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High-resolution thermal-expansion measurements of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ)

D. E. Schafer,* G. A. Thomas, and F. Wudl
Bell Laboratories, Murray Hill, New Jersey 07974

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An analysis of our measurements of the b-axis expansivity α_b of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) within the Debye approximation suggests an unexpectedly high effective Debye temperature ($\Theta_b = 200 \pm 30$ K) and a large anharmonicity ($\Gamma = 5 \pm 1.5$) for the low-lying b-axis polarized acoustic phonons. These values for Γ and Θ_b indicate substantial softening of the lattice above 100 K and also suggest an expansivity contribution from intramolecular vibrational modes. No anomalous length changes were observed in the region of the metal-semiconductor transition (45–65 K) to within $\Delta L_b/L_b \cong 3\times 10^{-5}$.

The thermal expansivity of organic charge-transfer salts such as tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) is of interest because it reflects the nature of the binding forces responsible for the close interplanar spacing between the stacked molecules.[1,2] The temperature dependence of α_b also provides information about the lattice vibration spectrum, which is important in understanding the transport properties[3-7] of these materials. Our measurements of the expansivity $\alpha_b \equiv (dL_b/dT)/L_b$, where L_b is the b-axis (stacking axis) crystal length, yield two pieces of information regarding the TTF-TCNQ crystal lattice. From the data below 100 K, we have obtained an estimate of an effective Debye temperature for the low-lying b-axis polarized acoustic phonons of $\Theta_b = 200 \pm 30$ K, considerably higher than the average over acoustic phonons of all polarizations $\langle\Theta\rangle = 90$ K indicated by low-temperature specific heat measurements.[4] Above 100 K, we find a large additional increase in α_b which may be characteristic of organic materials with anharmonic binding forces between large flexible molecules, and which also implies that the number of phonons increases almost quadratically with T.

Our analysis is based on the standard expression for the expansivity[8]

$$\alpha_b = \frac{1}{C_b V_0} \sum_{q,p} \frac{dE_{q,p}}{dT}\Gamma_{q,p}, \tag{1}$$

where V_0 is the zero-temperature volume, $E_{q,p}(T) = n_{q,p}(T)\hbar\omega_{q,p}$, and $\Gamma_{q,p} = -(d\ln\omega_{q,p}/d\ln L_b)$. Since Γ is probably largest for modes involving the intermolecular restoring force for b-axis compression and expansion,[8] we restrict the sum $\sum_{q,p}$ to phonon branches having $\hat{b}$-axis polarization. C_b is an effective elastic constant for expansion of L_b, which is C_{22} to the first order, but which is made larger by the coupling of L_b to the simultaneous expansion of L_a and L_c as T increases.

Relative changes in L_b of the small ($0.2\times 2\times 0.02$ mm) TTF-TCNQ single crystals available were detected to within $\Delta L_b/L_b = 10^{-6}$, using a modified capacitance dilatometer (shown schematically in Fig. 1) whose upper capacitor plate (a 0.3-in. diameter quartz disc coated with Al thin film) was suspended over the fixed lower plate by three TTF-TCNQ crystals. The 0.14-mm starting gap was established reproducibly to within 2% by gluing the crystals in place as the upper plate rested on the lower one, and then inserting 0.14-mm shims in the dilatometer support posts. The capacitance of the two plates was measured in the conventional three-terminal arrangement relative to a 2-ppm stable reference capacitor, using a simple bridge circuit and a precision ac voltage divider. A grounding wire was connected to the crystals with silver paint, in order to suppress the effect of the crystals on the measured capacitance.

