Optical Properties of LiIO₃ in the Far Infrared

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The absorption coefficient of LiIO₃ has been measured at 300°, 80°, and 7°K for the ordinary and extraordinary ray. The corresponding indices of refraction at 300°, 80°, and 17°K were also determined. Upon cooling from 300° to 7°K, the absorption coefficients decrease drastically in the 10–150-cm⁻¹ spectral region. At 7°K the absorption coefficient is less than 1 cm⁻¹ for frequencies up to 80 and 90 cm⁻¹ for $E \parallel c$ and $E \perp c$, respectively. This characteristic is important for far-infrared generation by mixing of two laser frequencies.

Lithium iodate, LiIO₃, has become an important crystal because of its high second-harmonic efficiency for YAG:Nd³⁺ and ruby Lasers.[1,2] Moreover, it exhibits interesting electro-optical properties,[3] large piezoelectric constants,[4] and large electromechanical coupling factors.[4] LiIO₃ is an uniaxial crystal with space group $P6_3$ which can be grown from water solution[4] with good optical quality and with dimensions on the order of centimeters.[5]
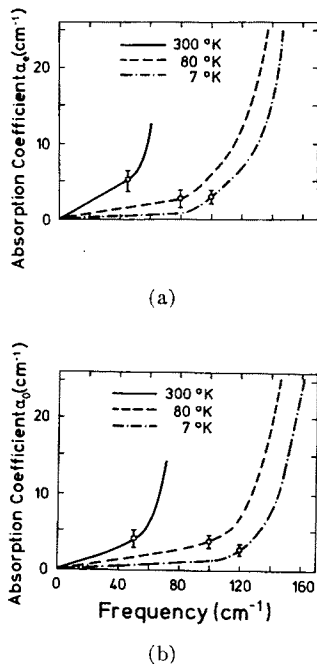

FIG. 1. The far-infrared absorption coefficients of LiIO₃ for the ordinary and extraordinary ray at 300°, 80°, and 7°K.

Recently, interest has been raised in potential materials for bulk generation of tunable far-infrared radiation by mixing of two optical laser lines, as has already been demonstrated in LiNbO₃ by Faries *et al.*[6] It has also been demonstrated in LiNbO₃ that stimulated polariton scattering is a means for efficient generation of far-infrared radiation.[7] In a recent Raman scattering experiment, Claus *et al.*[8] have observed polariton scattering in LiIO₃. Therefore, both of the above techniques might be successful in generating far-infrared radiation in LiIO₃. In comparison to LiNbO₃, LiIO₃ has the advantages of better optical homogeneity and higher resistance to damage from visible light.[3] Moreover, as will be demonstrated in this letter, LiIO₃ is transparent over a larger frequency range at low temperatures. There is, however, also a disadvantage. Phase matching of optical and infrared frequencies is only possible at a small angle θ from the c axis. The effective nonlinear constant for an $o-e\rightarrow o$ mixing process contains $\sin\theta$ and the intensity of the generated infrared radiation is proportional to $\sin^2\theta$. In order to determine the phase-matching angle θ, we have measured the refractive indices in the far infrared at 300°, 80°, and 17°K.

The far-infrared transmission of LiIO₃ has been measured in the 10–260-cm⁻¹ spectral range for both $E \parallel c$ and $E \perp c$ with a RIIC Fourier spectrometer employing a Golay cell as a detector.

Two LiIO₃ plates of different thickness (0.4 and 2.5 mm) and slightly wedge shaped in order to prevent interference effects were mounted on a movable holder in thermal contact with He exchange gas. Polarization of the far-infrared radiation was accomplished with a wire-grid polarizer electroformed on a Mylar substrate.

From the computed transmission spectra for the two different crystals, we have evaluated the absolute absorption coefficient α. Taking into account only single reflections at the entrance and exit surface of the crystal, the transmitted intensity is given by $I = I_0(1-R)^2 e^{-\alpha t}$, R being the reflectivity and t the crystal thickness. The absorption coefficient α is then given by

$$\alpha = \frac{\ln I_1/I_2}{t_2 - t_1},$$

where the indices 1 and 2 refer to the thin and thick samples, respectively. Whenever interference fringes occurred, a curve-smoothing technique was employed. In addition, a thinner sample (0.2 mm) was employed in order to better determine the absorption coefficient in less transparent regions.

