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Phase transition of $(\text{DMET})_2\text{Au}(\text{CN})_2$ at 180 K

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Abstract. The temperature dependence of the heat capacity of $(\text{DMET})_2\text{Au}(\text{CN})_2$ was measured. The existence of a phase transition at 180 K, suggested previously, was confirmed. The transition seems to be high order. The mechanism of the transition is discussed.

1. Introduction

$(\text{DMET})_2\text{Au}(\text{CN})_2$ is the first member [1] of the DMET family of the organic superconductors [2–5]. The remarkable feature of the DMET molecule is its asymmetry: a half of the molecule is that of TMTSF and the other half BEDT TTF (figure 1). The crystal structure of $(\text{DMET})_2\text{Au}(\text{CN})_2$ is shown in figure 2 [6]. In the crystal, the molecules stack alternately along the crystallographic *b* axis, which is the most conductive, and the crystal-growth axis. Since the unit cell contains two DMET molecules which are in the same column, there exist two types of molecular overlap.

$(\text{DMET})_2\text{Au}(\text{CN})_2$ is metallic down to 28 K under normal pressure [1]. X-ray [7] and magnetic resonance [8] studies revealed the transition to be due to the formation of a SDW (spin density wave). The transition is suppressed by a pressure of 5 kbar and the superconductivity appears below 0.80 K [1]. The *T*–*P* phase diagram has recently been determined through electrical measurements [9]. The pressure range where the transition from the SDW phase to the superconducting one takes place was found to be rather wide, i.e. 2.5–5.0 kbar [9].

Murata *et al* [10] pointed out the existence of a small anomaly (dip) in the resistivity curve at about 180 K and suggested that the anomaly resulted from some phase transition. The plot of the resistivity between 150 and 210 K is shown in figure 3. According to the so-called Elliott mechanism, a similar anomaly can be recognised in the linewidth of electron spin resonance (ESR) [11, 12]. The smallness of the anomaly implies a

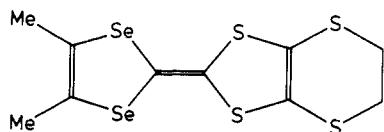


Figure 1. Molecule of DMET.

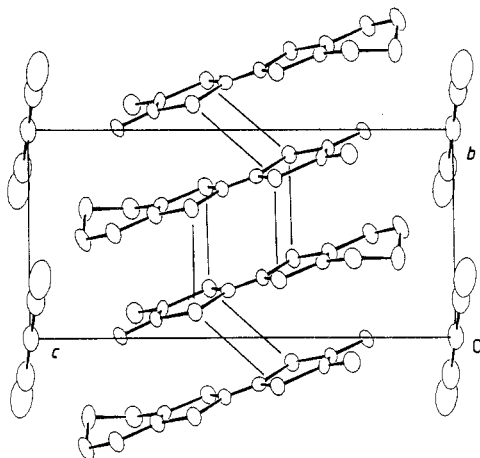


Figure 2. Crystal structure of $(\text{DMET})_2\text{Au}(\text{CN})_2$. Shorter interatomic contacts than the sum of van der Waals radii are indicated with full lines.

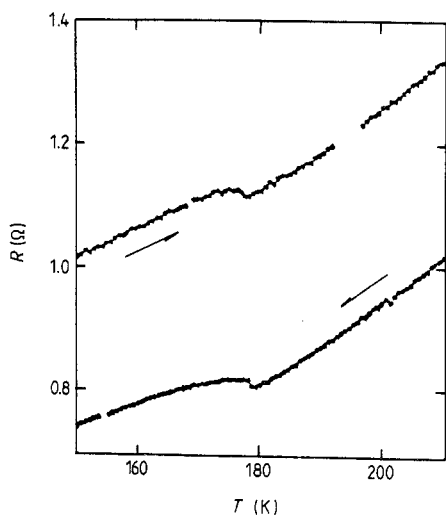


Figure 3. Resistivity of $(\text{DMET})_2\text{Au}(\text{CN})_2$. Arrows indicate the direction in which the measurements were made.

similarity in the crystal structure above and below the 'transition' [7, 13]. The anomaly was also detected in the temperature dependence of thermopower [14, 15]. In order to clarify the nature of the anomaly, especially to answer whether the anomaly is due to a thermodynamic phase transition or not, thermodynamic measurements are desired. The situation prompted us to carry out further study, preliminary results of which have been reported in [14]. In this paper, the experimental details and the results of AC calorimetric measurements on $(\text{DMET})_2\text{Au}(\text{CN})_2$ are described. The mechanism of the transition is discussed.

2. Experimental

In order to measure heat capacities of a small sample, an AC calorimeter with chopped-light heating was constructed. The method [16] is very suitable for small samples because the heat capacity of addenda is only that of the thermometer (thermocouple in this case).

