BCS theory and the SPA.

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[1] N. Boccara and G. Sarma, Physics (Long Is. City, N. Y.) 1, 219 (1965).

[2] For a review of the relevant literature, see N. R. Werthamer, Phys. Rev. B 1, 572 (1970).

[3] N. S. Gillis and T. R. Koehler, Phys. Rev. B 4, 3971 (1971), and Phys. Rev. B (to be published).

[4] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1958), Sect. 135.

[5] A. F. Devonshire, Advan. Phys. 3, 85 (1954).

[6] See for example R. Brout, *Phase Transitions* (Benjamin, New York, 1965).

[7] For dipolar forces, the linear term is replaced by $Q_0^2 \ln Q_0$. However, the transition remains first order.

[8] V. L. Ginzburg, Fiz. Tverd. Tela 2, 2031 (1960) [Sov. Phys. Solid State 2, 1824 (1961)].

[9] This condition applies strictly speaking only for $T < T_c$. For $T > T_c$ the critical region is determined by comparing fluctuations of the second and higher orders. If it is assumed that the critical region is roughly symmetrical about T_c, then Eq. (11) is also the condition for the validity of the factorization approximation.

[10] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[11] E. Pytte and J. Feder, Phys. Rev. 187, 1077 (1969), and Phys. Rev. B 1, 4803 (1970).

[12] For a discussion of the mean field approximation see also H. Thomas, in Proceedings of the Advanced NATO Study Institute on Structural Phase Transitions and Soft Modes, Geilo, Norway, April, 1970 (to be published).

Optical Rectification by Impurities in Polar Crystals

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When illuminated by an optical source, absorbing impurities in polar crystals produce a macroscopic polarization due to both the change in electric dipole moment from ground to optically excited states and a pyroelectric effect in the host lattice following thermalization of the excitation. The relevance of these mechanisms to relaxation processes is demonstrated by a measurement of the dispersion of optical rectification in $LiTaO_3{:}Cu^{++}$ over the range of rectified frequencies from 0 to 10^{12} Hz.

Previous studies[1-3] of optical rectification have dealt exclusively with the nonlinear properties of transparent electro-optic crystals. In this Letter we report efficient optical rectification in polar crystals due to impurity absorption. The absorbing impurities produce a polarization proportional to optical intensity due to two effects. If the relaxation of the optically excited impurites is largely nonradiative, a pyroelectric polarization results from the heating of the host lattice following thermalization of the excitation. Also, the acentric character of a polar host polarizes an impurity ion, producing an electric dipole moment which may be different in the excited state than in the ground state, and hence results in a macroscopic polarization upon optical excitation. This effect, which does not occur in nonpolar materials has been observed[4] in chromium-doped $LiTaO_3$ and $LiNbO_3$. Although the pyroelectric effect is well known for its detector applicatons,[5] its relevance to fast nonradiative relaxation has not been considered previously.

For a two-level atomic system with a nonradiative relaxation time τ, the macroscopic polarization P, due to these two effects, is determined by the approximate equation

$$\frac{\partial P}{\partial t} + \frac{1}{\tau} P = \frac{\alpha \Delta \mu I(t)}{\hbar \omega_0} + \frac{\alpha}{C_v}\left(\frac{\partial P_3}{\partial T}\right)\frac{1}{\tau}\int I(t)\,dt, \tag{1}$$

where α is the optical absorption coefficient for incident light of intensity $I(t)$ and frequency ω_0, $\Delta\mu$ is the difference in dipole moment of the impurity ions between ground and excited states, $\partial P_3/\partial T$ is the pyroelectric coefficient of the host lattice, and C_v is the specific heat. For simplicity we have excluded the effects of saturation and coherent population fluctuations in Eq. (1). Also, the time interval of interest is assumed to be short relative to both thermal and acoustic transients, i.e., the adiabatic, clamped-material properties are used in (1).

Alternatively, these mechanisms can be represented in the frequency domain by second-order nonlinear susceptibilities for difference frequency generation of the form[6]

$$P_j(\omega) = \chi_{jkl}(\omega = \omega_1 - \omega_2)E_k(\omega_1)E_l^*(\omega_2),$$

$$\chi_{3kl}(\text{pyroelectric}) = \frac{\omega_0}{c_v}\left(\frac{\partial P_3}{\partial T}\right)\frac{1}{\omega}\,\frac{1}{1+i\omega\tau}[\chi_{lk}(\omega_1) - \chi_{lk}^*(\omega_2)], \tag{2}$$

$$\chi_{jkl}(\text{dipolar}) = \frac{\Delta\mu_j}{i\hbar}\,\frac{\tau}{1+i\omega\tau}[\chi_{lk}(\omega_1) - \chi_{lk}^*(\omega_2)], \tag{3}$$

where χ_{lk} is the complex linear optical susceptibility of the absorbing impurities. The pyroelectric polarization is directed along the polar (3) axis of the crystal. The symmetry properties of the excited-state dipole effect are determined by the point group of the impurity site.

