TABLE I. Bulk critical fields and Kunzler fields for "high-field" superconductors.

	$H_c(T=4.2°)$	$H_K(T=4.2°)$	H_K/H_c
Mo_3Re	466	15 000[b]	32
Nb+25% Zr	2500[e]	70 000[c]	28
Nb_3Sn	6000[a]	>200 000[d]	33

[a] R. M. Bozorth, A. J. Williams, and D. D. Davis, Phys. Rev. Letters **5**, 148 (1960).
[b] J. E. Kunzler, E. Buehler, F. S. L. Hsu, B. T. Matthias, and C. Wahl, J. Appl. Phys. **32**, 325 (1961).
[c] P. R. Aron and H. C. Hitchcock (private communication, to be published).
[d] J. E. Kunzler (private communication).
[e] Estimated from measurements on a polycrystalline sample.

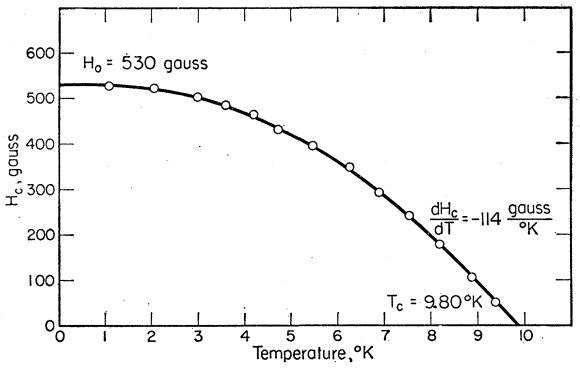

FIG. 1. Critical field vs temperature, Mo_3Re.

comparison is made utilizing approximate data for Nb+25% Zr and Nb_3Sn. For each of these materials, H_K is taken from the curve of critical current I_c versus applied magnetic field. H_K is defined as the field at which the plateau region of critical current ends and I_c commences its steep descent to zero. While H_K seems to depend somewhat on the physical and chemical inhomogeneities present in the material, a saturation point appears to be attained as the concentration of these inhomogeneities is increased. The H_K values in Table I are the maximum values so far reported for each material.

Apparently, H_K/H_c lies in the vicinity of 30 for the high-field superconductors which have been so far studied. This is surprising in view of the fact that the materials are of different metallurgical character and, moreover, were studied under different conditions. It suggests to us that perhaps the basic mechanism of the formation of high-field, superconducting filaments or plates is the same for these three materials, at least in the bulk state.

Finally, we note that the surprisingly low Kunzler field for the transition metal alloy, Mo_3Re, stems directly from a low value of the bulk critical field. We suggest that the region between Groups 6 and 7 is not favorable for extremely high Kunzler fields, and that the molybdenum-technetium system will exhibit γ, H_c, and H_K values similar to those of other high-field superconductors.

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Nonlinear Optical Effects

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A number of possible nonlinear light effects in solids are discussed where the optical properties of a medium depend upon the value of the incident E and H radiation field; as a consequence of the nonlinear properties of these effects and their intrinsic fast response times, the possibility exists of producing harmonic generation and mixing at infrared and visible frequencies. The theory of multiple-photon excitation of an electron from the valence to the conduction in a solid is developed. It is shown that this process exhibits an intensity-dependent absorption edge at photon energies below the minimal energy gap of a solid. The experimental conditions for observing such transitions are considered; presently available optical maser sources of radiation are of sufficient intensity to enable double-quantum processes to be experimentally observable in semiconductors and insulators.

WITH the present availability of intense monochromatic sources of radiation in the visible and infrared regions of the spectrum utilizing optical masers,[1–3] the E and H fields that can now be incident upon a substance are of sufficient intensity to allow a number of classical and quantum mechanical nonlinear optical effects to be observable. Under these conditions, the high-frequency permittivity, permeability, or conductivity of a medium can be field dependent. Maxwell's equations for the medium will no longer be linear and the principle of superposition will no longer apply, so that waves of different frequencies can interact. Quantum mechanically, a nonlinear response to an intense

[1] T. H. Maiman, Nature **187**, 493 (1960).
[2] R. J. Collins, D. F. Nelson, A. L. Schawlow, W. L. Bond, C. G. B. Garrett, and W. K. Kaiser, Phys. Rev. Letters **5**, 303 (1960).
[3] P. P. Sorokin and M. J. Stevenson, Phys. Rev. Letters **5**, 557 (1960).

optical radiation field can be considered as an interaction where energy levels are strongly mixed by the incident field, as distinct from weak-field interactions which can cause transitions between essentially static levels. In this paper, we shall discuss a number of nonlinear optical effects whose intrinsically fast response times can be comparable to optical periods; as a consequence, it should be possible to produce harmonic generation and mixing at infrared and optical frequencies. Recently, the generation of optical harmonics has been demonstrated by Franken *et al.*[4] using nonlinear dielectrics and purely classical considerations.

