Optical modes and dielectric properties of ferroelectric orthorhombic KNbO$_3$†

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Both Raman scattering and infrared reflectivity measurements have been performed to determine the optically active branches of orthorhombic KNbO$_3$ at room temperature. Principal-axis phonons and oblique phonons were observed with a combination of 90° Raman scattering, back scattering, and forward scattering. Unobserved longitudinal modes and mode couplings were derived from the reflectivity measurements. The ferroelectric modes, namely those rendered highly anisotropic as a result of successive transitions, were identified and their corresponding wave vectors determined; strong interference with more isotropic modes was pronounced. Dielectric constants were derived from these measurements and the $A_1$ polaritons dispersion curve was also measured. The modes were grouped according to the cubic representations from which they are derived and compared with those of BaTiO$_3$. In particular, the modes were three times less damped. Of the original soft cubic ferroelectric mode, the component along the remaining soft direction was found at 56 cm$^{-1}$ and not overdamped ($\Gamma/\omega = 1$).

I. INTRODUCTION

Current interest in the structural instabilities of the perovskite structure has stimulated many investigations involving Raman scattering, neutron scattering, and x-ray scattering. In particular, ferroelectric BaTiO$_3$, provided a model for the original soft-mode theory of Cochran$^1$ and the Devonshire theory of ferroelectrics.$^2$ While it has been known for a long time that both BaTiO$_3$ and KNbO$_3$ exhibit similar properties,$^3$ the latter had not been included in these investigations until recently. Mixed crystals, namely,$^4$ (Ba:Pb)TiO$_3$ and K(Ta:Nb)O$_3$, have been compared with BaTiO$_3$, but orthorhombic KNbO$_3$ has waited upon the development of large, high-quality, single-domain crystals. As these have become available a picture of the KNbO$_3$ analog of the orthorhombic ferroelectric phase of BaTiO$_3$ is emerging. Attempts to achieve this phase by cooling BaTiO$_3$ below 5°C have not been particularly successful owing to the uncontrolled development of the ferroelectric domains. This exercise is less painful when the phase is stable at room temperature as in KNbO$_3$.

The cubic phases of BaTiO$_3$ and KNbO$_3$ can be characterized by a soft, overdamped ferroelectric mode whose (100) polarized components remain at low frequency for $k$ vectors out to the Brillouin-zone boundary. The spacial anisotropy implied by these measurements had been predicted earlier by Huller$^6$ to explain the apparent disorder suggested by the planes of diffuse x-ray scattering seen by Comès.$^9$ Nevertheless, a similar diffuse scattering was seen in KTaO$_3$, which possesses a less-soft, underdamped ferroelectric mode essentially isotropic at large wave vectors. A possible explanation was seen to lie in the extreme anisotropy of the transverse-acoustic branch. This remained flat and at low frequency for large wave vectors and (100) polarizations.$^{10}$ Since both these optic and acoustic branches possess the same symmetry, these seemingly different behaviors can be correlated by allowing the ferroelectric mode for $q=0$ to develop into a combination of optic and acoustic modes at finite $q$. A similar feature has been predicted recently$^{11}$ by self-consistent calculations on rocksalt structures.

The tetragonal phase of BaTiO$_3$ exhibits a stiffened $A_1$ component of this ferroelectric mode together with the remaining, low-frequency $E$ component. The latter retains the cubic anomaly of low energies and high damping for all $q$ values parallel to [100] and [010].$^{12}$ Raman scattering$^{13}$ from the $A_1$ modes has clarified their damping and coupling characteristics but yields a value for $\epsilon_{zz}^{\theta}$ (along the ferroelectric axis) which is lower than the value obtained at 250 MHz.$^{14}$ The temperature dependence of these modes yields essentially a constant value for $\epsilon_{zz}^{\theta}$ which also fails to agree with the rising value for increasing temperature measured at 250 MHz. In addition, the Raman scattering persists into the cubic phase with little change as the temperature goes through $T_c$.$^{15}$ This may be interpreted either as strong higher-order scattering or disorder-induced first-order scattering. The high value for the dielectric constant favors the presence of an enhanced low-frequency response which may reflect the extra elastic scattering of phonons seen in some perovskite lattices. Such a peak is generated in recent calculations$^{16}$ of
TABLE I. Conventional cell parameters and atomic displacements from cubic positions with Nb (Ti) at (0, 0, 0) in orthorhombic KNbO$_3$ and BaTiO$_3$.

