PHYSICAL REVIEW B VOLUME 39, NUMBER 14 15 MAY 1989-I

Brief Reports

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Far-infrared difference-band absorption in potassium iodide

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(Received 5 January 1989)

A far-infrared measurement of the temperature-dependent absorption in KI between 4.2 and 82 K shows a number of absorption edges which correlate very closely with calculations of the two-phonon difference-band effect in the limit of energy-conserving processes. A temperature-dependent peak in the absorption coefficient at 11.3 cm^{-1} corresponds to a weak difference-band contribution stemming from vertical transitions between the Σ_1(LA)-Σ_4(TA) symmetry branches in the region where the slopes are nearly parallel. This result demonstrates that at finite temperature a true gap does not exist in the energy-conserving two-phonon difference-band absorption spectrum for a rock-salt crystal which has a well-defined gap between the acoustic and optic branches.

Although the phonon difference-band far-infrared absorption process in alkali halide crystals has been studied for many years, it recently become evident that the available data were not good enough to distinguish between two fundamentally different mechanisms involving proposed energy-conserving and energy-nonconserving processes. The early investigators[1-3] had analyzed their data in terms of energy-conserving two- and three-phonon processes with reasonable success. Later calculations with the deformation dipole model[4] continued to emphasize this approach; however, since that time, other theoretical investigators[5,6] showed that the earlier experimental data could be described equally well in terms of lifetime-broadened two-phonon processes.

To resolve this ambiguity associated with the theoretical description of intrinsic millimeter- and submillimeter-wave absorption in dielectric crystals, we have measured the temperature-dependent absorption coefficient in long KI crystals at frequencies from 5 to 80 cm^{-1} and temperatures from 1.2 to 82 K. At about 15 K new absorption-edge features appear at frequencies smaller than previously measured[2] and, somewhat surprisingly, the lowest-frequency feature is characterized not by an edge but by an absorption coefficient peak at 11.3 cm^{-1} in good agreement with the frequency previously calculated[2] for energy-conserving difference frequency transitions from the TA to LA branch. Our straightforward observation of well-defined low-frequency edges and a peak indicate that lifetime-broadened phonon processes are not important at least up to temperatures comparable with the acoustic-phonon energy. Because these features maintain their integrity up to 82 K, our highest sample temperature, we conclude that over this temperature region the two-phonon energy-conserving process accounts for the dominant absorption mechanism in KI.

To compare the submillimeter-wave properties of this crystal which has a gap between the optic and acoustic branches to one which does not, a few additional low-frequency measurements have been carried out on NaCl. At the lowest frequencies, the frequency dependences of the absorption coefficient of the two crystals appear qualitatively similar, but the first edge in NaCl, at 20 cm^{-1}, comes from different transitions, some of which occur in a different part of the Brillouin zone (BZ).

The samples used in our experiments are Czochralski-grown single-crystal boules of KI and NaCl which were then tuned down on a lathe to cylinders 1.24 cm in diameter to slip into brass light pipes. The cylinder axis lies along a [100] crystal axis. This sizing procedure is known from previous etch-pit–analysis studies[7] to produce a high dislocation density in the crystal surface to a depth of about 0.1 cm, which can be removed by a high-temperature crystal anneal. Although the measurements reported were we made on unannealed samples, the dislocation-induced absorption is known to be weak and should not be temperature dependent.

Fourier-transform spectra of KI from 3 to 28 cm^{-1} were obtained at 0.44-cm^{-1} resolution using a lamellar grating interferometer. Data from 25 to 86 cm^{-1} were taken with a Michelson interferometer at 0.35-cm^{-1} resolution. The NaCl spectra were taken at 0.54-cm^{-1} resolution using the lamellar interferometer. A ^{3}He-cooled Ge bolometer detector was used throughout.

