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Far-infrared powder absorption measurements of some tetramethyltetraselenafulvalene salts [$(TMTSF)_2X$]

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We have measured the far-infrared [(10—100)-cm^{-1}] powder spectra of six compounds of the form $(TMTSF)_2X$, where $X = PF_6$, AsF_6, and SbF_6 (octahedral anions) and ClO_4, BF_4, and ReO_4 (tetrahedral anions), and TMTSF is tetramethyltetraselenafulvalene. The octahedral-anion spectra are all very similar, having four sharp resonances which have been attributed to three lattice modes and one internal mode. These assignments were made on the basis of isotope shifts upon deuteration and wave-number temperature dependence. The intensity of the lines is proportional to the dc conductivity and shows the spin-density-wave transition around 12 K. The spectra of the tetrahedral-anion compounds, on the other hand, show extra structure below the anion-ordering temperature T_{AO}; this is attributed to the activation of zone-boundary phonons due to zone folding which accompanies the formation of the ordered anion superlattice. In particular, a feature appears in each compound around 30 cm^{-1} which actually exists above T_{AO} but is very broad, and is interpreted as a zone-boundary acoustic phonon. This is believed to be responsible for the $\mathbf{E}||\mathbf{a}$ 30-cm^{-1} feature in the ClO_4 compound, previously observed by Ng, Timusk, and Bechgaard to be sensitive to magnetic field and possibly related to the superconductivity.

INTRODUCTION

The salts of the form $(TMTSF)_2X$, where TMTSF is tetramethyltetraselenafulvalene and X is an inorganic anion such as PF_6^-, AsF_6^-, and SbF_6^-, which are octahedral, or ReO_4^-, BF_4^-, and ClO_4^-, which are tetrahedral, form highly conducting pseudo-one-dimensional organic crystals, which have the same crystal structure and stoichiometry, but remarkably various physical properties upon cooling. Those with the three octahedral anions listed have metal-insulator (M-I) transitions around 12 K upon the formation of a spin-density wave (SDW) and become superconducting around 1 K under applied pressure.[1-9] The tetrahedral anions are, however, orientationally disordered in the compounds at room temperature and upon cooling pass through an anion-ordering transition. The ReO_4 compound has this transition[10] at 177 K forming a superlattice[11] with a unit cell of $2a \times 2b \times 2c$. This causes a metal-insulator transition with the formation of a charge-density wave (CDW). A semiconducting gap of over 1000 cm^{-1} is seen in the infrared conductivity[12] below the transition, together with a strong enhancement of the intensity of the totally symmetric (a_g) intramolecular modes of the TMTSF molecule. This is due to the coupling with the CDW, and has been seen in the infrared powder spectrum.[13] Upon the application of pressure the M-I transition is suppressed and the perrhenate becomes superconducting[14] near 1 K. The anion-ordering transition occurs in the BF_4 compound[1] at 38 K, much lower than for ReO_4, but it also forms a superlattice with the same unit cell,[15] and undergoes a metal-insulator transition. Under pressure, however, the transition is suppressed but no superconductivity is observed. Finally, the ClO_4 compound orders at 24 K but no metal-insulator transition accompanies it.[9,16,17] The unit cell of the superlattice[15,18] is $a,2b,c$. If cooled slowly into the "relaxed" state, superconductivity at ambient pressure is observed, whereas a "quenched" sample will undergo a SDW transition near 6 K into an insulating phase.[19]

Several compounds have been examined in the infrared region including numerous and detailed single-crystal studies,[12] and a thorough analysis has been made of the intramolecular vibrations of tetramethyltetrathiafulvalene (TMTTF) and TMTSF.[20,13] Fewer far-infrared studies have been performed. This spectral region contains several interesting and pertinent phenomena: semiconducting gaps, superconducting gaps, pinned CDW's, antiferromagnetic resonances, free-carrier absorption, low-lying intramolecular modes, and all of the intermolecular modes, including translational and librational optical phonons as well as acoustic phonons. Single-crystal far-infrared studies have been performed on $(TMTSF)_2ClO_4$,[21-24] $(TMTSF)_2PF_6$,[12,24] $(TMTSF)_2SbF_6$,[25] and $(TMTSF)_2AsF_6$.[26] There is a disagreement between some of the results obtained for the ClO_4 and the PF_6 compound. In part, this is because of the difficulty of these measurements when the crystals are small. While efforts continue on the single-crystal polarized far-infrared measurements, it was felt worthwhile to perform the much simpler powder measurements in this region since none presently exist. While these give information mainly for the transverse polarizations and give no indication of the absolute magnitude of the conductivity, useful insights have been obtained.

