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Infrared Reflectivity of Paratellurite, TeO₂†

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The polar-phonon spectrum of paratellurite has been obtained from polarized infrared reflectivity at 295 and 85 °K. The eight E and four A_2 modes are identified; the mode frequencies, oscillator strengths, and dampings are determined from a dispersion analysis of the data. The anisotropic frequencies of the coupled A_2 and E modes for oblique phonons in the extraordinary ray are also presented.

The polar-phonon spectrum of paratellurite has been obtained from the polarized infrared reflectivity at 295 and 85 °K. Paratellurite is a tetragonal, D_4^4, form of TeO_2 with four formula units in the elementary cell.[1] The zone-center optical phonons have the symmetries $4A_1 + 4A_2(z) + 5B_1 + 4B_2 + 8E(x, y)$, of which the infrared-active

branches are labeled with their polarizations where z is parallel to the crystal c axis. All of these lattice-mode symmetries are Raman active except for the pure $A_2(z)$ phonons. In this paper the eight E and four A_2 modes are identified; and the mode frequencies, oscillator strengths, and dampings are determined from a dispersion analysis of the
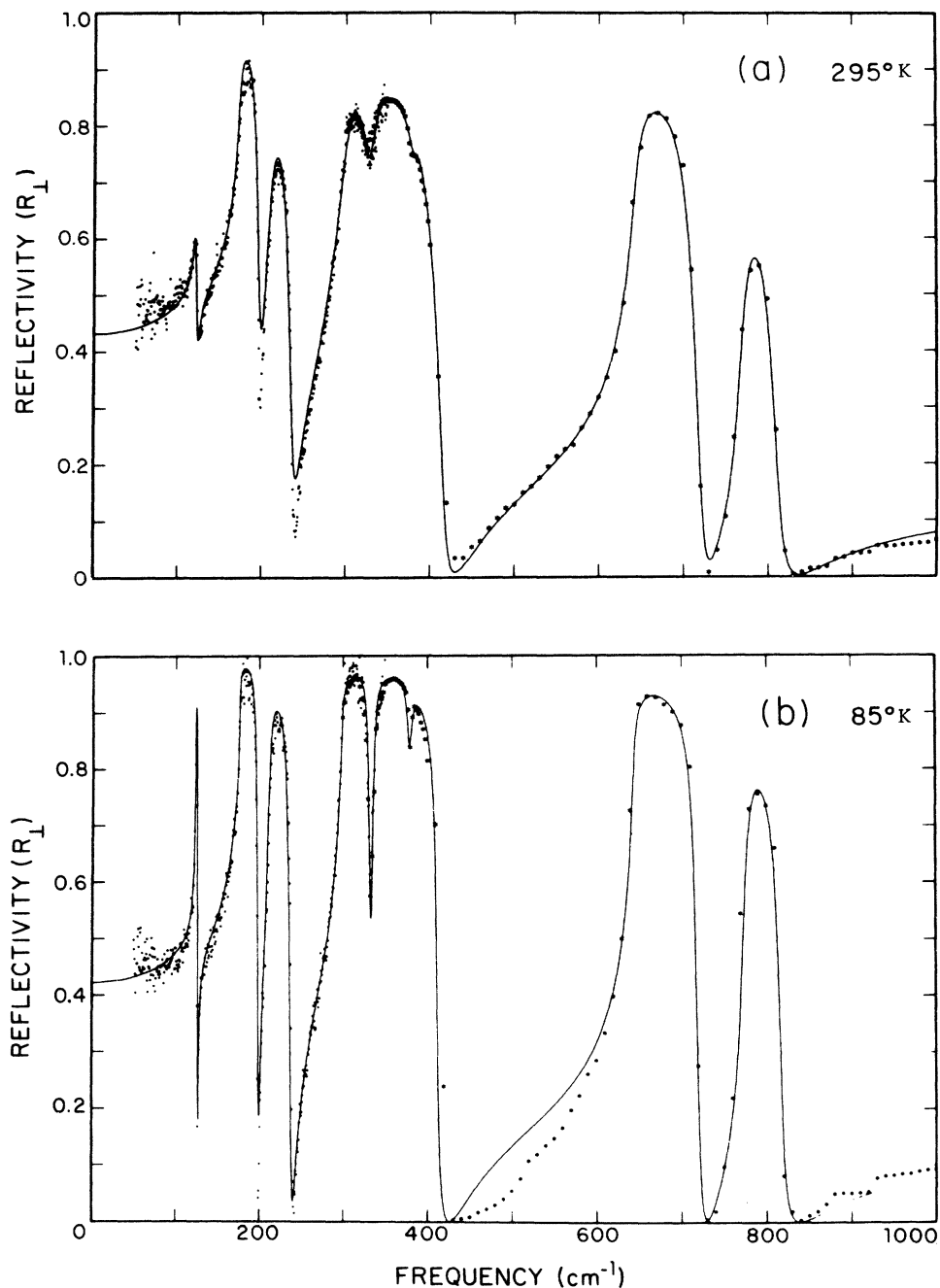
FIG. 1. E-mode reflectivity of paratellurite: (a) 295 °K, (b) 85 °K; solid curve is dispersion fit; dots are interferometer data; asterisks are spectrophotometer data.

