LBL-15279

Conf-821226--2

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

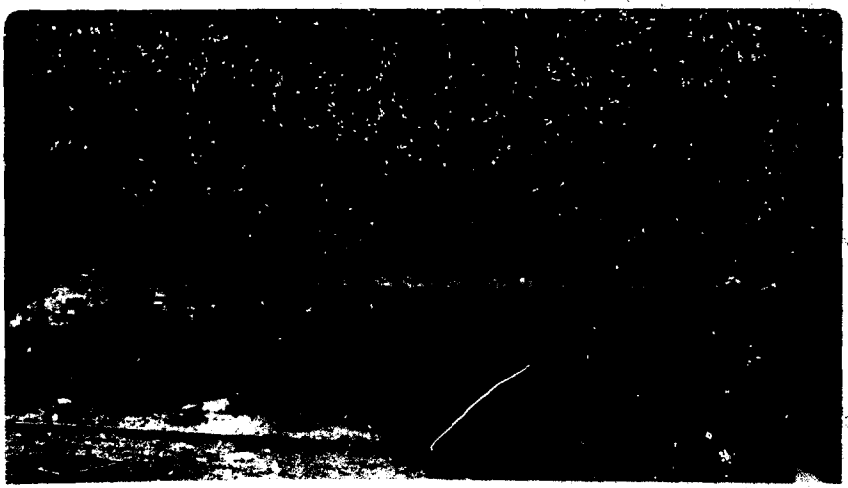
Materials & Molecular
Research Division

Presented at the International Conference on
Low Dimensional Conductors and Superconductors,
Les Arcs, France, December 12-18, 1982; and
to be published in Les Editions de Physique

# FAR-INFRARED PROPERTIES OF $(TMTSF)_2ClO_4$

W.A. Challener, P.L. Richards, and R.L. Greene

January 1983



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL--15279

DE83 009142

# FAR-INFRARED PROPERTIES OF $(TMTSF)_2ClO_4$

W.A. Challener and P.L. Richards

University of California
and
MMRD, Lawrence Berkeley Laboratory,
Berkeley, California 94720

and

R.L. Greene
IBM Research
San Jose, CA

January 1983

## DISCLAIMER

Résumé - La réflectance de $(TMTSF)_2 ClO_4$ a été mesurée entre 4 et 40 $cm^{-1}$. A 2K deux pics étroits sont observé à 7 et 29 $cm^{-1}$. Entre 2K et 80K l'intensité des pics diminue mais leur frequence ne change pas. Sous irradiation de rayons X l'intensité des pics diminue également. Un champ magnétique (jusqu'à 40 kOe) appliqué le long de l'axe c* ne change pas le pic à 29 $cm^{-1}$. Ces experiénces suggérent que les pics proviennent des vibrations moléculaires couplées aux électrons. Ces experiénces sont incompatibles avec l'interprétation expliquant l'origine /1/ du pic à 29 $cm^{-1}$ par un pseudogap supraconducteur.

Abstract - The far-infrared properties of $(TMTSF)_2 ClO_4$ have been measured for frequencies between 4 and 40 $cm^{-1}$. At 2K, phonon-like peaks in reflectance are seen at 7 and 29 $cm^{-1}$. Increasing the temperature to 80K causes these peaks to gradually disappear, but not to shift appreciably in frequency. Radiation-induced defects substantially reduce the height of the 29 $cm^{-1}$ peak. Experiments at 2.3K and 4.2K show no change in the 29 $cm^{-1}$ peak with a magnetic field of up to 40 kG applied parallel to the c*-axis. These results suggest a coupled electronic-molecular vibration origin for these features. They are incompatible with the recently proposed /1/ interpretation of the 29 $cm^{-1}$ feature as a quasi-one-dimensional superconductive pseudogap.

