transfer processes producing multiplicity changes. Evidence now exists that the F-center aggregation process induced by F light in the room-temperature range involves a photoinduced migration[12] which, during its earliest stage, results in the clustering of F centers.[4,13] With further irradiation, M centers begin to form, some probably located in these cluster regions. Thus, aggregation, in effect, locally increases these concentrations.

An F center might behave differently after excitation depending on whether it is isolated or whether it lies in a cluster region, which may or may not also contain M centers. F-center luminescence might be expected from the more isolated F centers; energy transfer with triplet formation, for F centers lying in cluster regions containing M centers. The reason why energy transfer produces M centers in the triplet state and does not appear to excite M centers to states within the singlet system is presently not clear.

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OPTICAL NONLINEARITIES DUE TO MOBILE CARRIERS IN SEMICONDUCTORS

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Optical nonlinearities due to conduction-band electrons have been observed in InAs, InSb, GaAs, and PbTe using 10.6-μ (ω_1) and 9.6-μ (ω_2) radiation from a Q-switched CO_2 laser. Difference frequencies $\omega_3 = 2\omega_1 - \omega_2$ at 11.8 μ and $\omega_4 = 2\omega_2 - \omega_1$ at 8.7 μ were measured for a variety of carrier concentrations at several temperatures.

We have observed optical nonlinearities arising from conduction electrons in semiconductors. The 10.6-μ (ω_1) and the 9.6-μ (ω_2) radiation from a Q-switched CO_2 laser focused into samples of single crystal InAs, InSb, GaAs, and PbTe generates difference frequencies at 11.8 μ ($\omega_3 = 2\omega_1 - \omega_2$) and at 8.7 μ ($\omega_4 = 2\omega_2 - \omega_1$) from the above nonlinearity. In addition, in InAs and GaAs the sum frequency at 3.53 μ ($3\omega_1$) was observed. The process we describe is of entirely different origin from the one responsible for most second-harmonic-generation[1] (SHG) and parametric-oscillation[2] experiments hitherto observed. The latter process is due to bound electrons and is often called the "electronic" effect.[3] The optical nonlinearities studied in our experiments seem to be caused by the nonparabolicity of the conduction band. The interaction we observe, which involves the closely spaced frequencies ω_1, ω_2, $2\omega_1 - \omega_2$, and $2\omega_2 - \omega_1$, permits near phase-matched mixing over significantly long crystals.

The Q-switched CO_2 lasers used were similar to the one described earlier.[4] The 10.6-μ radiation (P transitions of the 00^01-10^00 band) and the 9.6-μ radiation (P transitions of the 00^01-02^00 band) were focused to produce power densities in the range 10^4-10^6 W cm^{-2}, and peak electric fields of about 10^3-10^4 V cm^{-1} in the sample. The confocal distance[5] in all samples significantly exceeded the actual crystal length. Power levels were such that changes

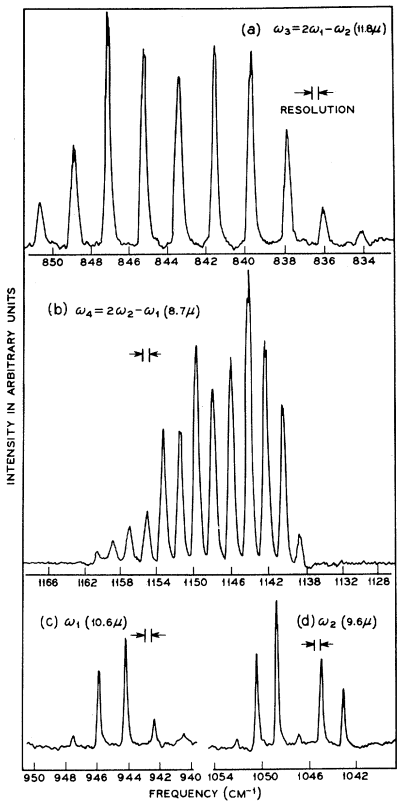

FIG. 1. Output from 1-mm-thick n-InSb (6×10^{16} cm^{-3}, ~80°K). (a) Mixed signal at 11.8 μ; (b) mixed signal at 8.7 μ; (c) input signal at 10.6 μ; and (d) input signal at 9.6 μ.

