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INFLUENCE OF MAGNETIC FIELD ON THE ELECTRONIC SPECIFIC HEAT OF THE ORGANIC METAL (BEDT-TTF)$_2$KHg(SCN)$_4$

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Specific heat measurements of a single crystal of the organic metal (BEDT-TTF)$_2$KHg(SCN)$_4$ have been carried out at low temperatures and under a magnetic field of up to 14 T. A jump in the specific heat of about 0.1 J/mol·K, which corresponds to the antiferromagnetic phase transition, has been observed. The magnetic field is found to decrease the transition temperature at any field orientation. The strongest effect was found to take place in the field direction along the highly conducting **ac**-plane.

1. INTRODUCTION

The organic metals (BEDT-TTF)$_2$MHg(SCN)$_4$, where BEDT-TTF stands for bis(ethylenedithio)-tetrathiafulvalene and M = K, Tl and Rb, are of significant interest due to their unusual properties in magnetic fields at low temperatures [1]. The Fermi surface characteristic of these compounds consists of a cylindrical (quasi-two-dimensional, Q2D) part and slightly corrugated open (quasi-one-dimensional, Q1D) sheets. The instability of the Q1D conducting band against the spin density wave (SDW) formation is thought to be the reason for a phase transition occurring below 10 K in these compounds. The strong anisotropic change of the magnetic susceptibility [2] resembles that previosly observed in the purely Q1D conductors such as (TMTSF)$_2$X [3] although the magnitude of the magnetic moment modulation extracted from the μSR experiment [4] is considerably smaller, $\mu_{SDW} = 0.003\mu_B$ (here μ_B is the Bohr magneton).

According to the B–T phase diagram originally proposed by Sasaki et al. [5] for the M = K salt on the basis of magnetoresistance studies at different temperatures, the phase transition into the SDW state is gradually suppressed by the magnetic field applied perpendicular to the highly conducting planes, and the normal metallic state is stabilized above 23 T in the entire temperature region. Many of magnetoresistance anomalies have been explained in the framework of the SDW model [6] and the phase diagram [5]. However, several serious problems remain. For example, the effect of magnetic field on the SDW ground state in these compounds near the transition temperature T_p is not clearly understood. For the quasi-one-dimensional (TMTSF)$_2$X salts, a magnetic field applied perpendicular to the highly conducting planes is known to stimulate rather than suppress the SDW instability due to the effective enhancement of the one-dimensional character of the electron motion. The theoretical model developed for one-dimensional systems [7, 8] and applied to (BEDT-TTF)$_2$KHg(SCN)$_4$ [9]

predicts a gradual increase of the SDW transition temperature with magnetic field. Other models considering magnetic breakdown between Q1D and Q2D parts of the Fermi surface [10, 11] or fluctuation effects [12] have been proposed as possible explanation for the field-induced reentrant transition. We note that all the theories mentioned above consider the effect of the field directed perpendicular to the highly conducting planes as the most significant effect. However, from the experimental point of view, no agreement has been established as to whether the perpendicular field component has the main effect on the low-temperature antiferromagnetic state near T_p.

The B–T phase diagram was recently revised on the basis of the comparative magnetoresistance and magnetic torque studies by Sasaki et al. [9] and Kartsovnik et al. [13]. Both investigations proposed that the low-temperature state differs from the normal metallic state even in the high-field region. However, no agreement has been reached as to the magnetic field effect in the low-field range. According to the diagram proposed by Sasaki et al. [9], at least two successive transitions take place upon cooling the sample in a finite field, where the magnetically ordered state is stabilized by the field. In contrast, only one transition was found by Kartsovnik et al. [13] in the temperature dependencies of the resistance and torque at fields below 10 T; the transition temperature shifted to slightly lower temperatures as the field was raised.

Thus, the effect of magnetic field on the low-temperature state of α-(BEDT-TTF)$_2$MHg(SCN)$_4$ is still an open question and further detailed studies are required in order to clarify the problem. We report here the results of an experimental study of the heat capacity of a α-(BEDT-TTF)$_2$KHg(SCN)$_4$ single crystal as a function of temperature under a magnetic field up to 14 T. A single prominent anomaly corresponding to one phase transition has been observed at all applied fields. The anomaly gradually shifts down as the field increases. Tilting the field from the direction normal to the highly conducting planes increased the magnitude of the shift .

