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FAR INFRARED RESPONSE OF $(TaSe_4)_2I$:

OBSERVATION OF THE CHARGE DENSITY WAVE OPTICAL PHASON

M. S. Sherwin* and A. Zettl

Department of Physics, University of California, Berkeley, Berkeley, California 94720

P. L. Richards

Department of Physics, University of California,
and Materials and Molecular Research Division,
Lawrence Berkeley Laboratory, Berkeley, California 94720

Abstract:

We report measurements of the far infrared (FIR) reflectance of the charge density wave (CDW) conductor $(TaSe_4)_2I$. In the CDW state, and for incident electric field polarized parallel to the crystal chain direction, the associated FIR conductivity shows a giant resonance at 38 cm^{-1}. We identify this mode with the CDW optical phason.

Over 30 years ago, Fröhlich[1] proposed a novel mechanism for charge transport in a coupled electron-phonon system having undergone a Peierls transition: a displacement of the phase of the charge density wave (CDW). The field of CDW dynamics has been an area of vigorous research since 1976 , when nonlinear DC conductivity was first observed in $NbSe_3$ and attributed to a sliding CDW Fröhlich mode[2]. More recent microwave studies[3,4] of the CDW materials $NbSe_3$, TaS_3 and $(TaSe_4)_2I$ have found a resonance in the ac conductivity, and this resonance has been attributed to the excitation of the pinned q=0 acoustic phason, first predicted by Lee, Rice and Anderson (LRA)[5] . In the past it has been assumed that, at frequencies above this resonance, the response spectrum would be rather featureless (with the exception of low-lying phonon modes) until normal carriers are excited across the Peierls gap at $h\nu=2\Delta$.

In this letter, we report measurements of the far infrared (FIR) conductivity of $(TaSe_4)_2I$ parallel to the crystal chain direction (c axis), in the frequency range[7] 8 to 350 cm^{-1}. We find a giant peak in the conductivity at 38 cm^{-1}, which is roughly 40 times larger than the frequency of the microwave resonance[4] and 50 times smaller than the frequency of the Peierls gap[6,7] associated with $(TaSe_4)_2I$. The FIR peak has approximately 80 times the oscillator strength of the microwave peak associated with the pinned phason mode. The temperature dependence of the FIR peak indicates that it is associated with the condensation of the CDW. We argue that the phason branch of the CDW dispersion must in fact be split into an acoustic and an optical branch, and we interpret the FIR peak as arising from the excitation of the q=0 *optical* phason. Based on the phason dispersion relation derived by LRA[5], we estimate that this optical phason should be observed near 39 cm^{-1}, consistent with our experimental results.

We have grown single crystals of $(TaSe_4)_2I$ (tetragonal space group) by conventional vapor transport techniques. The CDW transition temperature, determined from dc

resistivity measurements on crystals from the same preparation batch, was T_p=265K. Typical face sizes of the crystals used for our FIR studies were 5mm along the c axis and 2mm along the a axis . Several crystals were carefully oriented on both principal axes and mounted on a stycast epoxy plug to form a mosaic which covered roughly 70% of the area of a 1 cm diameter disk. The sample was placed in a continuous transfer Helium cryostat adapted in our laboratory for use with a Michelson Fourier spectrometer to measure polarized reflectance. Incident FIR radiation was polarized using a wire grid polarizer and reflected radiation was detected using a low noise composite bolometer operated at 1.5K. The sample temperature was varied from 10 K to room temperature, and reflectance was measured from 8 to 350 cm^{-1}. At each fixed sample temperature, the sample spectrum was normalized to that of a polished brass plug. After all data had been measured, gold was evaporated onto (only) the crystal faces of the mosaic and the reflectance of the sample was again normalized to that of the brass. This allowed correction for any non planar geometry of the composite sample. The details of the experimental technique will be described elsewhere[8].