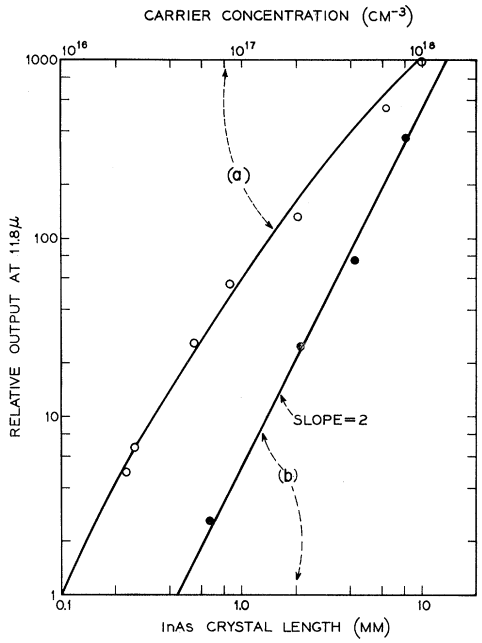

FIG. 2. Total 11.8-μ output from n-InAs, (a) as a function of carrier concentration along with the solid line showing the calculated output from Eq. (1) normalized at $n_e = 10^{16}$ cm^{-3}, and (b) as a function of length showing the expected l^2 dependence together with the experimental points.

in carrier density due to possible multiphoton electron-hole pair creation[6] were judged negligible in the more heavily doped samples and in large-band-gap materials. Measurements were carried out at ~300, ~80, and ~10°K.

Figures 1(a) and 1(b) show the output at 11.8 μ and 8.7 μ, respectively, from a 1-mm-thick sample of n InSb ($n_e = 10^{17}$ cm^{-3}) at ~80°K, when the crystal was irradiated with the 10.6- and the 9.6-μ laser lines shown in Figs. 1(c) and 1(d), respectively. The positions of the 11.8- and the 8.7-μ lines are given accurately by $\omega_3 = 2\omega_1-\omega_2$ and $\omega_4 = 2\omega_2-\omega_1$, respectively. With 1 kW (peak) at 10.6 μ and 0.1 kW (peak) at 9.6 μ (in all lines) the peak power obtained at 11.8 and 8.7 μ from InSb (~80°K) was 1-2 mW.

Figure 2(a) provides strong evidence that the nonlinear effect described in this paper arises from mobile carriers. Total 11.8-μ intensity is plotted as a function of electron density in n InAs. Care was taken to correct the experimental data for measured absorption at ω_1, ω_2, and ω_3. The nonlinear effect is seen to increase with increasing carrier concentration. Were the bound electrons responsible for the observed mixing (through a third-order nonlinearity), P_{ω_3} (corrected for absorption) should be independent of carrier concentration. Similar results were obtained from n-InSb for $n_e \geq 10^{16}$ cm^{-3}.

It is important to ascertain that the results obtained in n-InSb, n-InAs, and n-GaAs did not arise from a two-step process due to a bound electron nonlinearity, i.e., (a) $2\omega_1$ generation and (b) subsequent $2\omega_1-\omega_2$ mixing. We measured SHG ($2\omega_1$) at 5.3 μ and the difference frequency $\omega_3 = 2\omega_1-\omega_2$ at 11.8 μ as a function of the angle θ between $\vec{E}_{\omega_1,\omega_2}$ and the $\langle 100\rangle$ axis of the n-InAs sample.[7] As expected from the second-order nonlinear susceptibility tensor, $\chi_{BE}^{(2)}$, for $\bar{4}3m$ crystals, $P_{2\omega_1}$ vanished[8] for $\theta = 0$, but the P_{ω_3} at 11.8 μ (which was always linearly polarized along the same direction as $\vec{E}_{\omega_1,\omega_2}$) showed less than a few percent variation as θ was changed through 180°. This rules out the above two-step process for generation of the difference frequency, ω_3 (and