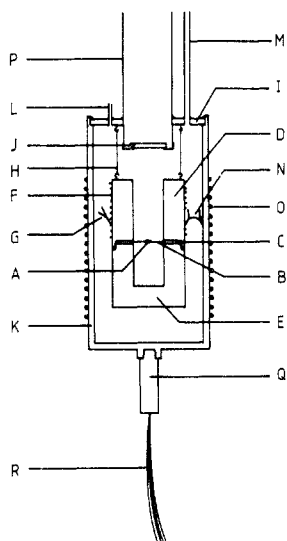


Figure 4. Sectional view of the major part of the AC calorimeter. A, sample crystal; B, thermocouple for detecting the temperature of the sample; C, gold-plated copper plate; D, E, gold-plated copper block; F, electrical leads; G, thermocouple for measuring the temperature of the block; H, stainless steel wires; I, copper flange; J, Pyrex window; K, copper mantle; L, stainless steel tubing; M, stainless steel tubing for gas outlet/inlet; N, thermocouple for measuring the temperature difference between the copper block and the mantle; O, constantan heater; P, stainless steel tubing (light path); Q, brass rod; R, copper wires.

The major portion of the calorimeter is shown in figure 4. The sample crystal (A) is directly adhered with thinned varnish to the crossed junction of the thermocouple (B) (type E, 12 μm in diameter) of which lead wires are adhered to a gold-plated copper plate (C) with insulating varnish; the junction of the thermocouple is in the centre hole (0.5 cm in radius) of the plate. The plate is tightly interposed between the upper (D) and the lower (E) parts of a gold-plated copper block (140 g in mass) which behaves as a heat bath; the temperature of the block is measured with a thermocouple (G) (type E, 0.1 mm in diameter). The lead wires of the thermocouple (B) are connected with thicker wires (0.1 mm in diameter) of the same material, which are again connected with copper lead wires (F) (0.1 mm in diameter) on the surface of the copper block. One pair of the leads of the thermocouple (B) is used for measuring the amplitude of temperature oscillation and the other pair for the temperature difference between the sample and the copper block. The copper block is hung with three stainless steel wires (H) from the copper flange (I) which has a window (J) for light entrance. The copper mantle (K) is soldered with Wood's alloy vacuum tight to the flange. The leads are taken out through epoxy resin sealing at the end of stainless steel tubing (L). The inside of the mantle is evacuated and an appropriate amount of helium gas is introduced through stainless steel tubing (M). The temperature difference between the copper block and the mantle is monitored with a thermocouple (N) (type E, 0.1 mm in diameter) and controlled constant by supplying electric current to a heater (O) (140 Ω in total resistance) wound non-inductively on the mantle. The assembly is placed in a Dewar vessel. Chopped light is supplied with a stabilised halogen lamp through stainless steel tubing (P), of which the inside is kept evacuated.

The amplitude of the temperature oscillation is measured with a digital lock-in amplifier (LAD-1A, Shinku-riko Co Ltd) which operates between 0.01 and 99.99 Hz and is capable of driving a chopper.

The performance of the calorimeter was examined through the experiments on bis(4-chlorophenyl)sulphone [17, 18]. The accuracy and the precision for the relative temperature dependence of the sample heat capacity were found within 2 and 0.2 per cent, respectively, between 100 and 250 K.

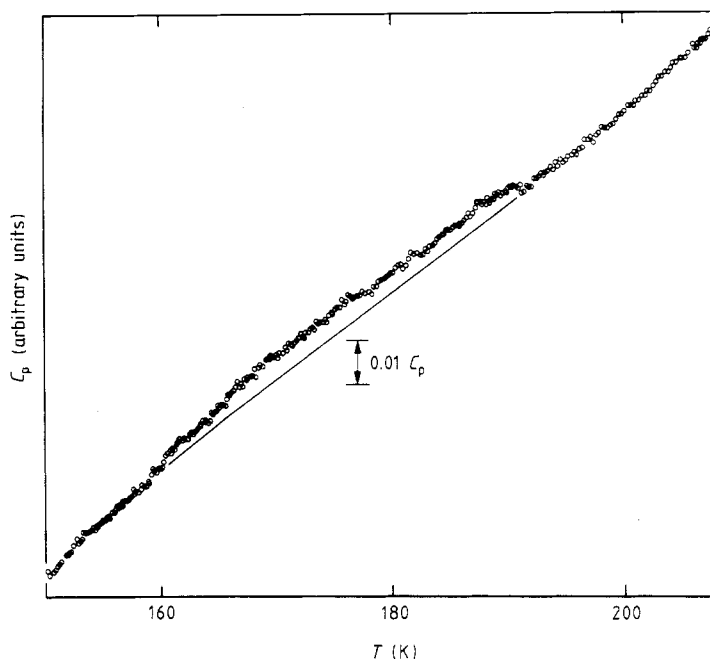


Figure 5. Temperature dependence of the heat capacity of $(\text{DMET})_2\text{Au}(\text{CN})_2$.