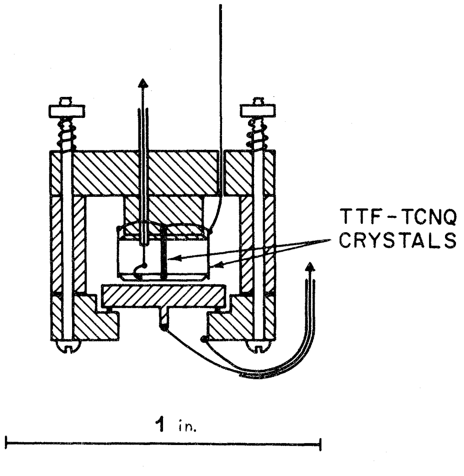

FIG. 1. Capacitance dilatometer used to measure α_b, showing upper capacitor plate suspended on three TTF-TCNQ crystals. Shading represents OFHC copper.

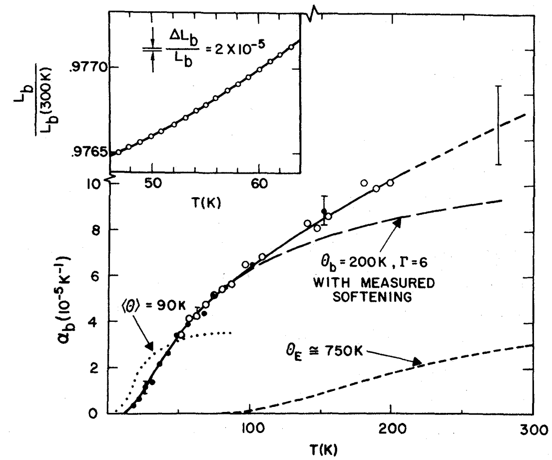

FIG. 2. b-axis expansivity of TTF-TCNQ single crystals, showing (dashed line) fit using an anisotropic Debye spectrum for the b-axis polarized acoustic phonon branch, $\Theta_b = 180$ K, see text; and (dotted line) expected behavior for an isotropic phonon spectrum consistent with the average value over all acoustic branches $\langle\Theta\rangle = 90$ K indicated by the low-temperature specific heat. Inset: length changes of one set of TTF-TCNQ crystals in the vicinity of the conductivity drop and the specific-heat anomaly, described to within the experimental accuracy by a smooth quadratic function.

The temperature was measured with an accuracy of 0.1 K using a platinum resistance thermometer mounted on the dilatometer. Quartz glass fibers were used in place of the crystals in a calibration run, giving expansivities of the oxygen-free high-conductivity (OFHC) copper dilatometer parts within 10% of published values.[9] Subtraction of quartz-fiber data from TTF-TCNQ data (about a 20% subtraction) on two different sets of crystals and capacitor plates gave the data of Fig. 2. The temperature dependence of the data reproduced to within 10%, except above 200 K where the sample-mounting epoxy softened slightly. All the data were consistent with the lower resolution data of Cook *et al.*,[10] as well as the unit cell changes observed in x-ray structure determinations.[1]

In order to analyze the behavior of $\alpha_b(T)$ in a systematic way, we first fitted the data below 60 K, where flexural-modulus measurements[12] suggest that C_b is relatively temperature independent,[13] and where only the low-lying $\hat{b}$-polarized acoustic modes should contribute. For these modes, we used an anisotropic Debye spectrum $\omega_b^2(q) = S_b^2 q_b^2 + S_\perp^2 q_\perp^2$, where $q_\perp^2 = q_a^2 + q_c^2$, and assumed that only the b-axis sound velocity S_b, and not $S_\perp$, varied with dL_b/L_b to give the relation $\Gamma_q = \gamma_b(S_b q_b/\omega_b)^2$, where $\gamma_b = -d(\ln S_b)/d(\ln L_b)$.

The best fit to the temperature dependence of α_b was obtained with $S_b = (3.2 \pm 0.4) \times 10^5$ cm/sec and was fairly insensitive to $S_\perp$ for $S_\perp$ close to 1.8×10^5 cm/sec, the value suggested for $(S_a S_b S_c)^{1/3}$ by the low-temperature specific heat.[4] The magnitude of α_b implies a value of $\gamma_b \cong \alpha_b C_b V_0/N_0 k_B \cong 5.0 \pm 1.5$, using $C_b \cong (5 \pm 1) \times 10^{10}$ dyn/cm^2 from the flexural modulus measurements.[12] For a linear- (i.e., Debye) phonon dispersion curve, the phonon cutoff energy at the zone boundary $q = \pi/b$ is $\Theta_b \equiv \pi S_b/k_B b = 200 \pm 30$ K.