<table>
<thead>
<tr>
<th></th>
<th>KNbO$_3$ X ray</th>
<th>KNbO$_3$ Neutron</th>
<th>BaTiO$_3$ X ray</th>
<th>BaTiO$_3$ Neutron</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z_K$, K (Ba) at (0, $\frac{1}{2}$, $\frac{1}{2}$) + $Z_{(0)}$</td>
<td>0.017</td>
<td>0.014</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>$Z_{(1)}$, O$<em>{(1)}$ at (0, $\frac{1}{2}$, $Z</em>{(1)}$)</td>
<td>0.021</td>
<td>0.036</td>
<td>0.020</td>
<td></td>
</tr>
<tr>
<td>$Z_{(2)}$, O$<em>{(2)}$ at ($\frac{1}{2}$ + $X</em>{(2)}$, 0, $\frac{1}{2}$ + $Z_{(2)}$)</td>
<td>0.035</td>
<td>0.034</td>
<td>0.023</td>
<td></td>
</tr>
<tr>
<td>$X_{(2)}$</td>
<td>0.004</td>
<td>-0.0024</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>5.697</td>
<td>5.669</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>3.971</td>
<td>3.990</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>5.720</td>
<td>5.682</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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response functions for one-dimensional lattices of coupled anharmonic oscillators. Nevertheless, a complete analysis for BaTiO$_3$ has not been attempted.

The orthorhombic phase which BaTiO$_3$ reaches at 5°C has not been investigated in any great detail, but the similar phase in KNbO$_3$ which forms at 220°C has been the subject of recent light scattering and similar investigations. The neutron results indicate a similarity with KTaO$_3$.

The transverse-acoustic branch at large wave vector which propagates in (010) sheets is flat, damped, and at low frequency when polarized along [010], the remaining soft direction in the crystal. The present article contains the details of our light scattering and infrared-reflectivity measurements which have exposed the complete optic-mode structure and shown the spacial anisotropy of the ferroelectric $q = 0$ mode to be similar to that of this transverse-acoustic (TA) branch at large $q$ values. The previous investigation wrongly ascribed missing modes to other peaks in the Raman spectrum and the neutron data placed the soft-mode frequency lower than our value of 56 cm$^{-1}$, which is close to the TA-mode frequency of 1.6 THz at finite $q$. In addition we find that all the modes are underdamped at room temperature even though the ferroelectric mode is overdamped in the cubic phase. Transverse modes related to this ferroelectric mode possess linewidths of 30 cm$^{-1}$ while the other modes have linewidths of 3 cm$^{-1}$. This high value is 3 times less than that for the broad modes in tetragonal BaTiO$_3$.

The infrared data provide an important contribution to this phonon unraveling: The LO modes possess weak Raman intensity but their position can be fairly precisely determined from the infrared reflectivity. This enables all the principal-axis phonons and oblique phonons to be correlated so that the anisotropies of the excitations can be exposed. Then the remaining broad peaks in the Raman spectrum can be confidently relegated to either first-order scattering allowed by broken symmetry or strong second-order scattering involving the low-frequency branch.

II. BACKGROUND

Orthorhombic KNbO$_3$ possesses C$_{3v}$ symmetry with principal axes [101], [101], and [010] defined in the pseudocubic system. The primitive cell has one molecule of KNbO$_3$ and 15 deg of vibrational freedom according to $5A_1 (z) + 5B_1 (x,y) + A_2$. We choose to define the polarization direction [101] as $z$ and [010] as $y$. This choice of notation is consistent with the conventional cell symmetry of $Bmm2$ chosen by Katz and Megaw. The letters in parentheses represent phonon polarizations and appropriate infrared (IR) activity. One vertical mirror plane (010) is composed of niobium and oxygen (O$_{(11)}$) and oxygen (O$_{(11)}$) atoms. Oxygen (O$_{(11)}$) and potassium atoms together with the niobium constitute the other vertical mirror plane (010) and complete the structure. Table I is a resume of lattice parameters and distortions from cubic symmetry compared with those for BaTiO$_3$.

The orthorhombic modes (and the tetragonal BaTiO$_3$ modes) can be grouped according to the cubic modes from which they are derived. Then it becomes apparent that the $A_1 (z) + B_1 (x) + A_2$ modes derived from $T_{2g}$ are expected to be comparatively isotropic with little (TO-LO) splitting since they possess no IR strength in the cubic phase. Indeed we shall see that these lines are very narrow and possess splittings of only several...
cm\(^{-1}\) near 280 cm\(^{-1}\). Of the three \(T_{1u}\) modes, one is comparatively isolated with small (LO-TO) splittings (~10 cm\(^{-1}\)) near 180 cm\(^{-1}\). The other two modes are broader and possess strong ir strengths and highly anisotropic transverse components. Since these modes would be isotropic in the cubic phase, they have been strongly affected by the ferroelectric phase transitions. Consequently these TO modes are loosely termed the ferroelectric modes. All the longitudinal modes are essentially isotropic and consequently they possess mixed symmetry in oblique directions. Apart from the longitudinal mode associated with the isolated \(T_{1u}\) mode, the remaining ones are stabilized by macroscopic electric fields derived from eigenvectors which are, presumably, also isotropic.

### III. EXPERIMENT

The flux-grown, untwinned crystal used in these experiments was a 5×5×7 mm\(^3\) cube with natural \{100\} pseudocubic faces. No attempt was made to create artificial surfaces so as to minimize the effects of strain birefringence and surface imperfections. Hence a combination of 90° scattering, backscattering, and forward scattering was necessary to detect all the phonons in Raman scattering. The \(A_i(z)\) polaritons were observed in forward scattering. The following scattering geometries yield all the phonons propagating along principal axes.

