PHYSICAL REVIEW VOLUME 135, NUMBER 2A 20 JULY 1964

Infrared Studies of Perovskite Titanates

C. H. PERRY AND B. N. KHANNA*

Spectroscopy Laboratory† and Research Laboratory of Electronics,‡ Massachusetts Institute of Technology, Cambridge, Massachusetts

AND

G. RUPPRECHT§

Tyco Laboratories, Inc., Waltham, Massachusetts

(Received 18 October 1963; revised manuscript received 9 March 1964)

The infrared reflection and transmission spectra of $CaTiO_3$, $SrTiO_3$, and $PbTiO_3$ have been measured from 4000 to 30 cm^{-1} at room temperature. The reflection data have been analyzed by means of a Kramers-Kronig method, from which the frequencies of the normal optically active vibrations were derived in agreement with data obtained from transmission spectra. Three infrared active vibrations were observed for cubic $SrTiO_3$ as required by group theory. However, in the case of $CaTiO_3$ and $PbTiO_3$, which crystallize as slightly distorted perovskite structures to become orthorhombic and tetragonal, respectively, additional bands were found which had not been observed previously. These distortions from ideal cubic symmetry would split degenerate modes to possibly give additional frequencies. The results are compared with those of other workers. From the presented data two features emerge: (1) Two normal modes ν_1 and ν_2 are essentially constant for these titanates independent of the cation. (2) The vibration of lowest frequency, ν_3, which is responsible for the ferroelectric behavior, appears to decrease with increasing cation mass. This suggests a mode assignment as proposed by Last.

INTRODUCTION

SEVERAL infrared absorption studies[1–3] on perovskites and other related structures such as rutile have been carried out recently to determine the frequencies of the normal modes of vibration of these interesting materials. Last[1] considered the vibrations of the cubic perovskites (e.g., $SrTiO_3$) in terms of the modes of vibration of the TiO_3 octahedra and reached the conclusion that there should be three triply degenerate infrared-active vibrations. From his infrared studies he assigned the frequencies as follows: a Ti-O stretching mode, ν_1, at 610 cm^{-1}; a Ti-O bending mode, ν_2, at 395 cm^{-1}; and a cation-TiO_3 lattice vibration, ν_3. The frequency ν_3 was beyond the range of his spectrometer.

More recently Barker and Tinkham[2] and Spitzer *et al.*[3] have made thorough investigations of the infrared reflectivity of $SrTiO_3$. Both groups placed the highest frequency at about 550 cm^{-1} and assigned it to a Ti-O stretching vibration. They also found evidence for two more frequencies near 178 cm^{-1} and 90–100 cm^{-1}. The higher of these could be seen directly in the reflectivity curve and was assigned to a cation-TiO_3 vibration by Spitzer *et al.*,[3] whereas the low frequency was obtained only from analysis of the reflection data by a Kramers-Kronig[4] and classical dispersion treatment. It was further shown by Barker and Tinkham[2] and more recently by Cowley[5] that this low-frequency mode exhibits a temperature dependence which has been predicted by Cochran[6] from the temperature dependence of the dielectric constant.

An investigation of the Raman spectrum of $SrTiO_3$, which substance is not expected *a priori* to exhibit its fundamental frequencies therein, was reported by Narayanan and Vedam.[7] Although the spectrum obtained was very weak and broad, it was interpreted by these authors as being primarily a first-order Raman spectrum arising from deviations from ideal cubic symmetry, for instance caused by strain. Certain frequencies are in reasonably close accord with the infrared values of Last.[1] They selected frequencies at 620, 335, and 90 cm^{-1} as those corresponding to Last's ν_1, ν_2, and ν_3. In addition, they asserted that a normal mode rejected by Last as a "torsional motion of the unit cell" (i.e., as an optically inactive motion of symmetry species F_{2u}) should in fact be included among the infrared-active modes, all of which are of symmetry species F_{1u}. The $4F_{1u}$ modes attributed to the observed Raman lines were based on the assumption that the distortion of the unit cell was small enough to give only four distinct vibrational frequencies but was sufficiently large to cause a violation of the selection rules for first-order Raman effect. On the basis of their Raman data, they placed the frequency of this fourth vibration at 441 cm^{-1}, in agreement with the calculations of Rajagopal

---

[*] Present address: Department of Physics, Indian Institute of Technology, Kanpur (U.P.), India.

