Splitting of the TO Mode in Calcite by the Polarization Field

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This paper describes an investigation of the behavior of an infrared-active E_u mode of the internal vibrations in a calcite crystal when a wave vector is inclined at an angle θ to the crystallographic c axis. It has been deduced through theoretical consideration that the polarization field splits the E_u mode into two components which have dipole moments with orthogonal polarizations $P_{\parallel}$ and $P_{\perp}$, and that the value of $\omega_{TO}(P_{\parallel})$ changes with θ, while the values of $\omega_{LO}(P_{\parallel})$, $\omega_{TO}(P_{\perp})$, and $\omega_{LO}(P_{\perp})$ remain unchanged. In order to see whether or not this prediction is valid, the values of the above frequencies for various values of θ were obtained by analyzing the reststrahlen bands observed in five specimens with reflecting surfaces of θ equal to 0°, 24.5°, 44.5°, 65.5°, and 90°, which were found to be in accordance with the curves given by theoretical calculation.

I. INTRODUCTION

Calcite has a crystal structure which belongs to the D_{3d}^6 ($R\bar{3}C$) space group, with two molecules per primitive cell.[1] It can be shown group theoretically that there are 30 phonon modes with wave vector $\vec{q} = 0$ distributed among the various irreducible representations of the D_{3d} point group as follows:

$$\Gamma_{30} = A_{1g} + 2A_{1u} + 3A_{2g} + 4A_{2u} + 4E_g + 6E_u \ .$$

One A_{2u} and one E_u mode correspond to rigid translations of the whole crystal. The A_{1g} and E_g modes are Raman active, while the A_{2u} and E_u modes are infrared active and have a dipole moment parallel and perpendicular to the crystallographic c axis, respectively. All of the A_{1u} and A_{2g} modes are Raman and infrared inactive.[2]

Among the infrared-active modes, one A_{2u} and two E_u modes arise from the internal vibrations of the CO_3^{-2} ions. The vibration to be dealt with in the present investigation is the E_u mode which has the resonance frequency of 1410 cm^{-1}. It gives rise to an intense reststrahlen band by reflection from a surface cut perpendicular to the c axis, as is represented by curve A in Fig. 1. The surface cut parallel to the c axis gives the same reflectivity curve for light polarized perpendicular to the c axis, while it gives the reflectivity curve B for light polarized parallel to the c axis. It is well known[3] that the reststrahlen band obtained from a rhombohedral face (1011) has a shoulder as represented by the curve C. For this, no reasonable explanation has as yet been given.[4]

From recent observations, we have found that the reflectivity curve C consists of two kinds of reststrahlen bands orthogonally polarized to each other. One of them, polarized parallel to the [1$\bar{1}$00] direction, has a resonance frequency of 1410 cm^{-1} and coincides with curve A. The other, which is polarized parallel to the [$\bar{1}\bar{1}$01] direction,

has a resonance frequency of 1493 cm^{-1}. It cannot be ascribed to the A_{2u} modes, since such a band does not appear in curve B. Therefore, it is conceivable that this reststrahlen band might be attributed to some effect due to the removal of the degeneracy of the E_u mode. A theoretical consideration of this problem and the experiment which has been carried out to see the validity of the consideration are what we wish to present in the following.

II. THEORY

In the theoretical treatment, we shall consider the reflection of light at normal incidence by a plane crystal surface which is cut to have a normal inclined to the crystallographic c axis in general. In Fig. 2, the P plane represents the plane of the paper and the crystal surface is placed perpendicular to this plane. The coordinates are set so that the z axis be parallel to the crystallographic c axis, and the y axis be perpendicular to the P plane. θ is the angle between the z axis and the normal n of the reflecting surface. In the case of normal incidence, the phonons which resonate with the light wave have the wave vector normal to the reflecting plane; hence, θ represents the angle between the direction of the phonon wave vector and the crystallographic c axis. Let K be a pair of CO_3^{-2} ions in a Bravais cell. It should be noted here that the positive and negative ions in a single CO_3^{-2} ion are distributed in the x-y plane and that, for the E_u mode now concerned, their displacement vector is limited within the x-y plane by the symmetry of this crystal. Since n is always at right angles to the y axis, the waves of the y component of the displacement vector may be considered to be TO phonons. On the other hand, the waves of the x component of the displacement vector are neither TO nor LO phonons[5] because the x axis is inclined at $(90° - \theta)$ to the n axis. By decomposing the x component of
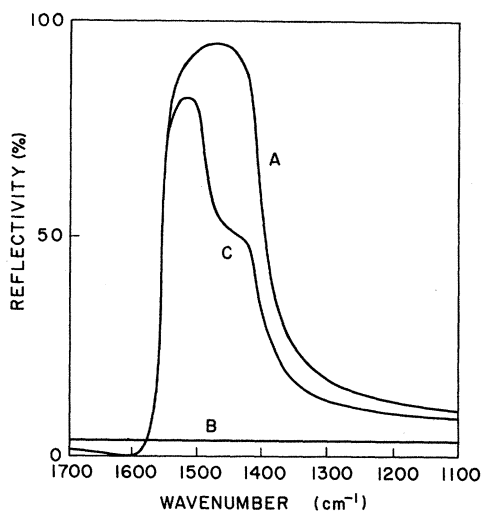
FIG. 1. Reflection spectra in the region 1100 to 1700 cm⁻¹. A is a spectrum obtained by a surface cut perpendicular to the c axis. B is that obtained by a surface cut parallel to the c axis for the light polarized parallel to the c axis. C is that obtained by a rhombohedral face.