90° Stokes scattering:
\[
\begin{align*}
x + z (yy) x + z & \quad \text{yields } A_1(\text{TO}), \\
x + z (yy) x + z & \quad \text{yields } A_1(\text{LO}), \\
x + z (y, x + z) x + z & \quad \text{yields } B_1(\text{TO}) + A_2, \\
x + z (yx) y & \quad \text{yields } A_2.
\end{align*}
\]

Backscattering:
\[
\begin{align*}
y(zz) y & \quad \text{yields } A_1(\text{TO}), \\
y(zx) y & \quad \text{yields } B_1(\text{TO}).
\end{align*}
\]

Forward scattering:
\[
\begin{align*}
y(zx) y + \Delta x & \quad \text{yields } B_1(\text{LO}), \\
x + z (y, x + z) x + z + \Delta y & \quad \text{yields } B_2(\text{LO}) + A_2.
\end{align*}
\]

The spectra were recorded with an argon laser (Coherent Radiation, model 53) and double monochromator (Spex, model 1401) equipped with a cooled photomultiplier (ITT, model FW130). Usual precautions were taken to reduce the detection of spurious argon fluorescence. In the collinear scattering geometry, a combined mask and aperture was used to remove the unscattered beam and define the collection geometry. The large indices of refraction and high birefringence can cause problems. Large collection angles will allow spurious polarizations to be found in the scattered light. Strong internal reflection of the incident beam will scramble forward and backward scattering in the collinear geometry and LO's and TO's in the 90° geometry. The consequences of these effects are apparent in the results and great care was exercised to isolate these spurious signals in the spectra. The frequencies are probably accurate to ±3 cm\(^{-1}\).

The ir spectra were recorded on Perkin-Elmer spectrometers. Data between 250 and 1000 cm\(^{-1}\) were obtained from a modified model 200-B and data below 250 cm\(^{-1}\) were obtained from an automatic recording model 180. No attempt was made to obtain high-resolution spectra since the results were only required to confirm the location of the LO-mode frequencies. The low-frequency data are inaccurate owing to poor sensitivity and inadequate normalization.

### IV. RESULTS

In the limit of small mode damping, Raman scattering yields the frequencies of the TO and LO modes which are the poles and zeros of the dielectric function responsible for the behavior of the ir reflectivity. In a more complex multimode situation with significant damping and mode coupling, the poles and zeros become complex and are not extracted easily from the reflectivity data. In addition, the modes seen by Raman scattering do not yield the full characteristics of the dielectric function directly. A review of the use of response functions to handle this situation has been given by Barker and Loudon.\(^{23}\) We have chosen to let the experimental situation dictate the level of complexity used to analyze the problem. In particular the Raman scattering has been analyzed with a set of damped harmonic oscillators. Mode coupling was introduced only to analyze the crossing of the main \(A_1\) polariton branch with a sharp mode near 190 cm\(^{-1}\). A two-oscillator fit was used rather than a complete polariton description. The latter was used by Chaves \textit{et al.}\(^{15}\) to analyze the similar problem in BaTiO\(_3\), where mode coupling was apparent even in the TO spectrum. There, a single coupling parameter was used to analyze both the TO spectrum and the polariton spectra. In K\(\text{NbO}_3\), where the mode damping and coupling is greatly reduced, such an analysis was not considered appropriate.

The infrared strengths of the \(A_i\) modes were estimated from Raman scattering from the zeros of the real part of the dielectric function calculated...
by neglecting the damping of the sharp modes. The subsequent prediction of the ir reflectivity is superimposed on the experimental data in Fig. 3. It is immediately apparent that the sharp mode strengths have been overestimated and that mode couplings cannot be neglected in the interpretation of the reflectivity data.

This situation was expected from the work of Barker and Hopfield on BaTiO₃, KTaO₃, and K(Ta:Nb)O₃ (KTN), where mode couplings were first observed. Consequently a least-squares analysis was performed along principal axes, varying mode parameters and including imaginary couplings between overlapping modes. The sharp mode parameters were not obtained with any great accuracy because the resolution of the data was inadequate. These modes, however, contribute little to the dielectric response away from their respective frequencies. The TO frequencies were not allowed to change and imaginary coupling was chosen because Barker had shown that good agreement with experiment could apparently be achieved in perovskites by using parameters obtained in an uncoupled analysis and then merely including the imaginary coupling to improve the fit. By writing $\epsilon(\omega) = \epsilon_\infty + 4\pi\hbar\frac{Q_\nu Q_\nu'}{G_{\nu\nu}'(\omega)}$, with $G_{\nu\nu}'(\omega) = (\omega^2 - \omega_\nu^2)^2 + i\omega\gamma_\nu$, it is apparent that this procedure will not affect $\epsilon(0)$, but rather the properties of the complex zeros and poles of $\epsilon$. The zeros of the real part of $\epsilon(\omega)$ were reevaluated with these parameters neglecting the damping of the sharp modes, and the resulting frequencies were assumed to represent the LO modes. It has been suggested by Chaves et al. that real and imaginary mode coupling can be distinguished in BaTiO₃ by polariton scattering. In KNbO₃, where the mode damping and coupling are lower, neither the TO nor the polariton scattering is significantly affected by this coupling. Consequently we were unable to make this distinction; other sources of broadening tend to disguise the effects even in BaTiO₃. Estimates of $\epsilon(0)$ were obtained by applying the Lyddane-Sachs-Teller (LST) relation to both these frequencies and the Raman data, in addition to evaluating $\epsilon_\infty + 4\pi\hbar\frac{Q_\nu Q_\nu'}{G_{\nu\nu}'(0)}$.