In view of the average value over all polarizations $\langle\Theta\rangle = 90$ K indicated by the specific heat, this value of Θ_b represents substantial anisotropy in the stiffness of the crystal binding. Although other modes could contribute to α_b at these temperatures and confuse the fit, a purely acoustic contribution with Θ_b less than about 170 K is seriously inconsistent with the slow initial rise of the data. The value $\Theta_b = 200$ K is high compared to usual Van der Waals interaction energies and may bear out previously published ideas[2] about so-called "polarization" bonding in aromatic solids with less than Van der Waals interplanar spacing between neighboring molecules. However, in spite of the possibly high value of Θ_b, the large expansion still indicates fairly anharmonic binding.

Above 100 K, the elastic constant C_{22} must soften significantly, according to the relation $\Delta C_{22}/C_{22} \cong -2\gamma_b \Delta L_b/L_b$. The reasonable agreement between the net room-temperature softening estimated in C_{22} (28% ± 10%) and that observed in the flexural modulus[12] (38%) suggests that the length dependences of E_b and C_{22} are not made drastically different from each other by the coupling of L_b to L_a and L_c.[13] Thus it is reasonable to use the temperature dependence of E_b to estimate the softening in the effective elastic constant C_b. This has been done in attempting to fit α_b above 100 K, as shown in Fig. 1. The deviation of α_b from the expected acoustic contribution has roughly the shape expected for a set of Einstein modes of $\Theta_E \cong 750$ K, and is reasonably attributed to internal vibrational modes of the TTF and TCNQ molecules. This type of behavior, where internal vibrations make the molecules effectively larger, has been observed in the expansivity of polymer crystals in directions transverse to the polymer chains.[11]

We have taken particularly high-resolution data over the range 45–65 K to look for any length anomaly associated with the apparent structural changes[15] and the small specific-heat anomaly.[14] Careful analysis of the data, some of which are shown in the inset in Fig. 1, indicates no sudden changes in $\Delta L_b/L_b$ to within 3×10^{-5} and in α_b to within 10^{-5} K^{-1}. The same anharmonicity which gives rise to the thermal expansion should couple a structural distortion at any wave vector to L_b. A simple treatment in terms of an anharmonic two-body nearest-neighbor potential gives an expression for this coupling of $\Delta L_b/L_b = (-\gamma_b/2)(\delta/b)^2 [1-\cos(qb)]$, where δ is the amplitude of a static distortion at wave number q, and b is the original lattice spacing. This expression gives an upper limit on the sudden appearance of any short wavelength ($q \gtrsim \pi/3b$) distortion of $\delta/b \approx 5\times10^{-3}$. A smaller anomaly in α_b of the order 5×10^{-6} would be expected within an Ehrenfest estimate for a second-order phase transition at 55 K, assuming a specific-heat anomaly[14] $\Delta C_p \approx 0.05R$ and a Young's modulus anomaly[12] $\Delta E_b/E_b \approx 0.01$.