also ω_4), due to bound electron second-order nonlinearity. Additional evidence against the two-step process is obtained from the observation of 11.8-μ radiation from n-PbTe (~10°K, and $n_e = 10^{17}$ cm^{-3}) which is centrosymmetric and thus produces no second harmonic. The 11.8-μ intensity from PbTe was typically about 10^{-2} of that obtained from n-InSb ($n_e = 10^{17}$ cm^{-3}). The smallness of this signal can be attributed to the strong absorption (~20 cm^{-1}) in the 10-μ region in our PbTe sample.

The calculated coherence lengths for 11.8- and 8.7-μ generation at room temperature are given in Table I for InAs, InSb, and GaAs. Because of the closeness of ω_1, ω_2, $2\omega_1-\omega_2$, and $2\omega_2-\omega_1$, phase-matched mixing is possible over significant lengths of the crystals even in absence of birefringence. In Fig. 2(b) we show the total 11.8-μ intensity which is seen to vary as l^2 as expected for phase-matched mixing.

Since InAs, InSb, GaAs, and PbTe have a cubic symmetry, the third-order bound-electron nonlinear susceptibilities, $\chi_{BE}^{(3)}$ are expected to be relatively isotropic.[9] To estimate these $\chi_{BE}^{(3)}$, we used an extension of Miller's phenomenological approach[10] for $\chi_{BE}^{(2)}$. Table I(A) gives a summary of our experimental results for 11.8-μ generation in the first column, along with $\chi^{(3)}$ necessary to account for the observed $P_{\omega_3}/P_{\omega_2}$. In the second column are given the estimated $\chi_{BE}^{(3)}$ and the corresponding $P_{\omega_3}/P_{\omega_2}$. Because of the uncertainties involved in estimating $\chi_{BE}^{(3)}$, we compare only the relative values for different materials. Thus, for InAs and InSb the observed P_{ω_3} is ~10^3 times that expected from $\chi_{BE}^{(3)}$. However, for GaAs, the observed $P_{\omega_3}/P_{\omega_2}$ nearly equals that calculated from $\chi_{BE}^{(3)}$. This strongly suggests that in InAs and InSb the $\chi_{BE}^{(3)}$ cannot account for the observed strength of the parametric mixing process. Similarly, the observed power at $3\omega_1$ cannot be explained by $\chi_{BE}^{(3)}$ as seen from Table I(B).

Recent calculations[11] of the effect of nonparabolic[12] conduction bands in narrow-gap semiconductors predict optical nonlinearities of nearly the same order of magnitude as those we have observed. A mobile carrier being accelerated by an optical electric field expe-

Table I. Comparison between measured[a] and calculated nonlinear effects in InAs, InSb, and GaAs. The numbers in parentheses give the $\chi^{(3)}$ required in each case.[b] $P_{\omega_1} = 10^3$ W, $P_{\omega_2} = 10^2$ W, focal area $= 10^{-3}$ cm^2.

Material	l_{coh}[c]		I Observed	II Calculated (bound electron)	III Calculated (nonparabolic)
			(A) $P_{\omega_3}/P_{\omega_2}$		
	ω_3	ω_4			
InAs ($n_e = 2.6\times10^{16}$)	2.9 cm	3 cm[d]	2×10^{-6} (1.8×10^{-10} esu)	6×10^{-9} (10^{-11} esu)	5.5×10^{-5} (9.4×10^{-10} esu)
InSb ($n_e = 6\times10^{16}$)	1.3 mm	4.6 mm[e]	2×10^{-5} (8×10^{-10} esu)	5×10^{-8} (4×10^{-11} esu)	7.8×10^{-4} (5×10^{-9} esu)
GaAs ($n_e = 1.5\times10^{16}$)	1 cm	1 cm[f]	2.5×10^{-9} (7×10^{-12} esu)	3×10^{-9} (7×10^{-12} esu)	8.5×10^{-8} (3.8×10^{-11} esu)
			(B) $P_{3\omega_1}/P_{\omega_1}$		
	$3\omega_1$				
InAs	12 μ[d]		1.5×10^{-8}	10^{-12}	2.3×10^{-9}
GaAs	37 μ[f]		2.5×10^{-10}	6×10^{-12}	3.6×10^{-11}