Reflectance curves for $(TaSe_4)_2I$ at various temperatures, for radiation polarized parallel to the c axis, are presented in Fig.1. At room temperature the reflectance is high and fairly featureless except for a slow decrease with increasing frequency from .9 at 30 cm^{-1} to .7 at 300 cm^{-1}. The precursor of a low temperature peak at 143 cm^{-1} is evident. As the sample is cooled through T_p=265 K, the reflectance between 30 and 90 cm^{-1} begins to increase, and the drop in the reflectance near 100 cm^{-1} begins to sharpen. As the sample is cooled further, this drop develops into an extremely sharp edge, with the reflectance at 110K dropping from near unity at 92 cm^{-1} to .2 at 96 cm^{-1}. Two smaller peaks appear between 140 and 200 cm^{-1}. The reflectance changes little between 110K and 10 K. Fig. 2 (solid line) shows the measured reflectance at 10K. The reflectance rises from .9 at low

frequencies to near unity at 40 cm^{-1} and remains near unity until 95 cm^{-1}, with the exception of a small dip at 79 cm^{-1}. At frequencies beyond the reflectance edge, two sharp peaks are evident, at 143 and 190 cm^{-1}. Above 200 cm^{-1} the reflectance slowly rises with increasing frequency and then levels off, with no sharp features.

Reflectance was also measured perpendicular to the c axis in $(TaSe_4)_2I$ at various temperatures above and below T_P. As expected for this quasi one-dimensional material, the perpendicular spectrum shares no common features with the parallel spectrum described above. The perpendicular reflectance data will be presented elsewhere[8].

The pattern of a rise in the reflectance from .9 at 20 cm^{-1} to near unity above 40 cm^{-1} followed by a reflectance edge suggests the presence of a mode with a giant oscillator strength in the region between 25 and 50 cm^{-1}. The other peaks in the spectrum (for example at 143 and 190 cm^{-1}) indicate modes with smaller oscillator strength. In order to extract the complex dielectric function $\epsilon=\epsilon_1+i\epsilon_2$ from the reflectance data, we have fitted the reflectance to a model with 4 Lorentz oscillators and a background dielectric constant ϵ_∞:

$$\epsilon_1(f)=\epsilon_\infty + \Sigma_n \frac{S_n[1-(f/f_{0n})^2]}{\{[1-(f/f_{0n})^2]^2+f^2/f_{0n}^4\tau_n^2\}} \qquad (1)$$

$$\epsilon_2(f)=\Sigma_n \frac{(S_n/f_{0n}\tau_n)f/f_{0n}}{\{[1-(f/f_{0n})^2]^2+f^2/f_{0n}^4\tau_n^2\}} \qquad (2)$$

where f is the frequency, f_{0n} is the resonant frequency of the nth mode in the model, the oscillator strength of the nth mode is $S_n(2\pi f_{0n})^2$, and τ_n is the damping time of the nth mode.

The dashed line in Fig. 2 shows the reflectance fit computed from ϵ using the fitting parameters listed in Table 1. The computed reflectance is sensitive to the chosen parameters of Table 1. For example, changes in the parameters of the 38 cm^{-1} mode

of only 5% visibly degrade the quality of the fit.

Fig 3 shows ϵ_1 and ϵ_2 calculated from Eqs. 1 and 2 using the fitting parameters of Table 1. The peak values of the conductivity arising from each mode are also presented in Table 1. As is apparent from Fig. 3, ϵ_2 (and hence the conductivity) is dominated by a giant peak centered at 38 cm^{-1}. We shall consider this strong mode in detail shortly. The weaker modes at 79, 143 and 190 cm^{-1} are most probably associated with low lying phonon modes[9]. At frequencies much less than the 38 cm^{-1} resonance peak, ϵ_1 of Fig. 3 is approximately equal to 600, consistent with the high reflectance at low FIR frequencies. Between 38 and 96 cm^{-1}, the dielectric constant is negative, giving rise to the near unit reflectance in this frequency range. The small dip at 79 cm^{-1} results from the weak (phonon) mode at that frequency. At 96 cm^{-1}, the dielectric constant crosses the real axis, leading to the sharp reflectance edge observed in Fig. 2.