It is apparent from expressions (2) and (3) that the dispersive properties of these susceptibilities are intimately related to the relaxation time τ of the impurities. The pyroelectric effect varies as ω^{-1} in the region $\omega\tau < 1$, reflecting the integrated character of this mechanism. Above this point, $\omega\tau > 1$, it drops off rapidly as ω^{-2}. The excited-state dipole effect, however, is flat up to $\omega\tau = 1$, and then drops off as ω^{-1} in the region $\omega\tau > 1$. In principle, it is possible to determine both the nonradiative relaxation time τ and the magnitude of $\Delta\mu$ from a measurement of the dispersion of the nonlinear susceptibilities. Since a measurement of this type can be made into the millimeter and submillimeter wave range of rectified frequencies, subpicosecond relaxation measurements are possible. An important fundamental limitation on the speed of the pyroelectric effect in addition to impurity relaxation is the rate at which energy thermalizes at the impurity site and diffuses into the host lattice to perturb the ferroelectric soft modes which are responsible for the pyroelectric polarization. A measurement or upper limit of this response time is possible in a system with a fast impurity relaxation and small $\Delta\mu$. More complicated multilevel systems such as those involving vibronic (i.e., electronic and vibrational) transitions can also be studied by these techniques.

For a preliminary study of some of these effects, the Cu^{++} ion in $LiTaO_3$ was chosen since its linear absorption spectrum has a relatively strong broad absorption band centered at 10 000 cm^{-1}, suitable for excitation with a 1.06-μm Nd:Glass laser. Also the absence of fluorescence from the excited $^2T_2$ state (O_h group) suggests the possibility of a fast nonradiative electronic relaxation. A strong charge-transfer band dominates the spectrum from 0.4 μm into the uv.

Crystals of undoped and copper-doped $LiTaO_3$ were grown by the Czochralski technique[7] and poled to produce single-domain material. The most heavily doped crystal, 2.24% weight Cu, had an absorption coefficient at 1.06 μm of 60 cm^{-1}. Crystals of centimeter dimensions were readily grown. The low-frequency dielectric and pyroelectric properties of the doped crystals were measured and found to be identical to the undoped crystals.[8]

The source of optical radiation was a 1.06-μm mode-locked Nd:Glass laser of standard design which emitted a train of pulses with a mean width of 10 psec, a peak power of 10^8 W, and a mean spectral width of 25 cm^{-1}. The range of intensities incident on the crystals was between 10^8 and 10^9 W/cm^2.

A measurement of the electronic relaxation time of the $^2T_2$ state of the Cu^{++} ion was made by populating the $^2T_2$ state with a 1.06-μm pulse ($^2E \rightarrow {}^2T_2$) and measuring the excited-state absorption from $^2T_2$ to the charge-transfer (CT) band with a delayed 0.53-μm second-harmonic pulse. Because of the large cross section of the parity-allowed $^2T_2$ to CT transition, a $^2T_2$ population of only a few percent was required. The relaxation time was obtained from the dependence of the excited-state absorption on the delay and found to be 30 ± 10 psec as shown in Fig. 1.

Using the 1.06-μm mode-locked pulses as a source, the optical rectification properties of $LiTaO_3{:}Cu^{++}$ were measured over the range 0 to 10^{12} Hz of the intensity spectrum of the incident pulses. As a reference, the corresponding signals due to the electro-optic effect in an undoped $LiTaO_3$ crystal were measured in an identical experiment. The low-frequency (0 to 1 GHz) current response of the undoped and doped crystals was measured in real time with a high-speed oscilloscope (Fig. 2). The crystals were electroded on their c faces, transverse to the laser axis. The dominant pyroelectric effect in the doped crystal produces a current pulse which resembles a bandwidth limited version of the optical pulse, whereas the electro-optic effect in the undoped crystal differentiates the intensity pro-

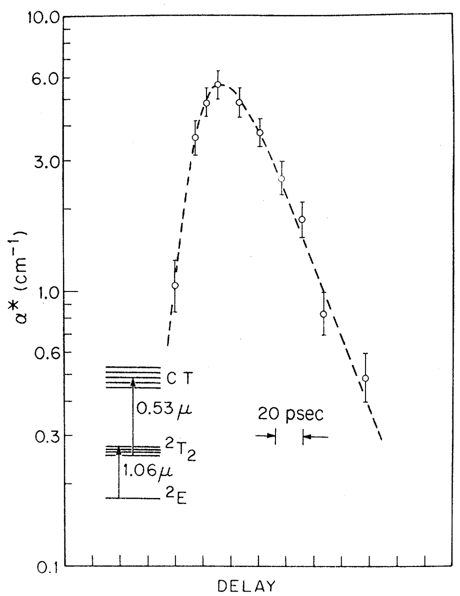

FIG. 1. Measurement of the electronic relaxation time of the $^2T_2$ state of the Cu^{++} ion in LiTaO$_3$ by excited-state absorption. Horizontal axis, delay time between pumping 1.06-μm pulse and 0.53-μm probing pulse. Vertical axis, excited-state absorption coefficient.

file of the incident optical pulse. In both cases the observed widths and amplitudes were limited by the impulse response of the oscilloscope of 300 psec.

