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Calorimetric study of the phase transitions in HMTTF - TCNQ

K. Biljaković-Franulović, S. Tomić, M. Prester and D. Djurek

Institute of Physics of the University, Zagreb, Yugoslavia

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Résumé. — Nous avons fait des mesures à haute résolution de la chaleur spécifique du conducteur quasi unidimensionnel HMTTF-TCNQ, entre 30 et 80 K. Nous avons observé deux anomalies étroites de largeurs comparables à 49 K et 43 K.

Abstract. — High resolution specific heat measurements have been performed on the quasi one-dimensional conductor HMTTF-TCNQ between 30 and 80 K. Two narrow anomalies of comparable widths were found at 49 K and 43 K.

The organic charge transfer salt TTF-TCNQ (tetra-thiofulvalenium-tetracyanoquinodimethane) is one of the most widely investigated quasi one-dimensional conductors. Structural [1] and calorimetric [2] measurements on this compound show the existence of at least three phase transitions at 54, 49 and 38 K. In the usual interpretations [3, 4] these transitions are attributed to the separate ordering of TCNQ and TTF stacks. HMTTF-TCNQ (hexamethylene-tetra-thiofulvalenium-tetracyanoquinodimethane) is another interesting salt derived from TTF-TCNQ which can provide deeper understanding of the behaviour of two stack systems. Structurally [5], HMTTF-TCNQ has an orthorhombic unit cell with alternating chains in both transverse (*a* and *c*) directions. This is in contrast to TTF-TCNQ [6] where the unit cell is monoclinic and the chains alternate in only one transverse (*c*) direction. Various properties of HMTTF-TCNQ have been studied recently. Limiting ourselves to the question of phase transitions we refer to measurements of the electrical conductivity [5, 7] and diffuse X-ray scattering [8], which indicate the existence of two transitions at about 49 and 43 K. On the other hand, measurements of static susceptibility and EPR give only one transition at 44 K [7] and at 50 K [9] respectively.

In order to clarify this point we have performed specific heat measurements in the transition region. The method used was the improved DC relaxation technique described elsewhere [2]. The small monocrystal needles of HMTTF-TCNQ we used were synthesized and grown by L. Giral *et al.* (Montpellier, France) and K. Bechgaard *et al.* (Copenhagen,

Denmark). For the specific heat experiment 3.61 mg of the crystals were powdered and then lightly pressed into a 15 μm gold foil container. A thin film of silver paint, uniformly spread over the container, was used as the sample heater. The temperature difference between the sample and the sink was monitored by an Au 0.03 % Chromel thermocouple while the absolute temperature of the sink was determined with a germanium thermometer. The cooling and heating rates were about 0.5 and 1 K/h, respectively. Heating pulses applied to the sample led to a rise in temperature of about 0.1 K. Finally, the resolution obtained was about 6 parts in 10^4 .

We have performed two experimental runs in the range from 30 to 80 K. In addition, the parasitic heat capacity of the container, silver paint, etc. was measured in an independent run and then subtracted from the total. Comparing our specific heat at 30 K with the extrapolated value of low temperature data [7] we find good agreement to within 5 percent. The resulting data show two specific heat anomalies at 49.5 and 43 K (Fig. 1). The hysteresis shown in the figure may be an experimental artifact caused by shifts in the germanium thermometer calibration between cooling and heating. The height of the specific heat anomaly at 43 K is several times larger than that at 49 K. We note that the peak heights of the logarithmic derivative of the resistance have similar relative values and occur at the same two temperatures [5]. This can be expected according to the analysis of critical behaviour in TTF-TCNQ by Horn and Guidotti [10]. Furthermore, the widths of both transitions are just as narrow as those in TTF-TCNQ [2]. We also note

Fig. 1. — Specific heat data in the transition region. The background line is not well defined, so it was not subtracted from the specific heat.

that the 43 K transition is nearly a factor of two wider than that at 49 K. All of these facts lead to the conclusion that in HMTTF-TCNQ we are dealing with two, three-dimensional, phase transitions. It seems to us that the crossover picture [8] is in disagreement with the observed specific heat anomaly at 49 K, which theoretically is not expected to occur at a crossover temperature [11].

