remains the same.

After mechanically damaging a sample we also observe a shift of the peak to larger fields. Just as in the irradiation experiments, the temperature dependence shows an increase in the intercept A without a change in B.

(8) *Other metals.*—Experiments in Bi, Ga, and K would seem to fit the Cu story, and we suggest that the effects observed in Refs. 3-5 are due to the same mechanism. We have examined such data to find that Eq. (4) also gives reasonable agreement with observed field values.

In conclusion, we would like to acknowledge the many useful discussions we have had with E. A. Kaner, H. J. Fischbeck, A. B. Pippard, and M. Ya. Azbel'. In particular, M. Ya. Azbel' has pointed out to us that the contribution to dZ/dH of surface electrons should diverge as $H^{-1/2}$.

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Dispersion of the Lowest-Order Optical Nonlinearity in InSb

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Second-harmonic generation has been studied in InSb. The fundamental source was a CO_2 laser, and the second-harmonic photon energies were near the band edge. The nonlinear susceptibility d_{14} is the largest known and shows significant frequency dependence. In a 2.6% range of photon energies, $|d_{14}|$ changes by 31% while the linear susceptibility at the second harmonic, $\chi^{\mathrm{lin}}(2\omega)$, changes by only 2.8%. In addition $d_{14}=|d_{14}|e^{i\varphi}$ is complex with $\varphi\cong -50°$.

Second-harmonic generation (SHG) has been directly measured in InSb as a function of photon energy for second-harmonic (SH) photon energies near the fundamental band-gap energy. The experiment yields the frequency dependence of both the magnitude and the phase of the nonlinear susceptibility $\chi^{(2)}(-2\omega, \omega, \omega)$. The interference technique used in the phase measurement has heretofore been used,[1-4] but the dispersion of the phase was not studied. The present results show that InSb has the largest optical $\chi^{(2)}$ of any material measured and that $\chi^{(2)}$ exhibits significant dispersion in the small range of photon energies ($\hbar\omega$, 0.1144 to 0.1173 eV; $2\hbar\omega$, 9.2288 to 0.2345 eV) utilized for this experiment. These results cannot be explained by simple models which ignore the $\vec{k}$ variation of electron-momentum matrix elements.

InSb has the zinc-blende structure (point-group symmetry $\bar{4}3m$) for which there is only one independent, nonvanishing component of $\chi^{(2)}$, namely, $\chi_{xyz}^{(2)}=d_{14}$. The coherence length for SHG (l_{coh}), the absorption coefficient at the SH [$\alpha(2\omega)=\alpha_2$], and d_{14} were all measured. The results are shown in Figs. 1 and 2. Each point is the average of three independent sets of measurements on the same sample. The error bars indicate the maximum uncertainty resulting from various sources of errors.

The sample geometry and experimental procedure are those described by Wynne and Bloembergen[3] (WB) with some important modifications. All measurements were made in transmission with the beam from a Q-switched CO_2 laser traversing two wedge-shaped samples, as shown in Fig. 1 of WB. The laser provided single-frequency operation on the lines $P42$ (0.11440 eV) to $P18$ (0.11727 eV) of the $00^0 1\text{-}10^0 0$ vibrational band of

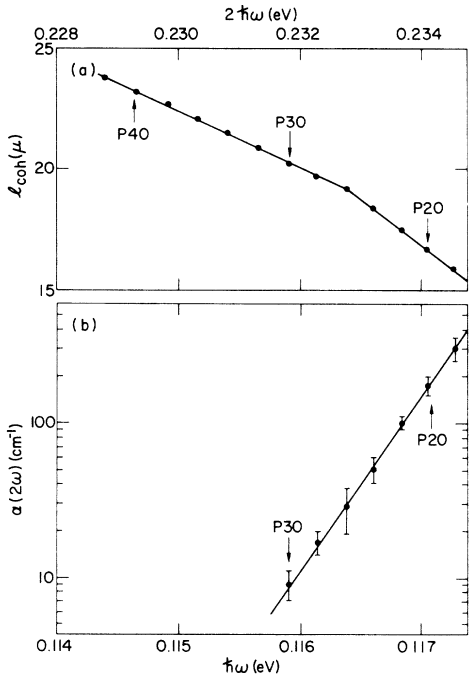

FIG. 1. (a) l_{coh}(InSb) and (b) α_2(InSb) plotted against $\hbar\omega$ and $2\hbar\omega$. In (a) the relative uncertainty is ±1%. The absolute uncertainty in l_{coh} is ±3%. The solid line in (a) is a smooth curve and in (b) is a least-mean-squares, straight-line fit.