data. The anisotropic frequencies of the coupled A_2 and E modes for the oblique phonons in the extraordinary ray are also given. [2]

Three previous studies of the Raman and infrared spectrum of paratellurite have recently been published. Krauzman and Mathieu[3] assigned frequencies to the A_1, B_1, and B_2 phonons on the basis of Raman scattering; and they found two A_2 and seven E modes using both infrared and Raman data.

Their infrared spectra were reported between 230 and 1000 cm^{-1} but only the portion between 450 and 850 cm^{-1} was displayed. The Raman spectrum of paratellurite was then examined by Pine and Dresselhaus[4] who reinterpreted the A_1, B_1, and B_2 assignments in the light of several anomalous selection-rule violations. From the Raman experiments they also identified six E modes and inferred the position of the four A_2 modes by observ-
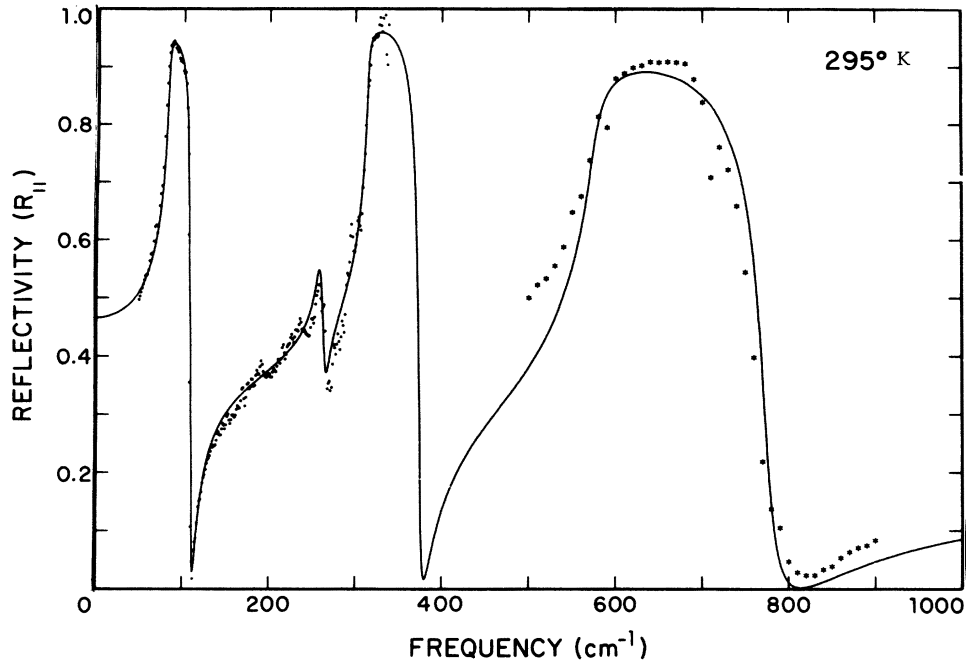
FIG. 2. A_2-mode reflectivity of paratellurite, 295 °K; solid curve is dispersion fit; dots are interferometer data; asterisks are spectrophotometer data.