To avoid the possibility of a change in detector sensitivity due to the radiation from the heated sample, the samples are placed outside the detector cryostat in an in-dependent variable-temperature cryostat. The blackbody radiation emitted by the room-temperature brass light pipe insures a nearly constant thermal flux on the detector. The sample temperature is determined using a calibrated 1-kΩ carbon resistor. For each sample, the frequency- and temperature-dependent absorption coefficient $\alpha(\omega,T)$ is determined by dividing spectra taken at the higher temperature by one at 4.2 K. Then

$$\alpha(\omega,T)-\alpha(\omega,4.2\ \mathrm{K}) = -(1/l)\ln[I(\omega,T)/I(\omega,4.2\ \mathrm{K})]\ , \qquad (1)$$

where l is the sample length and $I(\omega,T)$ is the intensity at the detector. Since this method requires only that the temperature be varied, without moving the sample, uncertainties due to changes in sample alignment are eliminated. For the (3–28)-cm^{-1} region 9.675-cm-long KI sample is used over the entire (4.2–82)-K temperature range, while for the higher frequencies the sample lengths are 0.297 cm for the (15–35)-K range and 0.123 cm for the (64–82)-K range. Both samples are used for the 47-K spectrum with the short sample used for the higher-frequency portion of the spectrum. These shorter samples are given a 1°–2° wedge to eliminate interference fringes, in which case the average length is used to calculate α. For the NaCl measurements in the region below 32 cm^{-1}, a single 11.1-cm-long sample is used.

The low-temperature absorption coefficient $\alpha(\omega,4.2\ \mathrm{K})$ for KI is determined later by ratioing spectra of samples of two different lengths (9.675 and 1.298 cm) and is added on to the temperature-dependent data to obtain $\alpha(\omega,T)$. This correction is negligible for frequencies below 80 cm^{-1} in KI and was not performed for the present low-frequency NaCl data.

The experimental results are shown in Fig. 1 where a semilogarithmic plot of the absorption coefficient versus frequency for the different temperatures is displayed. Examination of these results shows that the weak edges at 75 and 64 cm^{-1} correspond to the low-frequency cutoffs for the LO-TA and LO-LA processes, respectively. The prominent absorption edge at 42 cm^{-1} corresponds to the low-frequency cutoff for the TO-TA difference process. Particularly apparent is the edge at roughly 31 cm^{-1} corresponding to the cutoff for TO-LA processes. Also visible at 11.3 cm is the *high-frequency cutoff* for the LA-TA process.

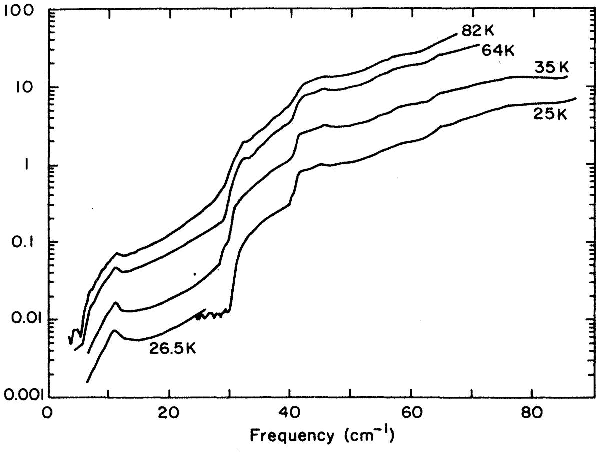

FIG. 1. Semilogarithmic plot of the far-infrared absorption coefficient of pure KI at different temperatures. The sample temperature is varied from 4.2 to 82 K. The spectral resolution is 0.44 cm^{-1} for frequencies between 3 and 26 cm^{-1}, and 0.35 cm^{-1} at higher frequencies. These spectral features are compared in Table I with two-phonon energy-conserving difference-band predictions.

The lowest-frequency feature at 11.3 cm^{-1} can be seen more clearly in the linear plot shown in Fig. 2 where the temperature dependence of the low-frequency absorption coefficient is shown. Both the position and the temperature dependence are consistent with the two-phonon difference process. The fact that this peak retains its characteristic shape up to our highest temperature provides direct evidence that the energy-nonconserving two-phonon difference-band processes do not produce a significant contribution over this temperature interval.

