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Infrared Absorption of the Hydroxyl Ion in Alkali Halide Crystals*

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The O—H stretching band and its immediate sidebands have been studied for OH$^-$ impurities in NaCl, KCl, RbCl, KBr, KI, and NaBr from 1.4 to 300°K. Sideband splittings range from 12 cm^{-1} in NaCl:OH$^-$ to 37 cm^{-1} in KBr:OH$^-$, and correlate with dips in the low-temperature thermal conductivity and with far-infrared absorption bands. Preliminary results on the electric-field-induced dichroism in KCl:OH$^-$ and RbCl:OH$^-$ give a dipole transition moment perpendicular to the O—H axis for the main sideband. There is evidence that several sidebands in NaCl:OH$^-$ are themselves combination bands with one or more 2–3-cm^{-1} tunneling levels. The first overtone yields values of $\omega_e = 3790$ cm^{-1} and $\omega_e x_e = 85.5$ cm^{-1} for OH$^-$ in KBr. These values explain very well the OH$^-$/OD$^-$ isotope shift of the main stretching band in KBr and KCl. The main-band oscillator strengths are small, on the order of 5×10^{-3} for most crystals, but this value is consistent with a theoretical calculation of the dipole moment by Cade. The main bands broaden rapidly with increasing temperature, possibly indicating a prominent lifetime-limiting role played by the sideband levels. The sideband levels themselves are tentatively suggested to be due to a center-of-mass resonance in KBr:OH$^-$ and to a librational resonance or fast tunneling level in KCl:OH$^-$.

INTRODUCTION

THE hydroxyl ion in alkali halide crystals is responsible for many effects that are not yet understood, or at best are only partly understood. Several years ago one of us discovered an extremely strong decrease in the helium-temperature thermal conductivity of NaCl doped with NaOH[1]—the conductivity was reduced by a factor of 100 by what we now identify as 10 parts per million hydroxyl ions.[2] At that time, however, the hydroxyl ion could not be positively identified as the phonon scattering agent. The obvious experiment of looking for the O—H stretching band in the 3-μ infrared region was then tried, but straightforward measurements at room temperature showed nothing. We have since been studying this impurity ion more intensively by means of thermal conductivity and infrared absorption measurements.

Recently the OH$^-$ ion in alkali halides has become the subject of many investigations by various workers. Careful measurements of the electric-field-induced dichroism of the ultraviolet OH band have shown that the hydroxyl ion goes into the lattice substitutionally with its axis along $\langle 100\rangle$, except possibly for KI.[3–5] The OH$^-$ ion increases the low-temperature dielectric constant of KCl[6,7] and KBr.[8] Cooling by adiabatic electric depolarization has been achieved,[9–11] and low-lying tunneling levels have been observed by paraelectric resonance measurements.[12–16] Anelastic relaxation effects have been observed in KCl and NaCl containing OH$^-$.[17,18] The ultraviolet "OH" band has been studied in some detail.[19–27] The related luminescence measurements are also of some interest.[28–30]

In this paper we report our results on the 3-μ infrared O—H stretching band. Several abstracts have been published on this band by our group[31–33] and by the

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Utah group.[34,35] Additional work has appeared in unpublished theses.[36,37] The related thermal-conductivity work will be published later,[38] but preliminary abstracts have already appeared.[2,32,39,40] A short report on the results of both types of measurement on KCl:OH$^-$ and KCl:OD$^-$ has already appeared.[41] Two sidebands were associated with the main O—H stretching band: One, at a splitting of 32 cm^{-1}, is discussed in the present paper; the other, at a splitting of 293 cm^{-1}, was assigned to a (stretching+libration) transition.[32,42] The librational transition near 300 cm^{-1} has been observed directly in some crystals.[34] Our results on the librational transition will be the subject of a separate paper.[43] The 32-cm^{-1} sideband in KCl:OH$^-$ was correlated with resonance scattering of phonons as revealed by thermal-conductivity measurements.[2] This energy level is revealed by direct far-infrared absorption measurements[44]; its analog apparently occurs in other host crystals.[32] It cannot be explained[41] by a simple model of the Devonshire type[45] in which the hydroxyl ion rotates in a cubic crystal field. In this paper we shall look for distinguishing characteristics and trends exhibited by this "non-Devonshire" or "30-cm^{-1}" level.

The spectra for OH$^-$ in KCl, RbCl, and KBr are somewhat similar and will be presented first. We have results upon isotopic substitution of deuterium for hydrogen in KCl and KBr and preliminary results on the electric-field-induced dichroism in KCl and RbCl.

The NaCl spectra are quite different and will be discussed in some detail. The KI spectra are different in yet other ways. Some data on NaBr:OH$^-$ will also be presented.

After presenting and discussing the data, we then give additional discussions of the first overtone of the main band, the main-band isotope shift, and its oscillator strength, all of which are well understood quantitatively, and of the linewidth, which is understood qualitatively. The paper concludes with some speculations about the origin of the "30-cm^{-1}" levels.

EXPERIMENTAL TECHNIQUES

Infrared data in the 3500–4200-cm^{-1} range were taken on a custom spectrophotometer built around a Perkin-Elmer model 99G double-pass monochromator modified to chop at 33 Hz.[37] A 300-lines/mm grating was used, and the source was a 500-W 120-V quartz-tungsten lamp operated at 55 V or less.[46] A filter removed light of frequencies greater than 5000 cm^{-1}. Calibration was achieved with HCl and water-vapor lines and was accurate to about $\frac{1}{3}$ cm^{-1} when special care was taken. The data have been corrected to give vacuum frequencies. Ordinarily, accuracy was $\frac{1}{2}$ to 1 cm^{-1}. Frequency differences are good to about $\frac{1}{2}$ cm^{-1}. The emerging monochromatic beam was focused on the sample in the cryostat, and refocused on a lead sulfide detector operated at liquid-nitrogen temperature. The beam could be moved to bypass the sample but still pass through the cryostat windows by turning two plane mirrors in such a way as to keep the beam focused on the detector.

Good photometric accuracy was obtained with a null technique by adding a variable-amplitude square wave 180° out of phase to the detector signal and feeding the sum through a preamplifier into a lock-in amplifier. The system was adjusted for a null with the sample bypassed and then again with the beam passing through the sample in such a way that the sample transmission coefficient appeared directly as the setting of a 10-turn potentiometer.

Atmospheric water-vapor bands were eliminated almost entirely by fast flushing of the light path with very dry air. Monochromator slit widths were 100 μ or less, giving a theoretical resolution of 0.8 cm^{-1} or better. Practical resolution seemed to be about 1 cm^{-1}.

A few measurements were made on a Beckman IR7 or IR9 recording double-beam spectrophotometer. With these instruments, the entire Nernst glower output was incident on the sample, and the resulting radiation limited the low-temperature performance. In addition, the light-path flushing was not as good as with our custom spectrophotometer.

Three cryostats were used to cover the temperature range of 1.4–380°K. Lowest temperatures required an immersion helium cryostat because of room-temperature radiation reaching the sample through the cryostat windows and because of the low sample thermal conductivity caused by the hydroxyl impurity.

The inner tail of the immersion cryostat had two bonded sapphire windows[47] and was sealed to the helium can with an indium O-ring seal. Sapphire disks[48] were used as cold windows on the surrounding nitrogen-temperature tail and on the outer vacuum jacket. These had not received the usual final polish in order to avoid interference fringes that appear when stock windows are used. The optic axes of all the windows were oriented to prevent depolarization of the beam during the dichroism experiments.

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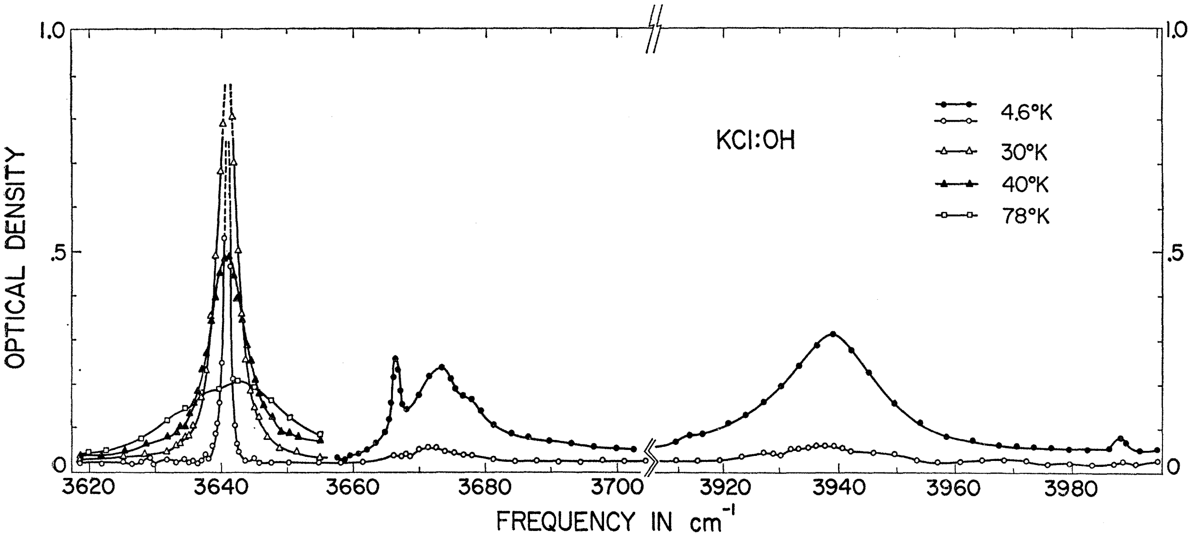

FIG. 1. The infrared absorption of KCl:KOH. The curve labelled with the solid black dots refers to a 14-mm-thick sample with 1500-ppm OH^-; the other curves refer to a 12-mm-thick sample with 250-ppm OH^-.