EXPERIMENTAL

Samples of $(\mathrm{TMTSF})_2X$ and $(\mathrm{TMTSF}\text{-}d_{12})_2X$ ($X=\mathrm{ClO_4}$, $\mathrm{BF_4}$, $\mathrm{ReO_4}$, $\mathrm{AsF_6}$, $\mathrm{SbF_6}$, and $\mathrm{PF_6}$) were prepared by electrocrystallization using a modified H cell.[27] The reaction was typically carried out under a nitrogen atmosphere in anhydrous dichloromethane ($5\times10^{-2}M$ in electrolyte, $4\times10^{-3}M$ in TMTSF—at the anode) at a constant current of 2.2 or 4.0 μA. The electrolysis was discontinued at $\sim50\%$ conversion. The $R_4\mathrm{N}X$ electrolytes were purified by recrystallization or chromatography followed by recrystallization prior to use. Initially, TMTSF was prepared in our laboratory. However, commercially available (Strem Chemicals, Inc.) material is now routinely used. The TMTSF-d_{12} was prepared from deuterated 3-methanesulphonyl-2-butanone (from 2,3-butandione-d_6) using a modification of literature procedures.[28] Deuterium-incorporation levels in the intermediate products were estimated by proton-magnetic-resonance spectroscopy and/or high-resolution mass spectrometry. The deuterium content of 4,5-dimethyl-1, 3-diselenole-2-selone, the immediate precursor to TMTSF-d_{12}, was estimated from an analysis of the $\mathrm{C_4}$ m/z mass spectral cluster. The level of deuterium incorporation of the TMTSF-d_{12} ($\sim90\%$) is assumed to be that of the 2-selone precursor.

The crystals were ground in Nujol and the mull transferred to a wedged piece of TPX (the Mitsui and Co., Ltd. trademark for methyl pentene polymer) which was then mounted in a Janis Supervaritemp Dewar. The tail of the Dewar sat at the focus of a modified Beckman RIIC FS720 Fourier spectrophotometer operating in the polarizing Martin-Puplett mode.[29] A gallium-doped germanium bolometer at 4 K was used to detect the radiation. In the experiments with the tetrahedral-anion compounds, the samples were cooled slowly (<1 K/min) through the transition so that the anions were ordered. Fast cooling produced spectra with much broader features.

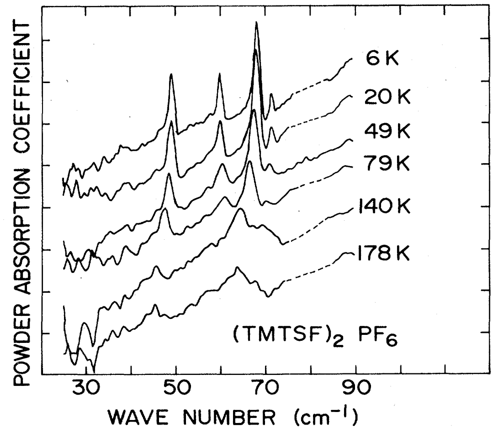

FIG. 1. Absorption coefficient of $(\mathrm{TMTSF})_2\mathrm{PF_6}$ powders in Nujol on a polyethylene backing showing four resonances. The dashed line at 80 cm^{-1} replaces an incompletely canceled polyethylene absorption line. The curves are displaced for clarity.