Using this qualitative information about the phonon spectrum, it is fairly straightforward to estimate a range of magnitudes and temperature dependences of the b-axis resistivity $\rho_b(T)$ of TTF-TCNQ which would be consistent with a conventional single-particle picture of the electrical transport. Although this picture, with single-particle electron-phonon scattering as the dominant resistive mechanism, is fully appropriate for most conductors,[8] it does not take into account some of the unusual behavior observed in TTF-TCNQ, such as the large Kohn anomaly observed at room temperature in neutron scattering[16] and the apparent strong frequency dependence of the conductivity in the far infrared.[17] Nonetheless, a free-carrier estimate of $\rho_b(T)$ is useful as a point of reference for the predictions of other possible models of the electrical transport.[18]

In the conventional free-carrier picture, the most temperature-dependent factor in the resistivity is the transport relaxation rate $1/\tau_{ep}$ due to electron-phonon scattering.[8] Since $1/\tau_{ep}$ is an average over many possible initial and final electron states, it is fairly insensitive to the details of the Fermi surface. Thus for any Fermi surface with sufficient anisotropy that small-angle scattering of electrons is somewhat suppressed, the temperature dependence of $1/\tau_{ep}$ due to scattering involving one phonon branch is given approximately by the expression for the strictly one-dimensional case

$$\frac{1}{\tau_{ep}} \propto \frac{1}{T}\,\frac{\exp(\Theta_F/T)}{[\exp(\Theta_F/T)-1]^2}\,, \qquad (2)$$

provided that the energy distribution of those phonons which span the Fermi surface along b is narrow enough to be replaced by its average, Θ_F. For the b-polarized acoustic phonons, Θ_F would be about 90 K for the case of a simple phonon dispersion curve $\omega(q) = (2\Theta_b k_B/\pi\hbar)\sin(\frac{1}{2}qb)$ and one-half electron transferred[15] from TTF to TCNQ. For the higher-frequency modes at $\Theta_E \cong 750$ K there would presumably be little dispersion, giving $\Theta_F \cong 750$ K for these modes at any value of charge transfer.

This wide variation of phonon frequencies from branch to branch of the phonon spectrum gives a corresponding wide range of possible ratios $\rho_b(300\text{ K})/\rho_b(60\text{ K})$, based on Eq. (2): for purely acoustic or purely intramolecular mode scattering, $\rho_b(300\text{ K})/\rho_b(60\text{ K}) \cong 7$ or 5000, respectively. However, a combination of roughly equal acoustic and intramolecular contributions gives the best fit to the relatively sample-independent[3-6] part of $\rho_b(T)/\rho_b(300\text{ K})$ (i.e., for $100\text{ K} < T < 300\text{ K}$) and indicates a ratio of $\rho_b(300\text{ K})/\rho_b(60\text{ K}) \cong 20$ and a temperature dependence of ρ_b that varies roughly as T^2. An estimate of the magnitude of τ_{ep} for a deformation potential type of electron-phonon coupling[19] gives $\tau_{ep} \cong \hbar/kT \cong 2\times10^{-14}$ sec or $\rho_b = 10^{-3}\ \Omega$ cm at 300 K. The major experimental results not accounted for by these estimates (as far as the dc conductivity is concerned) are the generally higher observed room-temperature resistivity[3,5,6] [$(2-3)\times10^{-3}\ \Omega$ cm which implies an effective mean free path[5] less than $\hat{b}$[18]], and the higher observed resistivity ratios [$\rho_b(300\text{ K})/\rho_b(60\text{ K}) \lesssim 50$ have been corroborated in more than one laboratory[4,22]]. It is also useful to estimate the expected contribution of phonon anharmonicity to the pressure dependence of ρ_b within the free-carrier description. Here we expect the acoustic modes to have the dominant pressure dependence, and Eq. (2) gives a contribution $d\ln\rho_b/dP \cong -2\Gamma C_{22} \cong -0.2$/kbar from these modes. This value coincides with that observed experimentally,[20] although there must be additional pressure dependence from band structure changes.[21]

In conclusion, the low-temperature b-axis expansivity of TTF-TCNQ may bear out previous conjectures of relatively strong bonding in aromatic organic solids. However, this bonding is sufficiently anharmonic to cause a large thermal expansion, resulting in softening of the solid at higher temperatures. This type of lattice behavior may be characteristic of the organic charge transfer salts, and may play a role in determining their transport properties.

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*Also at the University of Rochester, Rochester, N. Y. 14627.

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