For the electric-field-induced dichroism experiments, electrodes were painted on the sides of the sample with silver paint.[49] The surfaces were then overpainted with G.E. 7031 varnish. Data were obtained by measuring the absorption in the usual way for a given polarization direction, turning on the field, and measuring the changed sample transmission. Small changes of absorption could be verified by repeated application and removal of the field.

Measurements from 4.5 to 78°K were made in a cryostat equipped with a helium exchange gas switch.[50] One end of the sample was clamped to the heat sink with indium for thermal contact. There were LiF windows on the 4.2 and 78°K heat shields and on the outer vacuum jacket. All openings were masked to match the solid angle-area product at the sample to that of the focused light beam. Most hydroxide-doped samples could be cooled to 4.6°K with the bath at 4.2°K and with the exchange gas in. There was no important change along the sample, as measured with germanium resistance thermometers, except for heavily doped NaCl:NaOH with its extremely low helium-temperature thermal conductivity. Temperatures above 4.6°K were easily maintained within 2% by manual adjustment of the exchange gas pressure and heater power input to the heat sink.

A small liquid-nitrogen Dewar was used from 78 to 380°K. It had exchange gas coupling from the sample chamber to the nitrogen bath and was similar to one used for thermal conductivity measurements by Caldwell.[50]

Our methods of crystal growth and hydroxide-concentration determination have been described in detail elsewhere.[27] Most crystals were grown in mullite crucibles in an argon atmosphere by the Czochralski technique. Reagent-grade salt was used as starting material. Reagent-grade hydroxide was added in the form of fresh pellets or aqueous solution. Hydroxide concentrations were ultimately based on pH titrations. Aqueous solutions of the crystals were titrated with 0.02*N* HCl to determine the neutral end points. The strength of the ultraviolet OH band was calibrated by this technique and used as a secondary standard. The as-grown crystals were cleaved and measured without further heat treatment.

RESULTS

KCl

Typical data for KCl:KOH are shown in Fig. 1. These are the earlier data[41] corrected for spectrometer calibration. The main stretching band is at 3641 cm^{-1}. It has a strongly temperature-dependent linewidth and an integrated area that appears to decrease at low temperatures. We now believe that this loss of area is not real for the following two reasons: (1) Recent measurements with high (0.17 cm^{-1}) resolution by Härtel give no such loss of area.[35] (2) The first overtone in the similar system KBr:KOH shows little or no loss of area upon cooling (see below). Our apparent loss of main-band area can be attributed to a linewidth effect. If the true peak optical density is not small compared with unity and if the true linewidth is less than the instrumental resolution, the calculated absorption curve will have an area less than that of the true absorption curve. Our data in Fig. 1 and in subsequent illustrations are not corrected for this, but the curves are shown dashed where we believe them to be in quantitative error.

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The two broad high-energy sidebands visible in Fig. 1 are those mentioned in the Introduction. The one at 3839 cm^{-1}, a splitting of 297.5 cm^{-1} from the main band, is believed to be the (stretching+libration) combination band. The other broad sideband at 3672.5 cm^{-1} (a splitting of 31.5 cm^{-1}) was shown to be a combination band first by thermal conductivity measurements,[2] which showed a dip in the conductivity at 14°K, and then by the far-infrared measurements of Bosomworth,[44] who found a band at 32 cm^{-1}. His results are compared with our sideband data in Fig. 2. The over-all agreement is quite good. The narrow sideband peak at 25 cm^{-1} is not seen in the far infrared. It is not yet clear what its origin is. If it is indeed a true combination band, then it must have different symmetry from the main 32-cm^{-1} band to make it inactive in the far infrared. It may not be a true sideband, but rather part of the main band shifted by interactions of some OH^- ions with impurities. It shows an electric-field-induced dichroism, however; this supports the interpretation that this is a true sideband.

Other small, sharp bands near the 3641-cm^{-1} main band have also been observed and may also be due to impurities, but we should mention that at high OH^- concentrations Härtel found weak bands a few cm^{-1} from the main band with integrated areas scaling linearly with OH^- concentrations.[35] These might therefore be intrinsic to KCl:KOH.

Preliminary results for the electric-field-induced dichroism for the 32-cm^{-1} sideband are shown in Fig. 2. From dichroism measurements in the ultraviolet, Kuhn and Lüty found a $\langle 100\rangle$ orientation for the O—H axis and an effective dipole moment (using the external field E_a) given by $\mu=0.82$ eA.[3] With our applied field of $E_a=73$ kV/cm$=0.73$ mV/A, we obtain an alignment energy

$$U=\mu E_a=0.6\text{ meV}=k_B\times(7°\text{K})$$
$$(k_B=\text{Boltzmann's constant}).$$

Then with E_a along (100), alignment would be greater than 95% at 1.4°K. If all the moments were free to align, if the line was not otherwise changed, and if the transition moment for the 32-cm^{-1} band were transverse to the O—H axis, one would expect the following changes in absorption constant:

$$\Delta\alpha(\perp)=0.5\alpha \quad\text{and}\quad \Delta\alpha(\|)=-\alpha.$$

The values of $\Delta\alpha$ in Fig. 2 are about $\frac{2}{3}$ these predicted values; this is satisfactory agreement for a preliminary experiment of this type. We thus tentatively conclude that the transition dipole moment for the 32-cm^{-1} band is perpendicular to the O—H axis. This presumably would hold for both the sideband and the direct far-infrared band. Stress-induced dichroism measurements by Härtel agree with this conclusion.[36]

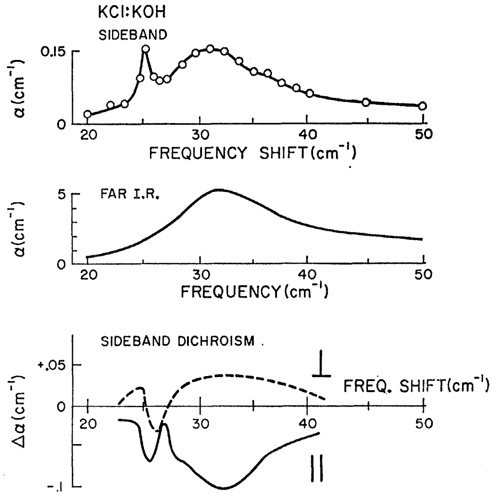

FIG. 2. Studies of the 32-cm^{-1} sideband in a 710-ppm KCl:KOH crystal. Upper curve: near-infrared sideband plotted as a function of frequency difference from the 3641-cm^{-1} main band. Center curve: far-infrared absorption at 1.7°K, according to Bosomworth (Ref. 44). Bottom curves: dichroism induced at 1.4°K in the sideband by an $\langle 100\rangle$ applied electric field E_a of 73 kV/cm. $\perp$ means E_{light} perpendicular to E_a; $\|$ means E_{light} parallel to E_a. The light path was 11 mm long and was located between the electrodes, which were 1.1 mm apart and 8.5 mm long.

No field-induced dichroism could be assigned to the main band at 3641 cm^{-1}. Any change in the true area under the peak would be difficult to observe, if, as explained above, the line is strong and much narrower than the instrumental resolution. To within $\frac{1}{3}$ cm^{-1}

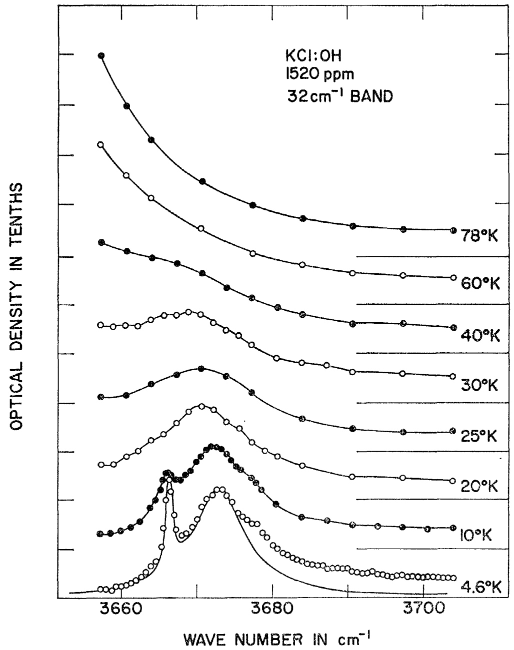

FIG. 3. Temperature dependence of the 32-cm^{-1} sideband in KCl:KOH. Crystal thickness, 14 mm. For clarity, each curve is successively displaced upwards by 0.1 optical density units. The solid curve at the bottom is the sum of two Lorentzians.