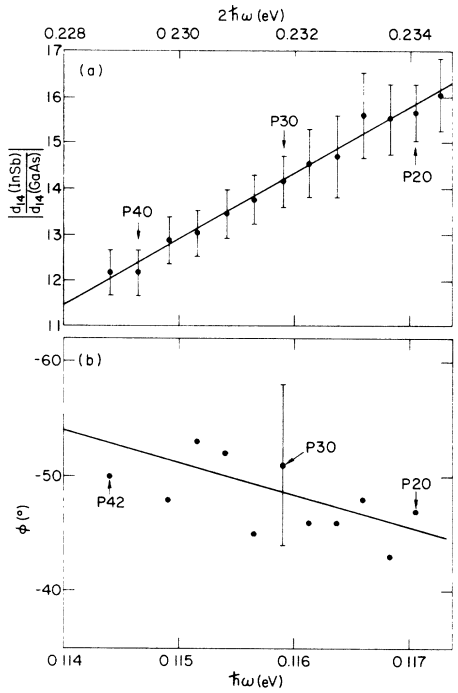

FIG. 2. (a) $|d_{14}(\text{InSb})/d_{14}(\text{GaAs})|$ and (b) φ plotted against $\hbar\omega$ and $2\hbar\omega$. The phase convention chosen is $d_{14} = |d_{14}|e^{i\varphi}$ and $\varphi = 0$ for GaAs. The solid lines are least-mean-squares, straight-line fits. Values for $P40$ and $P18$ are absent in (b) because of excessive uncertainty.

CO_2. The sample temperature was ~5°K. More experimental details are given below.

Since $\hbar\omega$ is only half the band-gap energy, one expects dispersive effects at $2\hbar\omega$ to dominate. This is confirmed for the linear optical properties by the results of Fig. 1. Figure 1(a) gives the variation of $l_{coh} = \frac{1}{4}\lambda_0/[n(2\omega)-n(\omega)]$, where the n's are indices of refraction and λ_0 is the vacuum wavelength of the fundamental. The change in $n(2\omega)-n(\omega)$ is much larger than the known variation[5] of $n(\omega)$ in this frequency range. In addition, whereas no absorption was detectable in InSb at the fundamental, Fig. 1(b) shows the onset of interband absorption at the SH. The linear dependence of $\ln(\alpha_2)$ on $2\hbar\omega$ is often observed close to a fundamental absorption edge.[6]

The measurements of d_{14}(InSb) were made relative to d_{14}(GaAs). At room temperature where the nominal carrier concentration was $n = 2\times10^{13}$ cm^{-3}, the GaAs reference sample showed no absorption at 10.6 μm or at 5.3 μm. Measurements of l_{coh} in GaAs showed an approximate 1% variation as the fundamental wavelength varied from $P42$ and $P18$. Since the band gap of GaAs is far removed, at ~1.4 eV, it is reasonable to attribute the observed dispersion of $|d_{14}(\text{InSb})/d_{14}(\text{GaAs})|$ to InSb. Figure 2(a) shows that at the lowest frequency measured $|d_{14}(\text{InSb})/d_{14}(\text{GaAs})| = 12.2\pm4\%$. The most precise measurement,[7] using a CO_2 laser, gives $d_{14}(\text{GaAs}) = (3.2\pm1)\times10^{-7}$ esu. Thus one finds $|d_{14}(\text{InSb})| = (3.9\pm1.2)\times10^{-6}$ esu for the fundamental at $P42$. This makes it the largest $\chi^{(2)}$, resonant or nonresonant, measured in any material. The largest previous value was measured with a CO_2 laser in Te which was found to have $d_{11}(\text{Te})/d_{14}(\text{GaAs}) = 7.2\pm4\%$.[7]