Because the selection rules for second-order phonon processes are so restrictive for the rocksalt structure,[8] the positions of the observed features can be compared in some detail with the predictions of the energy-conserving two-phonon difference-band calculations of Eldridge and Kembry,[2] whose results are summarized in Table I. Inspection of this table shows that all of our observed features are in reasonable agreement with their model predictions.

From a practical point of view, our temperature-dependent data illustrate that, although a true gap does not exist in pure KI, the crystal can be used to produce low-pass filters with an edge at more than one frequency. For example, KI at liquid-helium temperature has been used for many years to produce a cutoff filter at 100 cm^{-1}. Because the transverse-optic mode of alkali halide crystals does not occur at frequencies below 60 cm^{-1}, lower-frequency cutoffs for Fourier-transform spectro-

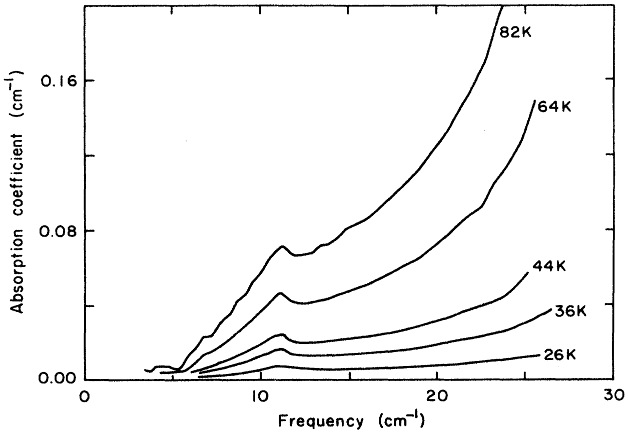

FIG. 2. Temperature dependence of the absorption coefficient of KI in the millimeter- and submillimeter-wave regions. The sample is 9.675 cm long. Note the peak feature at 11.3 cm^{-1} corresponds to the high-frequency cutoff for LA-TA difference-band processes.

scopic applications have been produced by using glassy materials with their inherently weaker frequency dependences and hence poorer cutoff efficiencies. From Fig. 1 it is apparent that a 1-cm-long pure KI single-crystal filter in contact with a liquid-nitrogen reservoir would provide a 30-cm^{-1} cutoff filter with much improved throughput.

To look for differences between a crystal with a complete gap between the optic and acoustic branches and one without, additional measurements have been made on a long NaCl crystal at a few temperatures. The frequency dependence of the difference-band absorption coefficient for three temperature differences is shown in Fig. 3. One extrinsic feature in these spectra is the temperature-dependent absorption line near 9.3 cm^{-1} which stems from the lowest-lying tunneling multiplet of an unwanted OH^- impurity.[9] A difference-band edge at 20 cm^{-1} is apparent in the three traces and the frequency dependences shown in Fig. 3 are similar to those already displayed in Fig. 2. Inspection of the NaCl dispersion curves obtained from neutron-scattering measurements[10,11] shows that the highest transition in the $\Sigma_1(\text{LA})$-$\Sigma_4(\text{TA})$ region, which accounts for the 11.3-cm^{-1} feature in KI, now occurs at 46 cm^{-1}, too large to account for the edge observed in Fig. 3. It appears that the LA-TO transitions at $W_1 W_2'$, at $\Sigma_1(\text{LA})$-$\Sigma_4(\text{TO})$, as well as the transitions at $\Sigma_4(\text{TA})$-$\Sigma_4(\text{TO})$, have large joint densities of states and are in the correct frequency region to produce the observed edge. So although the optic and acoustic branches are mixed for this case, there is still an absorption edge associated with the appearance of the first large joint density of states.

TABLE I. Comparison of measured absorption features in KI with those predicted by the two-phonon difference-band energy-conserving processes. The first three columns are from Ref. 2. The last column summarizes the data in Fig. 1.