## Introduction

The charge-transfer compound $(TMTSF)_2 ClO_4$ is the first organic conductor which becomes superconducting at ambient pressure (with $T_c \sim 1K$). Because of the unusual properties of this, and related salts based on the TMTSF complex, the nature of the highly conducting metallic state above $T_c$ is still a matter of controversy. One hypothesis /2/ suggests the picture of highly mobile carriers with a two-dimensional band structure, while an alternate viewpoint /3/ suggests a form of quasi-one-dimensional superconductivity.

In order to examine these questions we have made far infrared (FIR) measurements on samples of $(TMTSF)_2 ClO_4$ grown at IBM. We used a conventional Michelson Fourier transform spectrometer with mylar beamsplitters and a composite doped-Ge bolometer operated at 1.2K. The experimental apparatus has been described in detail elsewhere /4/. Reflectance measurements were made on a 0.5 $cm^2$ mosaic of about ten optically aligned fibers. The fibers were attached to a sheet of black epoxy resin with vacuum grease to insure good thermal contact. This in turn was cemented to a rotatable brass sample wheel. A carbon resistor and heater attached to the wheel were used to monitor and control the sample temperature. The entire assembly was located in an evacuable chamber in a liquid helium bath so that the sample temperature could be varied from 2K to over 100K. The radiation was incident at 7.5° from the normal. The spectra were normalized by using a brass reflector which could be rotated into the sample position.

Transmittance measurements were made on a similar sample mosaic. In this case, fibers were attached with vacuum grease to a copper grid polarizer on a mylar substrate. The fibers were oriented perpendicular to the polarizer grid so that a crossed-grid arrangement was produced /1/. In this way the E-field of the transmitted light was forced by the copper grid to be parallel to the fiber axis of the $(TMTSF)_2 ClO_4$. Fibers were placed in contact with each other to minimize light leakage. The average transmittance of the sample from 4 to 40 $cm^{-1}$ was about 3%. The grid constant of the copper polarizer was 3.8 μm and the mylar substrate had a thickness of 4 μm. Both of these dimensions are much less than the wavelengths of the FIR radiation involved. Fiber dimensions, on the other hand, as well as random inter-fiber spacings were comparable to the FIR wavelengths, so interference structure was observed which could be removed by computing ratios of spectra measured at different temperatures or magnetic fields.

The transmittance sample was mounted in an evacuable chamber inside a superconducting magnet and its temperature could be varied from 2.3K to over 100K. A carbon resistor attached to the brass light pipe surrounding the sample monitored the sample temperature. Exchange gas was used to obtain the lowest temperatures (below 20K) and to insure good thermal contact between the sample and thermometer. The magnetic field was oriented perpendicular to the broadest face of the crystal fibers, which was thought to be parallel to the c*-axis for most of the fibers in the mosaic.

## Data

The initial FIR reflectance measurements /5/, made as a function of temperature, showed phonon-like peaks at 7 and 29 $cm^{-1}$ (0.9 and 3.6 meV) which were present at and below 60K (Fig.1). The reflectance peaks had widths of 3 to 5 $cm^{-1}$ fwhm with

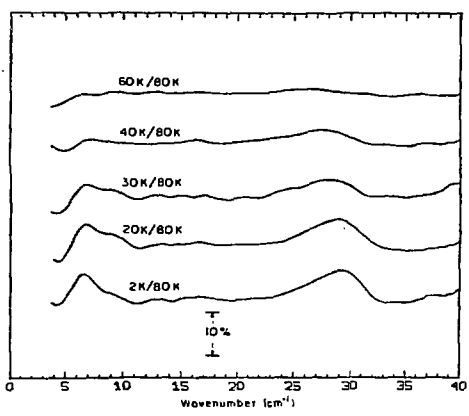



Fig. 1 - FIR reflectance vs. temperature of $(TMTSF)_2 ClO_4$, showing peaks at 7 and 29 $cm^{-1}$.

peak heights at 2K of 8% of the background reflectance. Above 20K the peaks gradually disappeared. A sample-in/sample-out normalization procedure determined definitely that the peaks were present at low temperatures, rather than at high temperatures (a fact which cannot be established from ratios of spectra measured at different temperatures).