2. EXPERIMENTAL

The single crystal used for the experiment was obtained by galvanostatic electrolysis (j = 1.0 μA/cm^2) of a solution of KSCN, Hg(SCN)$_2$ and 18-crown-6 (10 mmol/l each) in 1,1,2-trichloroethane/MeOH (abs.) (9:1; 25 ml) in the presence of BEDT-TTF (13 mg) at a temperature of 25 °C.

To measure specific heat, the standard ac-modulation technique [14] was used. The magnitude of the temperature modulation was 0.5–2%, the modulation frequency was ν = 0.04 Hz and the calorimeter-to-bath relaxation time τ was a few seconds in the studied temperature region of 6–14 K so that $2\pi\nu\tau > 1$. The calorimeter consisted of a bare chip of Cernox thermoresistor and a carbon heater. The thermal link between the calorimeter and the bath was provided by 50-μm manganin wires, which were used also as electrical leads to the thermometer and heater. A single crystal of (BEDT-TTF)$_2$KHg(SCN)$_4$ with the mass of 0.9 mg was fixed by a small amount of the Apiezon N grease to the thermometer and a smaller amount of the same grease was used to fix the heater to the sample. The absolute value of the specific heat of the sample was determined with an accuracy of 5% and was approximately a factor of 4 larger than the admixture. The temperature error due to the magnetoresistance of the Cernox thermoresistor did not exceed 0.1 K at 14 T and was taken into account in the data analysis.

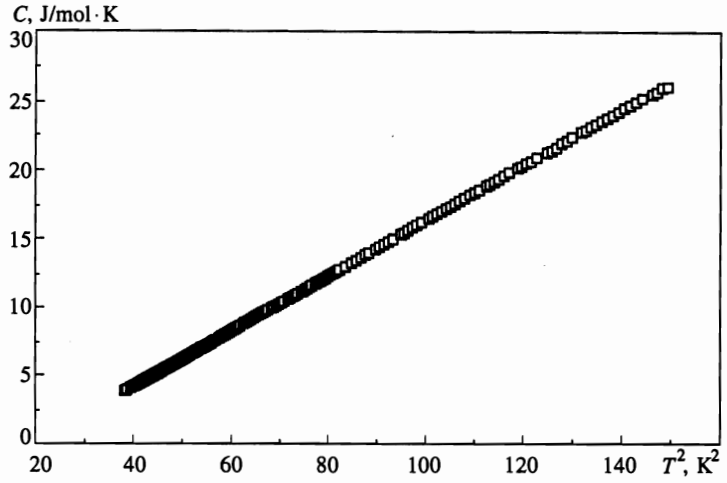

Fig. 1. Specific heat of $(BEDT\text{-}TTF)_2KHg(SCN)_4$ versus temperature squared

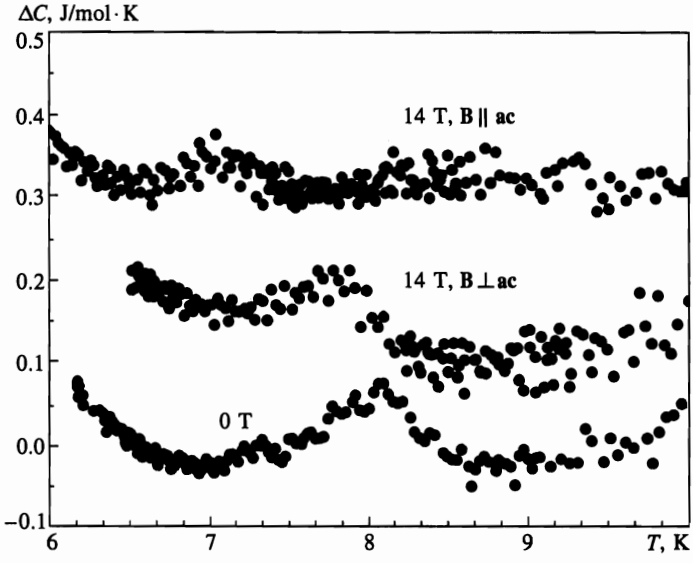

Fig. 2. Specific heat of $(BEDT\text{-}TTF)_2KHg(SCN)_4$ after subtraction of the monotonic background at zero field and at field $B = 14$ T directed parallel and perpendicular to the **ac**-plane

