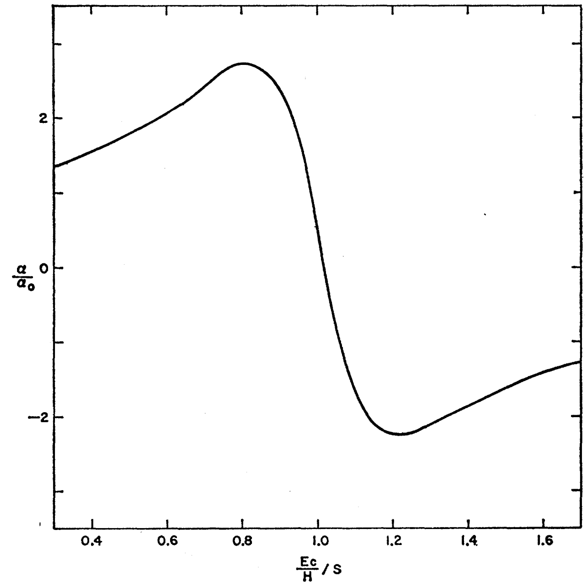

FIG. 1. Plot of bracketed term in Eq. (12) for the following values of parameters: $D=1$ cm²/sec, $\tau_r=10^{-8}$ sec, $k=10^4$ cm^{-1}, $s=10^5$ cm/sec.

be shown that the recombination rate will be given by

$$dn/dt=(-1/\tau_r)[(n-n_0)+N_r\epsilon(\mathcal{E}_n-\mathcal{E}_p)],$$

where N_r is a reduced density of states given, in terms of the density of states at the Fermi level in the conduction and valence bands, by $N_r^{-1}=N_c^{-1}+N_v^{-1}$. If we use this recombination rate in Eqs. (5a) and (5b), the amplitude of $n-n_0$ is altered and in Eq. (7) the factor $n_0\mu$ is replaced by $(n_0\mu+N_r/k^2\tau_r)$. The form of the attenuation constant is not altered, but an additional term given by

$$\alpha'=\frac{eN_r(\mathcal{E}_n-\mathcal{E}_p)^2}{\tau_r\rho s^3}\times\left\{\frac{Dk[Dk+(1/k\tau_r)]-(Ec/H)[(Ec/H)-s]}{[Dk+(1/k\tau_r)]^2+[(Ec/H)-s]^2}\right\}$$

is now present and should be added to that given in Eq. (12). α' is similar to the expression given by Hopfield if diffusion is ignored. Because of the term $-Dk[Dk+(1/k\tau_r)]$, α' can be negative corresponding to amplification for Ec/H slightly less than s.

The ratio of the two contributions to the attenuation constant is approximately given by $\alpha/\alpha'\cong\tau_r n_0\mu k^2/N_r \cong\tau_r E_F\mu k^2$ where E_F is the average Fermi level in the valence and conduction bands. For sound waves with small k it is clear that the recombination which caused term α' will dominate the attenuation, whereas the transport term α will dominate at higher values of k. The value of τ_r which enters the ratio α/α' is presently unknown, although it is thought to be large ($\sim10^{-6}$ sec) since recombination employing phonons should be negligible at temperatures at which amplification should be observed and scattering by impurities between states far apart in momentum is highly improbable.

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Nonlinear Dielectric Polarization in Optical Media

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The physical mechanisms which can produce second-order dielectric polarization are discussed on the basis of a simple extension of the theory of dispersion in ionic crystals. Four distinct mechanisms are described, three of which are related to the anharmonicity, second-order moment, and Raman scattering of the lattice. These mechanisms are strongly frequency dependent, since they involve ionic motions with resonant frequencies lower than the light frequency. The other mechanism is related to electronic processes of higher frequency than the light, and, therefore, is essentially flat in the range of the frequencies of optical masers. Since this range lies an order of magnitude higher than the ionic resonances, the fourth mechanism may be the dominant one. On the other hand, a consideration of the linear electro-optic effect shows that the lattice is strongly involved in this effect, and, therefore, may be very much less linear than the electrons. It is shown that the question of the mechanism involved in the second harmonic generation of light from strong laser beams may be settled by experiments which test the symmetry of the effect. The electronic mechanism is subject to further symmetry requirements beyond those for piezoelectric coefficients. In many cases, this would greatly reduce the number of independent constants describing the effect. In particular, for quartz and KDP there would be a single constant.

THE recent observation by Franken, Hill, Peters, and Weinreich[1] of second-harmonic light generation in quartz raises the question of the physical mechanism involved in nonlinear dielectric polarization effects at optical frequencies. The purpose of this paper is to discuss briefly the possible types of mechanism, and to point out the special properties of one mechanism which may permit it to be experimentally separated

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[1] P. Franken, A. Hill, C. Peters, G. Weinreich, Phys. Rev. Letters **7**, 118 (1961).

from the others. It is understood that the region of the spectrum of interest is that available to optical masers near $10^4\ \mathrm{cm}^{-1}$.