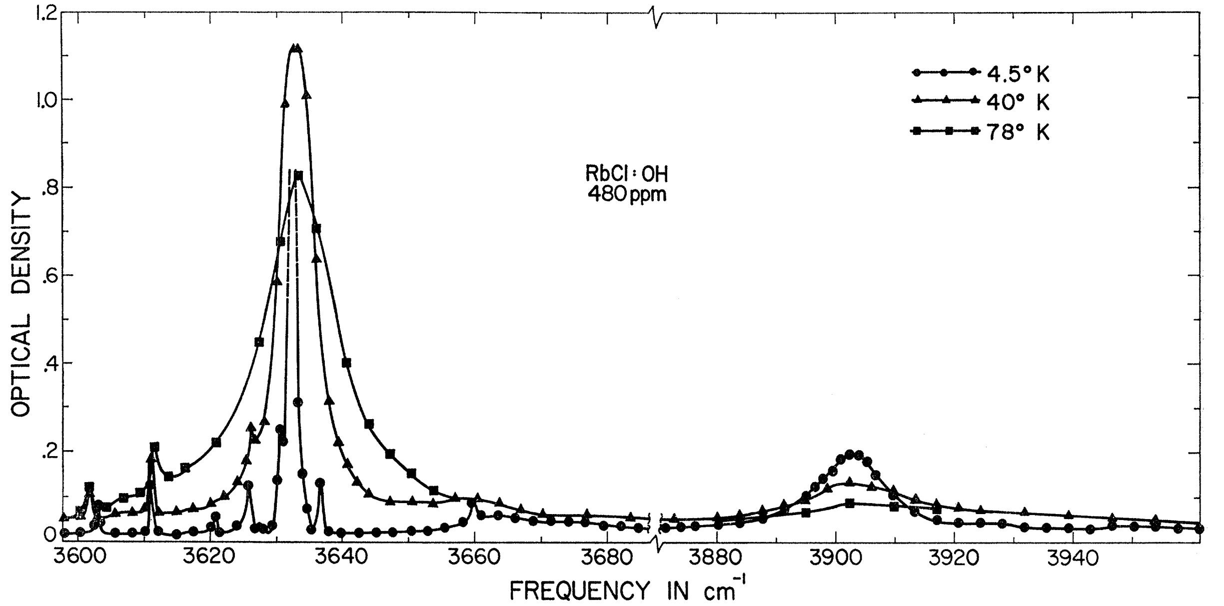

FIG. 4. The infrared absorption of RbCl:RbOH. Sample thickness, 14 mm.

there was no observable shift in the position of the main band.

Figure 3 shows the change with temperature of the 32-cm^{-1} sideband. At 78°K it has lost its separate identity, but it appears to be quantitatively greater than the tail of an assumed Lorentzian main band. The 32-cm^{-1} band thus seems to be at least partly present in a greatly broadened form at 78°K.

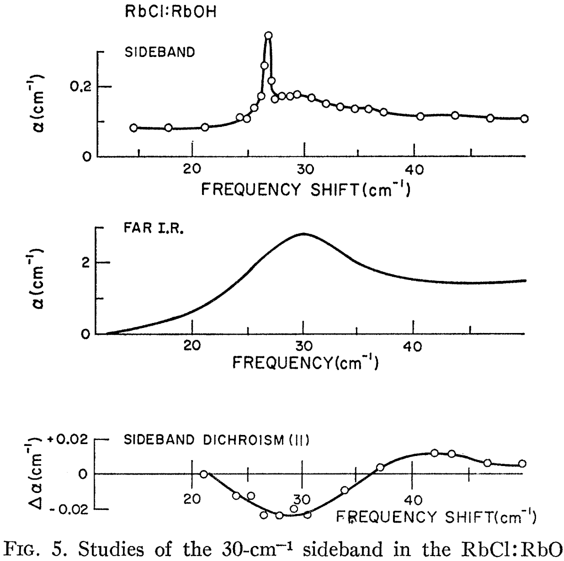

FIG. 5. Studies of the 30-cm^{-1} sideband in the RbCl:RbOH crystal used for Fig. 4. Upper curve: near-infrared sideband plotted as a function of the frequency difference from the 3632.5-cm^{-1} main band. Center curve: direct far-infrared absorption at 1.7°K, according to Bosomworth (Ref. 44). Bottom curve: dichroism induced at 1.4°K in the sideband by an applied ⟨100⟩ field E_a of 45 kV/cm. E_{light} parallel to E_a. (Sensitivity was too low to observe a perpendicular dichroism.) The light path was 14 mm long and was located between the electrodes, which were 1.8 mm apart and 11 mm long.

As the bottom curve in Fig. 3 shows, the main part of the 32-cm^{-1} band is fitted well by a Lorentzian curve, but a broad band remains at higher energies, as is also apparent from the far-infrared data.

In KCl doped with deuteroxide (OD$^-$) the main stretching band is at 2684.5±0.5 cm^{-1} at low temperatures. We found a broad OD$^-$ sideband at 9°K at a splitting of 23 cm^{-1}, but we were unable to resolve a narrow sideband line analogous to the 25-cm^{-1} OH$^-$ sideband line. The associated resonant dip in the thermal conductivity of this sample occurred at 10°K; the librational splitting was 231.6 cm^{-1}.

RbCl

The results shown in Figs. 4 and 5 on RbCl:OH$^-$ are analogous to those found on KCl:OH$^-$. The main band is at 3632.5 cm^{-1}; the librational sideband is 270.5 cm^{-1} higher at 3903 cm^{-1}. There is a low-energy sideband at a splitting of about 30 cm^{-1} that produces a dip in the thermal conductivity and a direct far-infrared band, as can be seen from Bosomworth's data[44] reproduced in Fig. 5. The sharp spike at 27 cm^{-1} in the sideband spectrum is not seen in the far infrared. There are also some sharp bands near the main band, especially at lower frequencies, which we tentatively assign to OH$^-$ ions near impurities. The RbCl starting material for this crystal was of nominal 99.9% purity, with Na and K as the main impurities. It is not hard to imagine that these impurities give rise to the extra sharp bands. No measurements were made on RbCl:OD$^-$.

The preliminary dichroism results in Fig. 5 are quantitatively disappointing. The field was large enough to produce a theoretical alignment along ⟨100⟩

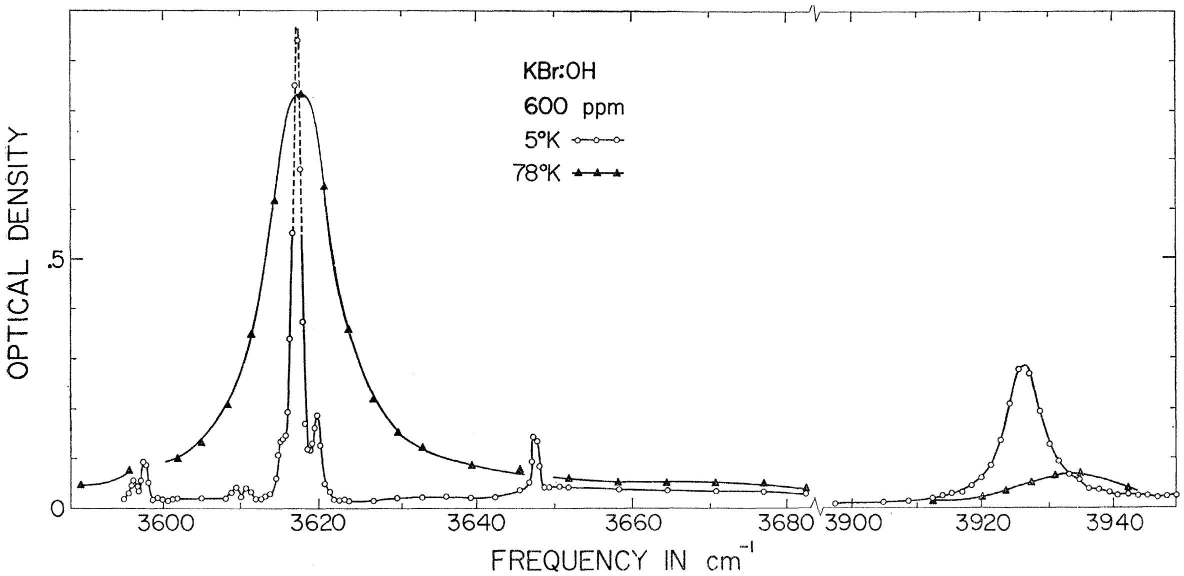

FIG. 6. The infrared absorption spectrum of KBr containing 600 ppm of KOH. Crystal thickness, 16 mm.

of 83% at 1.4°K. This should have produced a change in absorption constant at a 30-cm^{-1} shift of about 0.1 cm^{-1}, depending upon how much of the absorption at 30 cm^{-1} is due to the sideband proper. It is possible that the relatively large number of impurities present in this crystal prevented all the OH$^-$ ions from orienting in the applied field, without much changing the shape and position of the main absorption bands.

If we attribute the quantitative discrepancy to impurity effects, the qualitative dichroism results in RbCl can be understood by assuming that both the sideband and the direct far-infrared band consist of a superposition of two bands, one at 30 cm^{-1} with transition dipole moment perpendicular to the O—H axis and a broader band starting at about 35 cm^{-1} with a transition moment parallel to the O—H axis.

The dichroism data in Fig. 5 may also be interpreted as resulting from a simple shift of the 30-cm^{-1} peak to higher energy with applied field.

KBr

The infrared absorption of a KBr:KOH crystal is shown in Fig. 6. The main band is at 3617.5 cm^{-1}. The librator is at 309.25 cm^{-1} higher frequency. There is a very broad high-energy sideband at a splitting of 25 to about 60 cm^{-1}. It seems to be responsible for a thermal conductivity dip.[32] This band measured on a more heavily doped crystal is compared with the far-infrared data[44] on the same crystal in Fig. 7. The sideband shows an extra sharp line at a splitting of 30 cm^{-1} that is not found in the far infrared. This is quite similar in appearance to the 25-cm^{-1} band in KCl:OH$^-$ (Fig. 2) and the 27-cm^{-1} band in RbCl:OH$^-$ (Fig. 5).