Phonon symmetries	Predicted Feature (cm^{-1})	BZ position	Observed frequency (cm^{-1})
Δ_5-Δ_5	75[a]	0.7	75
Σ_4-Σ_4	42	0.5	42
$\Sigma_1(\text{LO})$-$\Sigma_4(\text{TA})$	63	0.6	64
$\Sigma_1(\text{LA})$-$\Sigma_4(\text{TO})$	30	0.5	31
$\Sigma_1(\text{LA})$-$\Sigma_4(\text{TA})$	12	0.5	11.3
L_1'-L_1	59		57
L_1'-L_3	74		75
L_3'-L_3	42		42
W_1-W_2'	46		45

[a] In Table III of Ref. 2, this value is given as 81 cm^{-1}, but inspection of Fig. 3 of Ref. 2 shows that the maximum actually occurs at 75 cm^{-1} for the temperature range of interest here.

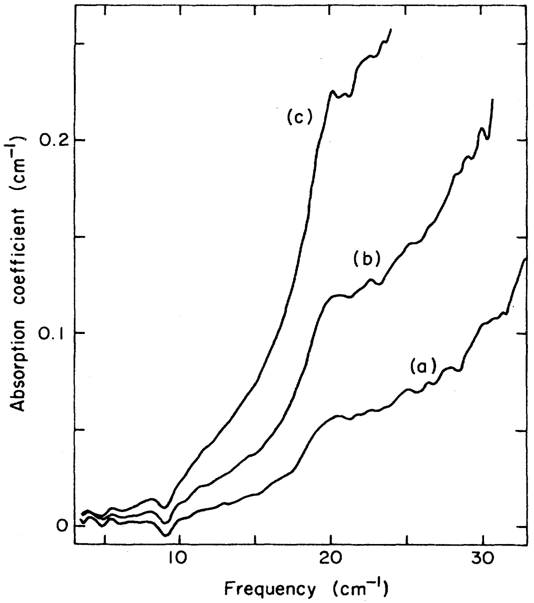

FIG. 3. Temperature dependence of the absorption coefficient of NaCl in the millimeter- and submillimeter-wave regions. Sample temperatures are (a) 31, (b) 35.5, and (c) 43 K. The sample is 11.1 cm long. The absorption line at 9.3 cm^{-1} is an extrinsic effect associated with OH^- impurities. The absorption edge at 20 cm^{-1} corresponds to the low-frequency cutoff for LA-TO difference-band processes.

In his early work on the difference band absorption in LiF, Eldridge[12] found for temperatures up to 300 K that energy-conserving three-phonon processes were not needed to explain the low-frequency experimental data. Our low-frequency results for KI are consistent with the LiF findings.

One reason that both energy-conserving and energy-nonconserving two-phonon difference processes appeared to fit the available data in rocksalt crystals was that in their later work on KI Eldridge and Kembry[2] did not make measurements below 70 cm^{-1} at 12 K nor below 30 cm^{-1} at 77 K and hence missed seeing the well-separated 11.3-cm^{-1} peak shown in Fig. 2. The slowly varying absorption coefficient that they did observe at higher frequencies led them to conclude incorrectly that no distinct features existed in the difference spectrum, a result which could be consistent with energy-nonconserving two-phonon processes.

On the other hand, these same investigators did correctly predict that a weak difference-band contribution would stem from vertical transitions between the $\Sigma_1(\text{LA})$-$\Sigma_4(\text{TA})$ symmetry branches in the frequency region where the slopes are nearly parallel. Because this contribution now has been identified and because it depends on the energy difference between *acoustic modes*, one has the general result that at finite temperature there is no true gap in the two-phonon difference-band absorption associated with energy-conserving processes even in rocksalt crystals which do show a well-defined gap between the optic- and acoustic-phonon branches,

This research supported by the U.S. Army Research Office (U.S. ARO) under Grant No. DAAL03-86-K-0103 and by the National Science Foundation (NSF) under Grant No. DMR-85-16616 through the Materials Science Center at Cornell University.

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