywords: organic (super) conductors, α -(BEDT-TTF)₂NH₄Hg(SCN)₄, thermal expansion.

Introduction

Organic (super) conductors are a series of multi-components molecular compounds categorized as organic charge transfer salts. They have a variety of electronic phases produced by π -electrons/holes released from molecular orbitals of organic molecules (HOMOs/LUMOs). They usually form an alternatively stacked structure of organic molecule layers and counter-ion layer. The molecular arrangements in the organic molecule layer are closely related to the band structures determined by the various electron transfers between neighboring molecules in the conducting layers. Electronic state at low temperatures shows divers variations due to the difference of these struc-

tural features. The itinerant $\tilde{\pi}$ -carriers also have feature of electron correlations as well as the characters induced by strong electron-lattice coupling. The development of these molecule-based conducting compounds was initiated by the ideas of Little and Ginzburg [1,2] on the possibility of superconductivity in quasi-one-dimensional and two-dimensional heterogeneous structures in which layers with metallic and dielectric properties alternate. The well-known component molecule of most numerous organic (super) conductors is the organic molecule BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene, also often abbreviated as ET). The BEDT-TTF molecule consists of two five-membered and two six-membered rings, each of which

contains two sulfur atoms [3]. These molecules are almost planar, which makes it possible to pack them in the form of quasi-one dimensional stacking, or uniform or zig-zag stackings of dimerized units, etc. (Fig. 1).

The unpaired π -electrons of the HOMO delocalized over carbon and sulfur atoms of the BEDT-TTF molecule form a set of π -orbitals perpendicular to the plane of molecule [4,5]. The ET molecules are donors of a charge (one electron per two ET molecules [6]) and form ordered conductive layers in the crystal, separated by acceptor insulating layers (in our case, by the [NH₄Hg(SCN)₄]⁻ anions).

Organic conductors of the family α -(BEDT-TTF)₂MHg(SCN)₄ (where M⁺ = NH₄⁺, K⁺, Rb⁺, Tl⁺) are characterized as metallic salts with quasi-1D and 2D Fermi surface. Organic conductors α -(ET)₂KHg(SCN)₄ and α -(ET)₂NH₄Hg(SCN)₄ were first synthesized as possible superconducting modifications of the compound κ -(ET)₂Cu(SCN)₂ possessing a 10 K transition temperature [7]. Despite of the fact that these two salts have isostructure categorized as non-dimerized α -type packing their low-temperatures properties are very different. α -(ET)₂NH₄Hg(SCN)₄ is a superconductor with $T_c \sim 1.15$ K, whereas α -(ET)₂KHg(SCN)₄ has a metallic conductivity down to 100 mK [8,9]. Kondo et al., based on combined discussion by transport properties under uniaxial stress measurements and band structure calculations [10], suggested that the quasi-one-dimensional Q1D zone contributes to superconductivity [11].

The application of external pressure gives two effects on α -(ET)₂NH₄Hg(SCN)₄: first, when hydrostatic pressure is applied, superconductivity disappears, and secondly, at P larger than 0.2 GPa the band structure of this compound is modified, which leads to peculiarities of magnetic and transport properties in the nonsuperconducting phase [12]. It was also noted that the presence in the structure of compound α -(BEDT-TTF)₂(M)Hg(SCN)₄ groups NH₄⁺ (in contrast to monatomic M metal ions) introduce an orientational freedom that may induce disorder into the crystal, which leads to dis-

ordering of open π -electron orbits [12]. This ensures the possibility of superconductivity at low temperatures and normal pressure in α -(BEDT-TTF)₂NH₄Hg(SCN)₄. This assumption is confirmed by the relationship between the parameters a and c of the elementary crystal cell of this compound [13]. For compounds containing NH₄⁺ ions, a decrease in the lattice parameter ratio c/a enhances superconductivity, while an increase in c/a stabilizes the metallic state. Intermediate between them is the density-wave state. The characteristic changes in the electronic properties of these compounds can be systematically represented as a function of c/a . Due to anisotropic thermal compression, the ratio c/a for the NH₄ salt is much smaller than for M = K, Rb, Tl at low temperatures and normal pressure, which explains the transition of NH₄⁺ compounds to the superconducting state. In these compounds, the phase transition to a charge-ordered state is due to the competition between the kinetic energy of the system, and the Coulomb energy (external and internal) of nearest neighbors, ET molecules [14]. Based on the phase diagram [15], it can be concluded that as the electronic correlations increase, the ground state of these systems changes from the metallic (Fermi liquid) to the Mott insulator, in addition, there is a superconductivity region between these states [13,16].