The Ginzburg-Landau model earlier developed

for 3 D ordering in TTF-TCNQ [3] was recently applied to HMTTF-TCNQ [12]. Alternation of chains in the c -direction in the latter compound requires the inclusion of diagonal coupling between stacks of the same type into the free energy expansion. This led to the possibility of 3 D ordering with an incommensurate and temperature independent transverse wave vector q_a as observed [8] and both CDW amplitudes nonzero (but $\rho_Q \gg \rho_H$) below a single critical temperature T_c . An abrupt increase in the CDW amplitude of HMTTF chains (ρ_H) at a lower temperature T' gives rise to a second anomaly in the physical properties. Good agreement with our experimental results can be achieved by putting $T_c = 49$ K and $T' = 43$ K. We point out that specific heat peak observed at 43 K, called a transition in this paper, can also be attributed to the theoretically predicted second anomaly.

In conclusion, we have measured the specific heat of HMTTF-TCNQ and found two anomalies at 49 K and 43 K, consistent with measurements of electrical conductivity and diffuse X-ray scattering.

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References

- [1] COMES, R., SHIRANE, G., SHAPIRO, S. M., GARITO, A. F. and HEEGER, A. J., *Phys. Rev. Lett.* **35** (1975) 1518 ; ELLENSON, W. D., COMES, R., SHAPIRO, S. M., SHIRANE, G., GARITO, A. F. and HEEGER, A. J., *Solid State Commun.* **20** (1976) 53 ; KAGOSHIMA, S., ISHIGURO, T. and ANZAI, H., *J. Phys. Soc. Japan* **41** (1976) 2061.
- [2] DJUREK, D., FRANULOVIC, K., PRESTER, M., TOMIC, S., GIRAL, L. and FABRE, J. M., *Phys. Rev. Lett.* **38** (1977) 715.
- [3] BJELIŠ, A. and BARIŠIĆ, S., *Lecture Notes in Physics* (Springer, New York) **65** (1976) 291 ; *J. Physique Colloq.* **38** (1977) C7-253 ; *Phys. Rev. Lett.* **37** (1976) 1517.
- [4] BAK, P. and EMERY, V. J., *Phys. Rev. Lett.* **36** (1976) 978.
- [5] GREENE, R. L., MAYERLE, J. J., SCHUMAKER, R., CASTRO, G., CHAIKIN, P. M., ETEMAD, S. and LAPLACA, S. J., *Solid State Commun.* **20** (1976) 943.
- [6] KISTENMACHER, B. T., PHILLIPS, T. E. and COWAN, D. O., *Acta Cryst. B* **30** (1974) 763.
- [7] DELHAES, P., FLANDROIS, S., AMIELL, J., KERYER, G., TOREILLES, E., FABRE, J. M., GIRAL, L., JACOBSEN, C. S. and BECHGAARD, K., *J. Physique Lett.* **38** (1977) L-233.
- [8] MEGTERT, S., POUGET, J. P., COMES, R., GARITO, A. F., BECHGAARD, K., FABRE, J. M. and GIRAL, L., *J. Physique Lett.* **39** (1978) L-118.
- [9] TOMKIEWICZ, Y., TARANKO, A. R. and SCHUMAKER, R., *Phys. Rev. B* **16** (1977) 1380.
- [10] HORN, P. M. and GUIDOTTI, D., *Phys. Rev. B* **16** (1977) 491.
- [11] DIETERICH, W., *Adv. Phys.* **25** (1976) 615.
- [12] BJELIŠ, A. and BARIŠIĆ, S., *J. Physique Lett.* **39** (1978) L-347.