We begin by considering the linear theory[2] of dispersion in ionic crystals, which is based upon equations of the form

$$\partial^2 w/\partial t^2 = b_{11}w + b_{12}E,$$
$$P = b_{21}w + b_{22}E. \qquad (1)$$

Here E is the electric field, w represents an ionic displacement in the crystal, b_{11} is a restoring force coefficient, $b_{12}=b_{21}$ is an effective charge, and b_{22} is the high-frequency polarizability. The physical ideas are most clearly introduced by considering the quantities in (1) as just magnitudes rather than vectors and tensors. The same equation can be used to discuss classically the electronic as well as the ionic contributions to the dispersion. In any case, the underlying physical ideas are the following: (a) An energy function $U(w,E)$ exists for the crystal in an electric field, such that

$$P = -\partial U/\partial E, \quad \partial^2 w/\partial t^2 = -\partial U/\partial w, \qquad (2)$$

and (b) there exists a mechanism independent of w giving a polarizability essentially independent of frequency in the frequency range of interest. The independent mechanism gives rise to b_{22} in (1). The energy function, second order in (w, E), leading to (1) is

$$U^{(2)}(w,E) = -\tfrac{1}{2}(b_{11}w^2 + 2b_{12}wE + b_{22}E^2). \qquad (3)$$

We may now generalize Eq. (1) to include second-order polarization by adding third-order terms to U as follows:

$$U^{(3)}(w,E) = -\tfrac{1}{3}(f_1w^3 + 3f_2w^2E + 3f_3wE^2 + f_4E^3), \qquad (4)$$

where $f_1,\ldots,f_4$ are coefficients characteristic of the medium. The equations of motion are easily obtained from Eq. (2) and will not be given here.

There are four mechanisms represented by the coefficients $f_1,\ldots,f_4$, which can produce second-order polarization. The separate terms in $U^{(3)}(w,E)$ may be characterized briefly in the following way: f_1 represents *anharmonicity* in the restoring force; f_2 represents *second-order electric moments*, such as give rise to infrared absorption in diamond type crystals[3]; f_3 represents the *Raman scattering* interaction; and f_4 represents the *nonlinearity in the independent mechanism.* A reasonable assumption would be that, w, f_1, f_2, and f_3 refer to processes essentially ionic, while f_4 refers to relatively high-frequency electronic processes such as the intrinsic absorption of the crystal. To see how second-order polarization comes about consider, for example, f_1. The coordinate w contains a component at the frequency of E, and, therefore, the anharmonic force f_1w^2 contains a second harmonic component and introduces this component into w. The second-harmonic component of w then is introduced into P.

It is important to notice that the frequencies ν of present optical masers lie roughly an order of magnitude below the frequencies of the strong electronic transitions and an order of magnitude above those of the ionic motions. The f_4 mechanism, therefore, is entirely different in its dispersion from the ionic mechanisms. The latter should fall off with increasing frequency as some power of $(1/\nu^2)$, while the former should be essentially flat with frequency. It seems reasonable[4] to suppose that, if the absorption of light by the lattice is negligible, the ionic mechanisms for nonlinear polarization are also negligible. The f_4 mechanism, on the other hand, does not imply absorption and may be the dominant mechanism in very transparent crystals such as quartz[4].

As pointed out by Franken *et al.*,[1] second-order polarization can only occur in crystals of suitable symmetry. Regardless of its mechanism, the second-order polarization can be written in full coordinate form,

$$P_k = \textstyle\sum_{ij} d'_{ijk}E_iE_j, \qquad (5)$$

where, without loss of generality, we set $d'_{ijk}=d'_{jik}$. There are in the most general case 18 independent coefficients d'_{ijk}, which may be conveniently written in the condensed notation[5] for piezoelectric constants

$$d'_{11k}=d_{1k};\ldots;d'_{12k}=d_{6k}. \qquad (6)$$

The requirements of crystal symmetry on d_{ij} are the same as for piezoelectric coefficients. Unless f_4 is the dominant mechanism there are no further symmetry requirements, and the d_{ij} will be frequency dependent. On the other hand, if f_4 is the dominant mechanism an additional symmetry must be satisfied. Consider the third-order energy function associated with f_4, which in full notation may be written

$$U^{(3)}(E) = -\tfrac{1}{3}\textstyle\sum_{ijk} d'_{ijk}E_iE_jE_k. \qquad (7)$$

The coefficients in Eq. (7) are the same as in Eq. (5), since Eq. (5) is obtained from Eqs. (2) and (7). Clearly the coefficients in Eq. (7) may be chosen symmetric with respect to any rearrangement of indices. Therefore, in the most general case there are 10 independent coefficients as follows:

$$\begin{matrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{16} & d_{22} & d_{23} & d_{24} & d_{14} & d_{12} \\ d_{15} & d_{24} & d_{33} & d_{23} & d_{13} & d_{14}. \end{matrix} \qquad (8)$$

