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High-Resolution Thermal Expansion Measurements of TTF-TCNQ in the Transition Region

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High-Resolution Thermal Expansion Measurements of TTF-TCNQ in the Transition Region

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Relative high resolution dilatometric measurements of tetrathiafulvalenetetracyanoquinodimethane (TTF-TCNQ) in the transition region 30–60K are reported. No anomalous length changes are observed to within $\Delta L/L \simeq 2 \times 10^{-5}$ in all crystallographic directions.

Several phase transitions characterize the metal-insulator transition region in tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ).[1,2] The Peierls transition at $T_1 = 54$K is followed by two additional transitions at $T_2 = 49$K and at $T_3 = 38$K.[5] Also, some other anomalies have been observed in the vicinity of these phase transitions.[6,7] Structurally, at 54K the "$2k_F$ Kohn anomaly", first observed[8] via diffuse x-ray studies in the conducting phase above T_1, is partially condensed resulting in a $2a \times 3.4b \times c$ modulated structure (the b-axis is the conducting direction). Below T_2 the a component of the modulated structure grows until at T_3 the structure is stabilized at $4a \times 3.4b \times c$.

The variation of the lattice parameters associated with the above transitions has been the subject of several previous studies. Schafer *et al.*[9] made high

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resolution thermal expansion studies of TTF-TCNQ and found no anomalous length changes in the b-axis parameter to within $\Delta b/b \simeq 3 \times 10^{-5}$ in the temperature region 45 to 65K. Later, Schultz *et al.*,[10] by x-ray measurements of the lattice parameters, claimed to observe an anomalous behavior of the a and c-axes and of the angle β, associated with the 54K transition. (The crystal structure is monoclinic with the b-axis as the unique axis.) The relative changes were of the order 2×10^{-3} which is the order of the standard deviations in their experiment. More recently, careful neutron diffraction measurements of the lattice parameters were made by Pouget *et al.*[2] Contrary to the previous x-ray work, no anomalous behavior was found in the lattice parameters b and $a \sin \beta$ in the whole transition region 38-54K. The relative accuracy of the experiment is estimated at about 7×10^{-4}, for the parameter $a \sin \beta$. It is thus seen that even this more accurate measurement has put only a relatively high lower-limit on a possible change of the transverse lattice parameter at the phase transitions.

Since the Peierls transition at 54K is the result of the interaction of the one dimensional conduction electrons with the longitudinal acoustic phonons propagating along the b-axis it is likely that any static change of the lattice parameters in the transverse direction should be smaller than in the b direction. Thus, to obtain better lower limits for any anomalous behavior, we have carried out high-resolution dilation measurements along the three crystallographic axes of TTF-TCNQ in the transition region.

Two forms of single crystals[11] were used in this study. The first is the usually grown TTF-TCNQ with the b-axis along the needle direction. The second is a transverse deuterated material with the long needle axis along the crystallographic a-axis. Typical dimensions of the crystals were $5 \times 0.3 \times 0.1$ mm with the c-axis being the smallest. The thermal expansion measurements were made using a capacitance dilatometer which allowed the sample to rest freely on a baseplate without the use of any adhesive, and exerted a force of less than 10 grams on the sample faces. All the measurements were relative to the thermal expansion of the beryllium-copper dilatometer cell and various Mo and Ag shims which were used in order to minimize the background slopes to increase the sensitivity. Actual recorder tracings of the capacitance bridge output vs. temperature are shown in Figure 1 for the 3 different axes.

Our data show that the temperature variation of the crystal dimensions along each of the axes is smooth and no anomalies are observed at T_1, T_2 and T_3 or at any other temperature in the investigated range. We can therefore set an upper limit of $\Delta a/a \leq 2 \times 10^{-5}$, $\Delta b/b \leq 2 \times 10^{-5}$ and $\Delta c/c \leq 3 \times 10^{-5}$ for the anomalous relative changes in the unit cell dimensions. These results are in accordance with the earlier high resolution measurements of Schafer *et al.*[9] along the b direction, which put an upper limit of $\Delta b/b \simeq 3 \times 10^{-5}$. We are able to reduce the upper limit of 7×10^{-4} set for the relative changes of the