ing the mixed A_2-E phonons propagating at an oblique angle to the c axis. These results will be compared to the infrared data in this paper. Ayrault et al.[5] confirmed the latter Raman assignments[4] and presented the room-temperature infrared reflectivity from 50 to 900 cm^{-1}. Their data, which were not analyzed for the mode parameters, exhibit four modes in the A_2 spectrum and seven in the E polarization; so one E mode was missing. In the present study this "missing" mode is observed as a shoulder in the 300 °K reflectivity and as well as a well-resolved peak at 85 °K.

Two crystals were used in this experiment. The E modes were observed with unpolarized light on a c-cut platelet, 13×8×1.5 mm in the x-y-z directions, supplied by Arlt of Philips Laboratory,

Aachen, Germany. The A_2 mode was examined with radiation polarized along the c axis of a Czochralski-grown 9×8×7 mm x-y-z oriented sample. This crystal was grown according to the methods described by Arlt, Liebertz, and Schweppe,[6] Miyazawa and Iwasaki,[7] and Bonner et al.[8]

Far-infrared reflectivity measurements between 50 and 425 cm^{-1} were performed on a Beckman (R.I.I.C.) Model No. FS-720 Fourier-transform interferometer equipped with a near-normal-incidence reflectivity module. Interferograms were scanned asymmetrically; appropriate phase-correction fast-Fourier-transform programing was used. Polarization for the A_2-mode studies was achieved with a wire-grid polarizer. Low-temper-

TABLE I. E-mode dispersion parameters.

Infrared reflectivity data at 295 °K				Raman data at 295 °K[a]		Infrared reflectivity data at 85 °K				Raman data at 85 °K[a]	
ω_i(TO) (cm^{-1})	ω_i(LO) (cm^{-1})	γ_i (cm^{-1})	f_i	ω_i(TO) (cm^{-1})	ω_i(LO) (cm^{-1})	ω_i(TO) (cm^{-1})	ω_i(LO) (cm^{-1})	γ_i (cm^{-1})	f_i	ω_i(TO) (cm^{-1})	ω_i(LO) (cm^{-1})
121.0	123.0	3.5	1.11	122	122	124.0	126.5	0.4	1.28	123	126
174.0	197.0	4.5	8.99	174	197	177.0	199.0	1.0	8.05	177	200
210.0	237.0	13.0	2.16		239	212.0	238.0	4.0	2.02	215	239
297.0	327.0	16.0	4.09	297	336	299.0	332.5	3.0	3.95	299	340
330.0	379.0	16.5	0.31			335.5	379.0	4.5	0.25		
379.4	415.0	14.0	0.01			379.4	412.0	6.5	0.01		
643.0	720.0	13.5	1.28		718	644.0	720.0	5.0	1.27	642	718
769.0	812.0	16.0	0.20	766	809	774.0	817.0	7.5	0.21	769	811

[a]Reference 4.

TABLE II. A_2-mode dispersion parameters.

Infrared Reflectivity data at 295 °K				Raman data at 85 °K[a,b]	
$\omega_i(TO)$ (cm^{-1})	$\omega_i(LO)$ (cm^{-1})	γ_i (cm^{-1})	f_i	$\omega_i(TO)$ (cm^{-1})	$\omega_i(LO)$ (cm^{-1})
82. 0	110. 0	2. 5	12. 95	76	109
259. 0	263. 0	7. 5	0. 77	265	269
315. 0	375. 0	3. 0	4. 70	325	335
575. 0	775. 0	20. 0	3. 86	570	785

[a]Reference 4.