[†] The work of this laboratory is supported in part by a grant from the National Science Foundation, Number G-19637.

[‡] The work of this laboratory is supported in part by the U. S. Army Signal Corps, the Air Force Office of Scientific Research, and the Office of Naval Research.

[§] This work was supported in part by the Energetics Branch, Air Force Cambridge Research Laboratory under Contract AF19(628)2845.

[1] J. T. Last, Phys. Rev. **105**, 1740 (1957).

[2] A. S. Barker, Jr., and M. Tinkham, Phys. Rev. **125**, 1527 (1962).

[3] W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, Phys. Rev. **126**, 1710 (1962).

[4] T. S. Robinson, Proc. Phys. Soc. (London) **B65**, 910 (1952).

[5] R. A. Cowley, Phys. Rev. Letters **9**, 159 (1962).

[6] W. Cochran, *Advances in Physics* (Taylor & Frances, Ltd., London, 1960), Vol. 9, p. 387.

[7] P. S. Narayanan and K. Vedam, Z. Physik **163**, 158 (1961).

and Srinivasan.[8] The latter authors also estimated the other frequencies as 517, 512, and 74 cm^{-1}. The agreement of the calculated with observed values is not expected to be very close in view of the simplifications required to make the computation tractable.

No band near 450 cm^{-1} had been observed by previous workers in the infrared reflection spectra of $SrTiO_3$.[1–3] In this report we wish to point out experimental evidence against the existence of a band at $\sim$450 cm^{-1} in $SrTiO_3$. However, additional bands of varying intensity near this frequency are present in $CaTiO_3$ and in $PbTiO_3$, and are reported here for the first time.

EXPERIMENTAL

The room-temperature reflectances of calcium, strontium, and lead titanate have been measured from 4000–30 cm^{-1} relative to the reflectance of a reference mirror coated with aluminum. Transmission measurements over the same frequency range were made on finely divided powders of the three materials suspended in polyethylene and potassium bromide matrices.

Reflection and transmission data above 300 cm^{-1} were obtained on a Perkin-Elmer Model 112 double-pass instrument equipped with NaCl and CsBr prisms. The reflection spectra were recorded at an angle of incidence of about 45° on the sample. The transmission data were repeated on a Perkin-Elmer Model 521 double-beam spectrophotometer which scanned continuously from 4000–250 cm^{-1}. A reflection attachment which provided an angle of incidence of about 15° and required a sample only 18 mm×2 mm in area was used in the P-E 521 to repeat the reflection data down to 250 cm^{-1}.

A single beam grating instrument originally constructed in this Laboratory by Lord and McCubbin[9] and recently modified to vacuum operation with more convenient sample optics[10] was used from 500–30 cm^{-1}. The angle of incidence was again 15°. The two Perkin-Elmer instruments were flushed with evaporated liquid nitrogen to remove water vapor as much as possible. The complete removal of water vapor in the long-wave vacuum instrument provided smooth backgrounds so that more accurate transmission and reflection data could be obtained compared with a flushed single-beam instrument.

Reflection measurements at 5 cm^{-1} were made on all three materials with a "carcinotron" as a source of 2-mm waves at Lincoln Laboratory, MIT, and were found to be in good agreement with our far infrared results down to 30 cm^{-1}.

