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the lattice softness, since $dT_L/dP < 0$. However,
pressure enhances the lattice softness for $T < T_L$. The
suggested interrelationship between T_L and T_c is then
(i) T_c will be maximum at the state of maximum lattice
softness, i.e., when $T_c = T_L$, and (ii) the change of T_c
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Specific Heat of Tetrathiofulvalinium-Tetracyanoquinodimethane (TTF-TCNQ) in the Vicinity of the Metal-Insulator Transition*

R. A. Craven, M. B. Salamon, G. DePasquali, and R. M. Herman
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

and

G. Stucky and A. Schultz
Department of Chemistry and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801
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Measurements of the specific heat of tetrathiofulvalinium–tetracyanoquinodimethane
have been made from 45 to 70 K using ac calorimetric methods. A steplike anomaly in
the specific heat is observed with transition temperature 54.8 K. The results compare
favorably with predictions from a mean–field model when the crystal undergoes a Peierls
distortion.

Since the report of unusual conductivity phenom-
ena by Coleman et al.[1] in the organic charge-
transfer salt tetrathiofulvalinium-tetracyanoquino-
dimethane (TTF-TCNQ), considerable attention
has been focused on the possibility of a Peierls
transition[2-5] in this material. To date, no direct
evidence of such a transition has been found. In
this Letter, we report evidence for a phase tran-
sition at ~55 K in single crystals of TTF-TCNQ,
manifested by a step change in the specific heat.
We compare this result with the theoretical pre-
dictions based on a mean-field, one-dimension-
al, tight-binding model, agreement with which

gives evidence that a Peierls transition does in-
deed occur.

The temperature-dependent specific heat of
TTF-TCNQ was determined using the ac calori-
metric method[6] on single crystals and pressed-
powder samples. The data we present in this
Letter were taken using a 47-μg single crystal
grown from solution which was provided by the
University of Pennsylvania group,[7] and a 12-μg
single crystal which was prepared by the authors
using vapor-phase reaction techniques. In Fig. 1
we show the specific heat of the Penn sample in
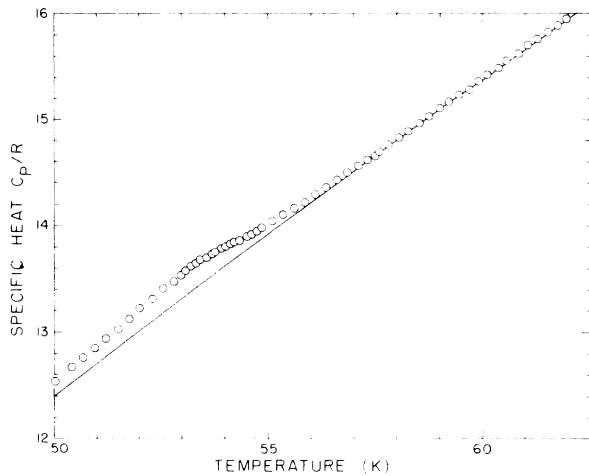the vicinity of the phase transition. Repeated

FIG. 1. Specific heat of TTF-TCNQ (Penn sample) in the vicinity of the phase transition.
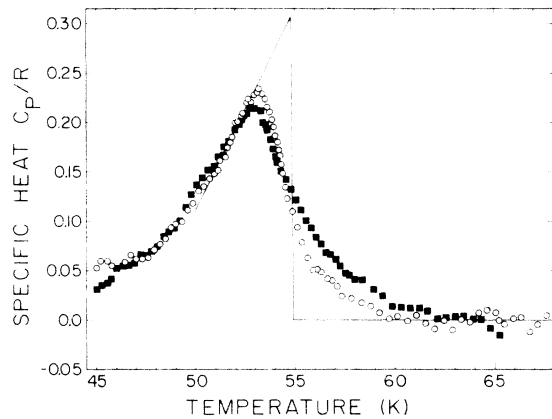

FIG. 2. Specific-heat data after subtraction of a quadratic background. The triangular function approximates the mean-field character of the transition. Squares, Penn sample; circles, Illinois sample.

passes through the transition were recorded digitally on a signal averager, with one tenth of the data points collected after five traversals of the transition shown in Fig. 1. Calibration of the ac data was achieved by comparison with the specific heat of a bulk sample at 50 K. This bulk sample was a pressed-powder pellet weighing 32.32 mg which was prepared from crystallites precipitated from acetyl-nitrile solution and found to be TTF-TCNQ by x-ray analysis. The absolute specific heat of the sample was measured using the heat-pulse method in an adiabatic calorimeter. Once the calibration point was chosen, the ac data and the results from the bulk measurements agreed to within the experimental uncertainties (± 5%) throughout the entire measurement interval.