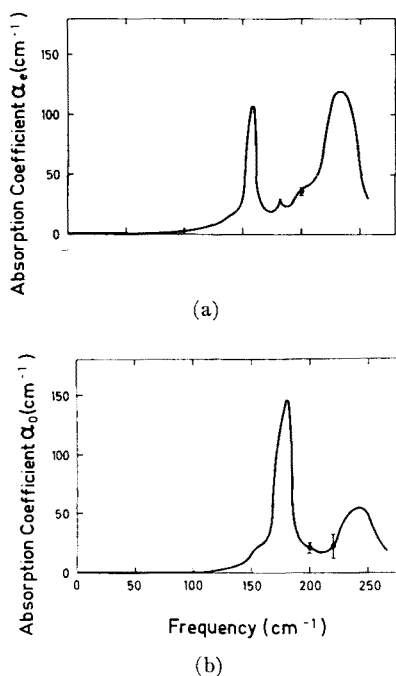Figures 1 and 2 show the resultant absorption co-

(a)

(b)

Fig. 2. The far-infrared absorption coefficients of LiIO₃ for the ordinary and extraordinary ray at 7°K. α_e has a weak maximum at 182 cm⁻¹ corresponding to the strong maximum in α_0 at the same frequency. This is due to the imperfect nature of the polarizer.

TABLE I. Far-infrared absorption bands and Raman lines in LiIO₃.

Present infrared investigation		Raman scattering[a] room temperature	
Frequency (cm⁻¹)	$T=7°K$	Frequency (cm⁻¹)	Assignment
158	$E \parallel c$	147	A
233	$E \parallel c$	243	A
182	$E \perp c$	172	E_1
~175[b]	$E \perp c$		
242	$E \perp c$		

[a] See Ref. 8.
[b] Shoulder.

efficients versus frequency in wavenumbers (cm⁻¹). At frequencies below 150 cm⁻¹, the absorption decreases drastically upon cooling from 300° to 7°K. Furthermore, one finds that the absorption coefficient is larger for $E \parallel c$ than for $E \perp c$, especially at frequencies approaching 150 cm⁻¹. At 7°K, $\alpha \leq 1$ cm⁻¹ for frequencies up to 80 and 90 cm⁻¹ for $E \parallel c$ and $E \perp c$, respectively. In addition, several absorption bands were observed and are given in Table I along with the Raman scattered lines reported by Claus et al. in the same frequency range. The apparent frequency differences may possibly be explained, in part, by a temperature dependence of the lattice and internal vibrations. Furthermore, for infrared-active phonons, the accompanying long-range electric fields lead to frequency shifts of some of the Raman-active phonons away from their $k=0$ values.[9] And in LiIO₃, which lacks a

center of inversion, a phonon can be simultaneously Raman and infrared active.

The absorption coefficients at a fixed frequency for various temperatures between 80° and 300°K show an increase which varies roughly linearly with temperature. This behavior may be explained by the assumption of a two-phonon difference absorption process.[10] However, the correlation between our absorption curves and the transitions between certain phonon branches is rather difficult for LiIO₃ because its complex phonon dispersion is still unknown.

We found neither any anomalous behavior of the far-infrared absorption and refractive indices, nor did we encounter any destructive phase transition upon cooling the LiIO₃ samples from 300° to 7°K.

The refractive indices n_0 and n_e were determined at 300°, 80°, and 17°K from the interference peaks of a thin plan-parallel plate of LiIO₃ ($t=0.4$ mm). Table II gives the refractive indices and compares them with the low-frequency dielectric constants measured by Haussühl[4] at 300°K and 10 Mc. As in the visible, where $n_0 > n_e$,[11] LiIO₃ is also negative uniaxial in the far infrared.