The multiple-photon excitation of an electron from the valence band in a solid is one example of an intensity dependent intrinsic interaction between radiation and matter. The optical absorption of a single photon by valence electrons has been extensively studied both theoretically and experimentally[5] and has included "direct" excitation by a single photon and "indirect" transitions in which phonons and photons simultaneously participate in the excitation. The case of excitation by two or more photons in band-to-band transitions seems not to have been considered, although multiple-quanta transitions between discrete levels have been studied in the radiofrequency region of the spectrum.[6] For the usual light intensities heretofore employed in most optical experiments and for photon energies greater than the energy gap, the higher-order processes corresponding to the absorption of two or more photons are usually negligible compared to first-order single photon processes. However, for photon energies less than the energy gap and at sufficiently high incident intensity, the multiple-photon excitation of a valence electron should be observable. Here we shall treat the case of the simultaneous absorption of two photons of the same or different frequency which are less than the energy gap; this type of transition can take place through a "virtual" state and does not require the presence of impurity levels within the forbidden gap.

Consider two monochromatic beams of light of N_1 and N_2 photons per unit volume incident upon a solid with the following band structure: three energy bands with extrema at $k=0$ playing the roles of a filled valence band, an empty conduction band, and a virtual conduction band. The absorption coefficient for photons of energy $\hbar\omega_1$, when two photons of energies $\hbar\omega_1$ and $\hbar\omega_2$ are simultaneously absorbed, can be calculated from conventional second-order time dependent perturbation theory and is given by:

$$K_1=\frac{4\pi n}{cN_1\hbar}\int\frac{d^3k}{(2\pi)^3}\left[\frac{|H_{vn}|^2|H_{nc}|^2}{[\Delta E+E_{nk}+E_{vk}-\hbar\omega_1]^2}+\frac{|H_{vn}|^2|H_{nc}|^2}{[\Delta E+E_{nk}+E_{vk}-\hbar\omega_2]^2}\right]\times\delta(E_g+E_{ck}+E_{vk}-\hbar\omega_1-\hbar\omega_2),\quad(1)$$

where n is the index of refraction, H_{vn} is the optical matrix element for transitions between a state $\mathbf{k}$ in the valence band and $\mathbf{k}$ in the virtual conduction band, H_{nc} is the corresponding matrix element coupling the virtual conduction band with the final conduction band. E_g is the energy separation of the valence and final conduction band at $k=0$, ΔE is the separation between the valence band the virtual conduction band extrema, and E_{ck}, E_{nk}, and E_{vk} are the energies of the conduction, virtual conduction, and valence band, respectively, measured with respect to their extrema. In this formulation, it is assumed that one is dealing with incoherent photons and that the optical transitions are vertical; the presence of coherence effects will bring in cross products of matrix elements and will increase the transition probabilities.

To explicitly evaluate K_1 for a given substance, the dependence of E_{nk}, E_{ck}, and E_{vk} must be specified together with the value of the optical matrix elements. If we assume spherical and parabolic energy bands for this solid, then:

$$E_{nk}=\alpha_n\hbar^2\mathbf{k}^2/2m,\quad E_{ck}=\alpha_c\hbar^2\mathbf{k}^2/2m,\quad E_{vk}=\alpha_v\hbar^2\mathbf{k}^2/2m,$$

where the α's are the inverse effective mass ratios. The optical matrix elements can be shown to be

$$|H_{vn}|^2=2\pi\hbar e^2N_1|P_{vn}|^2/m^2\omega_1,$$
$$|H_{nc}|^2=2\pi\hbar e^2N_2|P_{nc}|^2/m^2\omega_2.$$

For transitions between bands of opposite parity (allowed transition) $|P_{vn}|^2$ and $|P_{nc}|^2$, the squares of the momentum matrix elements are constant near the band edge, while for transitions between bands that have the same parity (forbidden transitions), the squares of the matrix elements can be assumed proportional to k^2 in the conventional manner. There are three types of transitions possible, depending upon the parities of the three energy bands; these can be designated as "allowed-allowed," "forbidden-allowed," and "forbidden-forbidden" indirect photon-photon transitions.

For the case of "allowed-allowed" transitions, substituting the above band energies and appropriate matrix elements in Eq. (1) and performing the integration, we obtain:

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

[5] J. Bardeen, F. J. Blatt, and L. H. Hall, *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4–6, 1954*, edited by G. H. Breckenridge *et al.* (John Wiley & Sons., Inc., New York, 1956), p. 146.

