Specific heat of the organic metal bis(tetrathiotetracene) tri-iodide from 20 to 100 K, the vicinity of the metal-nonmetal phase transition

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Specific-heat measurements on pressed pellet samples of highly disordered bis(tetrathiotetracene) tri-iodide (TTT_2I_3) have been made from 20 to 100 K using thermal relaxation methods. An anomaly at 50 K in the form of a broad bump is reported which is coincident with magnetic susceptibility structure and occurs approximately 25 K above anomalies in electrical and optical behavior. The specific-heat discontinuity is consistent with a mean-field model for a Peierls phase transition with correction for fluctuations.

I. INTRODUCTION

Most of the quasi-one-dimensional conductors synthesized to date have been found to undergo metal-nonmetal transitions upon cooling. Such transitions can result from the Peierls instability inherent in one-dimensional metals, and direct evidence to support this conclusion has been found in the organic charge-transfer-salt tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) and its selenium analog, the transition-metal complex KCP,[1,2] and tetrathiofulvalenium-thiocyanate [$TTF(SCN)_{0.588}$] and its selenium analog[3] which are similar to the organic metal studied in this work. That the metallic state is stabilized by impurities, structural disorder, and increased dimensionality is exemplified by the compound hexamethylene-tetraselenafulvalenium tetracyanoquinodinethane (HMTSF-TCNQ), which remains highly conducting at low temperatures.[4]

Details of heat capacity measurements from 20 to 100 K which provide direct evidence of a phase transition in the organic metal bis(tetrathiotetracene) tri-iodide (TTT_2I_3) are reported. Our specific-heat measurements reveal an anomaly at 50 K which is consistent in size with the prediction of a mean-field theory for the Peierls phase transition including fluctuations. The anomaly is coincident with the magnetic susceptibility transition reported by Isett.[5] Preliminary results have been reported elsewhere.[6]

Like TTF-TCNQ and its derivatives, TTT_2I_3 is an organic charge transfer salt. It is composed of segregated stacks of tetrathiotetracene and iodine molecules.[7] Conduction is achieved by means of holes which propagate along the TTT stack,[8] permitted by overlap of the π molecular orbitals. The iodine sublattice, though composed primarily of I_3^-, exhibits considerable disorder, manifested by vacancies along the iodine column.[7-9] The degree of disorder, discerned by x-ray diffraction studies, can be varied but not eliminated through the crystallization process.[8,9]

Systematic studies[8,9] of the role of disorder in the transport properties of TTT_2I_3 have shown that the temperature and magnitude of the conductivity peak and the metal-nonmetal transition temperature are depressed by increased disorder. Similar findings are indicated by thermoelectric power[8] and magnetic susceptibility[9] studies.

II. THEORY

An estimate of the specific-heat discontinuity ΔC expected at the Peierls transition temperature T_c is found by minimization of the free energy expanded in terms of the order parameter which characterizes the ordered phase. The coefficients in the free-energy expansion have been calculated for the Peierls transition by Allender, Bray, and Bardeen[10] and yield a specific-heat discontinuity of

$$\Delta C/R = 9.4N(0)k_B T_c \ , \tag{1}$$

where $N(0)$ is the density of states at the Fermi surface, k_B is Boltzmann's constant, and R is the gas constant. However, mean-field theory neglects fluctuations, which are very important in one dimension. Indeed, it is well known that phase transitions in one-dimensional systems are precluded by fluctuations. In the case of the quasi-one-dimensional conductor, they can be expected to lower the metal-nonmetal transition temperature.[11] Lee, Rice, and Anderson[11] concluded that, due to fluctuations, the observed transition temperature should be about one fourth that predicted by mean-field theory. This correction modifies the mean field ΔC to

$$\Delta C/R = 37.6N(0)k_B T_c \ . \tag{2}$$

In terms of the entropy $\Delta S = \gamma T_c$ [where $\gamma = 2N(0)k_B^2\pi^2/3$] associated with the Peierls transi-

tion, the theoretical values of ΔC are

$$\Delta C = 13.1 \Delta S/\pi^2 \ , \tag{3}$$

$$\Delta C = 56.4 \Delta S/\pi^2 \ . \tag{4}$$

without and with the inclusion of fluctuations, respectively.