A. $A_1$ modes

90° scattering in the pseudocubic (010) plane provides both TO and LO phonons (Figs. 1 and 2). The position of the two broad and strong modes reflects the stiffening of the cubic, low-frequency ferroelectric mode which has stiffened to 290 cm⁻¹ in this direction. The first TO is a sharp line located at 190 cm⁻¹, and the other sharp mode derived from the $T_{9y}$ cubic mode is at 299 cm⁻¹. The other broad line at 607 cm⁻¹ completes the $A_1$(TO) spectrum.

The proximity of the 290- and 299-cm⁻¹ modes obscures the latter. Further justification of the existence of this mode is provided by the oblique spectra shown in Fig. 14. Also, the first sharp phonon at 190 cm⁻¹ seems to be very weak in this geometry. Nevertheless, where other scattering components are obtained, such as (xx) or (zz), this phonon becomes very strong.

The $A_1$(LO) spectrum is entirely different. There are two sharp phonons at 193 and 296 cm⁻¹, located roughly at the positions of TO phonons. Then there is a sharp interference pattern at 417 cm⁻¹ and finally a broad phonon at 827 cm⁻¹. The phonon at 417 cm⁻¹ is hardly visible in other geometries, whereas in this (yy) polarization, it appears only as an interference with the background. The fact that it interferes so sharply is indisputable evidence of its existence as a first-order mode.

Both LO and TO spectra exhibit a broad background with pronounced peaks around 135, 450, and 550 cm⁻¹. The last one (strong in the LO spectrum) is probably a "leak" of the broad $B_1$(TO)
which derives from the $A_1$(TO) in oblique directions. Both the 135-cm$^{-1}$ peak and the one at 450 cm$^{-1}$ with its associated interference at 417 cm$^{-1}$ are strong in $(yy)$ but weak in the other scattering geometries; similar effects are seen in BaTiO$_3$.

It seems appropriate to assume the peaks are second-order Raman scattering involving the lowest $B_1$(TO) mode at 56 cm$^{-1}$. However, just as speculation has been raised concerning the background in BaTiO$_3$, so too one may speculate whether this background is indicative of a lack of ordering in the KNbO$_3$ lattice.

The $z$-polarized ir reflectivity is shown in Fig. 3. The gross features are exactly analogous to those found in BaTiO$_3$, SrTiO$_3$, KTaO$_3$, and KTN. The two modes which carry most of the ir strengths provide two broad reflectivity peaks which are only slightly perturbed by the sharp modes. Couplings between modes are very similar to KTN and KTaO$_3$, and it is seen that the Raman data provide a fair approximation for the reflectivity, justifying our choice of LO and TO modes. Nevertheless, the strengths of the sharp modes were obviously overestimated. This probably reflects an inaccuracy in our measurement of LO-TO splitting, rather than in our estimation procedure, which gives $\omega_{LO} - \omega_{TO} = 4\pi Q^2 / 2\epsilon \omega_{TO}$ for a sharp mode of strength $Q$ lying at frequency $\omega_{TO}$ where the background dielectric constant is real and equal to $\epsilon$.

An estimate of $\epsilon''(0)$ can be obtained from the low-frequency slope of the polariton scattering. This scattering is shown in Figs. 4(a) and 4(b). The smallest internal scattering angle at which useful data could be extracted was 15'. At this angle, the low-frequency behavior of the polariton was well established and our value $\epsilon''(0) = 20 \pm 2$

FIG. 3. $z$-polarized ir reflectivity of KNbO$_3$. Dashed curve derived from Raman data. Continuous curve derived from reflectivity analysis. Circles represent accurate data points. Dots represent data with uncertain normalization errors.