Earlier we investigated using a low-temperature capacitance dilatometer the low-temperature thermal expansion of quasi-two-dimensional organic conductors κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl and κ -(D₄-BEDT-TTF)₂Cu[N(CN)₂]Br along the crystallographic axes a and b in the temperature range 2–290 K [19,20]. The temperature dependences of the linear thermal expansion coefficients (LTEC) $\alpha(T)$ of these single crystals were determined and a correlation between the anomalies in their thermal expansion and the phase transformations was established. The purpose of this work was to investigate the influence of structural features and the phase state of α -(BEDT-TTF)₂NH₄Hg(SCN)₄ compound on the thermal expansion of this crystal.

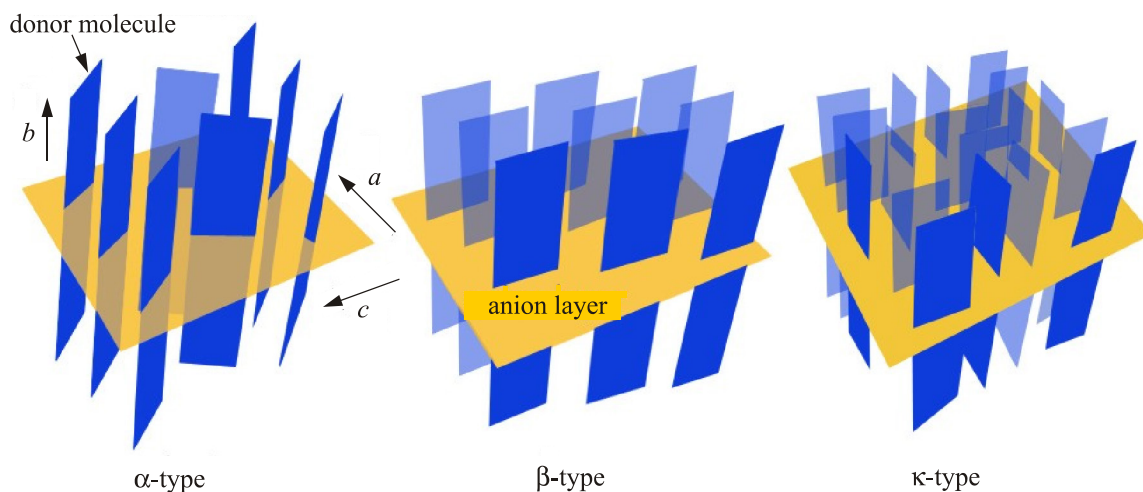


Fig. 1. Location of molecular layers in organic conductors of α -, β - and κ -type.

Experimentals

Organic salt α -(BEDT-TTF) $_2$ NH $_4$ Hg(SCN) $_4$ has an orthorhombic two-layered crystal lattice with four ET molecules in the unit cell. The layers of anions in this compound are located in the ac plane and are perpendicular to the b axis along which the flat BEDT-TTF molecules are located [18]. Conductive and insulating layers alternate along the b axis (Fig. 1). Positions of the crystallographic axes in the studied sample, the crystal structure and parameters of lattice was confirmed by x-ray diffraction (at room temperature $a = 10.103$ Å, $b = 20.557$ Å, $c = 9.935$ Å).

The study of linear thermal expansion coefficient of α -(BEDT-TTF) $_2$ NH $_4$ Hg(SCN) $_4$ single crystal was performed in the direction of the crystallographic b axis perpendicular to the crystal layers in the temperature range 2–250 K using a low-temperature capacitive highly sensitive dilatometer [19]. Since this direction is the inter-layer direction, the thermal conductivity seems sensitive to the change of the order-disorder arrangement of the anion layer. The change of this direction is also related to the 2D features in the transport and magnetic properties of this compound. The length of the sample in the measuring direction was $l = 0.7$ mm. The measured values of the coefficient of linear thermal expansion are shown in Fig. 2.

Results and discussion

Temperature dependence of LTEC of the single crystal sample of α -(BEDT-TTF) $_2$ NH $_4$ Hg(SCN) $_4$ do not have pronounced peaks observed earlier in the LTEC dependences of single crystals κ -(D $_4$ -BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br and κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Cl [19,20]. It decreases almost linear from room temperature down to about 100 K as is shown in the Fig. 2(a). The decrease become steep below about 70 K where the ethylene groups of BEDT-TTF molecules seem to be frozen or ordered. Since we could not detect peak like structure related to the ethylene dynamics in κ -type compounds, the lattice conffliction seems to be quite normal for molecular compounds. However, there are a number of features of $\alpha(T)$ (see Fig. 2) which must be related to the electron-lattice coupling of this compound.