Bosomworth's original published curve extends to higher frequencies than is shown in Fig. 7. There are broad peaks at about 67 cm^{-1} and 87 cm^{-1} that seem to be impurity-induced phonon absorption modes. The

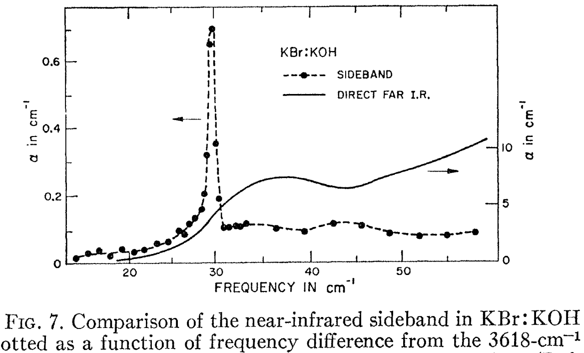

FIG. 7. Comparison of the near-infrared sideband in KBr:KOH plotted as a function of frequency difference from the 3618-cm^{-1} main band with Bosomworth's far-infrared absorption data (Ref. 44). Both measurements were on pieces from the same crystal containing 1500-ppm KOH.

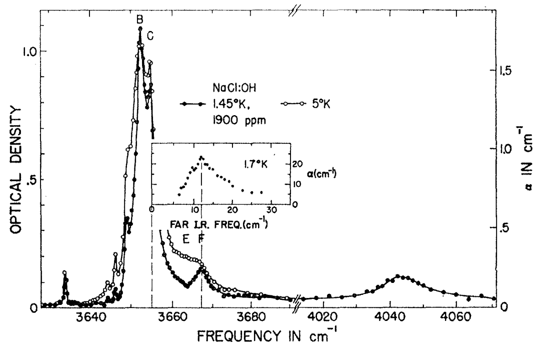

FIG. 8. Infrared absorption spectra of a 16-mm-thick crystal of NaCl doped with 1900-ppm NaOH. The inset shows Bosomworth's far-infrared absorption data measured on a crystal from the same boule (Ref. 44).

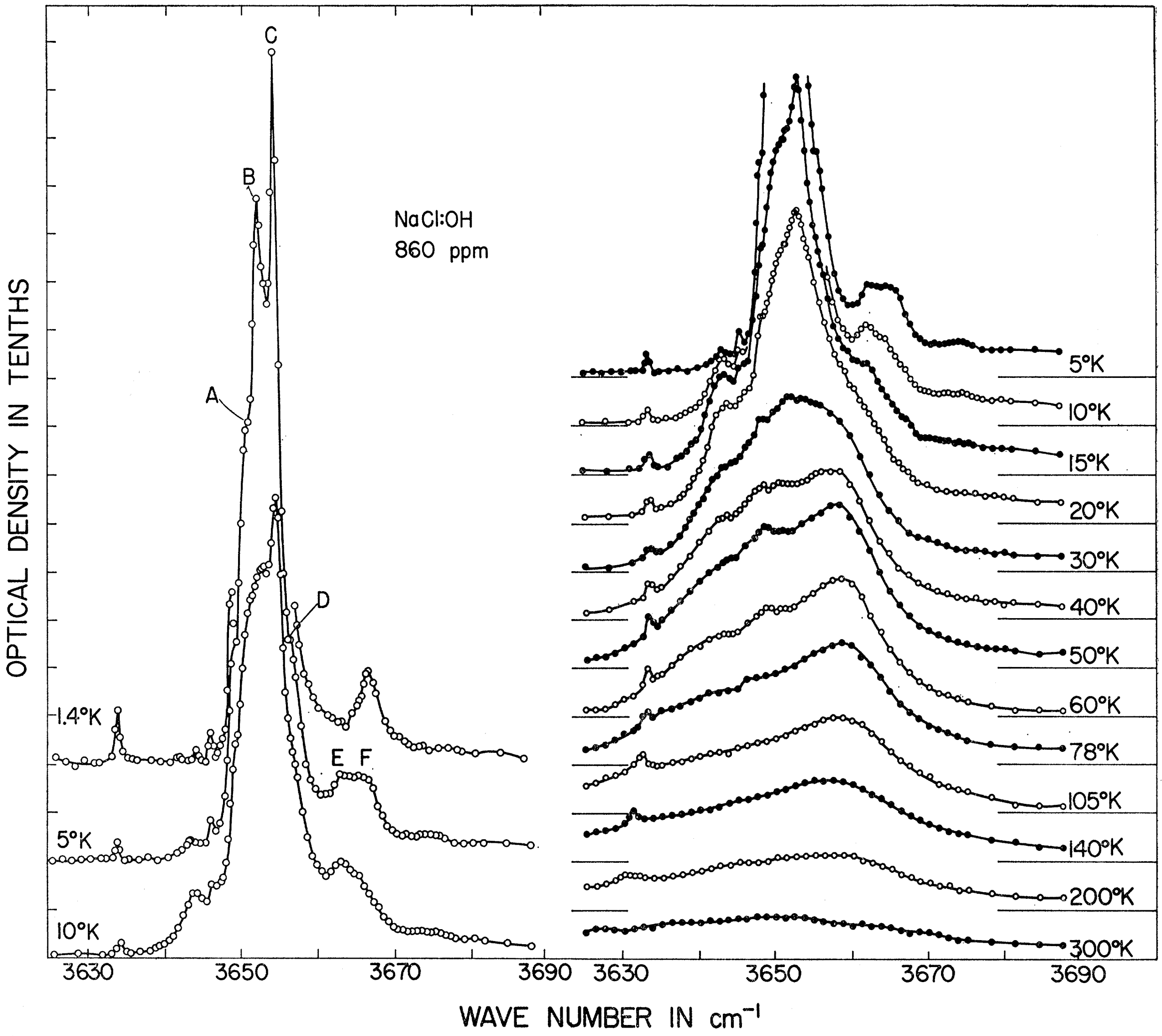

FIG. 9. Infrared absorption spectra of a 20-mm-thick crystal of NaCl containing 860-ppm NaOH. The 5 and 10°K data have been partially reproduced at the top right to show the temperature dependence of the sidebands.

weak sideband above 40-cm^{-1} splitting may be due to this same effect.

No field-induced dichroism measurements were attempted by us on KBr:KOH. Handler and Aspnes made measurements on the main band by the ac field modulation technique at room temperature and found a slight line narrowing for parallel polarization.[51]

The main stretching band in $KBr:OD^-$ was found at 2668.0±0.5 cm^{-1}. An extremely weak broad sideband was found at about the same place (37 cm^{-1}) as in $KBr:OH^-$ but the spectrum was too weak and noisy to allow the sideband peak position to be determined very accurately. This has been located more precisely at 35.5 cm^{-1} in the far infrared.[44] Since the OD^- data are not very precise, more detailed measurements would be desirable, but there is an indication of a sharp sideband at a splitting of 23 cm^{-1}. In this connection recall that Fig. 7 showed an OH^- sideband peak at a splitting of 30 cm^{-1}.

NaCl

In Figs. 8–12, we show the infrared absorption spectra of NaCl crystals containing various amounts of OH^-. These complex spectra depend strongly on temperature and on hydroxide concentration. Consider first the most heavily doped crystal shown in Fig. 8. Superficially this looks like the spectra seen for KCl, RbCl, and KBr; the apparent "main band" centered about 3652.5 cm^{-1} (line *B*) is broader, however, and has structure. There is a librational sideband at 4036 cm^{-1} and a closer sideband (line *F*) at 3666.5 cm^{-1}. The apparent similarity with other crystals vanishes for lighter dopings. Line *B* is not the main band then. Line *C* is the most prominant line for the 860-ppm crystal shown in Fig. 9; line *B* broadens and loses its

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[51] P. Handler and D. E. Aspnes, Phys. Rev. Letters **17**, 1095 (1966).

identity with rising temperature. Line *B* appears only as a shoulder in the data of Fig. 10 on a 470-ppm crystal and not at all in the data from a 60-ppm crystal shown in Figs. 10–12.

Bosomworth's far-infrared absorption curve at 1.7°K for a sample from our 1900-ppm boule is shown in the inset of Fig. 8.[44] If we identify the main peak at *F* as a combination band involving the 12-cm^{-1} far-infrared level, then line *C* at 3654.5 cm^{-1} (3655 cm^{-1} in Fig. 8) must be identified as the main O—H stretching band.

The identification of line *C* as the main band is tentative and makes it difficult to explain the origin of lines *A* and *B*. This identification is supported, however, by a comparison of our near-infrared data on the 60-ppm crystal with the far-infrared data of Kirby *et al.* at 4°K on the same crystal.[52] They found peaks at 9.2, 10.3, 12.2, 15.6, and 22 cm^{-1}. These are represented as shifts from line *C* by the arrows "*a*" through "*e*" at the bottom of Figs. 10 and 12; that is, "*a*" designates Kirby's 9.2-cm^{-1} line, etc. Assuming line *C* to be the main vibration band (V) in the near infrared, we find that lines *E* and *F* are probably $V+a$ and $V+c$, respectively. At 8°K the 60-ppm crystal shows weak lines *G* and *H* (Fig. 11). These freeze out by 5°K and appear to be the difference bands $V-c$ and $V-a$.