FIG. 4. (a) and (b): $(zz)$ spectrum of the $A_1$ polaritons in KNbO$_3$. $\phi$ represents the internal scattering angle.
TABLE II. $A_1$-mode parameters and dielectric properties derived from Raman scattering and ir-reflectivity measurements.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Mode 1</th>
<th>Mode 2</th>
<th>Mode 3</th>
<th>Mode 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{LO} - \text{Raman (cm}^{-1})$</td>
<td>190</td>
<td>290</td>
<td>299</td>
<td>607</td>
</tr>
<tr>
<td>$\omega_{TO} - \text{Raman (cm}^{-1})$</td>
<td>193</td>
<td>296</td>
<td>417</td>
<td>827</td>
</tr>
<tr>
<td>$\omega_{TO} - \text{ir (cm}^{-1})$</td>
<td>190</td>
<td>297</td>
<td>432</td>
<td>835</td>
</tr>
<tr>
<td>Linewidth (cm$^{-1}$) / Raman</td>
<td>3</td>
<td>30</td>
<td>4</td>
<td>33</td>
</tr>
<tr>
<td>Linewidth (cm$^{-1}$) / ir</td>
<td>$32 \pm 8$</td>
<td>$31 \pm 10$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mode strength $S = (4\pi q^2/\omega_{TO})^{1/2}$</td>
<td>$0.3$</td>
<td>$3.28 \pm 0.07$</td>
<td>$0.9 \pm 0.2$</td>
<td>$1.59 \pm 0.06$</td>
</tr>
<tr>
<td>Mode coupling (cm$^{-1}$)</td>
<td>$\gamma_{12} = 0$</td>
<td>$\gamma_{23} = 3$</td>
<td>$\gamma_{24} = 31 \pm 10$</td>
<td></td>
</tr>
<tr>
<td>LST value with $\omega_{LO} - \text{Raman}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LST value with $\omega_{LO} - \text{ir}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\epsilon_{\text{in}}(0)$ (24 $\pm$ 2)</td>
<td>17.0</td>
<td>18.2</td>
<td>18.5</td>
<td>20 $\pm$ 2</td>
</tr>
</tbody>
</table>

$^a$ Derived from $c'(\omega) = 0$.
$^b$ E. Wiesendanger, Ferroelectrics 6, 263 (1974).
$^c$ E. Wiesendanger, Ferroelectrics 6, 263 (1974).

Calculated from this slope is in agreement with a similar measurement by Winter et al. The other values of $\epsilon(0)$ are collected in Table II and can be compared with the clamped value measured by Weisendanger. A complete set of $A_1$-mode parameters are included in the same table.

Strong polariton behavior is exhibited by the two main modes. When the lower mode crosses the sharp mode at 190 cm$^{-1}$, strong interference occurs and can be seen in Fig. 4. This has been analyzed as a coupled-mode problem and the frequency of the uncoupled, main branch has been plotted in Fig. 5 to allow a smooth curve to be extended to the low-frequency data. Nevertheless, it should be remembered that the true polariton behavior involves discontinuous LO-TO splittings near both 190 and 280 cm$^{-1}$ (shown by arrows) similar to the main LO-TO splitting. Both the sharp modes play a minor role in the dielectric response except near their respective poles, and consequently their absence from the polariton presentation is justified; their associated slope changes are negligible. The dispersion is dominated by the stiffened ferroelectric mode. While this excitation does not become as sharp as expected in the limit $\omega, q \rightarrow 0$, this probably reflects the finite collection angle rather than a genuine broadening mechanism for wavelengths in excess of 200 $\mu$m.

FIG. 5. Polariton dispersion curve of the ferroelectric modes after decoupling from the sharp modes located at the frequencies indicated by arrows. $A_1(LO)$ and $A_1(TO)$ represent the asymptotes of the curve.

FIG. 6. 90° scattering. (xy) spectrum of the $A_2$ phonon in KNbO$_3$. 
B. \( A_2 \) modes

Since the \( A_2 \) mode is unique and ir inactive, the \((xy)\) Raman spectrum is expected to be particularly simple; it is presented in Fig. 6. It is completely devoid of background, indicating the lack of both second-order Raman scattering or first-order scattering allowed by broken symmetry and/or strain birefringence. The second-order scattering arising from \( A_1 \times A_2 \) and \( B_1 \times B_2 \) could occur from most of the Brillouin zone. The total absence of any \( A_2 \) background provides interesting possibilities for speculation on the origin of the prominent \( A_2(yy) \) background.

This \( A_2 \) mode is derived from the \( T_{2u} \) cubic mode and lies close to the frequency of its \( A_1 \) and \( B_2 \) partners. The equivalent mode in BaTiO\(_3\) is the \( E \) mode at 305 cm\(^{-1}\).

C. \( B_1 \) modes

The pure \( B_1(\text{TO}) \) modes can be seen by backscattering along the \( y \) direction. The \( y(zz)y \) spectrum is shown in Fig. 7. It is very similar to the \( A_1(\text{TO}) \) spectrum with two broad strong modes and two weak narrow modes. The main modes located at 243 and 534 cm\(^{-1}\) constitute the stiffened ferroelectric mode and are similar to the 290- and 607-cm\(^{-1}\) \( A_1(\text{TO}) \) modes. The first sharp \( B_1(\text{TO}) \) mode occurs at 187 cm\(^{-1}\) and the other sharp mode at 270 cm\(^{-1}\).

The broad, extra mode which is seen to interfere with the 187-cm\(^{-1}\) mode obviously possesses \( B_1 \) symmetry and is apparently the polariton associated with the 243-cm\(^{-1}\) mode. Internal reflection and a small \( xz \) birefringence allow this interpretation, which was confirmed by noting that the structure sharpened and moved to lower frequency

as the \( f \) number of the collection optics was increased.

The four \( B_1(\text{LO}) \) modes should be exhibited in the forward scattering geometry \( y(zz)y+\Delta y \) cor-

FIG. 8. Forward scattering. \((xz)\) spectrum of the \( B_1 \) oblique phonon propagating in \((010)\). Pure \( B_1(\text{LO}) \) modes are located at the positions of the arrows in the \( \phi=0 \) spectrum.