In the remainder of this paper we present a model to explain the origin of the giant peak in the conductivity at 38 cm^{-1}. The temperature dependence of this peak indicates that it is associated with the formation of the CDW, but its frequency marks it as quite distinct from the pinned phason mode at 1 cm^{-1} or the Peierls gap at 2000 cm^{-1}.

The dispersion relation for the CDW as calculated by LRA[5] predicts both an optical branch, the amplitudon, which consists of excitations of the amplitude of the CDW and is Raman active[9], and an infrared active acoustic or phason branch which describes excitations of the phase of the CDW. The dispersion relation for the phason is, in the absence of pinning and for long wavelengths[5],

$$\Omega_-(q)^2=(m/m^*)(v_F q)^2 \qquad (3)$$

where Ω_- is the phason frequency, m is the electronic band mass, m* the Fröhlich mass, v_F the Fermi velocity, and q the wavevector of the excitation. Because of impurity pinning, the phason frequency is not zero at q=0. The 1 cm^{-1} mode in $(TaSe_4)_2I$ has been identified as

the pinned acoustic phason[4]. The frequency of that mode increases with increasing sample impurity concentration, as expected for the pinned acoustic phason[10]. The giant conductivity mode observed in Fig. 3 is at a frequency approximately 40 times that of the pinned acoustic phason, and contains nearly 80 times the oscillator strength of the acoustic phason, as determined by the fitting parameters S and f_0 for the two modes[8].

The origin of the 38 cm^{-1} mode in $(TaSe_4)_2I$ may be understood as follows. In any crystal containing a CDW, the electronic density is modulated with a wavevector $2k_F$. This modulation gives rise to local electric dipoles. Hence, similar to the q=0 optical phonon mode in an ionic crystal, the phason mode with wavevector $2k_F$ will be very strongly coupled to the electric field. Since there is a static distortion with wavevector $2k_F$, the Brillouin zone for the CDW (ignoring the periodicity of the lattice) extends only from $-k_F$ to k_F, and acoustic phason modes with $k_F<q<2k_F$ are mapped onto an *optical branch of the phason*. Consequently, $2k_F$ maps onto k=0; clearly, a long wavelength electromagnetic wave can excite this mode associated with the static charge distortion. We hereafter call this mode the optical phason. Walker has predicted a related first harmonic phason[11].

Given the complicated nature of the phonon spectrum of $(TaSe_4)_2I$, it is difficult to accurately estimate the frequency of the optical phason. We may obtain a crude estimate by modifying Eq. 3 to include dispersion at the zone boundary. If we fit a sinusoidal dispersion relation to Eq. 3 at low frequencies, we find $\Omega_{-optical}(0)=(2/\pi)\Omega_-(2k_F)$. Assuming that $2k_Fv_F=(2\pi^2/\lambda^2)h/2\pi m$, where λ is the CDW wavelength ≈ 14 Å[12], h is Planck's constant, and taking $m\approx$ free electron mass and the microwave value[4] of $10^4 m$ for m^*, we find $\Omega_{-optical}(0)/2\pi=39$ cm^{-1}, which is remarkably close to the observed value.

The optical phason can be further analyzed using the theoretical framework developed

for the optical modes of ionic crystals. Ignoring the crystal lattice, the CDW in $(TaSe_4)_2I$ can be approximately treated as a diatomic crystal with positive and negative charges separated by $\lambda/2$. The point at which the reflectance rises to near unity at 38 cm^{-1} and the reflectance edge at 95 cm^{-1} are then respectively the TO and LO modes of the optical phason. As is clear from Figs. 3, the optical constants are dominated by the optical phason resonance at 38 cm^{-1}. The characteristics that distinguish the optical phason in $(TaSe_4)_2I$ from most optical phonons are its low frequency and giant oscillator strength. For example, the *lowest* TO frequency for an alkali halide crystal is 65 cm^{-1} for CsI, and for that resonance[9] S=4, compared with S=500 for the optical phason resonance (Table 1).