the displacement vector into two components Δx_n and Δx_m, however, it is understandable that the waves of this component provide two kinds of phonons: One is the TO phonons associated with the Δx_m; and the other the LO phonons associated with the Δx_n. The frequencies of TO and LO phonons thus produced will be designated by $\omega_{TO}(P_{\parallel})$ and $\omega_{LO}(P_{\parallel})$, respectively. In the polar vibrations, LO phonons give rise to the electric field due to the polarization along the wave vector.[6] Since the x axis is not perpendicular to the n axis, the real displacement in
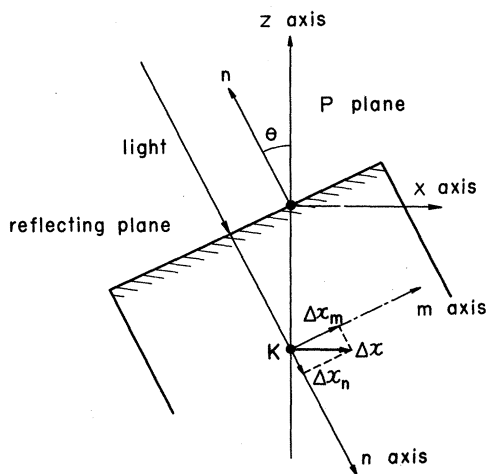

FIG. 2. Coordinate system. z axis is parallel to the crystallographic c axis. K represents a pair of CO_3^{-2} ions in a Bravais cell.
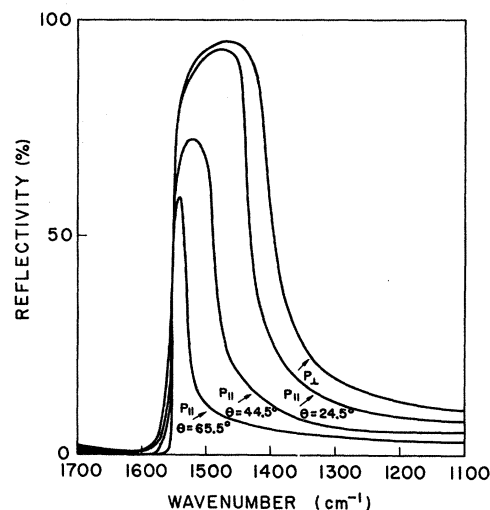

FIG. 3. Observed reflectivities in the spectral region 1100 to 1700 cm⁻¹ by the surfaces with different values of θ.

the direction of the x axis suffers a force due to the electric field of the polarization. On the other hand, the displacement in the direction of the y axis does not suffer such a force since it remains perpendicular to the n axis. Consequently, the value of $\omega_{TO}(P_{\parallel})$ is always higher than that of $\omega_{TO}(P_{\perp})$.

In general, the difference in the restoring force between the longitudinal and the transverse displacement in polar vibrations[6] is given as follows:

$$\mu(\omega_{LO}^2 - \omega_{TO}^2)\Delta x = 4\pi e^* P \ , \qquad (1)$$

where μ is the reduced mass of the mode, ω_{LO} is the frequency of LO phonon, ω_{TO} is that of the TO phonon, Δx is the relative displacement of the positive and negative ions, e^* the effective charge, and P the polarization. Therefore, the difference $\Delta f'$ of the force constant, between the longitudinal and
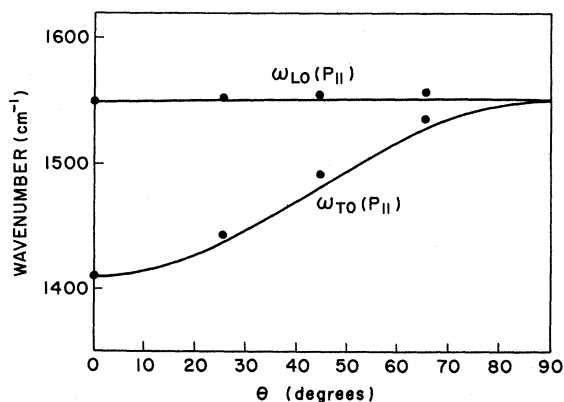

FIG. 4. Calculated curves of $\omega_{LO}(P_{\parallel})$ and $\omega_{TO}(P_{\parallel})$ and plots of observed values.