[6] N. F. Ramsey, Phys. Rev. **100**, 1191 (1955).

$$K_1=\frac{(2)^{7/2}\pi ne^4N_2|P_{vn}|^2|P_{nc}|^2}{cm^{\frac{1}{2}}(\alpha_c+\alpha_v)^{\frac{3}{2}}\hbar^2\omega_1\omega_2}$$
$$\times\left\{\frac{[\hbar\omega_1+\hbar\omega_2-E_g]^{\frac{1}{2}}}{\left[\Delta E+\frac{(\alpha_n+\alpha_v)}{(\alpha_c+\alpha_v)}(\hbar\omega_1+\hbar\omega_2-E_g)-\hbar\omega_1\right]^2}\right.$$
$$\left.+\frac{[\hbar\omega_1+\hbar\omega_2-E_g]^{\frac{1}{2}}}{\left[\Delta E+\frac{(\alpha_n+\alpha_v)}{(\alpha_c+\alpha_v)}(\hbar\omega_1+\hbar\omega_2-E_g)-\hbar\omega_2\right]^2}\right\}. \quad (2)$$

It is seen for Eq. (2) that the absorption coefficient for photons of energy $\hbar\omega_1$ is a function of the density of photons of energy $\hbar\omega_2$, exhibiting an intensity-dependent band edge which increases as some power of photon energies depending upon the symmetries of the energy bands, with a threshold at $\hbar\omega_1+\hbar\omega_2=E_g$. Expressions similar to Eq. (2) are obtained for the other two types of transitions with different constant terms and photon energy dependencies of the absorption. The ratio of the double-photon to a single-photon process[5] is proportional to the product of an optical matrix element and the photon density N_2 of the second beam.

To obtain the numerical values of the absorption coefficients using Eq. (2) for a particular substance, it is necessary to know the momentum matrix element and to specify the band structure parameters, α_c, α_v, α_n, ΔE, and E_g. For a specific substance, an estimate can be made of the desired parameters by experimentally measuring the fundamental absorption edge for the single photon process. The overwhelming factor that makes the photon-photon process potentially observable is the availability of high photon densities. The photon density we shall use in our estimate is the conservative figure of $N_2\approx10^{10}/\text{cm}^3$, since this represents ≈10 watts/cm^2 incident power which can easily be obtained with present unfocussed maser beams. However, in principle $\approx10^6$ watts/cm^2 can be obtained with a focussed beam. If we assume for a general solid $\alpha_c=\alpha_v=\alpha_n=1$, $E_g\approx1$ ev, $\Delta E\approx1$ ev, $N_2\approx10^{10}/\text{cm}^3$, expressing the optical matrix elements in terms of the f numbers for the transition with $f\sim1$, and let $\hbar\omega_1+\hbar\omega_2>1.0$ and <2.0 ev, we obtain $K_1\approx10^{-5}$ cm^{-1}. In this example, the resonant energy denominators are large; if in a substance the energy of the intermediate state is close to $\hbar\omega_1$ or $\hbar\omega_2$, the denominators can increase the contribution to the absorption coefficient.

A number of types of experiments suggest themselves to measure the effective double-quanta absorption coefficients; these include direct absorption, photoconductivity, and fluorescence. The common feature of these measurements is that excitation of a valence electron across the forbidden gap is detected due to the presence of photons of the same or different energies which are less than the energy gap. If a weak, variable frequency and a pulsed intense, fixed frequency are both incident upon the solid, the frequency and intensity dependence of the intrinsic photon-photon process should enable one to distinguish it from the multiple excitation involving excited impurity levels. Since the solid would be transparent to the incident radiation unless the simultaneous absorption of two photons takes place, no heating problem should be encountered. In principle, there is no such thing as a transparent intrinsic solid if one considers these higher-order radiation processes.

Magneto- and electro-optical effects have usually been considered in which the E or H fields are statically applied and the radiation field merely induces transitions between levels. If optical E or H fields of $\approx10^5$ volts/cm or $\approx10^4$ oersteds, respectively are incident upon a substance, the radiation field can cause a mixing of energy levels as well as transitions between levels. The above time-dependent perturbation treatment of the photon-photon absorption in a solid essentially reveals one facet of this strong-field type of interaction in which an intense radiation field of one frequency enables the absorption of radiation of a second frequency. In semiconductors and insulators, the intrinsic absorption edges are displaced by the application of external E field $\approx10^5$ volts/cm.[7] When an external H field $\approx10^4$ oersteds is applied to semiconductors, the valence and conduction bands split into Landau levels and magneto-oscillatory structure is observed.[8] The free carriers in a semiconductor represent a solid-state plasma which can exhibit a field-dependent collision frequency. The electronic nature of these effects indicates that the real and imaginary parts of the absorption can respond to the presence of a radiation field in a nonlinear fashion in a time of the order of the period of the incident radiation. Consequently, when a single intense frequency is incident upon a solid in a transparent region an emergent beam with harmonic content should be observable. If two intense maser beams of different frequencies are both incident within a volume of a solid where there is a phase coherence of the waves, mixing of the frequencies is possible. The difference frequency resulting from the beating of two optical masers through the agency of the above nonlinear effects can produce coherent radiation in the mm-wave and far infrared regions of the spectrum.

Note added in proof. Since this paper was submitted, the observation of one type of two-photon excitation has been reported by W. Kaiser and C. B. Garrett, Phys. Rev. Letters **7**, 229 (1961).

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