The giant oscillator strength of the optical phason can be understood to arise from the delocalized nature of the condensed electronic states in a CDW. An analogy may be drawn between the CDW and electrons weakly bound to ionic cores in IV-VI compounds. In SnTe, for example, a FIR resonance due to an optical phonon with TO frequency 26 cm^{-1}, LO frequency 139 cm^{-1} and S=1240 is observed[14]. Similar effects are not found in the alkali halides, where the electrons are in nearly atomic orbitals. The weak binding of electrons in IV-VI compounds means small ionic motion may be accompanied by a much larger readjustment of the electronic charge density, leading to a large oscillator strength. This large electronic polarizability is parameterized by a transverse effective charge[15] $e^*_T \equiv (\pi MS/N)^{1/2}\nu_{TO}$, where M is the mode mass, ν_{TO} is the TO mode frequency, and N is the density of oscillators. In the case of SnTe, $e^*_T \approx 8e$, where e is the bare electronic charge[14].

A similar effective charge parameterization should apply to the optical phason of the CDW[16]. However, in the absence of a theory valid for an incommensurate CDW, it is not clear how to assign a value for the mode mass M and thus it is difficult to estimate e^*_T. For a very rough estimate, if we assume the CDW to have the periodicity of

the unit cell[12], and for M we assume half the mass of the unit cell (which is equivalent to assuming all the atoms are participating equally in the oscillation), then $e^*_T \approx 70e$ for each of the 2 conduction electrons in the unit cell. This large value for the effective charge suggests a large oscillator strength for the optical phason, as observed in $(TaSe_4)_2I$.

The optical phason should be present in all CDW materials, and indeed our results have important implications with respect to ac conductivity studies of other CDW systems. FIR measurements have previously been performed on $NbSe_3$[17] and $K_{.3}MoO_3$[18]. In these materials, a reflectance edge with a temperature and frequency dependence very similar to that in Fig. 1 has been attributed to the pinned *acoustic* phason. This identification has been controversial. In $K_{.3}MoO_3$, for example, both a strong FIR mode[18] at 22 cm^{-1} and a radio-microwave resonance[19] have been interpreted as the pinned phason. A similar problematic interpretation occurs for $NbSe_3$ FIR [17] and microwave[3] data. We suggest that the FIR reflectance edges observed in these materials should be identified with the optical phason.

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Table 1

f_0 (cm^{-1})	$f_0\tau$	S	$\sigma(f_0)$ (Ohm^{-1}-cm^{-1})
38	13	500	4100
78	25	1.5	49
149	50	2.5	297
194	50	4	633

Table 1: Parameters of Eqs. 1 and 2 used for the fit to the reflectance of $(TaSe_4)_2I$ at 10K (Fig. 2) and the determination of the associated dielectric function (Fig. 3.). $\sigma(f_0)$ is the conductivity at f_0 arising from the resonance at f_0

FIGURE CAPTIONS

Fig. 1. Reflectance of $(TaSe_4)_2I$ at selected temperatures.

Fig. 2. Reflectance of $(TaSe_4)_2I$ at 10 K (solid line) and oscillator fit (dashed line) to that reflectance calculated from the parameters of Table I.

Fig. 3. Complex dielectric function $\epsilon = \epsilon_1 + i\epsilon_2$ for $(TaSe_4)_2I$ at 10K, as determined by the oscillator fit to the reflectivity. Both ϵ_1 and ϵ_2 are flat and featureless between 250 and 400 cm^{-1}.