[b]Frequencies inferred from oblique-phonon data; see text, and note change of temperature.

ature (~ 85 °K) studies were performed using a windowless cold-finger liquid-nitrogen Dewar.

E-mode reflectivity spectra between 300 and 1000 cm^{-1} were obtained on a Perkin-Elmer model No. 427A double-beam grating spectrophotometer equipped with a specular-reflectance attachment. A bottom-windowed (KRS-5) liquid-nitrogen cold-finger Dewar was used to obtain low-temperature data. The A_2-mode spectrum in the range 500–1000 cm^{-1} was taken on a Perkin-Elmer Model No. 421 spectrophotometer using the inherent polarization selectivity of the gratings. Reflectivity in all wavelength ranges was normalized to evaporated aluminum mirrors.

Infrared reflectivity spectra of the E modes in paratellurite at 295 and 85 °K are shown in Figs. 1(a) and 1(b). The data points are superimposed on solid curves representing a fit by a dispersion analysis. The reflectivity is computed from the dielectric tensor component[9]

$$\epsilon_\mu(\omega) = \epsilon_\mu(\infty) + \sum_i \frac{f_i\omega_i^2}{\omega_i^2 - \omega^2 - i\gamma_i\omega} = [n_\mu(\omega) + ik_\mu(\omega)]^2 \tag{1}$$

according to

$$R_\mu = [(n_\mu - 1)^2 + k_\mu^2]/[(n_\mu + 1)^2 + k_\mu^2]. \tag{2}$$

The two independent tensor components ($\mu = \perp, \parallel$) correspond to the electric field perpendicular to (for which the index i runs over the eight E modes) and parallel to (where i runs over the four A_2 modes) the c axis. The optical-frequency dielectric constants are taken from the refractive-index data of Arlt et al.[6] yielding $\epsilon_\perp(\infty) = 5.17$ and $\epsilon_\parallel(\infty) = 5.90$. The parameters used to fit $R_\perp$ are given in Table I along with the Raman data previously obtained.[4] The transverse-optical frequencies $\omega_i(TO)$ are the ω_i of Eq. (1) and the longitudinal-branch frequencies $\omega_i(LO)$ are taken as the zeros of $\epsilon_\mu(\omega)$ in the absence of damping,[10] that is, $\gamma_i \to 0$. Corrections for damping are on the order of γ_i^2/ω_i^2 and are too small to be measured here. The reflectivity spectrum in Fig. 1(a) is similar in appearance to that of Ayrault et al.[5] except for some minor differences in line shapes and relative peak reflectivities and, more importantly, for the shoulder at

~ 380 cm^{-1}. At low temperature this shoulder becomes a pronounced dip, as seen in Fig. 1(b), which indicates the presence of the heretofore missing E mode.

A similar analysis was applied to the A_2-mode spectrum in Fig. 2 resulting in the dispersion parameters given in Table II. Data in the 350–500-cm^{-1} range were extremely noisy due to filter and polarizer absorptions and are not shown. However, the A_2-mode edge at 375 cm^{-1} was clearly indicated in agreement with the earlier studies of Krauzman and Mathieu[3] and Ayrault et al.[5]

In a uniaxial crystal the extraordinary-ray dielectric constant depends on the angle θ between the phonon wave vector q and the c axis such that[2]

$$\epsilon_\theta = \epsilon_\perp\epsilon_\parallel / [\epsilon_\parallel\cos^2\theta + \epsilon_\perp\sin^2\theta]. \tag{3}$$