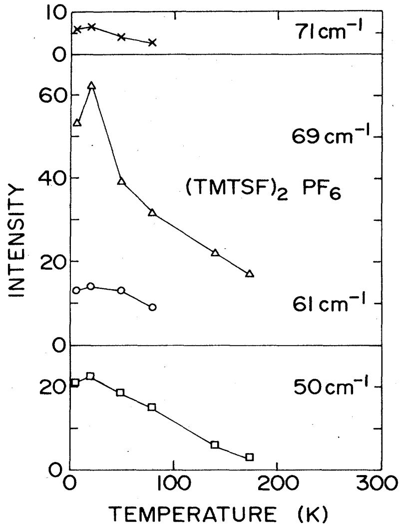

FIG. 2. Integrated intensity of the four lines of $(\mathrm{TMTSF})_2\mathrm{PF_6}$ seen in Fig. 1 versus temperature. The units are arbitrary but the same for each line. Note the turnover below the phase transition, which is at 12 K.

RESULTS

Figure 1 shows the results obtained for $(\mathrm{TMTSF})_2\mathrm{PF_6}$ at various temperatures above and below the M-I transition at 12 K, between 20 and 90 cm^{-1}. There is no striking evidence of this transition in the spectrum, in agreement with the results in the infrared.[13] Four resonances are observed. Due to the high conductivity[24] measured for $\mathbf{E}\parallel\mathbf{a}$, where $\mathbf{a}$ is the direction of the conducting chains, these resonant modes are polarized with $\mathbf{E}\perp\mathbf{a}$ and agree with those seen in the $\mathbf{E}\parallel\mathbf{b}'$ single-crystal-reflectivity spectrum[24] at 6 K. As the temperature is raised, the resonances shift and are thermally broadened.[30] Figure 2 shows the temperature dependence of the in-

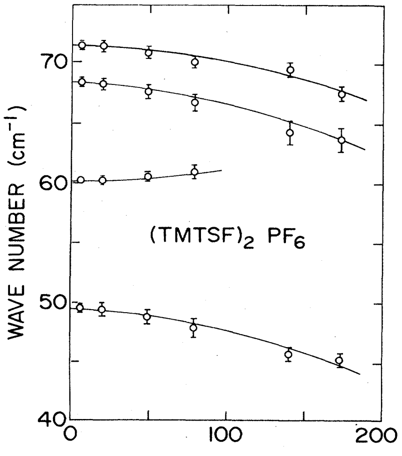

FIG. 3. Temperature dependence of the wave number of the four $(\mathrm{TMTSF})_2\mathrm{PF_6}$ lines seen in Fig. 1. Three lattice modes are indicated by the strong dependence. One internal mode is seen at 60 cm^{-1}.

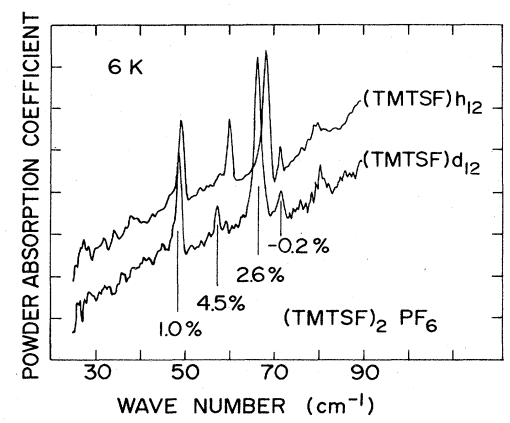

FIG. 4. 6-K powder spectra of protonated and deuterated $(TMTSF)_2PF_6$. The percentage decrease in wave number upon deuteration is indicated.

tegrated intensities of the lines, which is seen to follow that of the dc conductivity, including the turnover below 12 K, the only evidence of the transition. This coupling to the free carriers is similar to that previously observed for a lattice mode in TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane).[31] Figure 3 shows the temperature dependence of the wave number of the modes, with a strong dependence indicating three intermolecular (or "external" or "lattice") modes, and one intramolecular (or "internal") mode at 60 cm^{-1}. Figure 4 shows the deuterated spectrum at 6 K with the percentage shifts observed, while Table I lists the shifts expected for the various pure (unmixed) lattice modes, and Fig. 5 shows the two possible low-energy internal modes together with the calculated[32] isotope shifts. As in the case of TTF-TCNQ,[31] it is not really possible to distinguish between these two modes on the basis of an observed 4.5% shift, but since the deuteration was not complete, and the polarized spectra in TTF-TCNQ indicated the b_{3u} mode, it is probable that we are also observing $\nu_{72}(b_{3u})$. Table I indicates that two of the lattice modes involve motion of the TMTSF molecule alone and correspond to translational and librational motions, although they are undoubtedly mixed.[32] The irreducible representation of the translation and acoustic vibrations is given by