In order to search for magnetic field dependence, the transmittance of the $(TMTSF)_2$ $ClO_4$ sample with the crossed-grid arrangement was first measured at high temperatures (above 40K). The sample was then cooled to liquid helium temperatures, and its transmittance measured again, thereby verifying the presence of the 29 $cm^{-1}$ feature in the low temperature spectrum. With the sample still at this temperature, magnetic fields of 2 to 40 kG were applied parallel to the c*-axis of the fibers, and the transmittance of the sample was re-measured. Finally, the transmittance of the sample was measured in zero magnetic field, after warming the sample above 40K. The results of one such experiment are shown in Fig. 2. In this case, the sample was cooled at 0.3K/min from 40K to 15K, before cooling more quickly to 2.3K. To the limit set by the noise level (~1%) there is no change in the 29 $cm^{-1}$ feature in an applied field of 10 kG. A similar null result was found in applied fields of 2, 10 and 40 kG with the sample at 4.2K after quenching from 77K in about one minute.

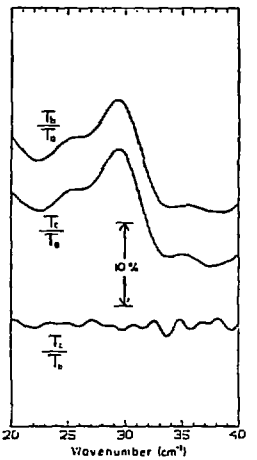



Fig. 2 - FIR transmittance ratios, showing no effect of magnetic field on the 29$cm^{-1}$ feature. $T_a$ is a transmittance spectrum at ~80K in zero applied field. $T_b$ is a transmittance spectrum at 2.3K in zero applied field. $T_c$ is a transmittance spectrum at 2.3K with a 10kG field applied parallel to the c*-axis of the crystals.

After cycling these samples many times in temperature, the height of the 29 $cm^{-1}$ reflectance peak was found to decrease substantially. This was possibly a result of surface degradation. However, no significant change in peak height with temperature cycling was found in transmittance experiments using the $(TMTSF)_2 ClO_4$ sample with the crossed-grid arrangement.

The effect of x-ray induced defects upon the 29 $cm^{-1}$ reflectance peak was also studied (Fig. 3). Measurements were made of the reflectance of virgin crystals, crystals with ~100 ppm defects, and crystals with ~1000 ppm defects. For virgin crystals the 29 $cm^{-1}$ feature had a peak height of 8% at 2K. With ~100 ppm defects, the peak height was only 3%. With ~1000 ppm defects, the peak was unobservable above the noise level of 1%.

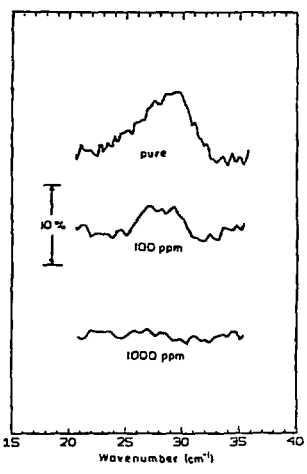



Fig. 3 - FIR reflectance vs. radiation-induced defects for samples with 0, ~100, and ~1000 ppm defects, showing the effect on the 29 $cm^{-1}$ feature.