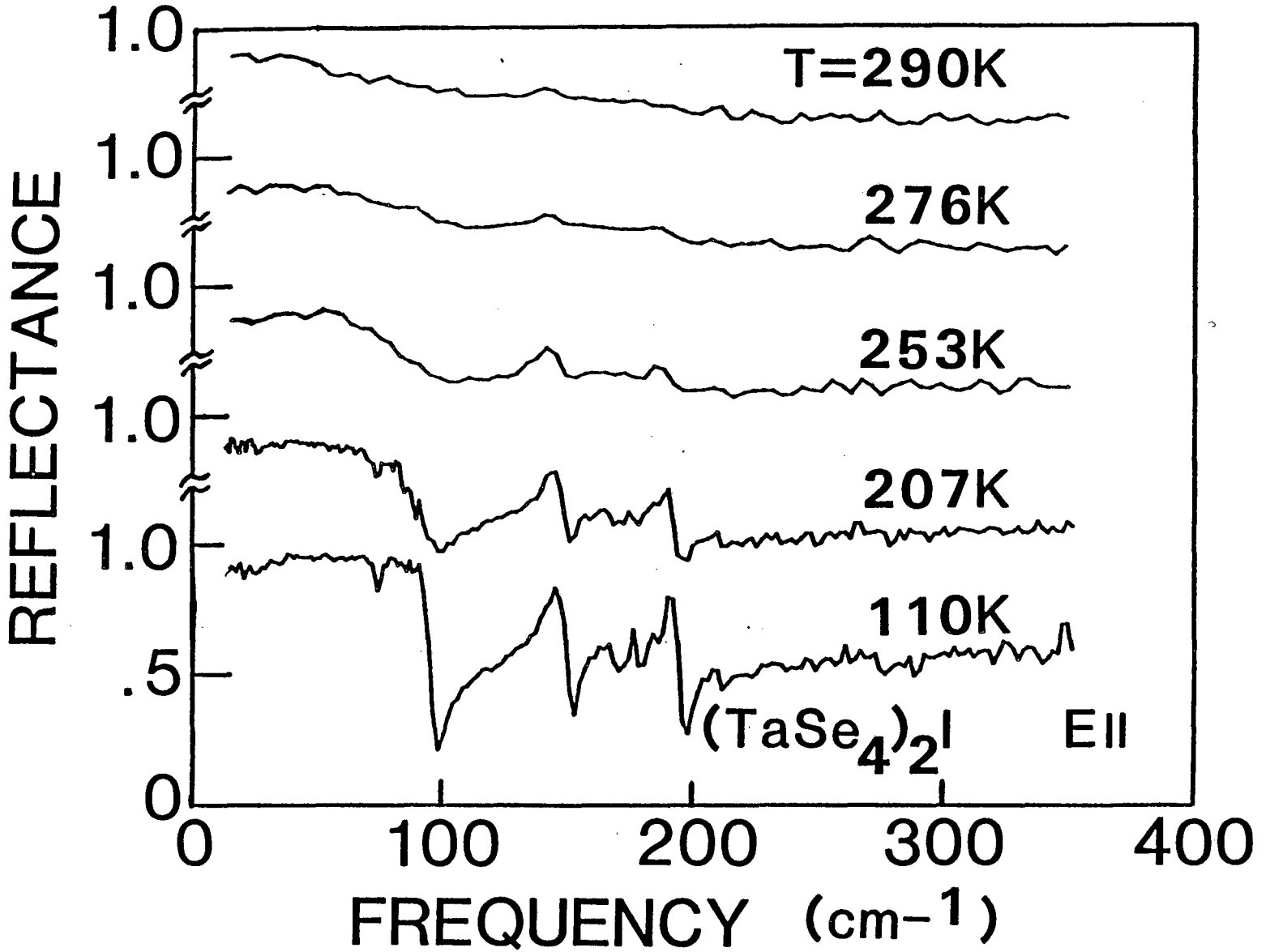
REFLECTANCE
1.0
1.0
1.0
1.0
1.0
.5
0
T=290K
276K
253K
207K
110K
(TaSe4)2I
E∥
0
100
200
300
400
FREQUENCY (cm-1)