TABLE I. Calculated and measured isotope shifts of the $(TMTSF)_2PF_6$ lattice modes. (Coordinates are shown in Fig. 5.)

Type	Molecules involved	ν_p/ν_d (calc.)	ν_p/ν_d (meas.)
Translational	2 TMTSF 1 PF_6	1.002	
Translational	TMTSF alone	1.013	1.010
Libration R_x	2 TMTSF 1 PF_6	1.001	
Libration R_x	TMTSF alone	1.044	
Libration R_y	2 TMTSF 1 PF_6	1.002	
Libration R_y	TMTSF alone	1.052	
Libration R_z	2 TMTSF 1 PF_6	1.002	
Libration R_z	TMTSF alone	1.024	1.026
?	2 TMTSF 1 PF_6		0.998

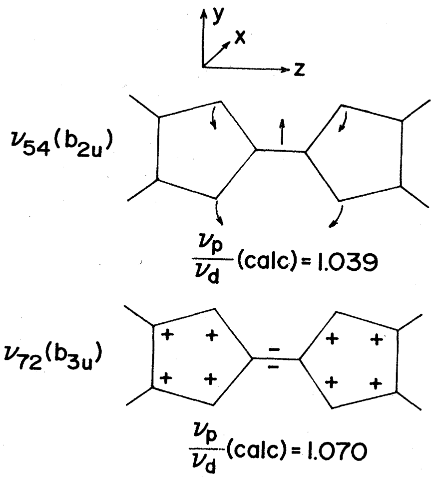

FIG. 5. Two lowest-energy internal modes of TMTSF (see Ref. 20), with the calculated wave-number shift upon deuteration, after Ref. 32.

$$\Gamma=(3A_g+3A_u)(\text{TMTSF})+3A_u(\text{PF}_6)\ , \qquad (1)$$

giving three Raman-active and three infrared-active modes. The representation of the rotational vibrations is given by

$$\Gamma=3A_u+6A_g\ , \qquad (2)$$

giving three infrared and six Raman modes. Thus one expects a total of six infrared-active modes with mixing of the translational and librational motions.

Figure 6 shows the 8-K spectra of the AsF_6 and SbF_6

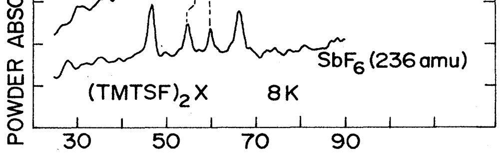

FIG. 6. 8-K absorption coefficient of $(TMTSF)_2PF_6$, $(TMTSF)_2AsF_6$, and $(TMTSF)_2SbF_6$, vertically displaced for clarity. All powders except the PF_6 were on TPX mounts. The nature of the resonances is indicated and dashed lines follow the features through the compounds. The molecular weight is included for reference.

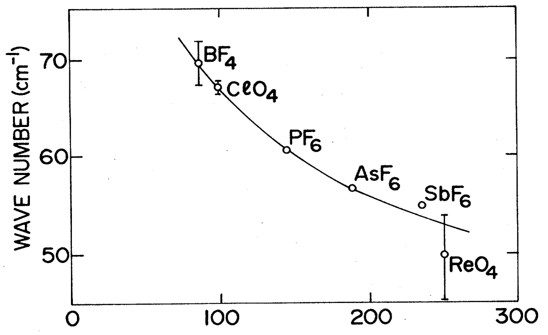

FIG. 7. Wave number of the internal mode versus anion mass. The dependence shows a weakening of the lattice component of the force constant as the lattice expands. The accuracy of the internal-mode wave number in the tetrahedral-anion compounds is poor due to the uncertainty in assignment, which resulted from the splittings and limited temperature range (see text).