[a] Accuracy of measurements: ±30% for P_{ω_1}, and P_{ω_2}; a factor of ~3 for P_{ω_3}, P_{ω_4}, and $P_{3\omega_1}$.

[b] P_{ω_3} is given by

$$P_{\omega_3} = \frac{256\pi^4(\omega_3)^2}{n_{\omega_1}^2 n_{\omega_2} n_{\omega_3} c^4}(3\chi^{(3)})^2 l^2 \frac{P_{\omega_1}^2 P_{\omega_2}}{(\mathcal{A}^2)^2},$$

where c = velocity of light, l = crystal length ($l < l_{coh}$), n_{ω_1}, n_{ω_2}, n_{ω_3} are the indices of refraction, and $\mathcal{A}^2$ is the cross-sectional area.

[c] $l_{coh} = \pi/\Delta k$.

[d] From dispersion data available from SHG experiments of C. K. N. Patel, Phys. Rev. Letters 16, 613 (1966).

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riences an increase in its effective mass, giving rise to a nonlinear term in its equation of motion. Solution of this equation of motion together with Maxwell's equations gives the following expression[11] for the field at $\omega_3 = 2\omega_1 - \omega_2$:

$$E_{\omega_3} = E_{\omega_1}{}^2 E_{\omega_2} \frac{3\pi m_e e^4}{2(m^*)^2 c n_{\omega_3}} \frac{l}{\omega_1{}^2 \omega_2 E_G} \times \frac{1 + 8E_F/5E_G}{(1 + 4E_F/E_G)^{5/2}}, \quad (1)$$

where e is the electron charge, m^* is the effective electron mass at the bottom of the conduction band, E_G is the band gap, and E_F is the Fermi energy. The third column in Table I gives the $P_{\omega_3}/P_{\omega_2}$ and $\chi_{\text{nonparabolic}}{}^{(3)}$ calculated from Eq. (1). The observed and calculated $\chi^{(3)}$ are in order-of-magnitude agreement for InAs and InSb. The degree of agreement is limited by the accuracy to which various quantities such as P_{ω_1}, P_{ω_2}, P_{ω_3} and the beam cross-section $\mathcal{A}^2$ (see Table I) can be determined experimentally. Moreover, the observed P_{ω_3} would be smaller than the calculated values given in Table I if the pulses of P_{ω_1} and P_{ω_2} did not occur simultaneously and were not in the same transverse mode. The above mechanism, through its dependence on m^* and E_G, accounts for the observation that the signal in GaAs is much smaller than that in InAs or InSb. On Fig. 2(a) where experiment P_{ω_3} vs n_e for InAs (~300°K) is given, the solid line shows the expected P_{ω_3} calculated from Eq. (1), normalized at $n_e = 10^{16}$ cm^{-3}. The agreement between experiment and theory supports the validity of the explanation based on the nonparabolicity of the conduction band. Finally, as shown in Table I(B), the power output at $3\omega_1$ calculated using the nonparabolic mechanism is in qualitative agreement with the observations in InAs and GaAs.

We have observed a new type of nonlinearity which arises from the conduction electrons in semiconductors. This makes possible greater flexibility in mixing experiments than in the experiments with the bound electron nonlinearity, since the conduction electrons are easily affected by external electric or magnetic fields. We have, in effect, obtained parametric amplification of 9.6- and 10.6-μ radiation in the $2\omega_1 - \omega_2$ and the $2\omega_2 - \omega_1$ processes, respectively. It should also be possible, using a pump at 10.6 μ, to obtain parametric oscillation at wavelengths close to the pump.

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