The specimen of $SrTiO_3$ consisted of a large highly polished single crystal 1 in. in diameter. The calcium and lead titanate samples were each made up of a mosaic of four polycrystalline samples cemented to an aluminum backing plate. The materials were ground and polished to a sample size of 1 in.$\times 1\frac{1}{4}$ in. so that full use could be made of the light beam with no vignetting.

Samples for transmission studies above 300 cm^{-1} were suspended in a KBr pellet by the usual techniques. Below 600 cm^{-1}, polyethylene was found to be the most convenient matrix. The press was brought up to about 120°C and the samples were pressed at 25 000 lb/sq in. at this temperature for approximately 5 min.

ANALYSIS OF DATA

The reflectivity data were transformed using a Kramers-Kronig relation.[4] The K-K relation used for the reflectivity R can be expressed as

$$\theta(\nu)=\frac{2\nu}{\pi}\int_0^\infty \frac{\ln[r(\nu')]d\nu'}{\nu^2-\nu'^2}, \tag{1}$$

where $\theta(\nu)$ is the associated phase angle and was obtained by using the IBM-7090 digital computer at the MIT Computation Center.

The reflectivity amplitude is characterized by $re^{i\theta}$, where $r=R^{1/2}$. This has been shown to be a good approximation even at 45°.

$$re^{i\theta}=(n-ik-1)/(n-ik+1), \tag{2}$$

$$n=(1-r^2)/(1+r^2-2r\cos\theta), \tag{3}$$

$$k=2r\sin\theta/(1+r^2-2r\cos\theta), \tag{4}$$

where n is the refractive index and k is the extinction coefficient.

The real and imaginary parts of the complex dielectric constant, ϵ' and ϵ'', can be written

$$\epsilon'=n^2-k^2, \tag{5}$$

$$\epsilon''=2nk, \tag{6}$$

and it is more revealing to show the results of the dispersion analysis in terms of the dielectric constant than in terms of n or k.

The integral in Eq. (1) was evaluated by representing $\ln r(\nu')$ by strainght-line segments between data points. The data were extrapolated to cover the infinite interval of Eq. (1). The reflectivity was assumed constant from 4000 cm^{-1} to ∞ and from 30 cm^{-1} to 0. The justification of the extension of the data was confirmed by comparing the limiting values of R predicted from known values of the high- and low-frequency dielectric constants where these values were known. It is assumed that $k \ll n$ at these limiting frequencies so that

$$R=(\epsilon^{1/2}-1)^2/(\epsilon^{1/2}+1)^2. \tag{7}$$

Each peak in the plot of ϵ'' versus energy (frequency) provided by the K-K analysis represents a resonance. The frequency of a given resonance is the frequency at

---

[8] A. K. Rajagopal and R. Srinivasan, Phys. Chem. Solids **23**, 633 (1962).

[9] R. C. Lord and T. K. McCubbin, Jr., J. Opt. Soc. Am. **47**, 689 (1957).

[10] C. H. Perry, Far Infrared Spectroscopy, Mass. Inst. Tech. Res. Lab. Electron. Quart. Progr. Rept. **70**, 19 (1963).

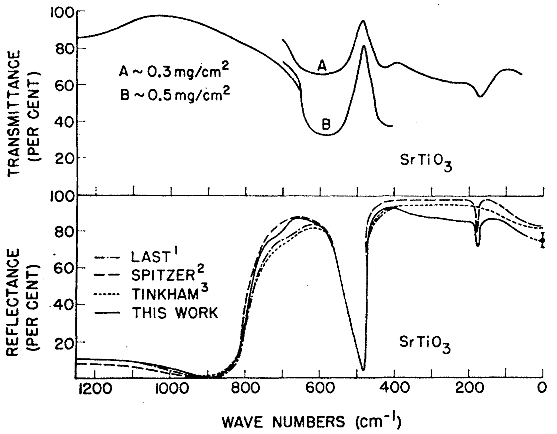

FIG. 1. The infrared transmittance and reflectance spectra of SrTiO₃ from 1250 to 5 cm⁻¹.