TABLE I. Lattice-vibration parameters obtained from the reflectivity data.

θ (deg)	$\epsilon_1 (P_\perp)$	$\epsilon_1 (P_{\parallel})$	$4\pi\rho(P_\perp)$	$4\pi\rho(P_{\parallel})$	$\omega_{TO}(P_\perp)$ (cm^{-1})	$\omega_{TO}(P_{\parallel})$ (cm^{-1})	$\omega_{LO}(P_\perp)$ (cm^{-1})	$\omega_{LO}(P_{\parallel})$ (cm^{-1})
0	2.63	2.63	0.55	0.55	1410	1410	1550	1550
24.5	2.63	2.56	0.55	0.40	1410	1443	1550	1552
44.5	2.63	2.45	0.55	0.20	1410	1493	1550	1553
65.5	2.63	2.24	0.55	0.06	1410	1535	1550	1555
90	2.63	2.18	0.55	0.00	1410		1550	

the transverse displacement is given as follows:

$$\Delta f' = \omega_{LO}^2 - \omega_{TO}^2 = \frac{4\pi e^*}{\mu\Delta x} P = \frac{4\pi\rho}{\epsilon_1}\omega_{TO}^2 , \qquad (2)$$

where ϵ_1 is the high-frequency dielectric constant and $4\pi\rho$ is the mode strength. If the electric field along the x axis due to the polarization is given by $4\pi P$, the electric field in the direction of n axis becomes $4\pi P \cos(90° - \theta)$, which leads to the electric field along the x axis due to LO phonons in the direction of the n axis being given by $4\pi P \sin^2\theta$. Therefore, for the TO phonons with wave vector along the n axis, the difference Δf of the force constant between the displacement along the x axis and that along the y axis is given as follows:

$$\Delta f = \omega_{TO}(P_{\parallel})^2 - \omega_{TO}(P_\perp)^2 = \Delta f' \sin^2\theta . \qquad (3)$$

Then, the dependence of $\omega_{TO}(P_{\parallel})$ on θ is given as follows:

$$\omega_{TO}(P_{\parallel}) = [\omega_{TO}(P_\perp)^2 + \Delta f' \sin^2\theta]^{1/2} ; \qquad (4)$$

and that of $\omega_{LO}(P_{\parallel})$ is given as follows:

$$\omega_{LO}(P_{\parallel}) = [\omega_{TO}(P_{\parallel})^2 + \Delta f' \cos^2\theta]^{1/2} = \omega_{LO}(P_\perp) . \qquad (5)$$

The value of $\Delta f'$ in the above equations can be given by the parameters $4\pi\rho$, ϵ_1, and ω_{TO} obtained by the reflection measurements for the light polarized perpendicular to the P plane using the relation

$$\Delta f' = (4\pi\rho/\epsilon_1) \omega_{TO}(P_\perp)^2 . \qquad (6)$$

From Eqs. (4) and (5), it is found that $\omega_{TO}(P_{\parallel})$ is dependent on θ, while $\omega_{LO}(P_{\parallel})$ is equal to $\omega_{LO}(P_\perp)$ without depending on θ. Since $\omega_{TO}(P_\perp)$ is independent of θ, the appearance of two kinds of reststrahlen bands by reflection from a rhombohedral face can be well explained.

III. EXPERIMENTAL PROCEDURE AND RESULTS

In order to confirm the validity of the theory described in Sec. II, the reststrahlen bands were observed by using crystal surfaces with different values of θ. The crystals used in the present work were large rhombs of optical-grade calcite occur-

ring naturally in Mexico. Five specimens were prepared which had reflecting surfaces of θ equal to 0°, 24.5°, 44.5°, 65.5°, and 90°. A rhombohedral face of a crystal was provided for the surface of θ equal to 44.5°. The reflecting surfaces were ground and polished carefully according to optical techniques to have the highest optical quality.

The reflectivity was measured by using an infrared-grating-spectrophotometer Japan Spectroscopic DS-601 fitted with a AgCl polarizer at the incidence angle of 11°.

The reflectivities in the spectral region 1100 to 1700 cm^{-1} obtained by five specimens are summarized in Fig. 3. The reststrahlen bands of five specimens polarized perpendicular to the P plane (see Fig. 2) perfectly coincide with one another, as represented by the curve $P_\perp$ in this figure. It implies that $\omega_{TO}(P_\perp)$ and $\omega_{LO}(P_\perp)$ are independent of θ as is expected theoretically. On the other hand, the reststrahlen band polarized parallel to the P plane, designated by $P_{\parallel}$, coincides with the curve $P_\perp$ when θ is zero, but deviates from the curve $P_\perp$ when θ is not zero. With increasing θ, the low-frequency side of the curve $P_{\parallel}$ is displaced towards higher frequency while the high-frequency side of the curve remains nearly unchanged. Moreover, the maximum intensity decreases with increasing θ, finally reaching zero at $\theta = 90°$.