Comparison of doped and undoped crystals at higher frequencies were made by measuring the spectral characteristics of the microwave and millimeter wave radiation produced by rectification of the optical pulses. The band from 2 to 4 GHz was measured with coaxial filters and a point-contact diode. X-band (4 to 10 GHz), and K-band (20 to 40 GHz) measurements were made by mounting the crystals in open wave guides and detecting the microwave radiation with point-contact diodes. A liquid-helium-cooled InSb photoconductor was used to detect the submillimeter waves.

In all cases except the oscilloscope measurement of Fig. 2, the dimensions of the LiTaO$_3$:Cu^{++} reference crystals were identical. The thickness in the direction of the laser axis was less than the coherence length and typically 0.1 to 0.3 mm (optical and microwave indices of refraction are 2.1 and 6.5, respectively). With both crystal and detector geometries identical, the relative magnitude of the nonlinear susceptibilities of the doped and undoped crystals is equal to the square root of the ratio of the intensities of the rectified signals, apart from a correction for the finite absorption depth in the doped crystal. In the case of the low-frequency real-time measurement, an additional thickness correction was made to account for the larger 4-mm undoped crystal which was needed to obtain a measurable signal.

In Fig. 3 the measured nonlinear susceptibility $\chi_{311}=\chi_{322}$, of a 2.24% LiTaO$_3$:Cu^{++} crystal is plotted, normalized to χ_{333} of an undoped LiTaO$_3$ crystal. The incident polarization for the doped crystal was chosen to be σ to minimize the contribution from the host nonlinearity. The low-frequency data (up to 1 GHz) was obtained from a numerical Fourier analysis of the real-time traces of Fig. 2. In general, the signal intensity depended quadratically on the incident optical intensity except at intensities approaching the damage threshold. Measurements with other dopings (0.3% and 1.2%) indicated that the susceptibility was proportional to copper concentration. The radiation from the doped crystals was strongly π polarized for both σ and π incident optical polar-

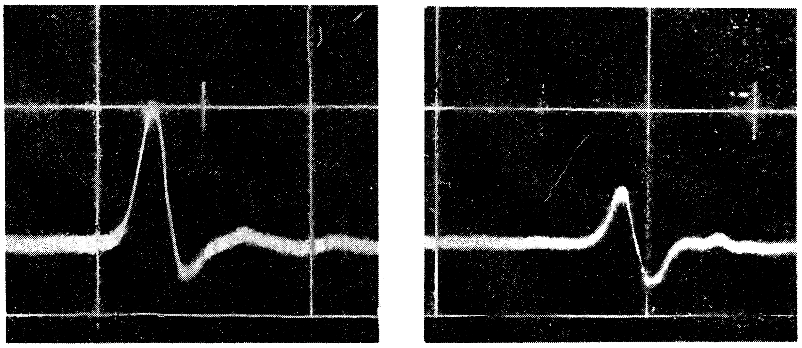

FIG. 2. Oscilloscope traces of the optical rectification from LiTaO$_3$:Cu^{++} (left) and undoped LiTaO$_3$ (right). Horizontal and vertical scales, 2 nsec/division and 10 V/division, respectively. Oscilloscope bandwidth, 1.1 GHz.

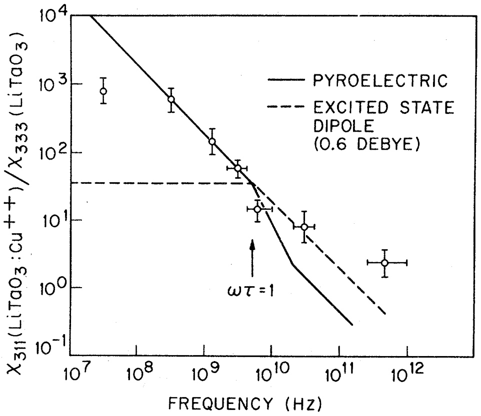

FIG. 3. Dispersion of the nonlinear susceptibility for optical rectification from $\mathrm{LiTaO_3:Cu^{++}}$ (2.24% Cu) normalized to an undoped $\mathrm{LiTaO_3}$ reference. Horizontal bars represent integrations over indicated bandwidths. Straight-line segments are used to accentuate critical points in theory.

izations. The polarization behavior of the undoped crystals was consistent with electro-optic data, showing a strong preference for π-incident optical polarization. For a pulse input of 10^{-3} J, the total rectified energy from the 2.24% Cu crystal was estimated to be between 0.1 and 1.0 erg in a 0.1-mm crystal.