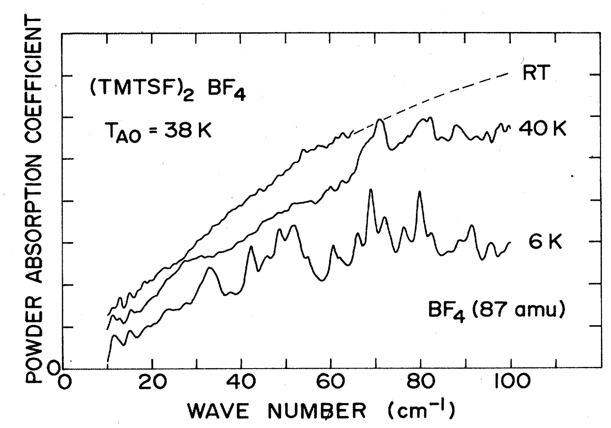

FIG. 9. Absorption coefficient of (TMTSF)$_2$BF$_4$ powders. The curves are not displaced and have the same scale and origin of absorption coefficient. The anion-ordering temperature is indicated. A dashed line extrapolates the room-temperature spectrum above 65 cm^{-1} due to the large noise resulting from the strong absorption. Cooling through T_{AO} was at <1 K/min.

compounds compared with the PF$_6$. The spectra are very similar each displaying four resonances, fairly close in wave number. The temperature dependence of the frequencies identifies the lattice modes. Two of them shift very little in going from one compound to another, confirming the negligible role of the anion. The third lattice mode, which involves both ions, shifts considerably between the PF$_6$ and the AsF$_6$ but little between the AsF$_6$ and SbF$_6$. In the latter case it is probably interacting with adjacent modes. The internal mode shifts slightly from one compound to another, as the force constants are modified slightly by the changing size of the unit cell. This is well-known behavior, seen, for example, in the ν_3 mode of the ReO$_4$ in alkali halides.[33] Figure 7 shows the wave number of the internal mode as a function of anion mass.

Turning to the tetrahedral-anion compounds, one finds very different behavior. Figure 8 shows the results for the ReO$_4$ at three temperatures. These curves are not displayed vertically, and have the same ordinate origin and scale. Above the transition, there is continuous and strong free-carrier absorption, increasing with wave number as expected. Below the transition this absorption decreases, displaying a semiconducting gap, and the vibrational resonances appear. Again, there are four main features at 10 K, but some of them have shoulders and there is additional structure at 28, 70, and 80 cm^{-1}. The results are similar for the BF$_4$ compound, seen in Fig. 9. The four modes are seen just above the transition at 40 K, near 70 and 80 cm^{-1}, broadened both by thermal motion and anion disorder. The free-carrier absorption is decreased by 6 K and the four modes have become multiplets. Additional features are seen at 33 cm^{-1} and be-

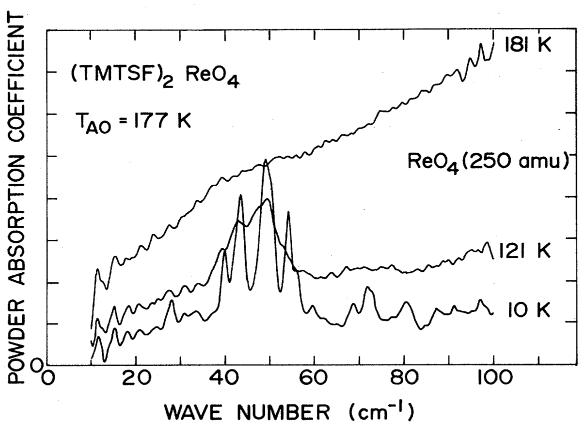

FIG. 8. Absorption coefficient of (TMTSF)$_2$ReO$_4$ powders. The curves are not displaced and have the same scale and origin of absorption coefficient. The anion-ordering temperature is indicated. Cooling through T_{AO} was at <1 K/min.

