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THE VELOCITY OF SOUND IN ORGANIC CHARGE TRANSFER SALTS $(TMTSF)_2FSO_3$ AND $(TMTSF)_2F_2PO_2$.

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The velocity of sound (v) along the needle a-axis was measured as a function of temperature in the title salts. The velocity of sound of $(TMTSF)_2FSO_3$ increases smoothly with decreasing temperature down to 86 K, where it increases sharply (first-order in character). Below the transition, v continues to increase with decreasing temperature, but at a rate faster than above the transition. From the data, the dimensionless electron-phonon coupling constant λ is extracted : $\lambda \sim .043$. Similary, for $(TMTSF)_2F_2PO_2$, v increases with decreasing temperature. However, unlike the FSO_3^- salt, at the metal-insulator transition ($\sim$ 137 K), v dips sharply before it sharply increases. The velocity of sound continues to increase below the transition.

The Bechgaard-phase salts $(TMTSF)_2FSO_3$ and $(TMTSF)_2F_2PO_2$ are unique in that they are the only members of the TMTSF family which have anions which possess a permanent dipole moment.[1,2] At ambient pressure, $(TMTSF)_2FSO_3$ undergoes a metal-insulator transition at $\sim$ 86 K associated with a (1/2,1/2,1/2) antiferroelectric dipole ordering of the anions.[1,3,4] Application of pressures $\sim$ 6 kbar suppresses the metal-insulator transition and superconductivity is observed [3,5] with onset temperatures > 3 K, although often the transitions are incomplete, and only a small (< 2 % of the sample volume) Miesner effect has been observed.[6] At 1 kbar pressure, $(TMTSF)_2F_2PO_2$ undergoes a metal-insulator transition [2] at $\sim$ 137 K, possibly associated with anion ordering.[7] Application of pressure depresses the metal-insulator transition to lower temperatures, but

no superconductivity is observed. Instead, at 14.5 kbar and low temperature, the resistivity (ρ) α ℓnT, suggestive of localization in two-dimensional systems.[2]

The velocity of sound along the a-axis was measured at ambient pressure using a vibrating reed technique.[8] The technique involves fixing one end of the sample with silver paint and measuring the frequency of the reed modes. The apparatus could be configured for finding the resonances (sweeping frequency) or tracking a resonance with varying temperature.

The sound velocity for $(TMTSF)_2FSO_3$ is shown in Figure 1. The room temperature valve of $v \sim 3.8 \times 10^5$ cm/sec ($\pm$ 25 %) is similar to that found for $(TMTSF)_2PF_6$ (ref. 9). The large uncertainty in the absolute valve reflects the difficulty in determining sample dimensions and the somewhat irregular sample shape. As the temperature is lowered, v increases smoothly down to 86 K. At 86 K, v jumps sharply. Below the transition, v continues to increase with decreasing temperature, at an initial rate faster than above the transition. The Figure 1 insert shows the velocity of sound in the neighbourhood of the transition for cooling and heating. The change in velocity of sound occurs discontinuously at $\sim$ 86 K. There is a hysteresis of .4 K between heating and cooling curves.

The velocity of sound of $(TMTSF)F_2PO_2$ is shown in Figure 2 for two different samples. These samples seemed particularly susceptible to microcracking, reflected by small discontinuities in the velocity of sound. As in the FSO_3^- salt, both samples show an overall increase in v with decreasing temperature. At $\sim$ 140 K, v in both samples drops sharply before increasing sharply, with sample 1 showing a bigger increase in v at the transition. Both samples show a continued increase in v below the transition. Measurements at low temperature were hampered by poor sample condition and high sample resistance.

The overall temperature dependence of v results largely from thermal expansion, as has been seen in TTF-TCNQ[10] and $(TMTSF)_2PF_6$ (ref. 9). In fact, both the FSO_3^- and PF_6^- salts have identical

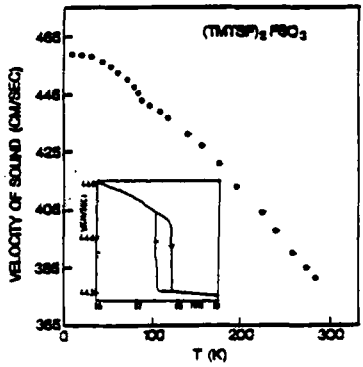

FIGURE 1 - v versus T for $(TMTSF)_2FSO_3$

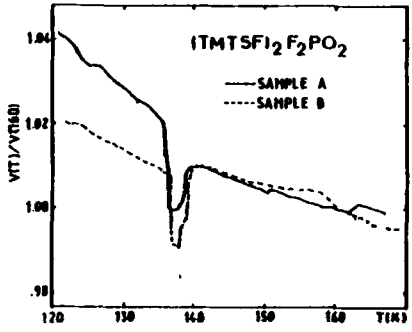

FIGURE 2 - v(T)/v(160K) versus T for $(TMTSF)_2F_2PO_2$

values of v(10K)/v(300K) = 1.24.