Below 3.5–4 K LTEC of α -(BEDT-TTF) $_2$ NH $_4$ Hg(SCN) $_4$ has small negative values (see the insert to Fig. 2(a)). It is assumed that the negative thermal expansion coefficient of this compound can be due to formation of hindered tunneling level of NH $_4^+$ or superconductive fluctuations coupled with charge disproportionation [15]. In the case of κ -type compounds, the negative thermal expansion is observed only below T_c . It is interesting to note that the attribute of charge fluctuations in the family of α -(BEDT-TTF) $_2$ MHg(SCN) $_4$ (where M — NH $_4$, Rb, Tl) most clearly manifest itself in NH $_4$ compound, since in ET-NH $_4$ salt the isolating anionic layer is thick among various of ET-based superconductor molecules. The period of the layer in the direction perpendi-

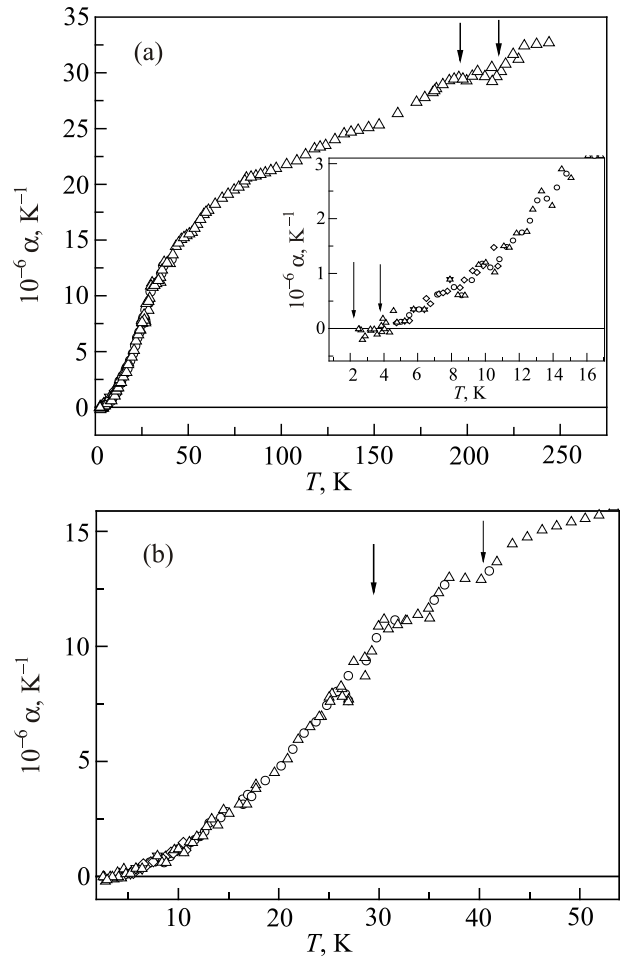


Fig. 2. The temperature dependences of LTEC in the intervals 2–250 K (a); 2–55 K (b). The interval 2–17 K is also shown in the inset to Fig. 2(a). Different symbols correspond to data from different series of experiments. Arrows indicate the temperature intervals of LTEC anomalies.

cular to the plane is about 20 Å. The heat capacity measurements of those compounds performed previously demonstrated that the fluctuation region of superconductivity ranges to the higher temperature region and hindered rotation contribution of heat capacity is observed as upturn of $C_p T^{-1}$ [21,22]. These thermodynamic features should be related to the appearance of negative thermal expansion region at low temperatures.

There are several anomalies (bends) of the dependence $\alpha(T)$ (Fig. 2(b)) in temperature range 25–45 K. The magnitude of these anomalies exceeds the experimental error. In this temperature range may be a kind of order-disorder arrangements of NH $_4^+$. The preliminary thermal conductivity measurement of the deuterated compound (ND $_4^+$) gives an anomaly around 25 K [24]. Probably the NH $_4^+$ containing compound show it at higher temperature than the deuterated compound and may show glass-like character, since the thermal expansion shows two-step behavior as is shown in Fig. 2(b)).