III. EXPERIMENTAL DETAILS

A. Samples

Specific-heat measurements are reported on two samples, each from a different batch of material. Each is a pressed pellet weighing approximately 5 mg. The samples were provided by Dr. R. B. Somoano of the Jet Propulsion Laboratory and were prepared in the same fashion as those classified as highly disordered according to the scheme devised by Khanna and co-workers.[8] These preparation techniques yield samples with highly reproducible properties, as evidenced by the x-ray and transport characteristics, which are very sensitive measures of the degree of disorder.[8] Our samples are therefore comparable to the highly disordered samples used in the electrical, magnetic, and optical studies of Refs. 8 and 12. Specific-heat data for the two samples agreed well in both magnitude and structure.

B. Measurement technique

The sample is bonded with Wakefield thermal grease to a sapphire substrate which is 0.635 cm in diameter and 0.0762 mm thick (Fig. 1). A thermocouple is made by spot-welding Chromel and Constantan wires, each of diameter 0.0254 mm, and the junction is attached to the substrate with epoxy. The

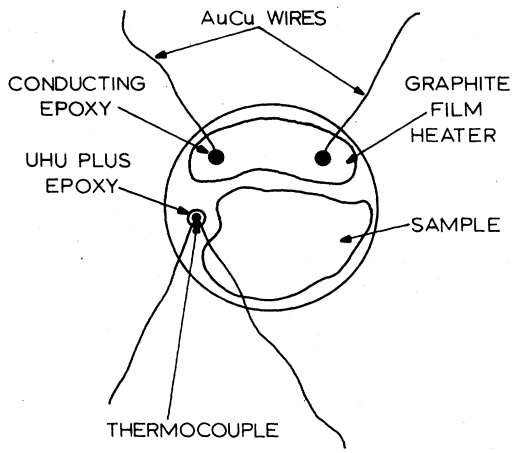

FIG. 1. Substrate with graphite film heater, thermocouple, and sample attached.

substrate heater is a graphite film with 0.0508-mm-diameter gold leads attached with conducting epoxy. The specific heat of these addenda is predetermined by running the experiment with no sample.

Specific-heat measurements were made using the thermal relaxation technique described by Bachmann and co-workers.[13] The sample and addenda are connected to a block at constant temperature T_0 by the weak thermal link provided by the small thermocouple and heater wires. The temperature of the sample and addenda is raised to $T_0 + \Delta T$ by application of constant power through the substrate heater until steady state is achieved. The power is then switched off, and the temperature difference ΔT decays exponentially to zero. The heat capacity C_s of the sample is then

$$C_s = K_w \tau_1 - C_A \ , \tag{5}$$

where K_w is the thermal conductance of the wires, τ_1 is the thermal decay time, and C_A is the heat capacity of the addenda.

The organic sample used in this experiment has an internal decay time τ_2 which is not short compared to τ_1. In this case, the thermal decay is not a simple exponential, but, provided the sample thermal conductance K_s is larger than K_w, the decay can be represented by a sum of two exponentials, one in τ_1 and the other in τ_2, as follows[14]:

$$\Delta T(t) = A \exp(-t/\tau_1) + B \exp(-t/\tau_2) \ .$$

Equation (5) is now modified to

$$C_s = K_w \tau_1 - C_A - K_w \tau_2 (K_w \tau_1 / C_A - 1) \tag{6}$$

with

$$\tau_2 = \frac{B \tau_1 / A}{K_w \tau_1 (B/A + 1)/C_A - 1} \ .$$

The constant A is found from

$$\Delta T(t >> \tau_2) \simeq A \exp(-t/\tau_1) \ ,$$

and B, from

$$\Delta T(0) = A + B \ .$$

The correction indicated in Eq. (6) is also applicable when the τ_2 problem originates from poor bonding between the sample and substrate.