The sharp discontinuous increase in v at the metal-insulator transition temperature, and the associated hysteresis indicates the transition in the FSO_3^- salt is first-order in character and unlike what has been observed in either of the charge density wave (CDW) transitions in TTF-TCNQ or the spin density wave (SDW) transition in the PF_6^- salt. The increase in velocity of sound at the transition can be understood as a stiffening of the lattice due to a loss of screening electrons associated with the opening of a gap at the Fermi surface. In general, an electron gas responds to an applied potential via a generalized response function or susceptibility, which for degenerate electrons is proportional to the density of states at the Fermi energy, D(0). For the strain field created by a sound wave, the electron screening softens the mode and hence reduces the sound velocity by :

$$\vec{v}_q^2 = v_{qo}^2 \ (1 - g^2\chi(0)) \qquad (1)$$

where g is the electron-phonon matrix element and $\chi(0)$ the Lindhardt function for non-interacting particles. In the metallic state, $\chi(0) = D(0)$ since the strain field has a long wavelength ($q \to 0$). On the other hand, when a gap opens on the Fermi surface, $\chi_o \to 0$ as $T \to 0$ and the low frequency phonons stiffen, consistent with an increase in v. The jump in velocity of sound is related to the

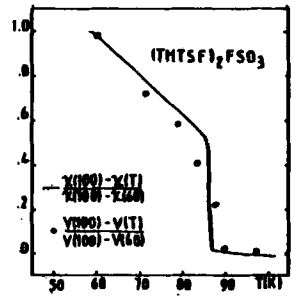

FIGURE 3 - Normalized v and χ versus T for $(TMTSF)_2FSO_3$

electron-phonon coupling constant χ by

$$\chi = g^2 D(0) = \frac{v_{qo}^2 - v_q^2}{v_{qo}^2} \qquad (2)$$

From Figure 1, a valve of $\chi \sim .043$ is extracted for the FSO_3^- salt, larger than the valve of .014 obtained for the PF_6^- salt.[9]

The normalized susceptibility,[1] $(\chi(100)-\chi(T)/(\chi(100)-\chi(60))$ and the normalized velocity of sound, $(v(100)-v(T)/(v(100)-v(60))$ are plotted versus temperature in Figure 3. Since the change in χ at $\sim$ 86 K results simply from a loss of density of states at the Fermi surface, the fact that the jump in v at $\sim$ 86 K is smaller than what is seen in χ indicates the change in v at $\sim$ 86 K involves both a change in D(0) and a lattice softening.

The anomalous behaviour seen in v in the $F_2PO_2^-$ salt, where a sharp dip preceeds the sharp increase at the metal-insulator transition, is similar to what has been seen at the CDW transitions in the layered dichalcogenides $TaSe_2$ and $NbSe_2$ (ref. 11), or the trichalcogenides [12] $NbSe_3$ and $TaSe_3$. However, the sharpness of the anomaly seen in the $F_2PO_2^-$ salt suggests the transition at $\sim$ 137 K may be first order in character.

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REFERENCES

1. F. Wudl, E. Aharon-Shalom, D. Nalewajek, J.V. Waszczak, W.M. Walsh Jr., L.W. Rupp Jr., P. Chaikin, R. Lacoe, M. Burns, T.O. Poehler, J.M. Williams and M.A. Beno, J. Chem. Phys. 76, 5497 (1982).
2. S. Cox, R.M. Boysel, D. Moses, F. Wudl, W.M. Walsh Jr. and L.W. Rupp Jr., Sol. St. Comm. 49, 259 (1984).

3. R.C. Lacoe, P.M. Chaikin, F. Wudl and E. Aharon-Shalom, J. de Physique C3, 767 (1983).
4. R. Moret, J.P. Pouget, R. Comès and K. Bechgaard, J. de Physique C3, 957 (1983).
5. R.C. Lacoe, S.A. Wolf, P.M. Chaikin, F. Wudl and E. Aharon-Shalom, Phys. Rev. B27, 1947 (1983).
6. K. Andres, F. Gross, H. Schwenk and F. Wudl, these proceedings.
7. J. Williams reported at this conference that no ordering of the anions was observed down to $\sim$ 125 K.
8. T. Tiedje, R.R. Haeving and W.N. Hardy, J. Acoust. Soc. Am. 65 1171 (1979).
9. P.M. Chaikin, T. Tiedje and A.N. Bloch, Sol. St. Comm. 41, 739 (1982).
10. T. Tiedje, R.R. Haering, M.H. Jericho, W.A. Roger and A. Simpson, Sol. St. Comm. 23, 713 (1977).
11. M. Barmatz, L.R. Testardi and F.J. Di Salvo, Phys. Rev. B12, 4367 (1975).
12. J.W. Brill, Sol. St. Comm. 41, 925 (1982) and J.W. Brill and N.P. Ong, Sol. St. Comm. 25, 1075 (1978).