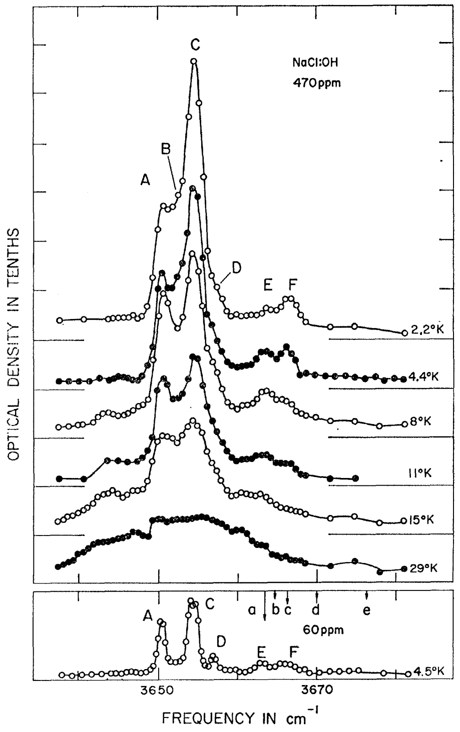

FIG. 10. Infrared absorption spectra of NaCl:OH^-. The top curves were taken on a 13-mm-thick crystal containing 470-ppm OH^-. The bottom curve refers to a 15-mm-thick 60-ppm crystal.

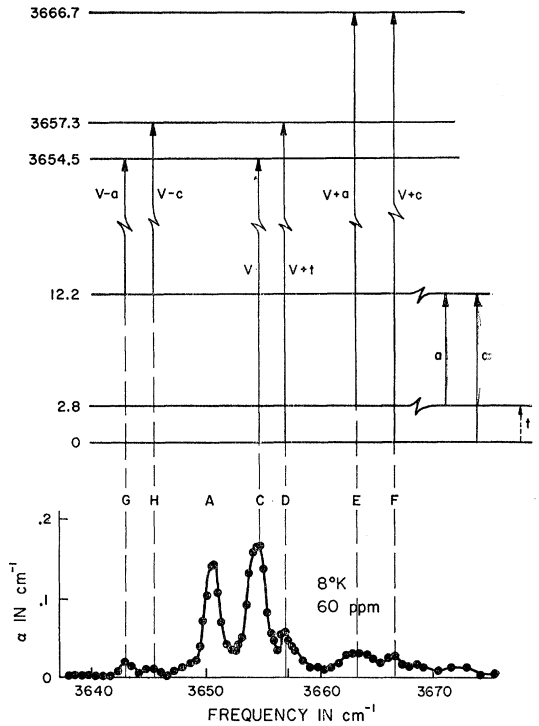

FIG. 11. Infrared absorption of the 60-ppm NaCl:OH^- crystal at 8°K. Some suggested energy levels and transitions are shown. See text for details.

An alternative assignment of the main stretching vibration V might be to line *A*. Then lines *E* and *F* would be interpreted as $V+c$ and $V+d$, respectively. Line *C* would presumably be a combination band of V plus a 4-cm^{-1} level. Low-temperature thermal conductivity measurements give no results that would suggest a 4-cm^{-1} level.[38] On the other hand, dips in the conductivity at 0.4–0.8°K and at 3–5°K have been found. These can be explained by resonance phonon scattering off centers with energy levels in the 1.2–2.5-cm^{-1} and 9–15-cm^{-1} ranges. Thus, on the basis of the present evidence we shall keep the assignment of *C* as the main band and simply accept levels *A* and *B* as of unknown origin.

In Fig. 11, we suggest an assignment of some of the low-lying energy levels to combinations of a 2.8-cm^{-1} tunneling level (t) with a 12.2-cm^{-1} level that is assumed to be the same as the 12.2-cm^{-1} level (c) of Kirby *et al.* This assignment is tentative and is intended only as a basis for discussion. It offers no explanation for band *A*. The temperature dependence of level *E* shows that it freezes out below 4°K, as can be seen from Figs. 8–10 and 12. It is therefore a difference band involving a lower level about 2–3 cm^{-1} above the ground state. This level is responsible at least in part for the thermal conductivity dip in the 0.4–0.8°K region. Level t may actually represent several levels in the 1–3-cm^{-1} range, but the present data are insufficient to reveal them.

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[52] R. D. Kirby, I. G. Nolt, R. W. Alexander, Jr., and A. J. Sievers, Phys. Rev. **168**, 1057 (1968).

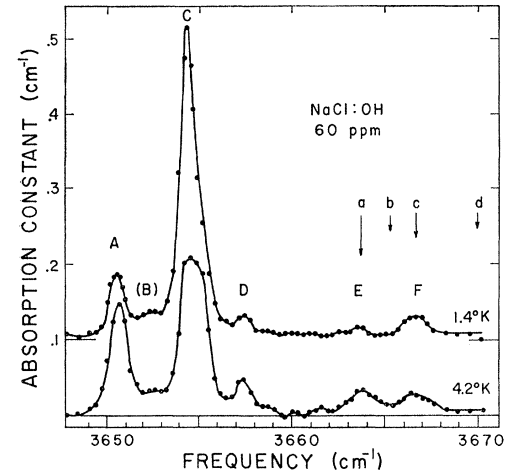

FIG. 12. Detailed spectra of the 60-ppm NaCl:OH$^-$ crystal. Base line of upper curve has been shifted 0.1 cm^{-1} for clarity.

Figure 9 also shows a broad, weak sideband in the 3670–3677-cm^{-1} region that may be a superposition of the combinations bands $V+d$ and $V+e$.

Additional absorption curves for the 60-ppm crystal, shown in Fig. 12, have a temperature dependence consistent with that of the 470-ppm curves of Fig. 10. Line E freezes out below 4°K, and line C grows relative to line A as the crystal is cooled below 8°K. There is a hint of level B at 3652.5 cm^{-1}.

The rapid changes with temperature shown by the NaCl:OH$^-$ spectra of Figs. 9 and 10 imply quite clearly that the low-lying energy levels responsible for the sideband structure are coupled very strongly to the phonons of the host crystal. This same coupling is responsible for the strong phonon scattering by these levels as revealed by thermal conductivity measurements. As mentioned in the introduction to this paper, it was not possible to identify the phonon scatterer in the original thermal conductivity work[1] as OH$^-$ by means of straightforward infrared measurements at room temperature. A glance at the 300°K curve of Fig. 9 clearly shows how easy it would be to miss the weak, broad band that remains at room temperature. Even the low-temperature absorption curves are about five times weaker than similar curves in most other alkali halides. This will be discussed below.

Figure 13 presents preliminary results on the electric-field-induced dichroism of the 860-ppm crystal. We should note that the alignment energy $U=\mu E_a$ was 0.45 eV$=$3.6 cm^{-1}. If one accepts the existence of a 2.8-cm^{-1} tunneling level (t) in NaCl, then the alignment energy U was close to t, and hence the experiments were not of the high-field type that would definitely produce large fractional alignments of the OH$^-$ ions. The data of Fig. 13 show that line F at 3666.5 cm^{-1} increases in a parallel field and decreases in a perpendicular field. The same is true for line B at 3652.5 cm^{-1}.

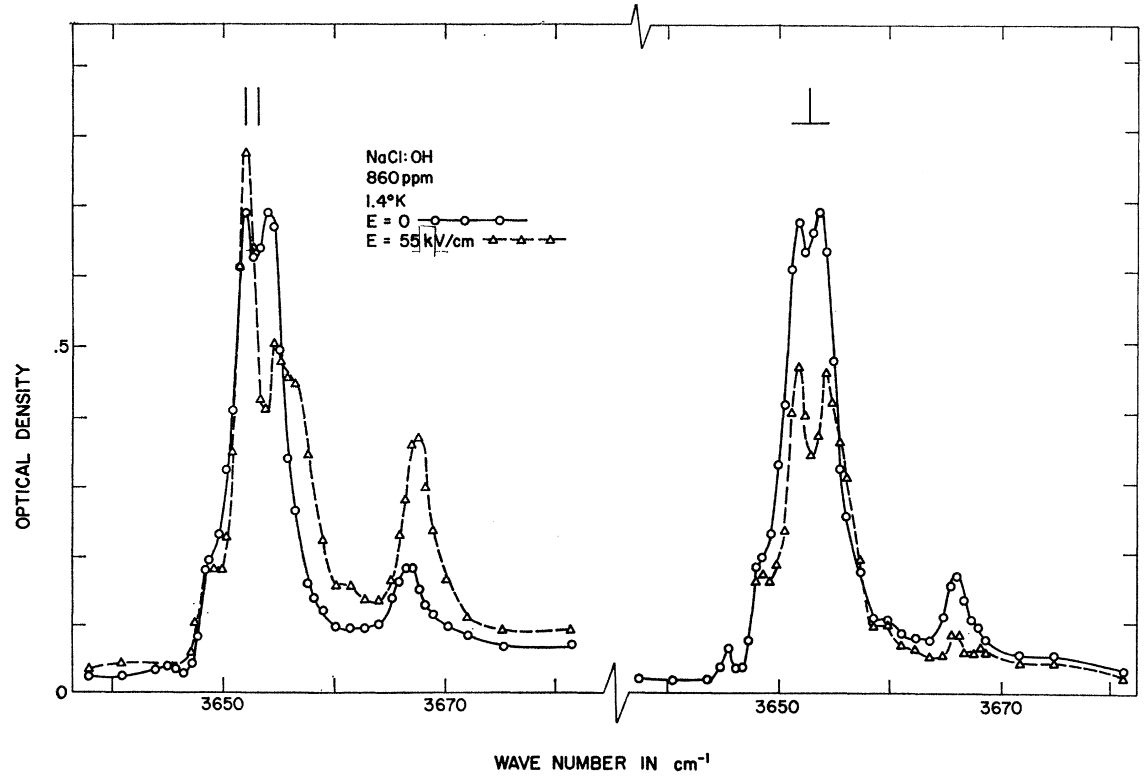

FIG. 13. Changes in the optical density of NaCl crystal containing 860-ppm OH$^-$ induced by an electric field. The light path was 18 mm long and was located between the electrodes, which were 1.4 mm apart and 14 mm long. Hence only about 14/18 of the length was under the influence of the field. $\|$ means E_{light} parallel to the applied field E_a; $\perp$ means E_{light} perpendicular to E_a.