3. RESULTS AND DISCUSSION

The total specific heat at zero field is presented in Fig. 1 (here 1 mol = N_A formula units where, N_A is the Avogadro number). The specific heat is plotted versus temperature squared. Since the plot is almost linear in such coordinates, we can approximate the monotonic

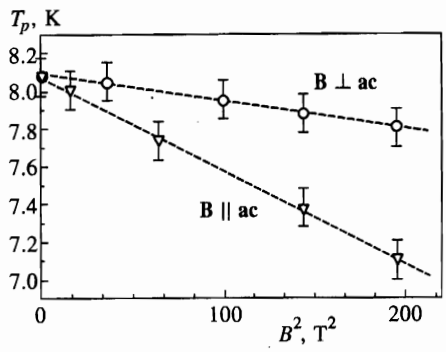

Рис. 3

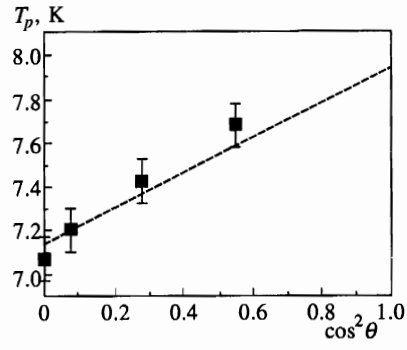

Рис. 4

Fig. 3. Field dependence of T_p versus magnetic field squared at two field directions

Fig. 4. Angular dependence of T_p versus cosine of the angle between the normal to the **ac**-plane and field direction

background as: $C = a + bT^2$. The specific heat, after subtraction of the background at zero magnetic field and at two orientations of the magnetic field $B = 14$ T, is shown in Fig. 2; the data are offset for clarity. The phase transition is manifested by a peak-like feature in the heat capacity. At zero field the maximum is at 8 K and it shifts to lower temperature in a magnetic field. The relatively large width of the anomaly is probably caused by the strong fluctuations. The magnitude of the specific heat jump at zero field is evaluated as C_0=0.1 J/mol·K or about 1% of the total specific heat. This value agrees with our previous measurements [15], but it is about a factor of 3 smaller than the value reported by Henning et al. [16]. On the other hand, Nakazawa et al. [17] may not have observed the anomaly since the scattering of their experimental data exceeded 1%. Figure 3 shows the field dependence of the maximum position at two field orientations: **B** is perpendicular to the highly conducting **ac**-plane and **B** is parallel to this plane. We see that in both cases the shift of the maximum position is proportional to the magnetic field squared, $T_p(B) = D(\theta)B^2$, where θ is the angle between the normal to the **ac**-plane and the magnetic field direction. For the field orientations shown in Fig. 3 we find

$$D(\theta = 0°) = (1.5 \pm 0.4) \cdot 10^{-3} \text{ K/T}^2 \tag{1}$$

and

$$D(\theta = 90°) = (5.0 \pm 0.5) \times 10^{-3} \text{ K/T}^2.$$

The angular dependence of the maximum position is shown in Fig. 4 for $B = 14$ T. The plot demonstrates an approximately linear dependence on the square of cosine of the angle θ between the normal to the **ac**-plane and the field direction.