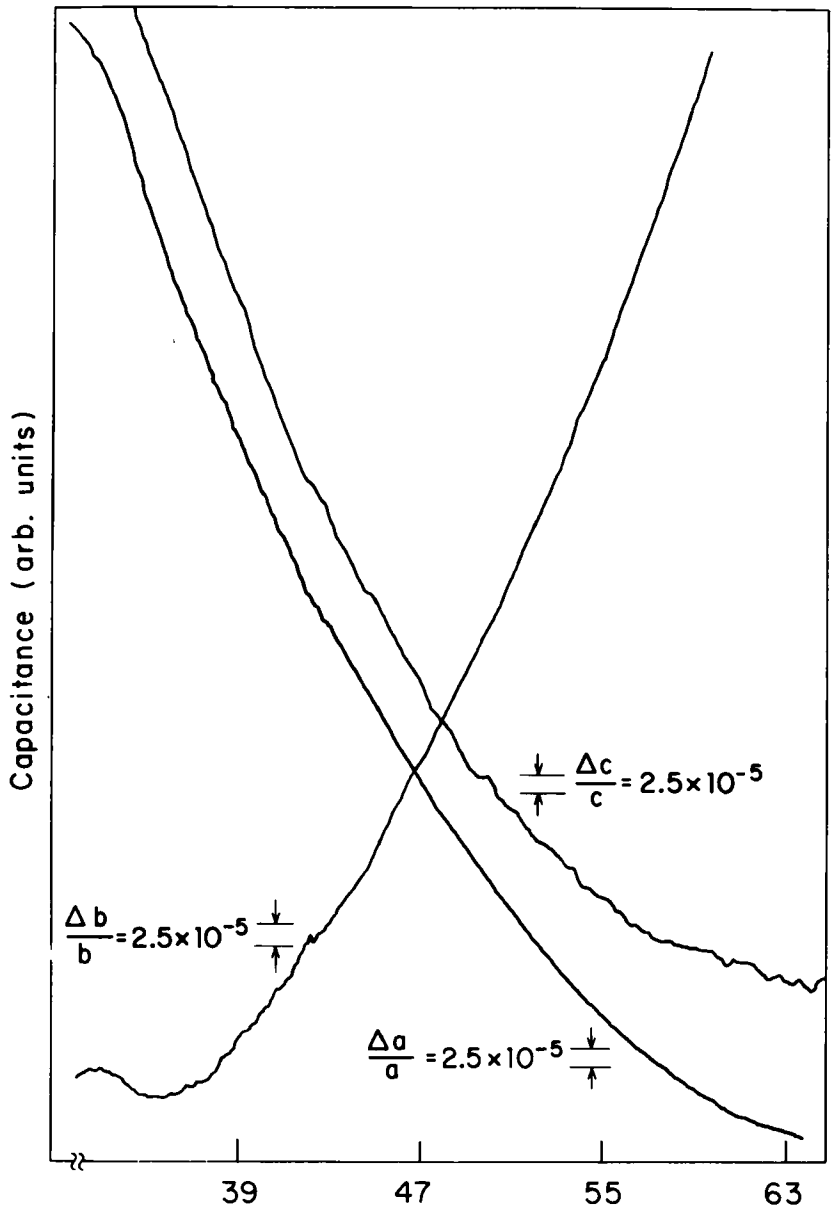

FIGURE 1 Thermal expansivity of TTF-TCNQ, relative to the dilatometer cell, from 30K to 65K, along the three crystallographic axes. The plots shown are the actual recorder tracings of the cell capacitance vs. the thermocouple voltage (or temperature as marked). The scale for each crystallographic axis is indicated.

parameter $a \sin \beta$ at T_1 by the neutron diffraction study[2] by more than an order of magnitude.

We conclude that in TTF-TCNQ the Peierls transition, which is essentially a soft mode structural transition driven by the one-dimensional electronic system and that leads to a noticeable distortion (modulated structure) of the high temperature unit cell, may be accompanied by only a minor change (less than 10^{-5}) of the average unit cell dimension.

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