FIG. 9. \( x \)-polarized ir reflectivity of KNbO\(_3\). Circles represent accurate data points. Dots represent data with uncertain normalization errors. Continuous curve is derived from reflectivity analysis.
TABLE III. $B_1$-mode parameters and dielectric properties derived from Raman scattering and ir-reflectivity measurements.

<table>
<thead>
<tr>
<th></th>
<th>Mode 1</th>
<th>Mode 2</th>
<th>Mode 3</th>
<th>Mode 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{\text{TO}}$ (Raman) (cm$^{-1}$)</td>
<td>157</td>
<td>243</td>
<td>270</td>
<td>534</td>
</tr>
<tr>
<td>$\omega_{\text{LO}}$ (ir) (cm$^{-1}$) a</td>
<td>190</td>
<td>264</td>
<td>413</td>
<td>842</td>
</tr>
<tr>
<td>Linewidth (cm$^{-1}$)</td>
<td>3</td>
<td>30</td>
<td>4</td>
<td>33</td>
</tr>
<tr>
<td>Mode strength $S = (4\pi Q^2/\omega_{\text{TO}})^{1/2}$</td>
<td>$1.40 \pm 0.3$</td>
<td>$4.66 \pm 0.08$</td>
<td>$1.58 \pm 0.10$</td>
<td>$1.91 \pm 0.04$</td>
</tr>
<tr>
<td>Mode coupling (cm$^{-1}$)</td>
<td>$\gamma_{12} \sim 5$</td>
<td>$\gamma_{22} \sim 2$</td>
<td>$\gamma_{24} = 33 \pm 6$</td>
<td></td>
</tr>
<tr>
<td>$\epsilon_{\infty}(0)$ (37.2) c</td>
<td>194.6</td>
<td>34.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\epsilon_{\infty} + \Sigma S_2^2$</td>
<td>34.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a, c See Table II.

responding to $\phi = 0$ in the oblique phonons shown in Fig. 8. Unfortunately none of the main peaks can be associated with these modes. The double peak at 534 cm$^{-1}$ is to be construed as the $B_1$(TO) mode and its associated polariton; similarly for the broad peak at 243 cm$^{-1}$ and its partner at 200 cm$^{-1}$. There remain, however, two features which may be interpreted either as $B_1$(LO) modes or the TO partners they become at $\phi = 90^\circ$. One is the sharp mode at 190 cm$^{-1}$ which interferes strongly with the polariton and the other feature is the shoulder on the high-frequency side of the TO mode at 267 cm$^{-1}$. Nevertheless, the main $B_1$(LO) modes whose positions are indicated by arrows are not seen in Raman scattering.

The $x$-polarized reflectivity is shown in Fig. 9. It is immediately apparent that this spectrum is virtually identical to the $A_{\perp}$ reflectivity and requires longitudinal modes near 413 and 842 cm$^{-1}$. These data are crucial to the elucidation of the $B_1$ spectrum. The reduction of these data as before is presented in Table III. This consistent picture of the $B_1$ modes confirms that, indeed, the scattering cross section of the LO modes must be small. This may not be too surprising if it is remembered that all Raman scattering is allowed only through the small distortions generated at the phase transitions. Rather than assuming a chance cancellation between deformation-potential scattering and electro-optic contributions to the LO scattering cross section, it may be more prudent to question the abnormally high scattering cross section of the main TO modes. A similar situation exists in BaTiO$_3$.26

D. $B_2$ modes

The $B_2$(TO) modes can be seen in $90^\circ$ scattering in association with the $A_2$ mode. The $x + z(y, x + z)$

FIG. 10. $90^\circ$ scattering. $(yx + yz)$ spectrum of the $B_2$(TO) and $A_2$ phonons in KNbO$_3$.

FIG. 11. $90^\circ$ scattering. Circles represent scattering from the soft ferroelectric $B_2$ mode in KNbO$_3$. Continuous curve derived from damped oscillator response with $\omega = 56$ cm$^{-1}$, $1/\omega = 1$. Dashed curve displays level of elastically scattered laser light.
TABLE IV. \(B_2\)-mode parameters and dielectric properties derived from Raman scattering and ir-reflectivity measurements.