Assuming that the phase transition is second order, we can relate the behaviour of the specific heat to the magnetic susceptibility by using the thermodynamic identity

$$C_i - C_j = -T\mu_0 \left(\frac{\partial H_{ij}}{\partial T}\right)_H \left[\left(\frac{\partial M_i}{\partial T}\right) - \left(\frac{\partial M_j}{\partial T}\right)\right]_H =$$

$$= -\frac{T\mu_0}{2}\left(\frac{\partial H_{ij}^2}{\partial T}\right)_H \left[\left(\frac{\partial \chi_i}{\partial T}\right) - \left(\frac{\partial \chi_j}{\partial T}\right)\right]_H, \quad (2)$$

where μ_0 is the magnetic permeability of vacuum, $H_{ij}(T)$ is the phase-separation line, and $C_i(C_j)$ and $\chi_i(\chi_j)$ are the specific heat and susceptibility of the phase $i(j)$, respectively. Although in our case the transition is significantly broadened in temperature, we will attempt to evaluate $\Delta\left(\partial\chi/\partial T\right)_H$ in the antiferromagnetic state from Eq. (2) using our data. For **B** parallel to the **ac**-plane we estimate

$$\Delta\left(\frac{\partial \chi}{\partial T}\right)_H \approx 2.6 \cdot 10^{-7}\ \mathrm{K}^{-1}$$

in the limit $B \to 0$, in agreement with the susceptibility data from [2] and [18]. For **B** perpendicular to the **ac**-plane we estimate

$$\Delta\left(\frac{\partial \chi}{\partial T}\right)_H \sim 0.8 \cdot 10^{-8}\ \mathrm{K}^{-1} \quad \text{as} \quad B \to 0.$$

We note that no significant change in the susceptibility in that direction was found in the magnetization measurements [2] in the field $B = 5$ T. In principle, this may be explained by a dependence of the transition temperature, which is much weaker than B^2 in fields below 5 T. Such an assumption is consistent with our data, as can be seen in Fig. 3. The uncertainty in the determination of the peak position does not allow us to make a definite conclusion about the field effect below 5 T.

Thus, our specific heat data show only one phase transition in a magnetic field in the range $0 < B < 14$ T. In contrast with the conclusion made by Sasaki et al. [9], no evidence of two successive transitions below 14 T was found. Therefore, we affirm that in the field range studied by us the only effect of magnetic field is that it gradually shifts the transition to a lower temperature. An important result is that the shift is dependent on the field direction.

The fact that the field parallel to the **ac**-plane has a stronger effect than the field perpendicular to the **ac**-plane seems to be consistent with the assumption about the easy-axis or the easy-plane antiferromagnetic order[1)] [19]. For the field along the **ac**-plane we can compare the obtained shift of the transition temperature with that predicted, within the mean field approximation, for the SDW state with an easy-axis ordering under the magnetic field parallel the spin alignment direction given by [20],

$$T_p(B) = T_0 \exp(-7\zeta(3)b^2), \quad (3)$$

where $b = \mu_B B/2\pi kT$. In low fields this expression reduces to [21]

$$\frac{T_p(B) - T_p}{T_p} \approx 0.2\left(\frac{\mu_B B}{k_B T_p}\right)^2, \quad (4)$$

which has a parabolic field dependence in agreement with our data. Substituting $T_p = 8$ K we obtain from Eq. (4) the shift of the transition temperature 0.01 K/T^{-2}, in reasonable agreement with the experimental value (1).

[1)] We note that although the SDW transition in Q1D organic metals is commonly characterized by an easy-axis antiferromagnetic ordering, recent torque experiments pointed out the possibility of a more complicated spin alignement in the **ac**-plane.

The influence of the magnetic field perpendicular to the **ac**-plane is rather different in our measurements than expected for the conventional SDW state. According to the theoretical prediction [7, 8], it also differs from the results reported by Sasaki et al. [9]. As mentioned above, other theoretical models [10, 11] predict a decrease of the transition temperature for this field direction. Probably the total effect of the magnetic field is a superposition of one of those mechanisms and the spin-field interaction.

In conclusion, we have found an anomaly in specific heat of $(BEDT\text{-}TTF)_2KHg(SCN)_4$ which corresponds to the antiferromagnetic ordering phase transition. This anomaly is shifted toward low temperatures in an applied magnetic field. The shift occurs at any direction of the magnetic field; the strongest effect is observed for the field parallel to the **ac**-plane. We suggest that for this field orientation the shift may be understood as resulting from the destruction of the SDW phase via the interactions of the electron spins with the external magnetic field. The reason for the decrease in the transition temperature in a field perpendicular to the **ac**-plane is yet to be clarified.

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