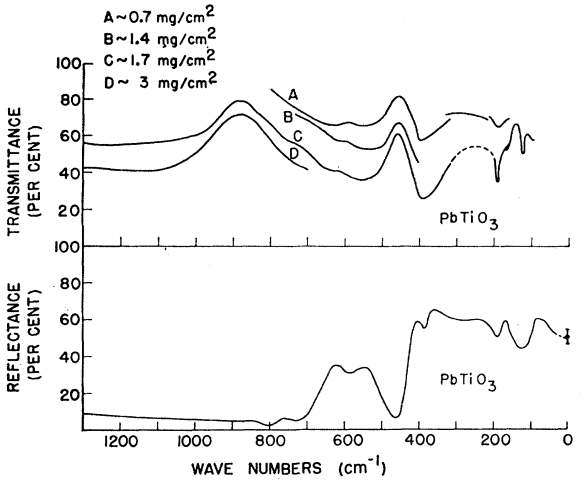

FIG. 2. The infrared transmittance and reflectance spectra of PbTiO₃ from 1250 to 5 cm⁻¹.

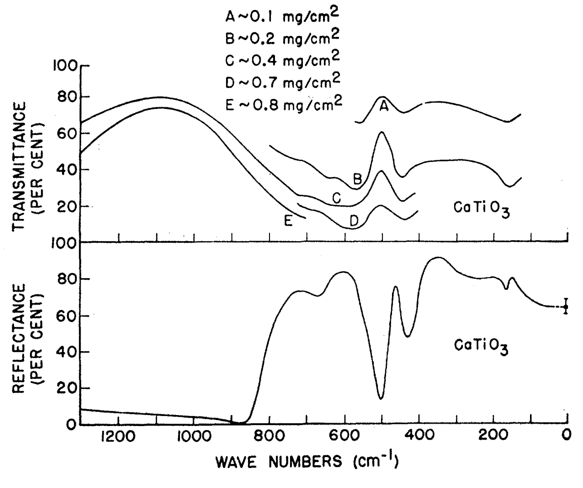

FIG. 3. The infrared transmittance and reflectance spectra of CaTiO₃ from 1250 to 5 cm⁻¹.

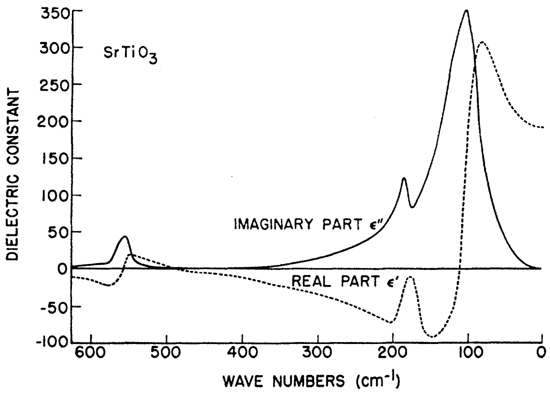

FIG. 4. Real and imaginary part of the dielectric constant of SrTiO₃ obtained from the reflectivity data in Fig. 1.

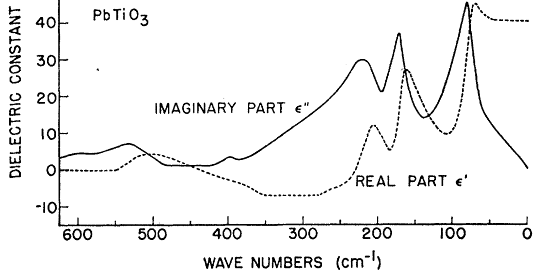

FIG. 5. Real and imaginary part of the dielectric constant of PbTiO₃ obtained from the reflectivity data in Fig. 2.