The presumed main band (C) at 3654.5 cm^{-1} weakens in both parallel and perpendicular fields. In a parallel field there is considerable growth of line D at 3657 cm^{-1}, or of a line very close to it. This line appears only as a broadening in the $E=0$ spectrum of this 860-ppm crystal (Fig. 11).

In deuteroxide-doped NaCl crystals we found no near-infrared absorption at all, even at helium temperatures and even for OD^- concentrations of 500 ppm. (The OD^- concentration was arrived at by subtracting the OH^- concentration determined from infrared data from the total OH+OD concentration determined from the ultraviolet OH band.) The peak OD^- absorption constant must have been less than 0.015 cm^{-1} for this 500-ppm sample, at least 100 times weaker than the peak OH absorption constant.

KI

A high concentration of OH^- ions was difficult to grow into KI, probably because of the large size difference between the OH^- and I^- ions. Concentrations of 90 and 310 ppm were achieved in two crystals, which gave the same spectra.

The main band in Fig. 14 occurs at 3603 cm^{-1}. It has two higher sidebands at splittings of 3.7 and 8.2 cm^{-1} that are strongly temperature-dependent. At 1.4°K, the 3.7-cm^{-1} sideband was completely frozen out, suggesting that it originates from a thermally populated low-lying level above the vibrational ground state. The 8.2-cm^{-1} band at 1.4°K indicates a splitting in the vibrational excited state, or perhaps it is the result of a different type of center altogether (i.e., not a sideband). In addition, weak, sharp absorption bands were found at splittings of +22 and −21 cm^{-1}, but these are not believed to be combination bands.

This behavior of KI:OH^- is unique among the alkali halides studied so far. It does not show the 30-cm^{-1}-type splittings revealed in KCl, RbCl, and KBr, and it is less complex than NaCl. Potassium iodide will probably require its own explanation that is not related to those for the other crystals.

NaBr

We could not obtain an OH^- concentration greater than 100 ppm in NaBr and as a result could study only the main band. We are able to say something about its strength and its half-width versus temperature in the discussion, but dopings were too weak for us to see any "32-cm^{-1}"-type sidebands. For this reason we do not show the actual absorption curves.

Low-Energy Sidebands

The spectra of most of the crystals show a sharp band 20–30 cm^{-1} below the main stretching band. An example is the band at 3598 cm^{-1} in Fig. 6. It does not broaden or shift betwen helium and room temperature. A similar band is found in NaCl:OH^- at 3634 cm^{-1} (Figs. 8, 9). This one does broaden and shift somewhat, but not as much as the main band. In KCl:OH^- there is a band at 3614 cm^{-1} at helium temperature that shows little broadening and no shift up to room temperature. It has been reported at 3610 cm^{-1} by Stekhanov and Maksimova[52a]; a similar band is found in RbCl:OH^- at 3611 cm^{-1} (Fig. 4).

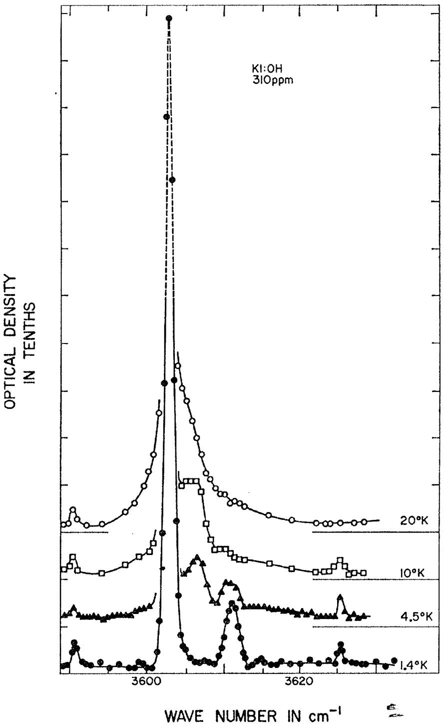

Fig. 14. Infrared absorption spectra of a 14-mm-thick sample of KI:KOH.

Since these bands do not freeze out at low temperatures, they cannot be difference bands involving a transition from a 20–30-cm^{-1} excited state. Because of the lack of strong temperature dependence, the responsible energy levels cannot be coupled strongly to phonons. The strong phonon coupling of all the other levels probably comes about because the hydroxyl ions are "loose" in the lattice and can undergo large amplitude oscillations or tunneling motions. These low-energy sidebands probably come from "tight" hydroxyl ions that may be coupled to impurity centers or possibly to aggregates of two or more hydroxyl ions.

DISCUSSION

There are some comments that can be made about the main band—about its position, isotope shifts, oscillator strength, and temperature-dependent half-width, for example.

[52a] A. I. Stekhanov and T. I. Maksimova, Fiz. Tverd. Tela **9**, 3668 (1967) [English transl.: Soviet Phys.—Solid State **9**, 2900 (1968)].

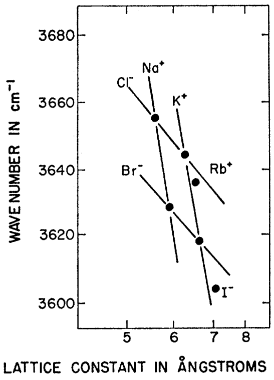

FIG. 15. Comparison of main-band stretching frequencies for OH^- in various alkali halides.

Frequency Shifts

In Table I, there is a list of our experimental values for the main O—H stretching frequency at liquid-helium temperature. By way of comparison, consider the value expected for free neutral OH,[53] namely,

$$\omega=\omega_e-2\omega_e x_e=3735-2\times 82.8=3569\ \mathrm{cm}^{-1}.$$

As used by Herzberg, x_e is a dimensionless parameter that describes the shift of ω from the purely harmonic result ω_e. There are no precise measurements or calculations for the free OH^- ion. On the basis of calculations using Hartree-Fock-Roothaan wave functions, Cade has predicted that ω_e for OH^- should be in the range 3733–3820 cm^{-1}.[54] With our $\omega_e x_e$ value of 86 cm^{-1} in $KBr\!:\!OH^-$ (see below) this would place the $0\rightarrow 1$ transition for free OH^- in the range 3560–3650 cm^{-1}. One generally expects the free-ion value to be lower than that for an ion in a crystal; if so, its value must be lower than 3603 cm^{-1}, our value for OH^- in KI.

From photodetachment measurements, Branscomb has estimated ω_e for free OH^- as $3735\pm 560\ \mathrm{cm}^{-1}$.[55]

TABLE I. OH^- main stretching band.

Host	Frequency (cm^{-1})	Area A (cm^{-2}) per 1000 ppm	Oscillator strength $f\times 10^3$
NaCl	3654.5 ± 0.5	10.1	0.65[a]
KCl	3641.0 ± 0.5	55	4.7
$KCl(OD^-)$	2684.5 ± 0.5	≈ 15	≈ 2.5
RbCl	3632.5 ± 0.5	53	5.7
KBr	3617.5 ± 0.5	33	3.3[b]
$KBr(OD^-)$	2668.0 ± 0.5	≈ 8	≈ 1.7
KBr (overtone)	7064		
NaBr	3626	6.2	0.45
KI	3603	18	3.0

[a] 0.91 at 5°K. [b] 5.3 at 273°K.

The observed frequencies are plotted versus the logarithm of the lattice constant in Fig. 15. Meistrich finds the main stretching band at 3728 cm^{-1} for OH^- in NaF at room temperature[56]; his result fits nicely on the Na^+ line. Note that Rb^+ and I^- do not fit well on the Cl^- and K^+ lines, respectively, but perhaps one should not make too much of this. We should also mention Stoebe's result of 3730 cm^{-1} for the room-temperature OH^- stretching frequency in LiF.[57]

Overtone and Anharmonicity

We were able to see a first overtone band at 7064 cm^{-1} in a 1500-ppm crystal of $KBr\!:\!KOH$ at nitrogen and helium temperatures. The integrated area under the overtone at 4°K was apparently 25% less than that at 78°K, but it was possibly within our experimental error that these areas were equal. The area of the overtone at 4°K was 1/400 that of the main-band fundamental at 78°K. Knowing the overtone frequency, we can now calculate a value of $\omega_e x_e$ for OH^- in KBr. This should not vary much for OH^- in other alkali halides, or for free OH^-:

$$\omega_e x_e=2\ \text{fundamental}-\text{overtone}=85.5\ \mathrm{cm}^{-1}.$$

We also obtain a value for ω_e:

$$\omega_e=\text{fundamental}+2\omega_e x_e=3789\ \mathrm{cm}^{-1}.$$

Hence,

$$x_e=85.5/3789=2.26\times 10^{-2}.$$

Isotope Shift

When the reduced mass of a diatomic oscillator changes from m to m_i due to isotopic substitution, ω_e changes to $\rho\omega_e$ and x_e changes to ρx_e, where $\rho=(m/m_i)^{1/2}$.[58] The fundamental frequency then changes from $\omega_e-2\omega_e x_e$ to

$$\rho\omega_e-2\rho^2\omega_e x_e=\rho(\omega_e-2\omega_e x_e)+(\rho-\rho^2)2\omega_e x_e.$$

For substitution of deuterium for hydrogen, $\rho=0.728$. This formula then predicts $O—D^-$ stretching frequencies of 2684.5 cm^{-1} in KCl and of 2667.5 cm^{-1} in KBr. The experimental values are $2684.5\pm 0.5\ \mathrm{cm}^{-1}$ and $2668.0\pm 0.5\ \mathrm{cm}^{-1}$, respectively.

