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Thermal Expansion in TMTSF-Dmtcnq & (TMTSF)₂PF₆

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THERMAL EXPANSION IN TMTSF-DMTCNQ & (TMTSF)₂PF₆

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We have measured the anisotropic thermal expansion of TMTSF-DMTCNQ and (TMTSF)₂PF₆ in the temperature range 10-300 K using an X-ray diffraction technique with a relative accuracy of 3 parts in 10⁴. Between 10 K and 300 K we find expansion in the a*, b* and c* directions to be respectively 2.5%, 0.2% and 1.7% for TMTSF-DMTCNQ and 3.7%, 1.6% and 1.3% for (TMTSF)₂PF₆

There are relatively few reports of thermal expansion measurements for the organic charge transfer salts, although TTF-TCNQ has been studied with X-ray techniques^{1,2} and by means of capacitance dilatometry in the stacking-axis direction³, and there are X-ray measurements on TTF-DETCNQ⁴. We present measurements on TMTSF-DMTCNQ which undergoes a Peierls transition at 42 K⁵ to give a commensurate 4x superlattice along the stacking axis (a)^{6,7}, and (TMTSF)₂PF₆, the first of the family of organic superconductors (above 9 kbar⁸) which at ambient pressure shows a transition to what is considered to be a SDW state, at around 15 K^{9,10}.

The studies were performed on single crystals using an X-ray Weissenberg film technique with Cu-K_α radiation. Sample temperature could be controlled over the range 10-300 K in an Oxford Instruments continuous flow helium cryostat. Temperature was measured by means of a GaAs diode mounted close to the sample. Exposures of a selected reciprocal lattice point reflection were made at a number of different temperatures with separate areas of the film exposed at each temperature¹¹. The resolution for relative changes in lattice parameter using a high angle ($\theta > 80^\circ$) Bragg reflection is about

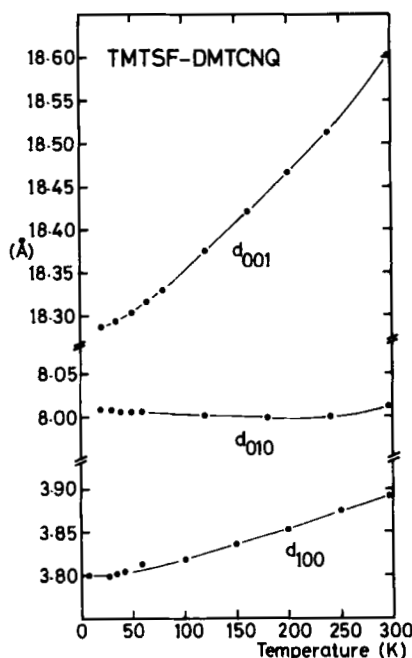


FIGURE 1 Temperature dependence of the inverse reciprocal lattice wave-vectors in TMTSF-DMTCNQ

3 parts in 10^4 . Changes in the angles α^* , β^* and γ^* for these triclinic structures^{12,13} may be estimated by following an off-axis reflection and making comparison with the relevant axial reflections. As this involves the use of different films, possibly with different shrinkages, the accuracy is reduced from the reciprocal lattice length determination. All data has been normalised to known room temperatures values^{12,13}.

Figure 1 shows the temperature dependence of the inverse reciprocal lattice wavevectors in TMTSF-DMTCNQ. These are related to the real space lattice parameters through

$$a = \frac{b^* c^* \sin \alpha^*}{V^*} \quad \text{etc.}$$

and

$$\cos \alpha = \frac{\cos \beta^* \cos \gamma^* - \cos \alpha^*}{\sin \beta^* \sin \gamma^*}$$

where V^* is the reciprocal lattice unit cell volume. No indication of anomalies in lattice parameter at the Peierls transition are evident within the accuracy of the experiment.

We have measured changes in the angles α^* and β^* to be less than 1° between 10 K and 300 K. The failure to detect

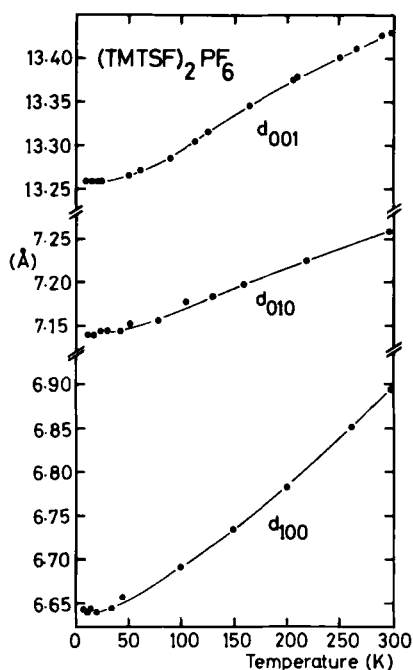


FIGURE 2 Temperature dependence of the inverse reciprocal lattice wave-vectors in (TMTSF)₂PF₆

changes in any of the lattice parameters, and hence unit cell volume, at the Peierls transition is consistent through the Clausius-Clapeyron relation with the very weak pressure dependence of the transition in the low pressure regime¹⁴. Lattice contraction along the stacking axis (a) of 2.5% between 300 K and 10 K is very similar to values reported for TTF-TCNQ of 2.4%¹ and TTF-DETCNQ of 2.6%³. Similarly, the very small thermal expansion observed in the b^* direction in TMTSF-DMTCNQ, which is the direction perpendicular to the stacking axis in which there is alternation of donor and

acceptor molecules, is also seen in the corresponding direction in TTF-DETCNQ³.

Thermal expansion data for (TMTSF)₂PF₆ is shown in figure 2. Corresponding changes in the triclinic angles are small, and less than 1.5° from 10 K to 300 K. There is no sign of an anomaly at the SDW transition at 15 K, as expected from the lack of any visible superstructure in diffuse X-ray studies⁷. The fractional changes in cell parameters from 10 K to 300 K, of 3.7%, 1.8% and 2.5% for the *a**, *b** and *c** directions are large and indicate a volume coefficient of expansion that is a factor of 2 larger than that for TTF-TCNQ, TTF-DETCNQ and TMTSF-DMTCNQ. The coefficient of thermal expansion is particularly large along the stacking axis (*a*), which presuming similar values of Gruneisen constant implies a significantly greater compressibility in (TMTSF)₂PF₆ along the stacking axis than in the two-stack systems, and hence greater intrastack electron-phonon coupling. We measure similar values of thermal expansion coefficient in the isostructural (TMTSF)₂ReO₄ above 200 K. This material undergoes a metal-insulator transition at around 180 K¹⁵, at which temperature the ReO₄ ions order to give a doubling of the unit cell in all three directions¹⁶. Preliminary measurements through the transition indicate a decrease in coefficient of thermal expansion below 180 K which is most marked in the *a** direction.

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