C. Cryostat

Liquid helium was used to produce temperatures in the range 20–77 K, and liquid nitrogen, above 77 K. A cross section of the vacuum can of the cryostat is shown in Fig. 2. The substrate is mounted in the heat-capacity cell located in the lower part of the can. The block temperature T_0 is measured with the silicon diode thermometer mounted in the wall of the

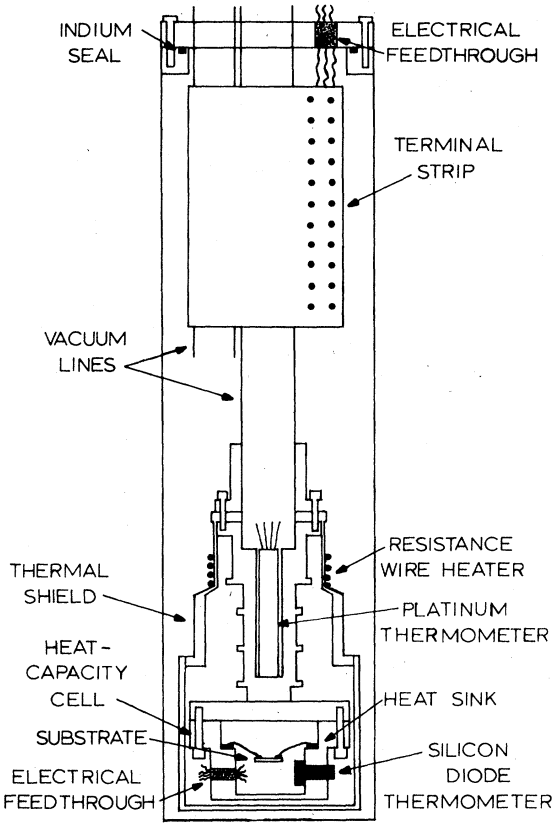

FIG. 2. Vacuum can of the cryostat.

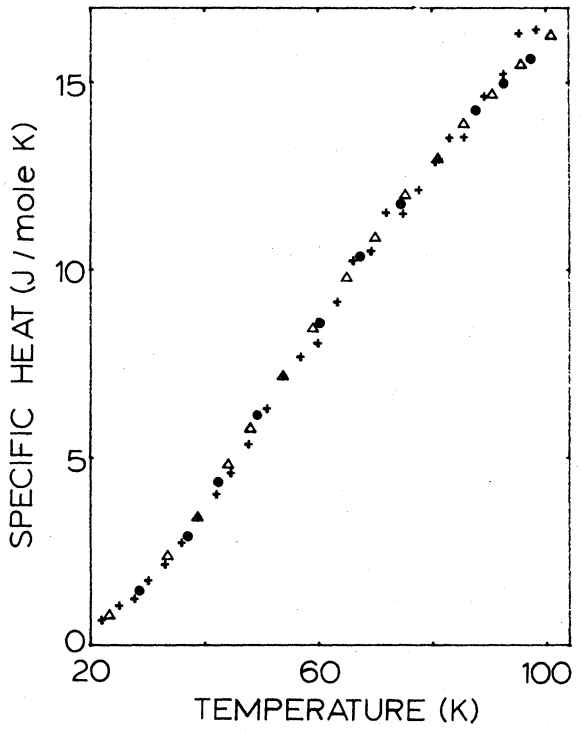

FIG. 3. Specific heat of copper as a function of temperature. This work +, Dockerty ●, Giauque and Meads Δ.

heat-capacity cell. The platinum thermometer was originally installed for this purpose but was too large to be located near enough to the substrate to accurately sense T_0. The resistance wire heater mounted on the two-piece thermal shield is used to control T_0. The temperature difference ΔT is measured directly with the thermocouple.

III. RESULTS

The accuracy of the absolute magnitude of the specific heat determined with the calorimeter described above was checked using a vacuum-annealed copper pellet chosen to have the same heat capacity as the TTT_2I_3 samples. These copper data compared with those of Dockerty[15] and Giauque and Meads[16] are shown in Fig. 3 and indicate an accuracy of 4% or better. The scatter in these data is 3% over the range of temperature shown. The internal decay time of the copper sample was not sufficiently long to require the τ_2 correction.