Since the electro-optic effect in the undoped $\mathrm{LiTaO_3}$ crystals ($\chi_{333} = 1.6 \times 10^{-6}$ esu)[9] is nondispersive in the frequency range spanned by our measurements, the results in Fig. 3 are a direct measure of the impurity contribution to the nonlinearity. In the region $\omega\tau < 1$ the results agree well with the expected pyroelectric behavior (the point at 30 MHz is in error as a result of a pyroelectric effect in the undoped crystal arising from residual impurities). The theoretical curve (solid line) also includes a contribution from a fast heating due to the relaxation of the vibrational energy within the excited vibronic state of the $\mathrm{Cu^{++}}$ ion. From the width of the optical band (4000 $\mathrm{cm^{-1}}$) we estimate the fraction of the absorbed energy involved in the vibrational relaxation is 0.25. Although this contribution extends the pyroelectric effect into the region $\omega\tau > 1$, its magnitude is too small to account for the experimental results (the intensity of the rectified signals from the doped crystal was almost three orders of magnitude larger than expected from a purely pyroelectric effect). As indicated by the dashed curve, the experimental data in the region $\omega\tau > 1$ suggest the existence of a dipole moment which differs between ground and excited states by approximately 0.6 D. This value is comparable to the $\Delta\mu$ of Cr in $\mathrm{LiTaO_3}$ and $\mathrm{LiNbO_3}$ measured by a different technique.[4] A second important result of this measurement is that the pyroelectric response of the host lattice is at least as fast as 30 psec. These materials are also of interest for nonlinear optics. Heavy doping can be used to both increase the magnitude of the nonlinearity and decrease the interaction length to less than the coherence length, eliminating the need for phase matching. A more detailed theoretical and experimental study of the effects demonstrated here is the subject of a forthcoming paper.

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[1] M. Bass, P. A. Franken, J. F. Ward, and G. Weinreich, Phys. Rev. Lett. 9, 446 (1962).

[2] M. J. Brienza, A. J. DeMaria, and W. H. Glenn, Phys. Lett. 26A, 390 (1968).

[3] K. H. Yang, P. L. Richards, and Y. R. Shen, Appl. Phys. Lett. 19, 320 (1971).

[4] A. M. Glass and D. H. Auston, to be published.

[5] See, for example, the three reviews by A. Hadni, E. H. Putley, A. M. Glass, and R. L. Abrams, in *Proceedings of the Symposium on Submillimeter Waves* (Polytechnic Press, New York, 1970).

[6] The contribution of the diagonal components of the dipole-moment operator to optical nonlinearities was considered in a general formulation by N. Bloembergen and Y. R. Shen, Phys. Rev. 133, A37 (1964).

[7] A. A. Ballman, J. Amer. Ceram. Soc. 48, 112 (1965).

[8] A. M. Glass, Phys. Rev. 172, 564 (1968).

[9] P. V. Lenzo, E. H. Turner, E. G. Spencer, and A. A. Ballman, Appl. Phys. Lett. 8, 81 (1966).

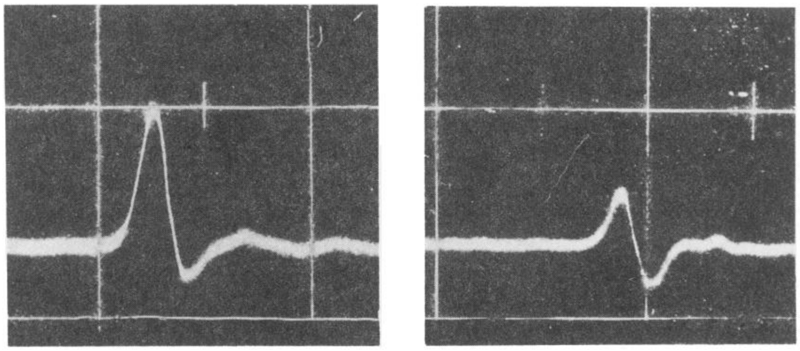

FIG. 2. Oscilloscope traces of the optical rectification from $LiTaO_3:Cu^{++}$ (left) and undoped $LiTaO_3$ (right). Horizontal and vertical scales, 2 nsec/division and 10 V/division, respectively. Oscilloscope bandwidth, 1.1 GHz.