It is understood that this matrix operates on a 6-component column vector E_1^2, E_2^2, E_3^2, $2E_2E_3$, $2E_1E_3$, $2E_1E_2$. It should be emphasized that Eq. (8) applies only to the f_4 mechanism.

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[2] M. Born and K. Huang, *The Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Chap. II., Sec. 7, 8, Appendix V.

[3] M. Lax and E. Burstein, Phys. Rev. **97**, 39 (1955).

[4] P. Franken (private communication).

[5] "Standards on Piezoelectric Crystals," Proc. Inst. Radio Engrs. **46**, 764 (1958).

When Eq. (8) is combined with the requirements of crystal symmetry, considerable simplification often results. Crystals with point symmetry D_4 (guanidine carbonate[6]) and D_6 are forbidden from exhibiting second-order polarization by the f_4 mechanism. In crystals with symmetry D_2 (rochelle salt[6]), D_3 (quartz), and D_{2d} (KDP[6]), the matrix Eq. (8) reduces to a single independent constant.

It should be quite feasible to carry out experiments which would test these predictions, and, thereby, determine if f_4 is the dominant mechanism. In the case of quartz, symmetry requires that all components d_{ij} (referred to crystallographic axes in which 3 is the optic axis and 1 is a binary axis) vanish except $d_{11}=-d_{12}=-d_{26}$ and $d_{14}=-d_{25}$. The second harmonic observed by Franken *et al.*[1] was entirely due to d_{11}. According to Eq. (8) d_{14} must vanish, since $d_{36}=0$ and $d_{25}=-d_{14}$ by symmetry. Therefore, it is proposed that the plane-polarized focused laser beam be made to pass through an X-cut quartz crystal plate as an *extraordinary ray* making an angle φ with the optic axis, where $0<\varphi<90°$. If $d_{14}\neq 0$, a second-harmonic *ordinary ray* will appear proportional in intensity to $d_{14}^2 \sin^2 2\varphi$. By means of an analyzer, this ray may be compared with the second-harmonic extraordinary ray proportional to $d_{11}^2 \sin^4\varphi$. To avoid difficulty with the optical activity, the plates should be considerably thinner than 1 mm.

It has been recognized[7] that second-harmonic generation is a related phenomenon to the *linear electro-optic* effect,[8] which is the change in birefringence proportional to an applied electric field. We consider whether these effects arise from the same mechanism. In the standard theory of the electro-optic effect[8,9] the inverse dielectric constant matrix a is expressed as a linear function of electric field through an electro-optic matrix r,

$$a_j = a_j^{(0)} + \sum_i r_{ji} E_i. \tag{9}$$

Here, a is arranged as a column matrix of six components in the usual convention[5], and r_{ji} is a 6×3 matrix. The r_{ji} can be expressed in terms of the d_{ij}, but the general case is too complicated to be of interest here. If, however, d has the form (8) and components are referred to the principal axes of $a^{(0)}$, the relation reduces to

$$r_{ji} = -4\pi A_j d_{ij}, \tag{10}$$

where $A_1 = a_1^{(0)2}; \ldots; A_6 = a_1^{(0)} a_2^{(0)}$, and the $a_j^{(0)}$ are the principal inverse dielectric constants.

The above discussion shows that by consulting the literature for the electro-optic constants of various crystals, it can be determined whether f_4 is the dominant mechanism for this effect. Since the data[10] for quartz, rochelle salt, and ADP are in disagreement with (10) and (8), we conclude that the usual linear electro-optic effect is not due to the f_4 mechanism, and probably involves ionic motion in an essential way. This view is strongly supported by the fact that r_{63} for KD_2PO_4 is over twice that for KH_2PO_4 (KDP) or RbH_2PO_4. This is not at all surprising, since the frequency of the applied field is well below that of the lattice vibrations. This does show that lattice polarization is inherently less linear than electronic polarization in crystals. Some question remains, therefore, as to the true mechanism for second-harmonic light generation, and it is suggested that the symmetry properties (8) of the electronic mechanism may prove helpful in answering this question.

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[10] *American Institute of Physics Handbook* (McGraw–Hill Book Company, Inc., New York, 1957), Vol. 6, p. 97.