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Multiphonon infrared absorption in highly transparent MgF_2

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We report the first detailed polarized-absorption measurements for MgF_2 in the 5–10-μm regime, at both room and liquid-nitrogen temperatures. The observed spectra are attributed to intrinsic multiphonon absorption, and differences in the polarized spectra are interpreted as indicating the persistence of selection rules into the three-phonon regime.

In recent years there has been considerable interest in highly transparent infrared materials[1–3] such as alkali halides and alkaline-earth fluorides, for potential utilization as windows, lenses, and fiberguides.[4] In a previous paper in this journal[3] we reported measurements of intrinsic multiphonon absorption in the highly transparent regime of the optically isotropic alkaline-earth-fluoride crystals CaF_2, SrF_2, and BaF_2. In this note we extend our investigations of multiphonon absorption in alkaline-earth fluorides to the optically anisotropic crystal MgF_2, which possesses the rutile structure. The one-[5] and two-phonon[6] polarized spectra of MgF_2 have been reported previously, as have preliminary measurements of unpolarized absorption spectra for MgF_2 in the 5–10 μm wavelength regime.[7] In this paper we report the first detailed polarized-absorption measurements for MgF_2 at both room and liquid-nitrogen temperature, for wavelengths between 5 and 10 μm. These are, moreover, to the best of our knowledge the first detailed measurements of absorption coefficients for two different polarizations to be reported for the three-phonon regime of any infrared material.[8]

The MgF_2 samples used for this investigation were high-purity Optovac material cut and polished with faces perpendicular and parallel to the optic axis. Infrared transmission spectra were obtained perpendicular and parallel to the c axis in the regimes of interest utilizing a Digilab FTS-14 Fourier spectrophotometer operated in the double-beam mode using a dry-nitrogen gas atmosphere. For the low-temperature measurements, the MgF_2 sample was clamped against an indium ring in contact with the coolant reservoir of a Dewar positioned at the focal point of the spectrophotometer sample compartment. The polarized spectra were obtained using a wire grid infrared polarizer placed between the sample and the detector. The sample was positioned with its axis 45 ° to the vertical axis of the spectrophotometer, and the polarizer set at 45 ° for spectra with $\vec{E}\parallel\vec{c}$ and 315 ° for $\vec{E}\perp\vec{c}$. The absorption coefficient α was obtained from the expression[9]

$$\alpha = d^{-1}\ln\left\{\frac{(1-R)^2}{2T} + \left[\left(\frac{(1-R)^2}{2T}\right)^2 + R^2\right]^{1/2}\right\}, \qquad (1)$$

where d is the sample thickness, T is the transmission, and R is the reflectivity. Computer-generated plots of the variation of α with frequency ω were obtained utilizing reflectivity values determined from the maximum transmission in the vicinity of 5 μm, where the absorption can be assumed to be negligible. Corrections are also made for 100% line and polarizer transmission variation with wavelength.

Results of the measurements are indicated in Fig. 1. The room-temperature spectra for $\vec{E}\parallel\vec{c}$ and $\vec{E}\perp\vec{c}$ are very nearly similar, and moreover display very little structure. At low temperature, however, the two spectra display notable structure, and differ distinctly (the differences are well in excess of the experimental error). These observations may be interpreted in terms of multiphonon absorption, as discussed below.

An overall exponential decrease of α with increasing frequency in the highly transparent regime is a familiar characteristic of intrinsic multiphonon absorption in solids.[1–3] The structureless, exponential-like spectrum at room temperature observed here for MgF_2 is consistent with similar behavior observed for many other ionic materials. As discussed elsewhere,[2] ionic materials display relatively little structure in their many-phonon spectra, and virtually none at all at room temperature and above. This behavior contrasts with that for semiconductors, where marked structure often persists into the three-phonon regimes, even at room temperature and above.[10] These differences in spectral characteristics are attributed to the larger anharmonicity and substantially broader vi-