The specific heat as a function of temperature of one of the pellets of TTT_2I_3 from 20 to 100 K is shown in Fig. 4. The data shown represent two runs

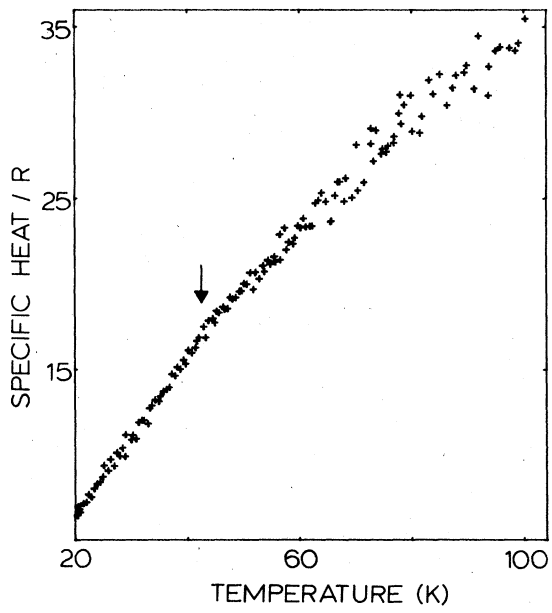

FIG. 4. Specific heat of TTT_2I_3 sample 1 as a function of temperature, both runs. The break in slope is indicated by the arrow.

on sample 1 and indicate reasonably good reproducibility within the scatter, which is 3% between 20 and 60 K. The scatter grows to 6% by 100 K, presumably due to the τ_2 problem since such large dispersions do not appear in the copper data.

The first indication of anomalous behavior is the apparent change in slope of the curve at about 45 K. This region is shown in detail in Fig. 5 for one run on each sample, revealing that the apparent change of slope in Fig. 4 is actually an anomaly in the form of a broad bump on top of the smooth background. Because small variations between the temperature of the maximum of the bump occur, the anomaly is more easily distinguished with data from a single run as plotted in Fig. 5. To obtain estimates for the specific-heat discontinuity ΔC and observed transition temperature T_{cobs}, the data in the ranges 20–30 and 50–65 K are arbitrarily fitted to a polynomial function of the form $C(T) = a_1T + a_2T^2 + a_3T^3 + a_4T^4$ which is then evaluated and subtracted from all the data in the range 20–65 K. The results of this subtraction for the data sets shown in Fig. 5 are shown in Figs. 6 and 7 and are quite sensitive to the choice

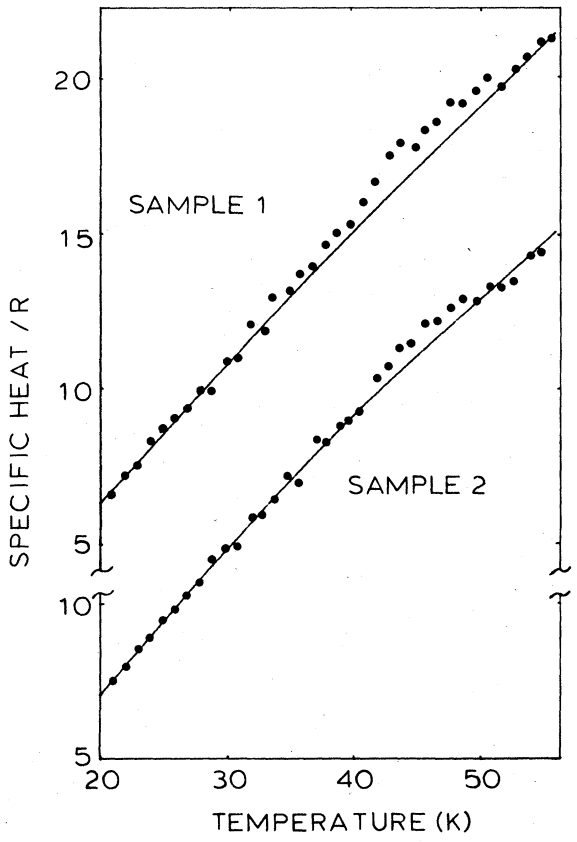

FIG. 5. Specific heat of TTT_2I_3 sample 1 run 2 and sample 2 run 1 as a function of temperature in the vicinity of the anomaly. The line represents the polynomial fit to the data in the ranges 20–30 and 50–65 K.