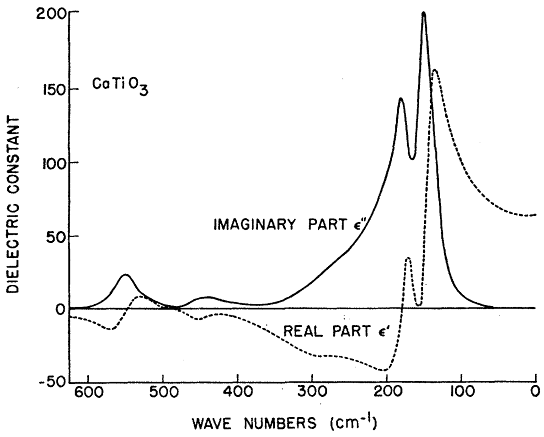

FIG. 6. Real and imaginary part of the dielectric constant of CaTiO₃ obtained from the reflectivity data in Fig. 3.

which the conductivity σ, $(\sigma_j = \epsilon_j''\nu/2)$ is a maximum.[11] The quantity ϵ_j'' is the contribution of the jth resonance to ϵ''.

In the approximation $\gamma_j/\nu_j \ll 1$, the maximum of ϵ_j'' also occurs at ν_j, where γ is given by the frequency half-width of the ϵ'' peak.

---

[11] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. XVII, p. 635.

TABLE I. Infrared and Raman frequencies in $SrTiO_3$ (cm^{-1}).

Modes	This work	Last[a]	Tinkham[c]	Sptizer[d]	Raman (Obs.) Narayanan and Vedam[f]	Calculated Rajagopal and Srinivasan[g]
ν_1 (stretch)	555±5	610[b]	550	544[e]	620	517
ν_2 (bend)	185±5	395[b]	175 100	88[e]	335	512
ν_3 (Sr-TiO_3)	100±5	···	no assignment given	178	90	74
ν_4 (bend?)	···	···	···	···	441	445

[a] Reference 1.
[b] Frequency maximum observed in reflectivity without K-K analysis of the data.
[c] Reference 2.
[d] Reference 3.
[e] Spitzer is not clear as to whether ν_1 and ν_2 should be interchanged.
[f] Reference 5.
[g] Reference 8.

DISCUSSION

The reflectance and transmittance curves are shown in Figs. 1–3. Figures 4–6 show the real and imaginary parts of the dielectric constant for the three materials. Measurements below 400 cm^{-1} are estimated to be accurate to about ±5% for the reasons reported earlier.[12]

The reflectance curve shown here for $SrTiO_3$ resembles those reported by the earlier workers.[1–3] Last[1] was unable to work below 300 cm^{-1} and was thus unable to detect the minimum at about 175 cm^{-1}. However, owing to the discrepancy between Last and the other groups with regard to a band at 400 cm^{-1}, we have studied the region from 500 to 300 cm^{-1} with special care, using three different instruments: The Perkin-Elmer 112, with a CsBr prism, the Perkin-Elmer 521, and our long-wave instrument with a grating of 40 grooves/mm blazed at 360 cm^{-1}. In the last instrument we used two reststrahlen plates of CaF_2, which has a very sharp short-wavelength cutoff at $\sim 20\,\mu$ (500 cm^{-1}).[13]

Reflection measurements over the same range were repeated at two different angles of incidence and also at liquid-nitrogen temperatures. No subsidiary maximum in the region of 450 cm^{-1} was found before the reflectance curve rose to a maximum at about 360 cm^{-1}.

Transmission measurements in this region showed a broad minimum at 400 cm^{-1}, in agreement with Last[1] and Barker and Tinkham.[2] However, Barker and Tinkham found that this minimum is sensitive to powder density and suggested that it might be a scattering effect. In $CaTiO_3$ and $PbTiO_3$, however, we could firmly establish that a band does indeed exist around 450 cm^{-1}, which can be observed both in reflection and transmission.