Oscillator Strength

It is convenient to define a quantity called the oscillator strength by the equation

$$f=\frac{Amc^2}{Ne^2\pi}\frac{9n}{(n^2+2)^2}.$$

Here e is the electronic charge in esu, c the velocity of

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[53] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., Princeton, N. J., 1950), 2nd ed., p. 506.

[54] P. Cade, J. Chem. Phys. **47**, 2390 (1967).

[55] L. M. Branscomb, Phys. Rev. **148**, 11 (1966).

[56] M. L. Meistrich, J. Phys. Chem. Solids **29**, 1119 (1968).

[57] T. G. Stoebe, J. Phys. Chem. Solids **28**, 1375 (1967).

[58] Reference 53, Sec. III, 2.

light, N the number of oscillators per unit volume, m their reduced mass, n the index of refraction, and A the area under the absorption curve (in cm^{-2}). Our experimental values for A and f are listed in Table I. A was determined from an assumed Lorentzian line shape: $A=(\pi/2)\gamma\alpha_{\max}$, where γ is the full width at half-maximum and $\alpha_{\max}$ is the peak absorption constant. Except where noted, these data refer to 78°K. They are reliable to about $\pm 25\%$.

For dipoles randomly oriented along $\langle 100\rangle$ directions or for a $J=0$ to $J=1$ rotation-vibration transition, we expect f to be given by

$$f=\frac{1}{3}\left(\frac{1}{e}\frac{dp}{dR}\right)^2,$$

where p is the molecular dipole moment with respect to the center of mass and R the internuclear spacing. Cade has calculated the dipole moment p_c versus R implied by his wave functions, where p_c is taken with respect to the geometrical center of the molecule.[54] By differentiating his curve and shifting to the center of mass, we obtain the results

$$\frac{1}{e}\frac{dp}{dR}=-0.143 \quad \text{for} \quad \mathrm{OH}^-$$

$$=-0.0905 \quad \text{for} \quad \mathrm{OD}^-,$$

giving theoretical f values of 6.8×10^{-3} and 2.7×10^{-3} for OH^- and OD^-, respectively.

Agreement with experiment is satisfactory except for NaCl:OH$^-$, NaBr:OH$^-$, and NaCl:OD$^-$. In the latter case, the experimental f value must be less than 1.5×10^{-5}. We suggest the following explanation for these discrepancies. The negative theoretical value of dp/dR implies that, as R increases, the increase in p from an outward-moving H$^+$ ion is more than balanced by an outward shift in the electron distribution. Presumably the four nonbonding π electrons shift outward enough for their contribution to p to overcompensate the H$^+$ motion. In some crystal lattices the π-electrons shift may be reduced, with less resulting overcompensation (or perhaps with undercompensation) and a smaller dp/dR. If this explanation is correct, the value of $f<1.5\times10^{-5}$ for NaCl:OD$^-$ would imply an almost exact cancellation of the two contributions to dp/dR.

Temperature-Dependent Width of Main Band

In Fig. 16, we plot the temperature dependence of the "half-width" (actually the full width at half-maximum) of the main band for RbCl, KCl, KBr, and NaBr. The data for KI and NaCl were left out because of the nearness of their sideband spectra to the main band. Because of instrumental resolution, the data in Fig. 16 are unreliable for half-widths on the order of 1 cm^{-1} or less.

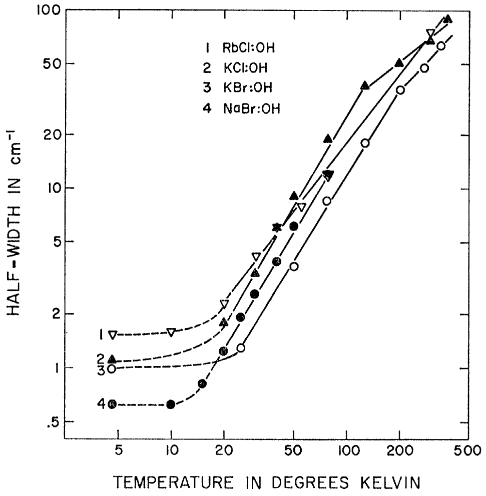

FIG. 16. Comparison of main bandwidths. "Half-width" = full width at half-maximum. The low-temperature data shown by dashed curves are probably not very reliable because of the approximate 1-cm^{-1} resolution limit of the spectrometer.

Although the temperature of the onset of broadening is uncertain, it is clear that above about 20°K the data show true thermal broadening of the lines. There is no simple expression that will fit these curves. Between 20 and 100°K the KCl, KBr, and NaBr curves have slopes of about 1.6; the RbCl curve has a slope of 1.25. At higher temperatures the slopes for KCl and KBr are closer to unity.

The early onset of line broadening might be related to the presence of the 30-cm^{-1} energy levels responsible for the near sidebands and for the direct far-infrared absorption in these crystals. These same levels are known from thermal conductivity measurements to interact strongly with phonons. The infrared line broadening may well be due to these same phonon interactions. The argument might go as follows. The lifetime of the excited vibrational state is assumed to be limited by phonon scattering off that state. In an elastic process a phonon of wave vector $\mathbf{k}$ would be absorbed and one with wave vector $\mathbf{k}'$ emitted, and the hydroxyl ion would finish in its excited vibrational state, but with a randomly shifted phase; this would limit its lifetime.[59] The elastic scattering process would go through the 30-cm^{-1} higher sideband level as a virtual intermediate state. The lifetime-limiting process could also be inelastic, involving the absorption of a 30-cm^{-1} phonon. A proper theory would automatically include both processes.

There is no shift of the main-band frequency as the temperature is changed from helium to nitrogen temperature. At higher temperatures the lines are too broad to measure accurately, but there appears to be a

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[59] R. J. Elliott, W. Hayes, G. D. Jones, H. F. Macdonald, and C. T. Sennett, Proc. Roy. Soc. (London) **A289**, 1 (1965).

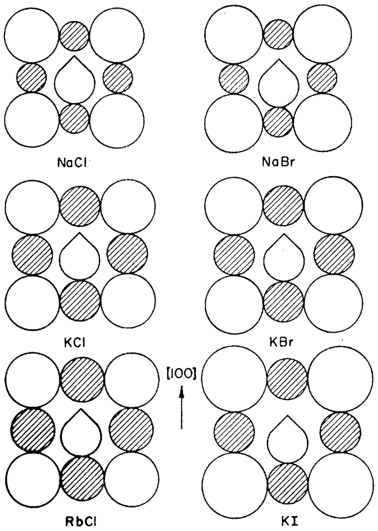

FIG. 17. Approximate relative sizes of the OH^- and host-crystal ions. The dark circles are cations; light circles are anions; the pointed circle is OH^-. The center of mass of the hydroxyl ion is shown displaced in the $[\bar{1}00]$ direction.

small shift to lower frequencies at room temperature, namely, by 7 cm^{-1} in KBr and 2 cm^{-1} in KCl.

SPECULATIONS ABOUT 30-cm^{-1} BANDS

Information about the 30-cm^{-1} or non-Devonshire bands is still insufficient for construction of a detailed model or models of the energy levels. KI seems to be in a class by itself; NaCl may or may not be, but it is at least complicated by high tunneling levels (2–3 cm^{-1}) interacting with perhaps several low "30-cm^{-1}" levels near 12 cm^{-1}. KCl, RbCl, and KBr have nearly the same levels at 32, 30, and 37 cm^{-1}, respectively. The band in KCl is the most pronounced (and interacts most strongly with phonons) and is accompanied by the least additional broad high-frequency absorption, whereas the KBr band has the most high-frequency background. Model building is further complicated by the uncertain interpretation of the sharp bands at 25, 27, and 30 cm^{-1} in KCl, RbCl, and KBr.

Consider now the two different OD^-/OH^- isotope effects that have been observed—23/32 for KCl and 35.5/37 for KBr. For a harmonic oscillator with a given spring constant, but with two different effective masses M_1 and M_2, the frequency ratio ω_2/ω_1 would be $(M_1/M_2)^{1/2}$. Thus the measured ratios suggest that if a harmonic oscillator model is valid, the effective mass should be the hydrogen mass in KCl and that of the entire ion in KBr.

Is a harmonic oscillator model reasonable? Low-lying resonance states have been found for some monovalent impurities in alkali halides. The most remarkable is the 16-cm^{-1} Li^+ resonance in KBr.[60] To explain it one must assume that the Li-Br force constant is less than 1% of the K-Br force constant of the host lattice. Frequency ratios ω_2/ω_1 for various isotopes exhibited by this and by other low-frequency resonances are close to the inverse square root of the impurity mass ratio $(M_1/M_2)^{1/2}$.[52] At first glance this result is easily explained using a simple Einstein oscillator model, but when harmonic couplings of the impurity to other than its nearest neighbors are considered, the effective mass of the oscillator has a contribution from the surrounding ions, and the resulting harmonic isotope effect is weaker than $(M_1/M_2)^{1/2}$.[61–63] These resonances show a rapid broadening with temperature; this suggests a strong anharmonic coupling to phonons. Such anharmonicity could lead to a stronger isotope effect, perhaps closer to $(M_1/M_2)^{1/2}$.[64] At any rate, it is an experimental fact that monatomic, monovalent impurity resonances behave as if they were simple Einstein oscillators.