The above far-infrared data suggest that LiIO₃ might be useful for difference-frequency generation in a similar way as described by Faries et al. for LiNbO₃. LiIO₃, being much more transparent than LiNbO₃ [12] between 50 and 100 cm⁻¹ at low temperatures, could be a better material for the generation of far-infrared radiation at

TABLE II. The ordinary and extraordinary indices of refraction of LiIO₃.

T (°K)	n_0	Frequency range	n_e	Frequency range
300	2.84 ± 0.1	25–65 cm⁻¹	2.5 ± 0.1	20–70 cm⁻¹
	$(\epsilon_1)^{1/2} = 2.87$[a]	10 Mc	$(\epsilon_3)^{1/2} = 2.56$[a]	10 Mc
80	2.9 ± 0.1	25–75 cm⁻¹	2.5 ± 0.1	14–90 cm⁻¹
17	2.9 ± 0.1	30–94 cm⁻¹	2.5 ± 0.1	20–90 cm⁻¹

[a] See Ref. 4.

frequencies approaching 100 cm^{-1}. The phase-matching angle at this frequency for an $o-e\rightarrow o$ mixing process would be about 11° with respect to the c axis.

The authors gratefully acknowledge the hospitality of Professor Genzel's group in Freiburg, valuable discussions with Professor K. Dransfeld, and financial support from the Deutsche Forschungsgemeinschaft.

* A financial grant was provided by the Deutsche Forschungsgemeinschaft.
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Elastic Field of a Point Defect in a Cubic Medium and its Interaction with Defects*

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(Received 15 September 1969)

Three equal orthogonal double forces without moment aligned along the cubic axes are used as a model for a point defect in a cubic medium. The method of Fourier transforms is used to obtain the solution for the displacement and stress fields. The solution is presented in a polynomial form. The elastic interaction between a point defect and an edge dislocation is computed for copper by making the displacement of the edge dislocation against the stress field of the defect. The interaction with the physically significant [11$\bar{2}$] edge dislocation on the (111) plane in copper is presented. The computer program was verified by the agreement of its results with those for the hypothetical [001] edge dislocation on the (010) plane, for which the stresses can be calculated in closed form. Near the slip plane, the calculated anisotropic interaction was almost twice that of a corresponding isotropic one. The elastic interaction between two point defects in copper is calculated, indicating regions of attraction of like defects along the cube axes and repulsion along the cube diagonals. Eshelby's perturbation analysis for materials with slight anisotropy predicts qualitatively similar effects, but the repulsion is much greater than that predicted by his approximate analysis.

The elastic interaction between defects in crystals is important to the theories of the mechanical properties of solids as well as to the theories of the kinetics of precipitation in solids.[1-4] A model to simulate a point defect which has been extensively used can be constructed by superimposing three orthogonal "double forces without moment."[5-7] Unfortunately, most of the analyses have been restricted to isotropic media because of the mathematical difficulties encountered in using anisotropic media, even though most crystals are so highly anisotropic[8] that the calculations are only poor approximations.

The elastic interaction energy between the stress fields of two defects can be calculated by volume integration but it is usually simpler to calculate the interaction by creating one defect by displacements in the presence of the stress field of the other. To find the interaction between a point defect and a dislocation in an anisotropic medium it is more convenient to use the stress field for the point defect and create the dislocation by displacements rather than the converse, because the stress fields for dislocations in anisotropic media are functions of orientation and the stresses are not known for many. In contrast, if we knew the stress field for a point defect, its interaction with any dislocation can be found by integrating over the surface of the dislocation's cut the stress component of the point defect which is parallel to the Burgers vector.

Attempts have been made to determine the elastic field of a point defect or of a point force in a cubic medium which then can be used to construct the model for the point defect. The usefulness of results have been limited because they are either approximate or cumbersome to employ. Burgers in 1939[9] obtained a two term expansion for the displacement caused by a unit point force in a cubic material. Lie and Koehler[10] and Mann,