Figure 1

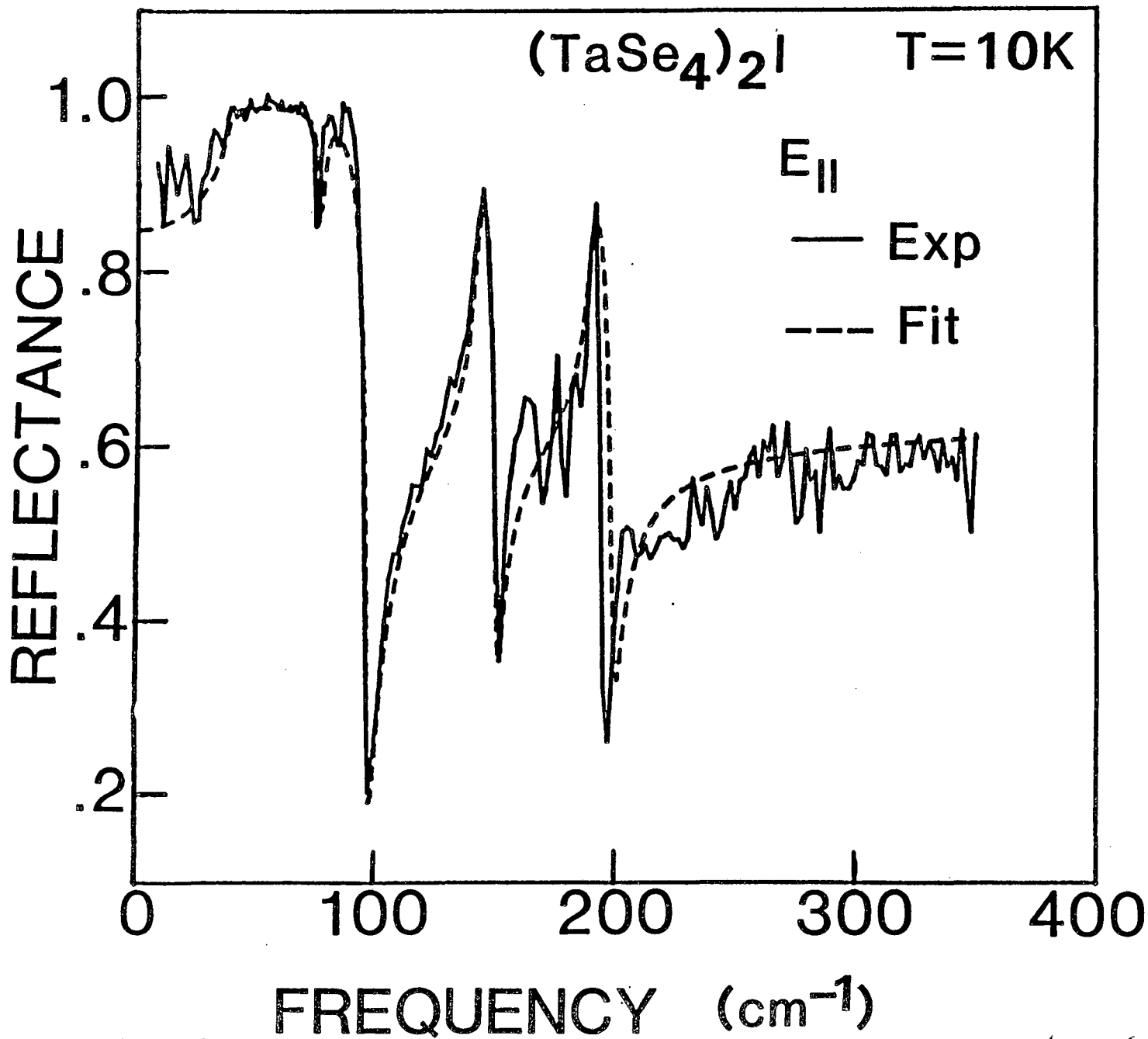
(TaSe4)2I
T=10K
E||
Exp
Fit
REFLECTANCE
1.0
.8
.6
.4
.2
0
100
200
300
400
FREQUENCY (cm-1)