The anomaly in the higher temperature region is considered as an electronic origin peculiar for nondimeric arrangement. In the case of α -type BEDT-TTF compounds, in addition to the local (on-site) Coulomb interaction U , the second important parameter that determines the properties of organic salts is the electronic repulsion V between the nearest neighbors. In the case of nondimerized structure, the metallic state may change to charge ordered insulating states through the increase of V/W ratio. In the region of a quantum critical point, superconductivity can be associated with the possible emergence of charge fluctuations [17]. When cooled, the electronic properties of these systems change due to several factors: (1) as for any metal, the scattering rate of charge carriers decreases, since the phonon oscillations are frozen; (2) a decrease in the volume of the crystalline cell increases proportionally the density of the charge carriers; (3) the optical throughput as well as the electrical conductivity of the crystals increase with increasing transfer integrals t and a decrease in the ratio V/t (the transfer integrals are defined as $t = ES$, where E ($= -10$ eV) is the empirical constant and S is the overlap integral [18]). Experimentally the $M = \text{NH}_4^+$ compound has the largest two-dimensional feature among α -type compounds, since the thick anions layers work to separate the π -electrons layers [18]. In the temperature range 200–220 K the dependence of $\alpha(T)$ shows a change in the slope and an increased scatter of the experimental values (Fig. 2(a)). Since this compound do not have dimerized structure, the charge disproportionation and fluctuations due to inter-molecular Coulomb repulsions may be important. According to the NMR experiments there is some kind of anomaly related to the charge disproportionation in this temperature region [15]. The hump structure (Fig. 2(a)) is probably explained by this circumstance since the charge disproportionation itself is electronic origin but should have large change in phonon structure. The change in the angle of inclination of temperature LTEC dependence can be due to freezing of free rotational motion of NH_4^+ ions coordinated by four SCN ligands and therefore appears in thermal expansion as a hump structure [24].

Conclusions

Thermal expansion of a single crystal of α -(BEDT-TTF)₂NH₄Hg(SCN)₄ was studied by the method of precision capacitive dilatometry in the temperature range 2–250 K along the crystallographic direction b axis (perpendicular to the crystal layers). The obtained temperature dependence of LTEC had a number of features due to the phase composition and structure of the compound. The negative LTEC values found below 3–4 K are possibly due to charge fluctuations as the measurement temperature approaches the temperature of transition to the superconducting state T_c . The kinks of the $\alpha(T)$ dependence in the temperature range 25–45 K are most likely associated with order-disorder arrangement of NH_4^+ ions. Weak maximum of the LTEC, detected at temperature

of about 200 K, can be caused by the processes of charge redistribution and associated intermolecular interaction fluctuations. The observed change in character of the $\alpha(T)$ dependence at 200–220 K is probably correlated with the disinhibition of the rotational motion of NH_4^+ ions with increasing temperature.

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Теплове розширення органічного надпровідника
 α -(BEDT-TTF)₂NH₄Hg(SCN)₄

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Методом прецизійної ємнісної дилатометрії в температурному інтервалі 2–250 К досліджено температурну залежність коефіцієнтів лінійного теплового розширення (КЛТР) монокристалла α -(BEDT-TTF)₂NH₄Hg(SCN)₄, де BEDT-TTF — бис(етилендітіо)тетрагіафульвален, уздовж кристалографічного напрямку *b* (перпендикулярно до шарів кристалу). Нижче 4 К виявлено від'ємні значення КЛТР, ймовірно, обумовлені флуктуаціями заряду при наближенні температури вимірювань до температури переходу в надпровідний стан T_c . Висловлено припущення, що перегини температурної залежності КЛТР, які спостерігаються в температурному інтервалі 25–45 К, пов'язані з процесами упорядкування-розупорядкування NH₄⁺ іонів. Пагорбоподібна аномалія КЛТР, яка виявлена при температурі близько 200–220 К, може бути викликана процесами перерозподілу заряду та пов'язаними з ними флуктуаціями міжмолекулярної взаємодії.

Ключові слова: органічні (над) провідники, α -(BEDT-TTF)₂NH₄Hg(SCN)₄, теплове розширення.

Тепловое расширение органического
сверхпроводника α -(BEDT-TTF)₂ NH₄Hg(SCN)₄

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Методом прецизионной емкостной дилатометрии в температурном интервале 2–250 К исследована температурная зависимость коэффициентов линейного теплового расширения (КЛТР) монокристалла α -(BEDT-TTF)₂NH₄Hg(SCN)₄, где BEDT-TTF — бис(этилендитио)тетрагифульвален, вдоль кристаллографического направления *b* (перпендикулярно слоям кристалла). Ниже 4 К обнаружены отрицательные значения КЛТР, вероятно, обусловленные флуктуациями заряда при приближении температуры измерений к температуре перехода в сверхпроводящее состояние T_c . Высказано предположение, что наблюдаемые в температурном интервале 25–45 К перегибы температурной зависимости КЛТР связаны с процессами упорядочения-разупорядочения NH₄⁺ ионов. Холмообразная аномалия КЛТР, обнаруженная при температуре около 200–220 К, может быть вызвана процессами перераспределения заряда и связанными с ними флуктуациями межмолекулярного взаимодействия.

Ключевые слова: органические (сверх) проводники, α -(BEDT-TTF)₂NH₄Hg(SCN)₄, тепловое расширение.