Arguing by analogy with these resonances, we might try to interpret the 37-cm^{-1} level in $KBr:OH^-$ as a center-of-mass resonance of the entire ion. This is supported by the fact that a resonance at 37 cm^{-1} exists in $KBr:F^-$.[65] The OH^- ion can be regarded in a first approximation as a distorted F^- ion with dimensions perpendicular to its axis comparable to the F^- dimensions and with larger dimensions parallel to the axis. If this explanation of the 37-cm^{-1} $KBr:OH^-$ level is correct, one would expect it to have a transition dipole moment perpendicular to the O—H axis. There might then be a higher-frequency resonance due to vibrations parallel to the axis; perhaps this is the origin of the broad far-infrared band at 50 cm^{-1} and higher frequencies. Unfortunately we have no dichroism results on KBr, but those on $RbCl:OH^-$ are consistent with this picture.

A search was made by the far-infrared group at Cornell University for a resonance near 30 cm^{-1} in $KCl:F^-$.[66] None was found. This result together with the strong isotope effect seems to rule out an explanation of the 32-cm^{-1} band in $KCl:OH^-$ as a center-of-mass resonance. If the band is due to a resonance, it seems that only the hydrogen part of the ion can be displaced. But is it plausible that anything resembling a hydrogen harmonic oscillator could have such a low frequency in a crystal?

Remembering the case of $KBr:Li^+$, we must answer, "Yes, provided that the net force constant is small enough." Is such a small force constant reasonable? To answer this question properly would require detailed

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[60] A. J. Sievers and S. Takeno, Phys. Rev. **140**, A1030 (1965).

[61] G. Benedek and G. F. Nardelli, Phys. Rev. **155**, 1004 (1967)

[62] M. V. Klein, in *Physics of Color Centers*, edited by W. B. Fowler (Academic Press Inc., New York, 1968), Chap. 7.

[63] M. V. Klein, in *Proceedings of the 1967 Irvine Conference on Localized Excitations in Solids*, edited by R. F. Wallis (Plenum Press, Inc., New York, 1968), p. 71.

[64] G. Benedek, in *Proceedings of the 1967 Irvine Conference on Localized Excitations in Solids*, edited by R. F. Wallis (Plenum Press, Inc., New York, 1968), p. 101.

[65] M. A. Levine (private communication), discussed in Ref. 62.

[66] A. J. Sievers (private communication).

numerical calculations, but we believe the answer may be affirmative for the following reasons.

Because of the reduced symmetry along its axis, there is no *a priori* reason for the center of mass of the OH^- ion to be at the halide lattice site. As several authors have pointed out, the center of mass may be displaced parallel to its axis in a $\langle 100\rangle$ direction.[12,15,67] This is illustrated for the hydroxyl ion in six alkali halides in Fig. 17, where the relative radii of the circles are the same as the Pauling or Goldschmidt ionic radii and where the host-crystal ions are shown in undisplaced positions. The OH^- ion is represented as an F^- ion with a conical cap revealing the location of the H atom. In this picture the very low-lying tunneling levels would correspond to combined translation and rotation transitions of the ion from one off-center position to another.

The librational oscillation occurring near 300 cm^{-1} (except for KI, where it may occur at a much lower frequency)[68] would then correspond to a torsional oscillation of the ion about an axis through its center of mass in which the O—H axis rotates away from the equilibrium (100) direction. It is revealing to compare this oscillator to the high-frequency infrared-active localized mode of the substitutional H^- ion (*U* center) that occurs at 502 cm^{-1} in KCl and at 563, 446, 382, and 476 cm^{-1} in NaCl, KBr, KI, and RbCl, respectively.[69] In this mode the H^- ion vibrates with respect to nearly static surroundings since at these high frequencies the host-crystal ions cannot respond sufficiently rapidly to follow. These values can be explained only by assuming that the net force constant between the H^- ion and its nearest neighbors is about 50% of its value for the anion in the perfect host crystal. In addition to the localized mode, a broad far-infrared absorption has been observed near the top of the acoustical phonon band in $KI:H^-$ and $KBr:H^-$.[70,71] This can be explained by the same calculation that gives the localized mode, namely, a harmonic Green's function calculation.[71] If such a calculation is made for a hypothetical H^- ion coupled with a weaker force constant than is the real ion, the localized mode will remain, but at a lower frequency; and the absorption in the acoustical band moves down in frequency and becomes a true resonance.[61,63]

Because the surrounding atoms can readily respond at low frequencies, they will participate in any such low-frequency H^- ion resonance, thereby increasing its effective mass, so that the zero-point oscillations will be smaller than those of a hydrogen oscillator. Nevertheless, the zero-point effects will be large enough to accentuate any anharmonicity in the potential; and, as mentioned above, anharmonicity will increase the calculated isotope effect over that obtained with a harmonic theory and an increased effective mass.

We suggest, therefore, that at least in some crystals such as KCl, the transverse motion of the OH^- ion about its center of mass may be like that of a "soft" *U* center and may have both a high-frequency localized mode (librator) and a low-frequency resonance (32-cm^{-1} band). In fact, a *U* center Green's-function calculation applied to the librator frequency gives a central force constant between the impurity and its nearest neighbors that is low enough to yield a resonance near zero frequency.[63,72] From Fig. 15 it is not clear whether the transverse nearest-neighbor ions of the hydrogen part of the OH^- ion are cations or anions; thus the *U* center results cannot be taken too seriously, but they may be suggestive.

Baur and Salzman have argued that the angular potential seen by the displaced OH^- ion is so anharmonic that the [100] direction is not a minimum. They further argue that there may be four equivalent minima making angles of about 40° with [100], separated by an approximate 100-cm^{-1} potential barrier.[73] Fast tunneling among the minima would then cause the 30-cm^{-1} level and other levels as well. The tunneling would be far removed from the slow type that can be described by a "LCAO" type of calculation; nevertheless, it must have a fairly strong isotope effect, stronger than $\omega_2/\omega_1 = M_1/M_2$ expected for a square well, because a potential with multiple minima is more anharmonic than a square well. Once again, even in a tunneling model, the surrounding atoms should move, thus increasing the effective mass and reducing the isotope effect.

We cannot at this time make even a tentative choice between a soft *U* center model and the fast tunneling model; indeed, the former will transform into the latter with increasing anharmonicity. Both models predict the observed perpendicular transition dipole moment for the 30-cm^{-1} bands in KCl and RbCl. Some such model may be close to the truth in KCl and perhaps in NaCl, but we feel that in KBr the center-of-mass resonance model works better. Actually there should be some admixture of transverse center-of-mass displacement with both torsional oscillation and torsional tunneling of the same symmetry, so that in KBr we may have one extreme where the true motion is primarily that of the center of mass and in KCl another extreme where the motion is primarily about the center of mass.

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There are several possible experiments to test these notions; we hope they will be done in the near future.

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Light Scattering from Polaritons in Centrosymmetric Crystals

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Polaritons in centrosymmetric crystals ($SrTiO_3$ and $KTaO_3$) have been studied by small-angle light scattering induced by external electric fields. Measurements of polariton dispersion curves in $SrTiO_3$ have produced new values for oscillator strengths of the infrared-active phonons. Absence of a measurable k dependence for the linewidth of the "ferroelectric" mode bears on the discrepancy between Raman and infrared linewidth measurements previously reported.

EXPERIMENTAL observation of polaritons[1–6] by means of small-angle Raman scattering has proven useful in three ways: It provides determination of the dispersion predicted by the classical oscillator equations[7] used to fit infrared (IR) data; it reveals interference between electro-optic and displacive contributions to the nonlinear susceptibility in the reststrahlen region[8,9]; and it is helpful in distinguishing between first- and second-order Raman features.[10] Since the polariton is a mixed excitation comprised of photon and IR-active TO phonon contributions, its observation in the Raman effect has previously been limited to noncentrosymmetric crystals (in which an excitation may be simultaneously IR- and Raman-active).

In the experiments described here, polaritons in centrosymmetric crystals have been studied for the first time by light scattering through the application of electric fields to induce Raman activity in the normally IR-active modes. The materials studied were $SrTiO_3$ and $KTaO_3$, which at the temperature of our experiments (8°K) belong to space groups $D_{4h}{}^{18}$ and $O_h{}^1$, respectively. Earlier electric-field-induced Raman scattering from the phonon modes in these crystals demonstrated that appreciable scattering cross sections could be induced by the field and revealed some puzzling behavior of the linewidth of the so-called "ferroelectric mode."[11,12] In addition to illuminating this question, the present work provides new values for the oscillator strengths of the IR modes which differ slightly from those obtained in IR experiments.[13]

The experimental techniques involved a combination of those described in Refs. 3 and 12. Samples were provided with Au over Cr evaporated electrodes to which were applied repetitively pulsed electric fields (of 250–2000 V across a 2.4-mm thickness of crystal) of 200-μsec duration every 3–10 msec. Linearly polarized light at 4880 Å from an argon ion laser was focused into the crystal mounted on a cold finger of a liquid-He Dewar. Light scattered through small angles was focused onto the slits of a double spectrometer. Aper-

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