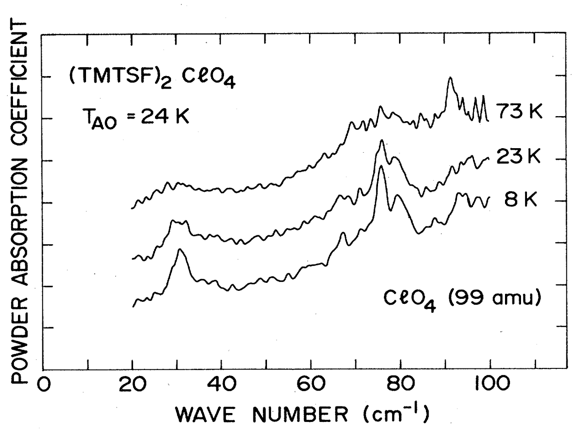

FIG. 10. Absorption coefficient of (TMTSF)$_2$ClO$_4$ powders. The curves are displaced for clarity. The anion-ordering temperature is indicated. Cooling through T_{AO} was at <1 K/min.

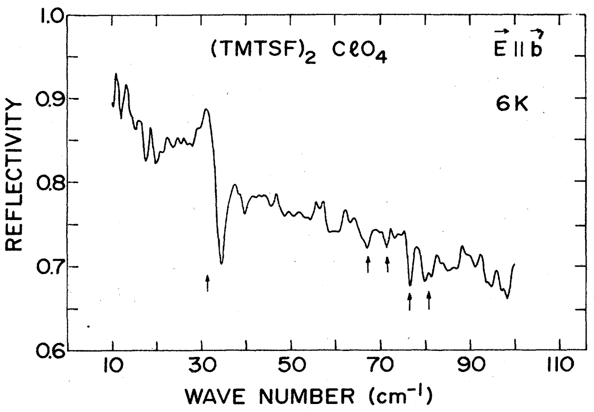

FIG. 11. Reflectivity of a relaxed single crystal of (TMTSF)$_2$ClO$_4$ at 6 K for radiation polarized with $\mathbf{E}\|\mathbf{b}'$, measured by a composite-bolometer method (see Ref. 24). Arrows indicate the wave numbers of the powder features. The other features in the spectrum are a result of incomplete cancellation of channeled spectra, plus some noise. Note the large resonance at 31 cm^{-1}.

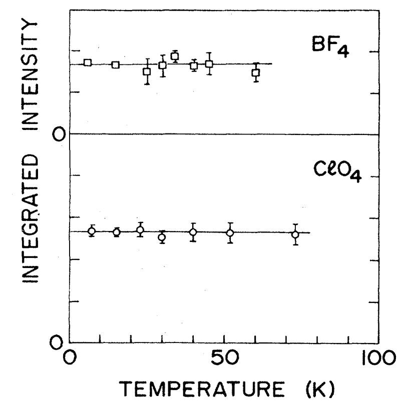

FIG. 13. Integrated intensity of the "30-cm^{-1}" feature in the powder spectra of the BF$_4$ and ClO$_4$ compounds. The intensity is constant well beyond T_{AO}. The data were taken up to a temperature beyond which the feature was too broad to measure.

tween 40 and 60 cm^{-1} below the anion-ordering transition. The ClO$_4$ has no M-I transition and so the free-carrier absorption changes little. The curves in Fig. 10 are therefore displaced for clarity. The four broad features are seen between 65 and 85 cm^{-1}, but below the transition an additional sharp feature appears around 31 cm^{-1}.

This 31-cm^{-1} feature is seen very strongly in our $\mathbf{E}\|\mathbf{b}'$ reflectivity spectrum,[24] part of which is shown in Fig. 11. It appears in both polarizations and was first seen by Ng, Timusk, and Bechgaard[21] and by Challener, Richards, and Greene.[22] Ng and Timusk found that for $\mathbf{E}\|\mathbf{a}$, the feature at 2 K was reduced by the application of a magnetic field of 7 kG, possibly linking it to the ambient-pressure fluctuating-superconductivity gap of the material. Challener, Richards, and Greene[23] found no magnetic field dependence, but it appears clear, both from their experimental procedure and from the structure in their spectra around 75 cm^{-1}, that they were measuring the $\mathbf{E}\perp\mathbf{a}$ feature, as seen by us. However, they suggested that the feature was a coupled-electron-phonon mode and suggested a comparison with other tetrahedral-anion compounds.