In order to examine the transition more closely we have arbitrarily subtracted from the data a smooth (quadratic) background extrapolated from the data points above 60 K. The resulting data are shown in Fig. 2. Approximately 20% of the data points for both the University of Illinois (eight traversals) and University of Pennsylvania (five traversals) samples are shown. The two samples behave very similarly, with the Illinois sample showing a slightly broader transition with the peak 0.25 K lower than the Penn sample, reflecting, perhaps, impurities present in the crystals of TTF and TCNQ used in the preparation of the Illinois samples, which had not been purified by sublimation.[8]

At the present time, estimates of the change in specific heat at the phase transition have only

been calculated from a mean-field model.[3,4] In order to facilitate comparison of our data with these predictions we attempted, in Fig. 2, to determine the specific-heat change in the absence of broadening by employing the illustrated triangular function. The slope of the curve for $T < T_c$ was determined by a least-squares analysis of the data from 51 K to the peak. The transition temperature was chosen to make the difference between the area under the measured specific-heat curve and that under the assumed triangular function the same above and below T_c. This transition temperature, $T_c = 54.8 \pm 0.4$ K, coincides with the crossing point of the two data sets. From this analysis we calculate

$$\Delta C/R \simeq 0.30 \pm 0.05. \tag{1}$$

A major source of uncertainty in these values is the arbitrarily chosen baseline for Fig. 2. The detailed shape of the peak is quite sensitive to the choice of background; what is reported is the best estimate of the background from extrapolation of data far from T_c.

Numerical integration of the data yielded a change in entropy associated with the specific-heat anomaly above 45 K of $\Delta S \cong 0.03R$. A significant fraction of the total entropy of the transition remained below' 45 K, however, where the background subtraction is highly uncertain. Since the thermodynamic behavior of a Peierls insulator is similar to that of a superconductor,[4] we approximated this contribution by assuming an exponential low-temperature specific heat,[9] $C_p/R \cong 0.28 \exp(-1.44 T_c/T)$, where the coefficient

was chosen to match the data at 45 K. This coefficient is approximately $6\gamma T_c$, smaller than the $8.5\gamma T_c$ found in the BCS model.[9] Using this functional behavior for C_p, we found an additional contribution of $0.02R$ to the entropy. Since the total entropy change is equal to γT_c, we estimated the density of states at the Fermi surface, assuming a single-band model, to be $\rho(E_F) = 3$ eV^{-1} electron^{-1}. This result is in agreement with both susceptibility[10] and thermopower[11] measurements.

Because large single crystals of TTF-TCNQ are not yet available, we measured the specific heat of the thin platelets, typically 0.3×0.02 mm^2 in cross-sectional dimensions and ranging to 1 cm long, which resulted from coevaporation and co-diffusion of TTF and TCNQ. Crystals, selected for size and uniformity, were mounted on a pair of thermocouples formed by spot welding lengths of 25-μm Chromel and Alumel wire, flattened to 5 μm in the junction region, using silicone vacuum grease as an adhesive. The sample-thermocouple combination was heated by pulses of light from a quartz-iodide lamp. One of the junctions of the crossed thermocouples detected the temperature oscillations of the system while the other formed the cold junction of a Chromel-Alumel thermocouple with its hot junction at the ice point. The thermocouple was calibrated separately against a platinum resistance thermometer. Because of the small size of these samples, the specific heat of the thermocouples contributed approximately 10% to the total heat capacity of the combination. This was removed by subtracting the heat capacity of the equivalent weight of Ni, the major component of the thermocouple alloys, since specific-heat data for these alloys is not available in this temperature range. While it clearly would have been interesting to examine the electrical resistivity of the samples used in this experiment, our mounting technique prevented quality electrical contacts from being applied at a later time.

Since the observed anomaly in Fig. 2 is small compared to the background lattice specific heat, many possible experimental configurations were investigated to assure that this peak was not spurious. In order to eliminate the possibility that a change in the power absorption due to a change in reflectivity[12] was responsible for the anomalous signal, we alternately placed infrared and optical blocking filters in the path of the heating pulses. As the anomaly was not dependent on the frequency of the incident light, it is unlikely that an anomalous reflectivity change is responsible

for the observed effect. Secondly, the orientation of the crystals caused the heat flow to be perpendicular to the high-conductivity axis which minimized the possibility of an anomaly due to changes in the thermal diffusivity of the sample. Further, the frequency dependence of the ac signal was strictly f^{-1} with no trace of lower powers of f which are associated with diffusive phenomena. There was, finally, no dependence on the chopping frequency in the data; the quantitative shape of the results was the same at 9 and 14 Hz.