<table>
<thead>
<tr>
<th>Mode</th>
<th>(\omega_{TO}) — Raman (cm(^{-1}))</th>
<th>(\omega_{LO}) — ir (cm(^{-1})) (^{a})</th>
<th>Lidewidth (cm(^{-1})) (^{b})</th>
<th>Mode strength (S = (4\pi \eta^2/\omega_{TO}^4)^{1/2})</th>
<th>Mode coupling (cm(^{-1}))</th>
<th>(\epsilon_{yy}(0)) (750 ± 50) (^{c})</th>
<th>(\epsilon_m+\Sigma S_3^2) = 726</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode 1</td>
<td>56</td>
<td>189</td>
<td>37</td>
<td>26.7 ± 0.5</td>
<td>(\gamma_{12} = 27 ± 8)</td>
<td>(\epsilon_m = 4.9)</td>
<td>(\epsilon_m+\Sigma S_3^2 = 726)</td>
</tr>
<tr>
<td>Mode 2</td>
<td>195</td>
<td>425</td>
<td>3</td>
<td>1.96 ± 0.30</td>
<td>(\gamma_{12} = 27 ± 7)</td>
<td>(\epsilon_m = 4.9)</td>
<td>(\epsilon_m+\Sigma S_3^2 = 726)</td>
</tr>
<tr>
<td>Mode 3</td>
<td>511</td>
<td>838</td>
<td>31 ± 10</td>
<td>1.63 ± 0.05</td>
<td>(\gamma_{12} = 27 ± 7)</td>
<td>(\epsilon_m = 4.9)</td>
<td>(\epsilon_m+\Sigma S_3^2 = 726)</td>
</tr>
</tbody>
</table>

\(^{a}\) See Table II.

+ \(z\) spectrum is shown in Fig. 10. Peaks at 36, 192, and 511 cm\(^{-1}\) can be associated with the \(B_2\) modes while the \(A_4\) mode at 283 cm\(^{-1}\) completes the spectrum. The line at 192 cm\(^{-1}\) shows interference with the broad wing of the low-frequency mode which is broader than the stiffened ferroelectric mode in the other directions. In general, this spectrum is analogous to the \(E\)-symmetry spectrum of tetragonal BaTiO\(_3\).

The low-frequency peak is associated with the ferroelectric mode which should stiffen in the rhombohedral phase. Both Stokes (+\(\omega\)) and anti-Stokes (-\(\omega\)) scattering have been analyzed in terms of a damped harmonic-oscillator response with a cross section \(\alpha(\delta^{\omega}) + 1\) \(\text{Im}(G)\). The success of this fitting procedure is seen in Fig. 11, where a frequency of 56 cm\(^{-1}\) and a width (\(\Gamma\)) of 57 cm\(^{-1}\) have been used.\(^{21}\) While the frequency may be in error by as much as 10%, the ratio \(\omega/\Gamma\) is accurately determined to be 1 ± 0.02, and consequently this mode is not overdamped. The oblique development of the mode away from the (010) plane confirms that it is the \(B_2\) (TO) soft mode. Also the resulting LST relation generates a value of \(\epsilon(0)\) which is in good agreement with the measured clamped value presented in Table IV. Our frequency of 56 cm\(^{-1}\) is at variance with the neutron results, which indicate a value of 0.7 THz (23 cm\(^{-1}\)) for the soft mode.

The three \(B_2\) (LO) modes should appear in the forward scattering geometry \(x+z(y, \vec{x}+z) x+z+\Delta y\),

\[A_x^2 B_2\]
\[P(P_y)P + \phi\]

\(\phi = 0^\circ\)

\(\phi = 30^\circ\)

\(\phi = 45^\circ\)

\(\phi = 60^\circ\)

\(\phi = 90^\circ\)

FIG. 12. Forward scattering. \((xy+yz)\) spectrum of the \(B_2\) oblique phonons and \(A_x\) mode propagating in (100). Pure \(B_2\) (LO) modes are located at the positions of the arrows in the \(\phi = 0^\circ\) spectrum.

\[\text{FREQUENCY (cm}^{-1})\]

\[\text{REFLECTIVITY}\]

\[\text{FREQUENCY (cm}^{-1})\]

\[\text{REFLECTIVITY}\]

FIG. 13. \(y\)-polarized ir reflectivity of KNbO\(_3\). Circles represent accurate data points. Dots represent data with uncertain normalization errors. Continuous curve is derived from reflectivity analysis.
corresponding to $\phi = 0$ in the oblique phonons shown in Fig. 12. Once again the spectrum is confusing because it is dominated by the components of the transverse ferroelectric modes which leak through via backreflection and incomplete polarization. In addition to the $A_1$ mode at 283 cm$^{-1}$, we are left with only one apparent $B_2(LO)$ mode, at 192 cm$^{-1}$. Like the $B_1$ modes, the main $B_2(LO)$ modes whose positions are indicated by arrows are not seen in Raman scattering.

The $y$ polarized ir reflectivity is shown in Fig. 13 and its analysis is summarized in Table IV. Apart from the low-frequency region dominated by the ferroelectric mode, the rest of the spectrum is reminiscent of the $x$- and $z$-polarized spectra, implying nearly isotropic LO modes.

Lack of agreement between experiment and theory in all the low-frequency reflectivity data probably reflects normalization errors in the measurements of about 10%. Lack of agreement at the high-frequency end is real. This feature, common to all directions, may represent a coupling of the modes to a higher excitation associated with plasma effects. The crystal was purposely grown in a reduced, conducting state to improve optical quality. It is known from the work of DiDomenico and Wemple$^{27}$ on KTN that similar perovskites exhibited an absorption band at 4 $\mu$m associated with either donor ionization or polaron effects. Consideration of similar effects may sharpen the high-frequency fall in reflectivity.