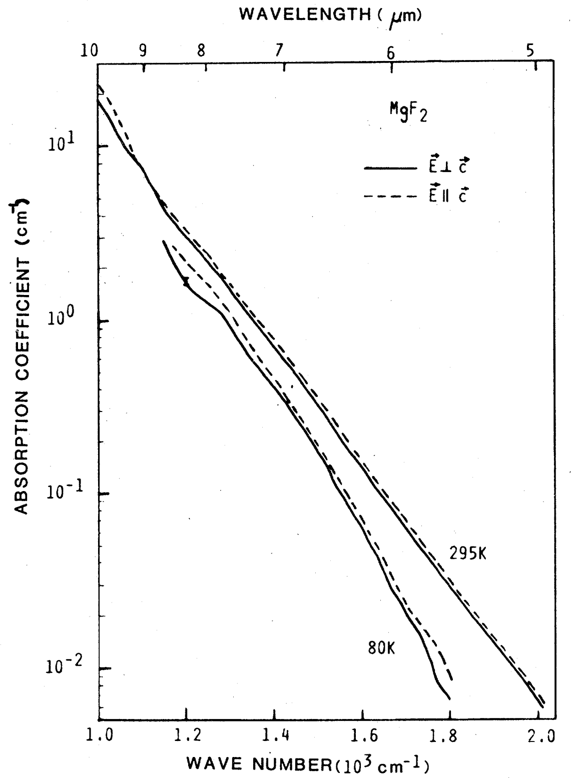

FIG. 1. Polarized absorption coefficient of MgF$_2$ as a function of frequency at two temperatures. A representative error bar is indicated for $\vec{E}\perp\vec{c}$ at 1200 cm^{-1}.

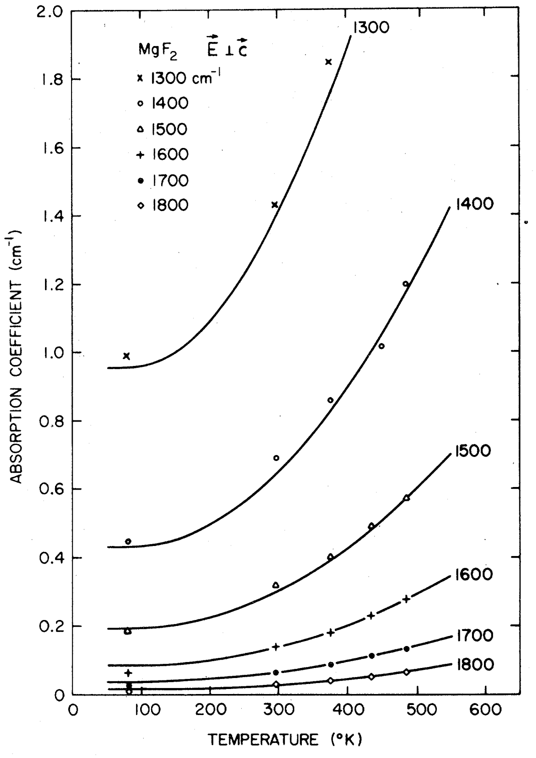

FIG. 2. Temperature dependence of absorption coefficient of MgF$_2$ for $\vec{E}\perp\vec{c}$ at selected frequencies. Solid lines are theoretical fits utilizing theory of Bendow (see Ref. 12).

brational density of states of ionic materials relative to that of semiconductors.

The present data may help clarify a previously unresolved issue, namely, the potential persistence of selection rules in multiphonon infrared absorption in the three or more phonon regime.[2] Since virtually all detailed studies of multiphonon absorption were carried out for cubic crystals, it was unclear whether structure in the spectra should be attributed to density-of-states effects or to selection rules. Certain semiconductor data appear to be well explained by just density-of-states effects,[10] while a theory of quasiselection rules in alkali halides appears capable of interpreting observed trends for certain of these materials.[11] We believe that the polarized spectra presented here indicate that selection-rule effects may persist into the three-phonon regime in infrared spectra. Presumably, if selection rules had broken down leaving only density-of-states effects, then the two spectra (i.e., for $\vec{E}\parallel\vec{c}$ and $\vec{E}\perp\vec{c}$) would have had similar shapes. The fact that these spectra differ suggests that selection rules are operative. Presumably, with increasing temperatures the spectral features broaden, thereby suppressing differences between polarized spectra.

To further verify that the observed spectra represent intrinsic multiphonon behavior, we have performed temperature-dependence measurements, and analyzed our results in an identical manner to Ref. 3, to which the reader is referred for details. We merely remark here that in essence the theory utilized fits all temperature data with just a single adjustable parameter, namely the effective oscillator ω_0. Our experimental data along with the calculated theoretical fits are displayed in Fig. 2, and the agreement is observed to be excellent.

In conclusion, we have measured polarized spectra in highly transparent MgF$_2$ and interpreted our observations in terms of intrinsic multiphonon absorption. We have observed differences between the polarized spectra which we attribute to selection-rule effects.

ACKNOWLEDGMENT

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