Thus both A_2 and E modes contribute to this anisotropic dielectric constant and ϵ_θ can be calculated from the parameters of Tables I and II. In the lossless case ($\gamma_i \to 0$) outside the polariton regime $\{qc/\omega \gg [\epsilon(0)]^{1/2}\}$, the poles of $\epsilon_\theta(\omega)$ or, equivalently, the zeros of the denominator of (3), are the peaks observed by large-angle Raman scattering.[2] The anisotropic frequencies of these extraordinary-ray oblique phonons in paratellurite at 295 °K are illustrated in Fig. 3. This figure differs from the previous calculation by Pine and Dresselhaus[4] principally in the 325–425-cm^{-1} re-
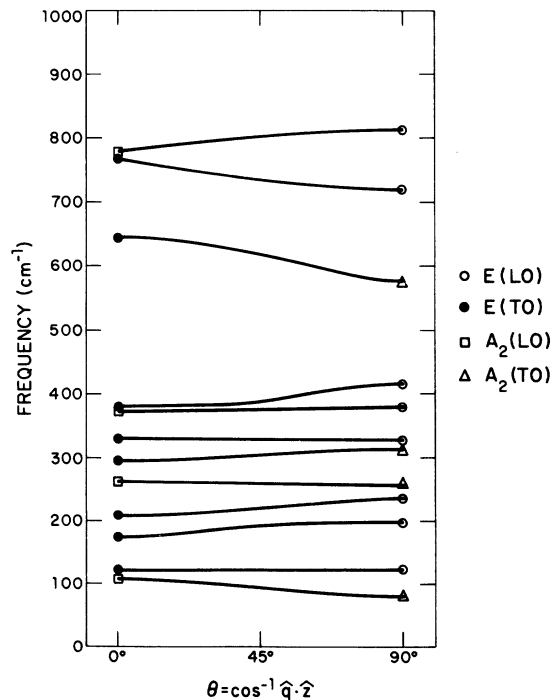

FIG. 3. Anisotropic frequencies of the extraordinary ray oblique phonons in paratellurite 295 °K.

TABLE III. Oblique polar-phonon frequencies (cm^{-1})
at $\theta = 45°$

Calculated from ir parameters at 295 °K
93, 123, 191, 220, 262, 304,
329, 379, 388, 619, 734, 802
Raman data at 85 °K[a]
91, 126, 193, 226, 267, 311, 337, 617, 730, 804

[a]Reference 4.

gion where two E modes were missing in the
Raman data. The A_2 mode frequencies inferred
from the oblique-phonon Raman data[4] at 85 °K and
compared to the reflectivity parameters in Table
II are in reasonable agreement except for the mode
with $\omega(LO) = 375$ cm^{-1}. This discrepancy results
from the coupling of this A_2 mode to the E modes
not observed by Raman scattering. The $\theta = 45°$
oblique-phonon frequencies as calculated from the
infrared parameters are generally in excellent
agreement with the $\theta = 45°$ Raman data allowing for
the change in temperature as seen in Table III.

The dc dielectric constants at 295 °K computed
from $\epsilon(0) = \epsilon(\infty) + \sum_i f_i$ are $\epsilon_\perp(0) = 23.3$ and $\epsilon_{||}(0)$
$= 28.2$. These are somewhat higher than the low-
frequency measurements of $\epsilon_\perp(0) = 21.5$ and $\epsilon_{||}(0)$

$= 25$ by Arlt et al.[6] but probably within experiment-
al error.

It should be noted that the dispersion analysis
was unable to fit simultaneously the reflectivity
peaks and their associated minima of the second
and third E modes in Figs. 1(a) and 1(b). It is not
clear whether this is an experimental difficulty or
an indication of multiphonon processes. Second,
the discrepancies between the Raman and infrared
frequencies of the highest-energy E mode is likely
due to calibration errors in the spectrophotometer.
Finally the 8–9-cm^{-1} discrepancy between the
Raman and infrared data for the fourth E-mode LO
frequency is much too large to be explained by the
experimental error of approximately ± 1 cm^{-1} for
the Raman data and less than ± 0.1 cm^{-1} for the
Fourier spectrometer. Ayrault et al.[5] indepen-
dently obtained the same Raman frequency. This
discrepancy was noted earlier by the authors[11] and
attributed to the interposition of the previously
missing E mode. However, the more recent dis-
covery of the 380-cm^{-1} structure makes the pres-
ent assignment more compelling, but leaves the
infrared-Raman discrepancy unexplained.

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