Analysis

A Kramers-Kronig analysis of the FIR reflectance of $(TMTSF)_2 ClO_4$ reveals sharp peaks in $Re(\sigma)$ centered at 7 and 29 $cm^{-1}$ with magnitudes of ~1000 and ~7000 $(\Omega cm)^{-1}$ and widths of 1 and 2 $cm^{-1}$ respectively, depending somewhat upon the high frequency extrapolation chosen for the reflectance. Such strong, sharp modes are typical of coupled electron-molecular vibrational modes found in the IR spectra of many organic charge transfer compounds. Examples include $(TMTSF)_2 ReO_4$, $(TMTTF)_2 PF_6$, and possibly $(TMTSF)_2 PF_6$ /6/. However, the low frequency of these modes in $(TMTSF)_2 ClO_4$ is unusual. The enormous oscillator strength of these modes is essentially electronic in origin /7,8/. The electron-phonon coupling in $(TMTSF)_2 ClO_4$ which gives rise to strongly IR-active modes is possibly a result of the dimerization /8,9/ of this compound. Since an onset of $Re(\sigma)$ with increasing

frequency would be expected for a superconducting pseudogap, the observed sharp peaks do not support the hypothesis of fluctuational superconductivity.

Radiation-induced defects are known to have a strong effect upon the electronic properties of $(TMTSF)_2 ClO_4$ and related salts. For example, a defect concentration of 100 ppm in $(TMTSF)_2 PF_6$ is sufficient to suppress the superconducting transition from 1K to below 20 mK, and at 1000 ppm defects, the spin density wave transition at 12K is suppressed /10/. Similar sensitivity to radiation damage might be expected for other electronic effects. It is not surprising, therefore, that defects suppress the 29 $cm^{-1}$ feature, which is largely electronic in origin.

An experiment /1/ very similar to the magnetotransmittance experiment described here did show a magnetic field dependence for the 29 $cm^{-1}$ feature, in contrast to our results. Several differences exist between these two experiments which may explain the different results. These include the sample temperature which was somewhat lower (1.2K to 2K compared with $T_c \sim 1K$) /1/, the rate of cooling (which has been found to have a significant effect upon the superconducting transition temperature /11/ and the appearance of a magnetic state below ~3.5K /12/), or in the samples themselves, which come from different sources. Aside from the field effect, most other results of the two experiments are in good qualitative agreement /10/.

## Conclusions

Reflectance measurements of $(TMTSF)_2 ClO_4$ between 4 and 40 $cm^{-1}$ reveal peaks at 7 and 29 $cm^{-1}$ at low temperatures. The peaks gradually disappear with increasing temperature above 20K, but are still evident up to 60K.

Radiation-induced defects suppress the 29 $cm^{-1}$ reflectance peak. A defect concentration of 1000 ppm is sufficient to reduce the peak height by more than an order of magnitude.

Magnetotransmittance measurements of the 29 $cm^{-1}$ feature at 2.3K and 4.2K show no magnetic field dependence.

A Kramers-Kronig analysis of the reflectance reveals strong, narrow peaks in $Re(\alpha)$ at 7 and 29 $cm^{-1}$. These are believed to be electron-molecular vibration coupled modes. The shape, strength and field independence of these features do not support an interpretation in terms of a superconducting pseudogap.

## Acknowledgments

Work supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and by the Office of Naval Research.

## References

(1) NG (H.K.), TIMUSK (T.), DELRIEU (J.M.), JÉROME (D.), BECHGAARD (K.), FABRE (J.M.) *J. Phys. Lett., 1982,* 43, L513.

(2) GREENE (R.L.), HAEN (P.), HUANG (S.Z.), ENGLER (E.M.), CHOI (M.Y.), CHAIKIN (P.M.), *Mol. Crys. Liq. Crys., 1982,* 79, 183.

(3) JÉROME (D.), SHULZ (H.J.), *Adv. in Phys., 1982,* 31, #4, 299.

(4) AURBACH (R.), Ph.D. Thesis, U. of Calif., Berkeley, 1975.

(5) GREENE (R.L.), CHALLENER (W.A.), RICHARDS (P.L.), *Bull. Am. Phys. Soc., 1982,* 27, #3, 641.

(6) JACOBSEN (C.S.), TANNER (D.B.), BECHGAARD (K.), *Mol. Crys. Liq. Crys., 1982,* 79, 25.

(7) RICE (M.J.), *Phys. Rev. Lett., 1976,* 37, #1, 36.