If one displays our results for the three tetrahedral-anion compounds together, as in Fig. 12, one sees that a "30-cm^{-1}" feature is indeed common to all three. Furthermore, if one plots the integrated intensity versus temperature, as in Fig. 13, one finds that it is constant up to a temperature beyond which it is too broad to measure.[34] The width of the feature grows sharply above the anion-ordering temperature and continues to grow with rising temperature, as shown in Fig. 14.

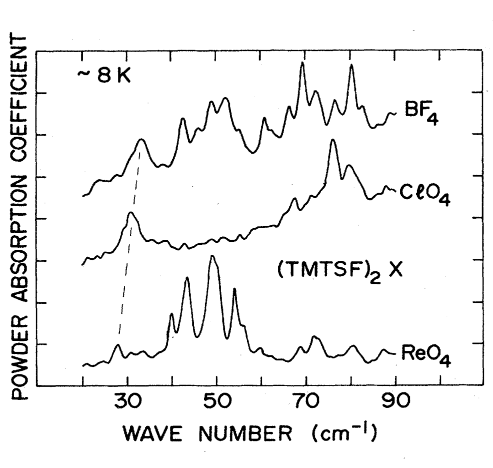

FIG. 12. Low-temperature powder absorption coefficients of the three tetrahedral-anion compounds, displaced for clarity. A dashed line joins the common "30-cm^{-1}" features. Notice also the large wave-number shift of the four normal lines between the ClO$_4$ and the ReO$_4$ compounds.

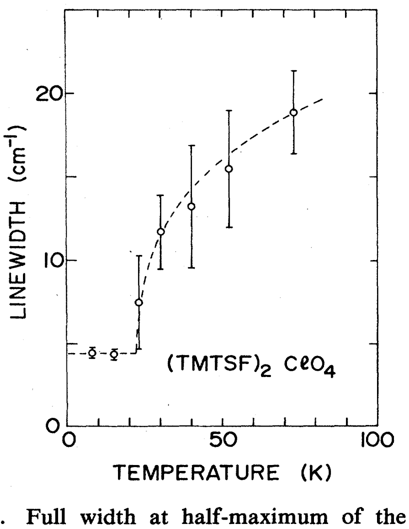

FIG. 14. Full width at half-maximum of the "30-cm^{-1}" feature in the powder spectrum of (TMTSF)$_2$ClO$_4$. The line was fitted to a Lorentzian on a sloping background. Above T_{AO} the line broadened quickly and was not a good Lorentzian. The error bars indicate this. The dashed line is drawn as a guide to the eye.

Our interpretation of the data is as follows. The superlattice formed by the anion ordering leads to zone folding in which ir-inactive zone-boundary phonons are folded back to the origin and some become ir active. This is the cause of the shoulders in the ReO_4 and the multiplets in the BF_4 spectra. The "30-cm^{-1}" feature would appear to be a zone-boundary acoustic phonon activated in this manner. It must couple very strongly with the electrons to have such a large oscillator strength. Above the anion-ordering transition, absorption would occur due to defect-induced one-phonon processes[35] along the entire phonon branch, proportional to the density of states. This would explain the sudden increase in width above the transition temperature and the apparent downward shift in wave number. As the temperature and disorder increase, longer-wavelength phonons will contribute. The integrated intensity should be constant above and below the anion-ordering temperature T_{AO}, since the absorption mechanism is unchanged, only the way in which momentum is conserved being different. Since the feature occurs near the same wave number for each compound, the zone-boundary (Z.B.) acoustic phonon would involve only the TMTSF molecules. We show in Fig. 15 the dispersion curves for a simple linear-chain model with a three-ion basis. The eigenvectors of the zone-boundary acoustic-phonon mode are shown in the figure and involve only the TMTSF molecules. If this is indeed the case, one would expect the "30-cm^{-1}" features to show at least a 1.3% decrease in frequency upon deuteration (see Table I). All three features, however, showed no downward shift at all, and the perchlorate feature actually increased by $(0.5\pm0.3)\%$. On the other hand, two of the regular perchlorate lattice modes had frequency shifts of 0% and an increase of $(0.6\pm0.2)\%$, respectively. Thus it would appear that a change in force constant is offsetting the mass increase. This is probably due to the shorter hydrogen bond upon deuteration, which contracts the lattice.