The small values for l_{coh}(InSb) mean that InSb is not very useful as an efficient generator of SH's. Of greater interest is the large change shown by d_{14}(InSb). This may be dramatized by normalizing out the local field effects through the use of Miller's delta,[8] defined by $\delta = |d_{14}|/[\chi^{lin}(\omega)]^2[\chi^{lin}(2\omega)]$. Neglecting the variation of $n(\omega)$ (= 3.95[5]), the change in l_{coh} gives a variation of $n(2\omega)$. Then one finds that the linear susceptibility $\chi^{lin}(2\omega) = \{[n(2\omega)]^2-1\}/4\pi$ varies from 1.235 to 1.269, or a change of 2.8%. Treating d_{14}(GaAs) as constant one finds that δ(InSb) varies from $\delta = 2.34\times10^{-6}$ esu for the fundamental at $P42$ to $\delta = 2.99\times10^{-6}$ esu at $P18$, or a change of 28%.

The phase of d_{14}(InSb) and its frequency dependence are given in Fig. 2(b). No structure is discernible in view of the large uncertainty, but it is apparent that d_{14} is complex and that its real part has the same sign as d_{14}(GaAs).

InSb has a direct band gap E_G at the point $\Gamma(k=0)$ in the Brillouin zone, with $E_G \simeq 0.236$ eV[9] at $T = 0$°K. The proximity of $2\hbar\omega$ to E_G suggests a resonant contribution of those electrons near Γ to the nonlinear susceptibility d_{14}. In view of the large imaginary part of d_{14}(InSb) and the changes in d_{14} and δ as functions of frequency, this contribution seems to dominate in d_{14}, whereas the corresponding contribution to $n(2\omega)$ is only a small fraction of the overall contribution of the valence electrons. $n(\omega)$ is related to the entire crystalline potential, whereas d_{14} is related only to the antisymmetric part of this potential. Thus the antisymmetric part seems to make a disproportionately large contribution to the electronic structure at Γ. The following information is intended for the reader concerned with the experimental details and should be read in conjunction with WB for a fuller understanding. To make a SHG measurement in a nonabsorbing region requires SH photon energies less than E_G. The CO_2 laser fulfills this requirement for InSb if the sample is cold enough. The laser had an intracavity diffraction grating for wavelength selection, and was otherwise similar to lasers frequently described in the literature.[10] In view of the negative temperature coefficient of the band gap,[11] it was desirable to have samples colder than the typical $T \cong 20$°K achievable with a helium cold-finger mounting. By mounting the samples in helium exchange gas, $T \cong 5$°K was achieved and the sample and windows were protected from thermal shock. The cryostat geometry is that given by Haupt and Wynne.[12] The samples were independently mounted with allowance for accurate vertical displacement. The samples were cut and polished with a wedge apex angle of ~0.25 rad and oriented so that the laser polarizations were along [111]. Ge, which is centrosymmetric, was used as the second wedge when it was desirable to have SHG only in the first wedge. Ge is transparent at 10.6 and 5.3 μm. With this arrangement, the first wedge was either InSb or GaAs, allowing relative SH power to be measured.

In order to minimize the effects of absorption the InSb wedges were kept as thin as possible, limited only by the tendency of the thin end to fracture. All data reported here were taken on a sample wedge with an apex angle of 0.0242 rad ± 3%. The sample was $l = 0.167$ mm thick at the thin end. The InSb was Ge-doped n-type, with $n = 7.3\times10^{13}$ cm^{-3} and mobility $\mu = 2.15\times10^5$ cm^2/V sec at $T = 77$°K. For those laser lines where absorption at the SH was important, it was possible to determine α_2 independently by examining the shape of the SH power $[I(2\omega)]$ versus l curves and by fitting them by the formula[13]

$$I(2\omega) = I_0[1 + e^{-\alpha_2 l} - 2\cos(l/l_{\mathrm{coh}})e^{-\alpha_2 l/2}]. \quad (1)$$

Equation (1) shows that when $\alpha_2 l$ is too large it is no longer possible to distinguish the maxima and minima of $I(2\omega)$ vs l associated with l_{coh}. This occurred, in practice, for SH photon energies greater than that of the SH of $P18$ (0.234 54 eV).