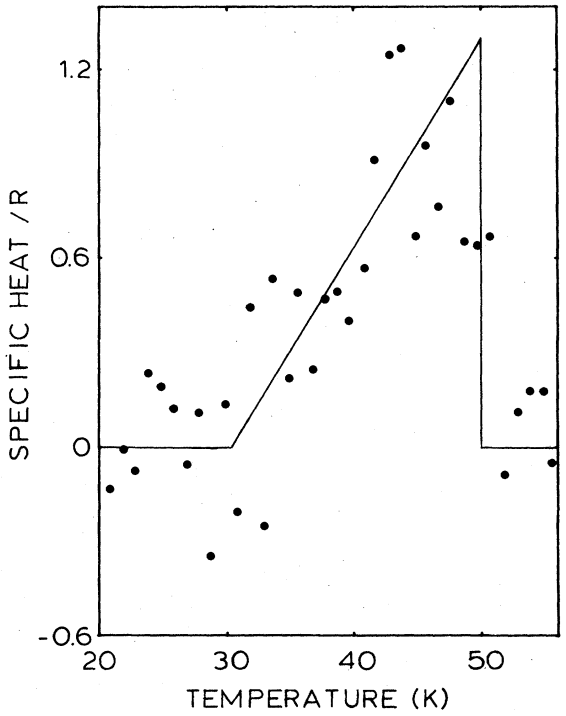

FIG. 6. Specific heat of TTT_2I_3 sample 1 run 2 after subtraction of smooth background, showing the triangle used in the analysis.

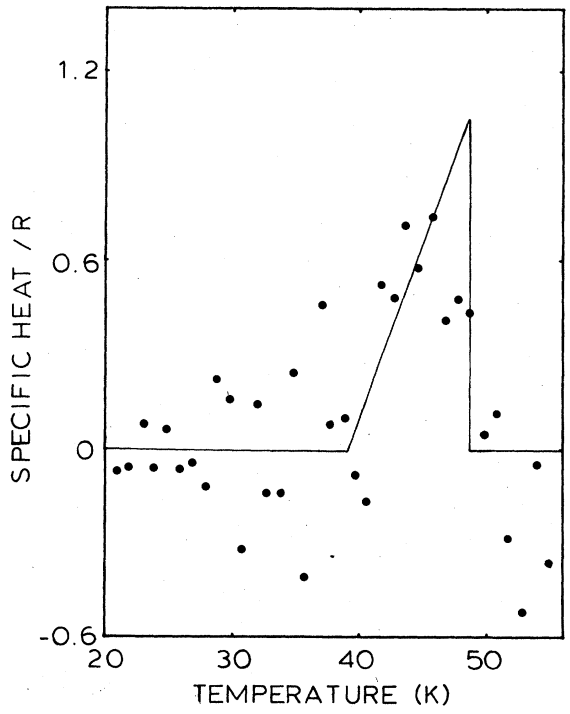

FIG. 7. Specific heat of TTT_2I_3 sample 2 run 1 after subtraction of smooth background, showing the triangle used in the analysis.

TABLE I. Critical temperature, entropy, and density of states results.

Sample	Run	T_{cobs} (K)	Entropy/R	Density of states $N(0)$ (states/eV molecule spin)
1	1	50±5	0.22±0.05	7.8±4
1	2	50±5	0.30±0.07	11 ±4
2	1	48±3	0.20±0.07	7.0±3
2	2	48±6	0.19±0.09	6.7±4

of background; however, we believe the background chosen best represents the data and serves to provide adequate estimates of the quantities of interest. The right triangular function is used to approximate the heat capacity of a Peierls transition in the absence of broadening for the purpose of estimating ΔC and T_{cobs} and is chosen to perserve the area under the curve. There is some arbitrariness about the choice of the triangle, but with the data scatter a more realistic function would not provide significantly better estimates. The uncertainty in T_{cobs} is determined from the width of the transition, $T_{cobs} - T_{peak}$, with the corresponding uncertainty in ΔC being $\Delta C(T_{cobs}) - \Delta C(T_{peak})$.