Transverse-acoustic (TA) phonons are known to be greatly affected by, and to play a role in, the superconductivity of simple metals. In niobium,[36] the [001] transverse-acoustic-phonon frequency *decreases* upon cooling, as opposed to the usual increase, throughout the range from room temperature to T_c, and decreases further on passing through T_c. The width of TA phonons with energy less than the superconducting gap is much narrower than that when their energy is above the gap, due to the lack of relaxation via normal electrons. We feel that Ng and Timusk observed an effect of the magnetic field on the electrons to which the phonon is coupling for its oscillator strength, and/or the electrons to which it is coupling when it relaxes. Whether this involves a superconducting gap, or normal electrons, is not clear.

Two final points may be made of the spectra in Fig. 12. One can see that the shift in frequency of the regular lattice phonons down from 65—80 cm^{-1} in the ClO_4 and BF_4 spectra to 40—55 cm^{-1} in the perrhenate spectrum is greater than the shift seen in Fig. 6 with the octahedral anions. The tetrahedral anion is therefore playing a greater role in these lattice phonons. The extra structure between 40 and 60 cm^{-1} in the BF_4 compound is either the superlattice activation of higher-energy, acoustic, zone-boundary phonons due to the larger superlattice unit cell of the BF_4 compound compared with the ClO_4 compound, bringing in phonons in other directions, or it is the sudden appearance of features with $\mathbf{E}||\mathbf{a}$, which can be seen due to the formation of the semiconducting gap. Similar comments apply to the 70- and 80-cm^{-1} structures in the ReO_4.

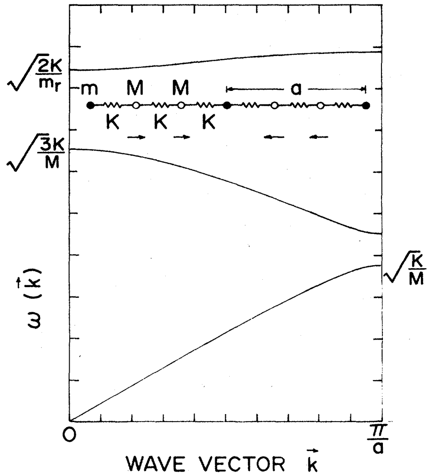

FIG. 15. Frequency dispersion curves for a simple linear-chain model with a three-molecule basis. The anions are represented by the mass m while the TMTSF molecule is represented by the mass M. The curves are drawn for $M=2m$. Equal force-constant springs join the masses. The reduced mass m_r is given by $(1/m+1/2M)^{-1}$. The eigenvectors for the zone-boundary acoustic phonon are indicated by arrows in the sketch.

CONCLUSION

The far-infrared powder spectra of $(TMTSF)_2X$, where $X=PF_6$, AsF_6, and SbF_6, are very similar and have been analyzed in terms of three normal lattice modes and one internal mode. The spectra of $(TMTSF)_2X$, where $X=ClO_4$, BF_4, and ReO_4, are quite different and involve sharp activated structure below the anion-ordering temperature. These additional sharp features are interpreted as the result of zone folding, due to the superlattice formed in the anion-ordered state, which activates previously inactive zone-boundary phonons. In particular, a feature common to all three compounds around 30 cm^{-1} is thought to be a transverse-acoustic zone-boundary phonon, which couples very strongly with the electrons. It is this absorption which was found to be sensitive to magnetic field in the perchlorate.

ACKNOWLEDGMENTS

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