The curves also show a maximum at about 600 cm^{-1} with a slight shoulder near 700 cm^{-1}, as well as a low-frequency minimum in reflection around 150 to 200 cm^{-1}. These results are substantiated by transmission data on pressed KBr and polyethylene pellets containing various concentrations of titanate powder. Minima in reflection coincide with maxima in transmission and vice versa. It is also apparent from Fig. 2 and Fig. 3 that samples with different concentrations show no appreciable frequency shift at the transmittance minima.

The maximum in reflectance at 605 cm^{-1} in $SrTiO_3$ which is in good agreement with Last, Spitzer *et al.*, and Barker and Tinkham (before K-K analysis of the data) has been unanimously assigned to the Ti-O stretching vibration by the previous authors.[1–3]

Table I compiles the frequencies of the normal modes in $SrTiO_3$ after a K-K analysis as obtained by different workers and their interpretation if available.

Results for $CaTiO_3$, $SrTiO_3$, and $PbTiO_3$ are compared in Table II. Only in $CaTiO_3$ and $PbTiO_3$ were bands around 450 cm^{-1} observed. These bands, as well as an additional band at 220 cm^{-1} in $PbTiO_3$, probably arise from systematic distortion from ideal cubic symmetry to the orthorhombic structure for $CaTiO_3$ and

TABLE II. Frequencies of the normal modes of $CaTiO_3$, $SrTiO_3$, and $PbTiO_3$ obtained from a K-K analysis of the reflection data.

		Infrared frequencies (in cm^{-1}) and symmetry of infrared modes		
Sample	Crystal symmetry[a]	ν_1 (Ti-O stretch)	ν_2 (Ti-O-Ti bend)	ν_3 (cation-TiO_3 lattice mode)
$CaTiO_3$	Orthorhombic	549±3 443±3 (B_1,B_2,A_1)	179±2 (B_1,B_2,A_1)	148±2 (B_1,B_2,A_1)
$SrTiO_3$	Cubic $O_h{}^1$ ($Pm3m$)	555±5 F_{1u}	185±5 (F_{1u})	100±5 (F_{1u})
$PbTiO_3$	Tetragonal	530±5 400±5 (E_u,A_1)	220±3 172±2 (E_u,A_1)	83±2 (E_u,A_1)

[a] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951), Vol. VII, p. a5.

---

[12] J. R. Durig, R. C. Lord, W. J. Gardner, and L. H. Johnston, J. Opt. Soc. Am. **52**, 1078 (1962).
[13] A. Mitsuishi, Y. Yamada, and H. Yoshinaga, J. Opt. Soc. Am. **52**, 14 (1962).

to the tetragonal structure for $PbTiO_3$, which would split degenerate modes to give additional distinct frequencies although the splitting need not be observed in every case. With respect to the observation of the four Raman lines ascribed by Narayanan and Vedam[7] to four F_{1u} modes made active by small deviations from ideal cubic symmetry, it can be pointed out that this same mechanism would render an optical mode of F_{2u} symmetry Raman-active also. Thus, there is no reason to suppose from either the infrared or Raman data of $SrTiO_3$ that Last's analysis of the infrared-active modes of $BaTiO_3$ and $SrTiO_3$ is incorrect. An ambiguity appears to exist as to whether an "internal vibration" or the cation-TiO_3 vibration is responsible for the ferroelectric behavior of these materials. In $SrTiO_3$ the ν_3 band has been interpreted as an internal vibration and the ν_2 band as the cation-TiO_3 vibration by Spitzer *et al.*[3] From Table II it can be seen that in all three titanates, the ν_1 and ν_2 vibrations are essentially constant as the cation changes from Ca with a mass of 40 to Sr with a mass of 88 to Pb with a mass of 207. However, ν_3 does depend sensitively upon the nature of the cation.