After l_{coh}(InSb), l_{coh}(GaAs), and α_2(InSb) were determined, the relative SH power measurements were reduced to $|d_{14}(\mathrm{InSb})/d_{14}(\mathrm{GaAs})|$ by using Eq. (7) of WB, modified to take absorption into account by Eq. (1). The indices of refraction used for GaAs were $n(\omega) = 3.275$ and $n(2\omega) = 3.30$.[3] l_{coh}(GaAs) was measured to be 106 μm ± 3%, in good agreement with WB.

The phase of d_{14}(InSb) was studied by the interference method described by WB. In the presence of absorption their results may be suitably generalized.[14] The first wedge was GaAs and the second was InSb. A plate of sapphire was inserted between samples in order to set GaAs on its minima or maxima of SHG. Then the sapphire was removed and the InSb was displaced to change l. The two curves of $I(2\omega)$ vs l(InSb) were compared in order to determine the phase shifts. The GaAs and InSb samples were absolutely oriented by chemical etching[15] to distinguish [111] from $[\bar{1}\bar{1}\bar{1}]$.

Previous attempts to calculate the low-frequency value of $\chi^{(2)}$ adopted localized models for the valence electronic structure. Levine's model[16] is the most successful. He calculated values of $\chi^{(2)}$ for a variety of materials. He predicts a value $d_{14}(\mathrm{InSb})/d_{14}(\mathrm{GaAs}) = 3.3$, in disagreement with the present measurements [although he correctly predicts the sign of the real part of d_{14}(InSb)]. This is not surprising because of the closeness of $2\hbar\omega$ to E_G. The use of localized models is expected to be valid only for $\hbar\omega, 2\hbar\omega \ll E_G$.

A previous study of the dispersion of d_{14} in InSb by Chang, Ducuing, and Bloembergen[1] was carried out using photon energies in or near the visible region. For these frequencies InSb is strongly absorbing at both the fundamental and SH. One

other measurement of d_{14}(InSb) exists.[17] This measurement includes the contribution of the infrared-active optical phonon and may not be compared directly to the present experiment.

Attempts to calculate the dispersive behavior of d_{14} have adopted general expressions for nonlinear currents using the Bloch representation for the electron states.[18] These calculations made the questionable assumption of $\vec{k}$-independent matrix elements so that the dispersive behavior of d_{14} was entirely due to the resonant energy denominators and the joint density of states. The present author has made two similar calculations, both based on a density of states and electron energy distribution as given by Kane's model[19] for InSb. One approach used an expression derived from the anharmonic oscillator model,[20] and the other used the Bloch-representation expression. Both gave results for the dispersion which showed far too small a change.

Using Kane's model, Rustagi[21] has shown that the inclusion of the spin dependent part of the kinetic momentum operator is crucial for the discussion of the contribution of Γ to d_{14}. He succeeds in relating d_{14} to the antisymmetric part of the crystalline potential. An extension of his procedure, where one actually finds the $\vec{k}$ dependence of the matrix elements, may be able to explain the observed dispersion of d_{14}. In addition, the experimental results suggest that there is another contribution. The data of Fig. 1(b) show sizable absorption for photon energies significantly smaller than E_G.[9] Also, d_{14} is complex, indicating some sort of resonant behavior below the band gap. A possible explanation may lie in the consideration of excitonic effects which have recently been shown to be of importance for $\chi^{(2)}$(CuCl).[22]

In conclusion, the dispersion of d_{14}, as well as of l_{coh}, has been studied in a narrow frequency range near E_G in InSb. The resulting changes are surprisingly large and warrant further investigation.

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