Figure 2

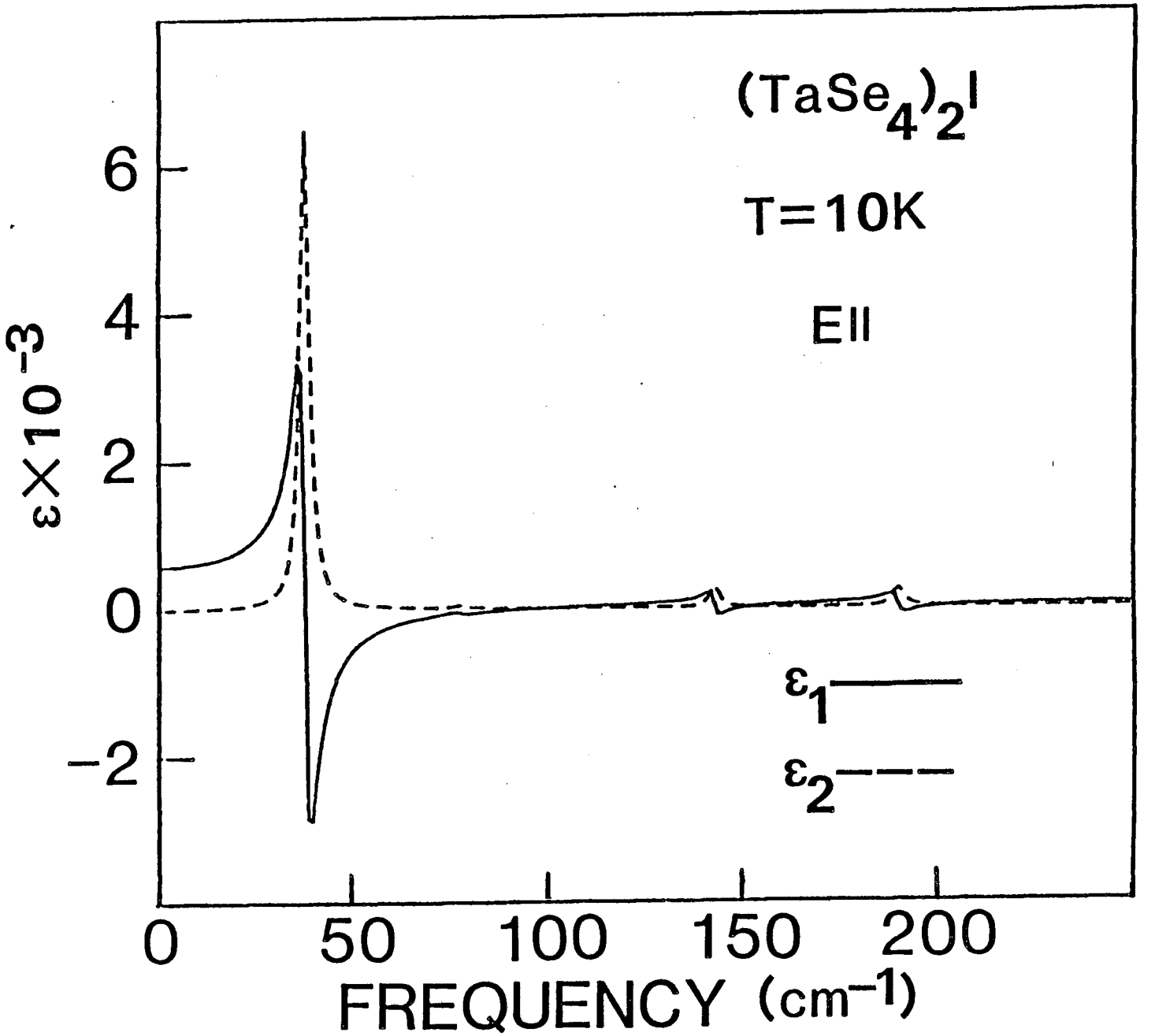

Figure 3

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