The values of ΔC and T_{cobs} estimated with the triangular functions are listed in Tables I and II for two data sets on each pellet and show consistency both between runs and for different samples. The entropy of the ordered phase is found by integration of the heat-capacity data after subtraction of the smooth background and division by temperature and is then used to estimate the density of states $N(0)$ from $\Delta S = \gamma T_c$ and the theoretical values of ΔC as given by Eqs. (3) and (4); these results are also listed in Tables I and II. In every case, the observed value of ΔC agrees with the estimated theoretical mean-field value which includes the effects of fluctuations, within the stated uncertainties.

The density of states calculated from thermopower data[5,8] is 1.5 states/eV molecule spin, lower than our values by almost a factor of 10. In better agreement is the value $N(0) = 3$ states/eV molecule spin determined from the paramagnetic susceptibility[4] χ_p using the Pauli relation $\chi_p = 2N(0)\mu_B^2$, where μ_B is the Bohr magneton. However, an estimate[4] of the on-site Coulomb repulsion indicates a value sufficient to enhance the paramagnetic susceptibility over the Pauli value. In this case, the true value of $N(0)$ would be smaller than 3 states/eV molecule spin.

Determination of $N(0)$ from the thermopower suffers from reliance on a simplified picture of the band structure and neglects the energy dependence of the scattering rate. Determination of $N(0)$ from magnetic susceptibility measurements requires that one accurately account for the diamagnetic and other paramagnetic contributions which although done in a consistent fashion can lead to large systematic errors in the value of $N(0)$. The principal advantage of the heat-capacity measurement is that it is based on thermodynamics and is relatively model independent. Thus, although there is a relatively large uncertainty due to scatter in the data and the fitting procedure we believe that the numbers given in Table I more accurately represent this system.

The specific-heat transition at 50 K is coincident with the abrupt decrease in the magnetic susceptibility reported by Isett.[5] These transitions are situated between the metal-nonmetal transition temperature of 24 K determined from the logarithmic derivative of the resistivity and the temperature of the conduc-

TABLE II. Comparison of observed values of specific-heat discontinuity $\Delta C/R$ with theoretical values.

Sample	Run	Observed	Discontinuity $\Delta C/R$ Mean field	Corrected mean field
1	1	1.1±0.2	0.31±0.07	1.3±0.3
1	2	1.3±0.4	0.43±0.1	1.7±0.4
2	1	1.0±0.4	0.29±0.1	1.1±0.4
2	2	1.3±0.3	0.27±0.1	1.1±0.5

tivity peak, 82 K, for highly disordered samples; the thermopower also peaks at 24 K. In addition, ESR and magnetoresistance structures have been found in this temperature range.[12] Since resistivity and thermopower are one-dimensional measurements, it is not surprising that these transitions occur at lower temperature than do either the two-dimensional magnetic susceptibility or bulk specific-heat measurements. Conducting paths may remain in the material below a bulk transition.

With an anomaly which is 6% of the background specific heat and with 3% scatter, it is possible that the magnitudes of the quantities reported here may have uncertainties as large as 50%. Nevertheless, we believe that the reproducibility of the data both between runs and between samples together with the coincident magnetic structure are sufficient evidence to substantiate a transition with a magnetic component. It is our guess that the anomaly reported here indicates a Peierls transition in highly disordered TTT_2I_3 at 50 K. It should be noted that no structural distortion in the TTT chain has been detected by x-ray diffraction down to 19 K,[17] but it is possible that the transition is shadowed by scattering from the heavier iodine atoms.[18] Specific-heat measurements on less disordered samples may reveal a more easily detected anomaly in support of our conclusion.

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