It was found that all of the reststrahlen bands excellently follow the reflectivity curve given by the dispersion theory assuming a single resonator. From the analysis, the resonance frequency ω_{TO}, the mode strength $4\pi\rho$, and the high-frequency dielectric constant ϵ_1 were found for an individual reststrahlen band, and are listed in Table I. In this table, the values of $\omega_{LO}(P_{\parallel})$ obtained by applying the Lyddane-Sachs-Teller relation are also shown. The values of $\omega_{LO}(P_{\parallel})$ and $\omega_{TO}(P_{\parallel})$ thus obtained are plotted against θ in Fig. 4. On the other hand, the theoretical values of $\omega_{LO}(P_{\parallel})$ and $\omega_{TO}(P_{\parallel})$, shown as solid curves in Fig. 4, were calculated by Eqs. (4)-(6), using the values of $4\pi\rho$, ϵ_1, and ω_{TO} obtained from the curve $P_\perp$. In this figure, it will be seen that the theoretical values are in excellent agreement with the observed values, which is considered to show the validity of the theoretical treatment described in Secs. I and II.

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Model for OH⁻, OD⁻, and CN⁻ Impurities in Alkali Halide Matrices

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A model has been developed for calculating the potential barrier-hindering angular motion and possible off-center displacement of the polar impurities in the alkali halide matrices. The general method of the multipole expansion of the intermolecular interaction has been employed. The calculations have been done for the OH⁻, OD⁻, and CN⁻ impurities in the KCl, KBr, NaCl, RbCl, and KI matrices. It has been found that the OH⁻ and OD⁻ impurities are displaced by about 0.2–0.3 Å from the normal-lattice site in the different alkali halide lattices. For the CN⁻ case, no appreciable displacement of the impurity c.m. is evidenced. In this case, the effect of the relaxation of the lattice near the impurity is also considered. This has been found to add a small tetragonal term of the type $(4\pi)^{1/2} K'' Y_0^2$ to the octahedral potential. The addition of such a small tetragonal term has recently been demonstrated by Pompi and Narayanamurti to explain successfully the rather unexpected infrared results and also the anomalous specific-heat results of Harrison *et al*. The calculated values of the barrier and the off-center displacement have been used successfully to explain the librational frequency and the tunneling splitting of these impurities in the matrices. The general validity of different approaches has been discussed in the light of the librational frequencies and their isotope effect.

I. INTRODUCTION

Ionic crystals containing a small concentration of dipolar impurities like OH⁻ and CN⁻ have attracted considerable experimental[1−9] and theoretical[10−15] attention. The presence of such impurities in the alkali halide crystals has been experimentally seen to cause changes in the dielectric constant, specific heat, and thermal conductivity at low temperatures. The interpretation of these and other phenomena like infrared absorption and paraelectric-resonance studies requires a definite knowledge of the potential in which the impurity ion performs different types of motions. These experiments also present strong evidence for a novel type of lattice distortion, when the mismatch in the size between the impurity and the replaced ion is large. Thus, when the OH⁻ impurity is substituted for the Cl⁻ ion in a KCl matrix, experiments suggest that the OH⁻ impurity shuttles around a number of equivalent off-center positions leading to observable dielectric, thermal, and mechanical effects. In this respect the behavior of the OH⁻ and CN⁻ ions is more or less similar to that of a Li⁺ ion dispersed in the ionic matrices.[16] A first-principles analysis of the origin of the off-center position of the center of mass (c.m.) and the angle-dependent part of the potential energy (i.e., the barrier-hindering angular motion of the dipolar impurity) is, therefore, of interest.

Attempts[17−19] have been made to calculate the potential barrier and the origin of such off-center displacements for a Li⁺ ion in the alkali halide matrices. Such calculations have been done within the framework of a Born-Mayer model with either an arbitrary but steep linear term to avoid collapse[18] or a modification for the polarization and the repulsion effects at short distances.[19]

For the dipolar impurities Lawless[20] used a point-charge–point-dipole model to calculate the rotational barrier for the OH⁻ impurity in alkali halide matrices. More recently, Chandra *et al*.[21] calculated the barrier height on a more realistic approach. The general method of multipole expansion was used to calculate the rotational barrier parameter K. This method could be applied to any diatomic impurity, provided its quadrupole and hexadecapole moments were known. This calculation gave a good estimate of the barrier height, except in the case of the KBr-OH⁻ system, where the calculated barrier parameter was about 25% less than