Compacted powder samples were prepared from the same precipitate mentioned earlier and also showed a peak in the specific heat, although somewhat broadened and shifted to lower temperatures (~ 51 K). These samples were compacted over the thermocouples to eliminate the vacuum grease and mounting procedure as a source of the specific-heat anomaly. The Penn sample was replaced with a blackened piece of 12-μm Mylar of the same mass. No effect was observed. The same sample was remounted on a copper-Constantan thermocouple and the peak remained. We conclude that the data of Figs. 1 and 2 represent an anomaly in the specific heat of the TTF-TCNQ crystals.

We compare these results with a model for the one-dimensional Peierls transition based on a tight-binding Hamiltonian which, although similar to other models,[2-5] leads to slightly different bands in the distorted phase. Recognizing that the Peierls state consists of "molecules" forming dimers we assume that the members of the pair of atoms forming a dimer can be labeled a and b, and that the jth pair is separated by $2L$ from each neighboring pair along a one-dimensional chain. The electronic Hamiltonian is, then,

$$\mathcal{H}_{el} = -t_+ \sum_{j\sigma}(a_{j\sigma}^\dagger b_{j\sigma} + b_{j\sigma}^\dagger a_{j\sigma})$$
$$-t_- \sum_{j\sigma}(a_{j\sigma}^\dagger b_{j-1,\sigma} + b_{j\sigma}^\dagger a_{j+1,\sigma}), \quad (2)$$

where $a_{j\sigma}^\dagger$ and $b_{j\sigma}^\dagger$ create electrons in the tight-binding orbitals of atoms a and b on the jth molecule, and the $t_\pm$ are the intramolecular and the intermolecular transfer integrals, respectively. If an exponential form is assumed for the transfer integrals between identical atoms a and b, the difference between t_+ and t_- due to lattice distortions is specified by writing $t_\pm = \frac{1}{2}(W \pm \Delta)$, where $\Delta = g\delta$, δ being the shift in position due to the formation of dimers and g a coupling constant, and $2W$ the bandwidth. Bloch states can now be formed from the simmetric and antisymmetric

combinations of a and b orbitals and we can solve for the energy bands,

$$\epsilon_k = \pm [W^2 \cos^2(kL) + \Delta^2 \sin^2(kL)]^{1/2}, \tag{3}$$

where $|k| \leq \pi/2L$. These bands reduce to the usual tight-binding band in the absence of the distortion and, unlike other models,[2-5] have a constant bandwidth at $k = 0$. Since the effectiveness of the gap in lowering the energy of electrons is reduced, the transition temperature is lowered from previous estimates[4] to

$$k_B T_c = (2.28 W/e) \exp(-1/\lambda), \tag{4}$$

where $\lambda = 2\rho(E_F)g^2/\hbar\omega(2k_F)$, with $\omega(2k_F)$ being the frequency of the phonon which gives rise to the Peierls distortion. Similarly, the gap at $T = 0$ is reduced by e^{-1}, leaving the relationship between T_c and the gap at $T = 0$ unchanged. We have calculated the coefficients A and B in the Landau free-energy expansion

$$F(T < T_c) - F(T > T_c) = A\Delta^2 + \tfrac{1}{2}B\Delta^4 \tag{5}$$

and find $A = \rho(E_F)(T/T_c - 1)$ and $B = 0.104\rho(E_F)/k_B^2 T_c^2$, which are nearly identical to the results of Ref. 4. The coefficient B is weakly dependent on W/kT_c; we report the value for $W/kT_c \sim 30$. From Eq. (5) we can predict the size of the specific-heat discontinuity at the transition to be given by $\Delta C/R = 9.6\rho(E_F)k_B T_c$. Using the density of states calculated from the entropy associated with the transition and the observed transition temperature, we find $\Delta C/R \cong 0.14$. According to Ref. 3, however, the mean-field transition temperature on which $\Delta C/R$ is based does not coincide with the observed transition, but should be 4 times larger, $T_c^{mf} \cong 4T_c^{obs}$. This gives $\Delta C/R \sim 0.56$, which is larger than the estimate in Eq. (1) made from the triangular function in Fig. 2. Thus the mean-field prediction and that of the Lee-Rice-Anderson[3] model bracket our experimental value.

The specific-heat results show conclusively that the conjectured phase transition in TTF-TCNQ does indeed occur, and with parameters that are quite close to the estimates of mean-field theory. Like the thermopower, which changes sign at about 56 K,[11] the specific heat yields a transition temperature which is lower than that at which there is a peak in the conduc-

tivity.[1] This suggests that the critical point is characterized by the point of maximum positive slope in the conductivity-versus-temperature curve, rather than by the peak. If so, much of the variation of T_c apparent for various samples would be resolved. This also suggests that when behavior which is precursive to the transition sets in, it results in increased resistivity, rather than in increased conductivity. The conclusion seems to be that the more mean field-like the transition, the more highly conductive it will be, which has, as a corollary, that long-range interactions (or at least, long-range coherence) of the interacting electrons is important in achieving high conductivities.

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