In this series of measurements of AC calorimetry, two samples having the similar size ($2 \times 0.5 \times 0.02 \text{ mm}^3$) were used and consistent results were obtained. The measurement frequency was about 3 Hz and the magnitude of the temperature oscillation about 10^{-2} K . The absolute value of heat capacity was not determined because of the difficulty in calibrating heat absorbed. Under an appropriate condition, the magnitude of the temperature oscillation in AC calorimetry is inversely proportional to the sum of heat capacities of sample and addenda [16]. The fulfilment of the condition was confirmed on the basis of the inverse proportionality between the measurement frequency and the magnitude of the temperature oscillation. Since the thermocouple for detecting the temperature oscillation of the sample is very thin, it is safely assumed that the measured temperature oscillation reflects solely the heat capacity of the sample; the inverse of the magnitudes of the temperature oscillation will be shown as the sample heat capacity in the following.

3. Results and discussion

The results of AC calorimetry in one typical run are plotted in figure 5. A very broad hump can be recognised between 160 and 190 K. Since no hump is expected for usual vibrational (intra- and inter-molecular) modes, three mechanisms for the enhancement may be considered; rotation of the methyl groups in the DMET molecule (four degrees of freedom per $(\text{DMET})_2\text{Au}(\text{CN})_2$), conformational change of the ethylenedithio group (two degrees of freedom) and phase transition. A typical magnitude of a hump is expected as R (gas constant) for one degree of freedom in the cases of the former two

mechanisms. Since the absolute value of the sample heat capacity is considered as about $5 \times 10^2 \text{ J K}^{-1} \text{ mol}^{-1}$ at 200 K from our experience, the observed 'anomaly' is too small to adopt the two mechanisms. Thus, it seems reasonable to attribute the 'anomaly' to a phase transition. Namely, the anomalous behaviours of $(DMET)_2Au(CN)_2$ [10–15] are considered to be accompanied by a thermodynamic phase transition.

Although AC calorimetry is impossible for detecting a latent heat due to first-order phase transition unless one uses special techniques, the anomaly detected in this study is smooth within 0.2 per cent and, consequently, is very likely that of a higher-order transition. The anomalous portion of heat capacity (excess heat capacity) is only 0.8 per cent of the total heat capacity of the sample when we draw a smooth interpolating curve as a normal portion as shown in figure 5. The smallness of the anomaly makes detailed discussion on its shape and the precise determination of the transition temperature impossible. The integration of the excess heat capacity yields roughly estimated upper limits of the enthalpy and the entropy of transition as 10^2 J mol^{-1} and $0.5 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. The value of the entropy of transition is much smaller than $R \ln 2$ ($\approx 5.8 \text{ J K}^{-1} \text{ mol}^{-1}$), a typical value for an order–disorder transition. Hence, it is hard to imagine some structural (positional) ordering as a possible mechanism of the transition. Indeed, no disorder was observed in the crystallographic study [6].

Now, it is possible to discuss a possible mechanism of the phase transition of $(DMET)_2Au(CN)_2$ at 180 K. Although a mechanism of an order–disorder type of structural phase transition is ruled out on the basis of the magnitude of the entropy of transition, it is hard to believe that the transition has a purely electronic origin. Hence, a mechanism of the transition will be of displacive type associated with soft mode(s). However the space group of the high-temperature phase, $P\bar{1}$, seems too low to possess some lattice instability owing to a purely structural origin. Some kind of electron–phonon coupling will play an important role in the phase transition. It was found that the SDW phase appeared in the pressure range where the (high-temperature) phase transition took place, and that the SDW and the high-temperature transitions simultaneously disappeared on applying pressure [10]. These facts suggest the importance of electron–phonon coupling in the high-temperature phase transition. It is noted that no superlattice nor change in space group was detected through the phase transition [7, 13]. Thus, the soft mode(s) which drive the transition will be at the centre of the Brillouin zone (Γ point) and of gerade symmetry for inversion (A_g species).

Taking into account the crystal structure and the importance of electron–phonon coupling, the following mechanism may be considered: the crystal is electronically dimerised below the transition, i.e. the electronic system is characterised with two transfer integrals. On the other hand, two transfer integrals are effectively the same in magnitude above the transition. The non-dimerised state is stabilised through electron–phonon coupling. The fact that the zero-wavevector modulation in $(DMET)_2Au(CN)_2$ is equivalent to that of $4k_F$ will also play an important role [19]. Although the mechanism considered is not symmetry breaking, it will be consistent with an appearance of a phase transition because the system has an effective superlattice below the transition.

The above model of the phase transition is only a possible (not an exclusive) one, but seems consistent with all the experimental data: the narrowing of the bandwidth implies an enhanced degree of localisation of electron, resulting in the upward anomaly in the resistivity and ESR linewidth on passing the transition temperature in the cooling direction. The model predicts an increase in Seebeck coefficient on cooling as observed in the experiments [14, 15]. The phase transition is of high order and displacive in nature. Raman spectroscopy will be necessary in order to assess the validity of the model.

Acknowledgments

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