Consequently, we feel it is reasonable to associate those frequencies which remain nearly constant with those structural elements which are common to all three materials, namely the TiO_3 octahedra, whereas the mode which varies should be connected with what is different in these titanates, namely the cation. This leads to a mode assignment as proposed by Last and confirmed by Hunt *et al.*[14] for the cubic perovskite $KMgF_3$: ν_1 and ν_2 are the stretching and the bending mode of the TiO_3 octahedron, whereas ν_3, the temperature-dependent mode, is identified with a vibration of the cation against the TiO_3 octahedron.

The comparison between ν_3 for $CaTiO_3$, $SrTiO_3$, and $PbTiO_3$ at room temperature is of course of a qualitative nature, since these frequencies are temperature-dependent. Among the three materials under investigation only $SrTiO_3$ and $PbTiO_3$ are known to be ferroelectric. Recent studies of the dielectric constant of $CaTiO_3$ have shown, however, that also in this material ϵ obeys a Curie-Weiss law but with a negative Curie-temperature ($-84°K$).[15] This means that the temperature-dependent soft mode, ν_3, in this material never tends to become unstable.

At room temperature, where the presented optical data have been obtained, $SrTiO_3$ and $CaTiO_3$ are in the paraelectric state above the Curie temperature whereas $PbTiO_3$ has undergone a phase transition from cubic to tetragonal at 763°K and is in a ferroelectric state. Under these circumstances it seems reasonable to compare the frequencies ν_3 of $CaTiO_3$ and $SrTiO_3$ at the same temperature above the Curie temperature that is at equal $(T-T_c)$. For $CaTiO_3$ room temperature is 384°K above the Curie temperature and $\nu_3 = 148 \pm 2$ cm^{-1}. $SrTiO_3$ has a Curie temperature of[15] 44°K and from Cowley's data[5] one finds that the ν_3 vibration at 428°K (i.e., 384°K above the Curie temperature) is 110 cm^{-1}.

Under the assumption of a mode assignment as discussed above, a simple spring constant model relates the force constants K_1, K_2, the reduced masses μ_1, μ_2, and the resonance frequencies ν_1, ν_2 for Sr-TiO_3 and Ca-TiO_3 in the form

$$K_1/K_2 = \mu_1\nu_1^2/\mu_2\nu_2^2 = 1.1\,,$$

so that under similar conditions the calcium and strontium in the perovskite lattice experience about the same binding forces. Megaw[16] has pointed out that because of the large polarizability and strong fourfold charge on the titanium ion there are reasons to believe that in the TiO_3 octahedra considerable covalent contributions to the binding forces between the titanium and the oxygen are present. Measurements of the field dependence of the elastic constant also seem to indicate that a strong covalent contribution to the binding energy exists.[17] In view of the present experimental evidence, it appears that Last's mode assignment represents the physical reality to a good approximation, but a complete normal coordinate analysis would be necessary to provide for an adequate description of the so-called "soft mode."

ACKNOWLEDGMENTS

The authors wish to thank Professor R. C. Lord for his advice and encouragement in this work, Dr. G. R. Hunt of the Spectroscopy Laboratory, MIT, for many helpful discussions and J. Ballentyne of the Insulation Laboratory, MIT, for the use of his K-K analysis program and for the reflection measurements taken at Lincoln Laboratory, MIT. We are much obliged to Dr. G. Wilkinson, King's College, London, for checking our dielectric constant results by using his K-K program on our reflectivity data.

---

[14] G. R. Hunt, C. H. Perry, and J. Ferguson, Phys. Rev. **134**, A688 (1964). Also reported in the Mass. Inst. Tech. Res. Lab. Electron. Quart. Progr. Rept. **72**, 19 (1964).

[15] G. Rupprecht and R. O. Bell, Phys. Rev. (to be published).

[16] H. D. Megaw, Acta Cryst. **5**, 739 (1952).

[17] R. O. Bell and G. Rupprecht, Phys. Rev. **129**, 90 (1963).