**E. Oblique modes**

Once the mode assignments have been completed along the symmetry axes, the position of all the oblique modes can be predicted. The theory of Merten$^{28}$ prescribes not only these frequencies but also the mixed symmetry of the modes. In the long wavelength, electrostatic limit the modes satisfy $\nabla \times E = 0$, restricting $E$ to the propagation direction. Then roots of the equation $\nabla \cdot E = 0$ provide the required mode frequencies since it reduces to $\varepsilon_E(\omega) = \sum a_k^2 \varepsilon_{kk}(\omega) = 0$ where $a_k$ are the direction cosines of the propagation direction with respect to the principal, orthorhombic axes and $\varepsilon_{kk}(\omega)$ are known from the previous principal-axis measurements.

We have considered two planes of oblique modes which were easy to measure in the forward direction with the natural crystal faces. The results were not analyzed in great detail, but mostly used to confirm the general description of the modes, especially the symmetry assignments and the im-

**FIG. 14.** Forward scattering. ($xx + zz + xz$) spectrum of $A_1$ and $B_1$ oblique phonons propagating in (100). Pure $A_1(\text{TO})$ and $B_1(\text{TO})$ modes at $\phi = 0^\circ$ develop into mixed $A_1$ and $B_1$ modes at $\phi = 90^\circ$.

**FIG. 15.** Schematic plot of spacial anisotropy of the optic modes in KNbO$_3$. Bold lines refer to quasitransverse ferroelectric modes. LO-TO splittings for the other modes (less than 20 cm$^{-1}$) together with their interference with the ferroelectric mode have been suppressed.
plied spacial anisotropy of the frequencies of the various modes. Phonon propagation in the (010) plane, shown in Fig. 8, provides an exposure of the development of $B_1$ modes. The other plane of propagation was (100): Figure 12 demonstrates the development of $B_2$ LO and TO modes into intermediate modes of mixed $A_1$, $B_1$, and $B_2$ symmetry. Figure 14 demonstrates the development of pure $A_1$(TO) and $B_1$(TO) modes at $\phi = 0^\circ$ into mixed $A_1$ and $B_1$ modes at $\phi = 90^\circ$.

The spacial anisotropy of these modes is summarized schematically in Fig. 15, and has been presented previously. The combination of $A_1 + B_1 + B_2$ modes at 190 cm$^{-1}$, corresponding to the lowest cubic $T_{1u}$ mode, is narrow (3 cm$^{-1}$) and possesses small LO-TO splitting, similarly for the $A_1 + A_2 + B_1$ combination around 280 cm$^{-1}$ derived from $T_{2u}$. These splittings have been omitted for clarity. The remaining modes, drawn in bold lines, carry both the infrared strength and the anisotropy of the crystal. They exhibit linewidths of the order of 30 cm$^{-1}$ and possess essentially isotropic longitudinal partners. Also omitted are the anticrossing features of the interaction of the sharp modes with the ferroelectric mode.

V. DISCUSSION

By finding all the vibrational modes of the crystal near $q = 0$ and correlating their spacial anisotropies, we have arrived at the point where the broad modes associated with the ferroelectricity can be correlated both with the similar modes in the tetragonal phase of BaTiO$_3$ and with two $T_{1u}$ modes in the cubic phases, while the sharp modes can be directly transposed to cubic $T_{1u}$ and $T_{2u}$ modes which are little affected by the phase transitions. Correlation with the neutron results has suggested that the ferroelectric branch may be flat over much of the Brillouin zone apart from the region where it would become degenerate with the rising transverse-acoustic branch. Consequently it would be interesting to try and confirm this by extending the neutron scattering measurements to 300 cm$^{-1}$ to detect the stiffened modes.

Using our results to estimate $\epsilon(0)$, we have arrived at values which compare very well with the direct measurement of the clamped dielectric constants. This situation is very different from BaTiO$_3$, where neither these values of $\epsilon(0)$ nor their temperature dependence agree with the direct measurements at 250 MHz. Consequently a careful study of the temperature dependence of the modes in KNbO$_3$ would provide a good test of whether or not the low-frequency dielectric properties are completely controlled by the optic modes alone. The crystals can be cycled through the higher-temperature phases many times but their optical quality deteriorates and uncontrolled twinning develops in the orthorhombic phase; twinning is even more pronounced in the rhombohedral phase. Twin formation is a serious problem: Not only does it scramble crystal axes but also causes the crystal to crack where the twin planes intercept.

We have mentioned the fickle behavior of background scattering which is dominant in the $A_1$(yy) polarized Raman spectrum shown in Fig. 16. This compares with a similar phenomenon in BaTiO$_3$, where the $A_1$ spectrum seen in both (xx) and (yy) possesses a strong background. This implies that the scattering is only present for components of the Raman polarizability along the soft axis where the dielectric constant is high. This background is less extensive and more structured in KNbO$_3$, with a definite peak around twice the soft-mode frequency in addition to other bands at higher frequency. Its origin, however, cannot be determined from our measurements.

Since this article was written, another report of the polariton spectrum of KNbO$_3$ has been published. Those results confirm the mode identification presented here. The numerical values, however, differ slightly from ours and neither mode damping nor coupling was considered.
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