PHYSICAL REVIEW B VOLUME 3, NUMBER 6 15 MARCH 1971

Spin-Flip Raman Scattering from Conduction Electrons in CdS and ZnSe

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(Received 16 September 1970)

Inelastic light scattering from free-carrier spin-flip excitations has been observed in the wide-band-gap semiconductors CdS and ZnSe in magnetic fields up to 100 kOe. In-doped ZnSe and CdS having carrier concentrations between 5×10^{17} and 4×10^{19} cm^{-3} were studied at temperatures between 5 and 80 °K using both 5145- and 4880-Å excitation from an argon-ion laser. Absolute values of the scattering efficiency are given for all samples. The efficiency is quite high, and for those samples exhibiting narrow spin-flip linewidth the peak scattering efficiencies appear large enough to make stimulated spin-flip Raman scattering feasible. The observed polarization selection rules show $\alpha_{ij}\neq 0$ only for $i\neq j$ and $\hat{j}\parallel\hat{H}$. The dependence of the Raman-frequency shift upon magnetic field implies effective g values for the conduction electrons of 1.86 and 1.18 for CdS and ZnSe, respectively. Several features of the spectra, including carrier-concentration dependence for the spin-flip cross section and linewidth, are not accounted for by existing theories.

I. INTRODUCTION

The utility of inelastic light scattering (Raman effect) for the study of magnetic excitations in solids has been amply demonstrated in recent years in a variety of experiments. Raman scattering from collective magnetic excitations of spin waves in antiferromagnetic insulators was first observed in 1966.[1] Magnetic scattering from localized impurities in semiconducting CdS was observed to be extremely strong.[2] Light scattering from the spin-split energy levels in the conduction-electron gas of narrow-band-gap semiconductors has also received much attention.[3] While seldom considered in the same discussion, these three phenomena are quite similar in that (a) they arise basically from the same mechanism (spin-orbit coupling), and (b) they provide a magnetically tunable Raman scattered frequency.

In this paper we report the extension of the spin-flip scattering by mobile carriers from the infrared (to which all previous work of this kind has been confined) to the visible and potentially to the ultraviolet regions of the spectrum. While the experiments reported here are in the visible region, extension to the ultraviolet would appear to be simple since ZnO and ZnS are transparent beyond 3700 Å, are available with carrier concentrations of up to 10^{19} cm^{-3}, and have similar values for those parameters determining spin-flip scattering to those found in CdS and ZnSe. One motivation for these experiments was the recent observation of light scattering in the visible from mobile carriers in CdS.[4] Both single-particle and collective (plasmon) electron excitations were demonstrated to scatter light strongly in the wide-band-gap II-VI compounds. The experiments reported here were performed on indium-doped CdS and ZnSe having carrier concentrations between 1×10^{17} and 4×10^{19} cm^{-3}. Spin-flip Raman scattering that was quite strong was excited with 5145- or 4880-Å laser light and was studied at temperatures between 5 and 80 °K in magnetic fields of up to 95 kOe. Values of the conduction-electron g factor were obtained for both materials, and the behavior of the spectrum with variations in carrier concentration, temperature, magnetic field strength and direction, and crystal orientation, was observed as well. The large scattering efficiency and the narrow spectral width for these spin-flip processes suggest the real possibility of a magnetically tunable Raman laser source operating in the visible or ultraviolet.

In Sec. II, we summarize our experimental results. In Sec. III, we discuss them in relation to other experiments and to theoretical predictions for scattering intensity, polarization selection rules, and stimulated Raman threshold. The concluding remarks are given in Sec. IV.

II. EXPERIMENTAL RESULTS

A. Apparatus

The Raman spectra reported here were excited using 50–100 mW of linearly polarized argon laser light at wavelengths of 5145 or 4880 Å. The laser light was focused onto single-crystal samples of CdS or ZnSe which were mounted inside a split-coil superconducting solenoid capable of a 100-kOe maximum field. The solenoid was mounted in a "varitemp" Dewar having four optical windows in the horizontal plane. Light scattered through 90°

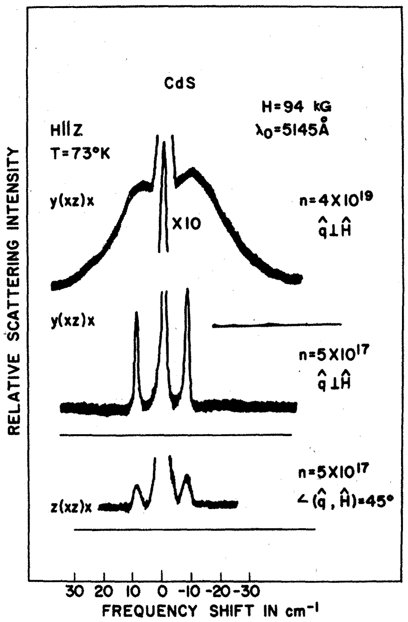

FIG. 1. Spin-flip spectra of In-doped CdS having room-temperature carrier concentrations of 4×10^{19} and 5×10^{17} cm^{-3}. The upper two traces are for $y(xz)x$ scattering geometry with H field parallel to the optic axis $\hat{z}$. The linewidths for the lower-carrier-concentration sample are completely instrumental; we estimate the actual linewidths for this sample as ≤ 0.2 cm^{-1}. The bottom trace is for the 5×10^{17}-cm^{-3} sample with spin-flip propagation direction $\hat{q}$ at 45° to $\hat{z}$ and $\hat{H}$. For this geometry a measureable linewidth of ~ 2 cm^{-1} is observed and cross sections are ~10 times weaker than for $\hat{q}\perp\hat{H}$. The gain for the top trace is 30 times that for the bottom traces (which have equal gains). Instrumental width is ~ 2 cm^{-1}.

was focused onto the slit of a double spectrometer. The transmitted signal was detected by a cooled S-11 photomultiplier, amplified, and displayed on a strip-chart recorder. The magnetic field direction was vertical in the laboratory. Variation and control of the sample temperature was achieved by a combination of variable-rate He-gas flow and corrective heaters mounted on the sample holder. Both Pt resistors and GaAs diodes were used as temperature sensors. The sample temperatures were measured to within ± 2 °K. The magnetic field was monitored by a magnetoresistance probe incorporated into the solenoid. However, we believe the accuracy of magnetic field values quoted here is no better than ± 1 kOe.

B. CdS Results

Several samples of CdS and ZnSe were examined for various combinations of magnetic field strength, crystal orientation, sample temperature, and carrier concentration. Representative spin-flip Raman spectra from CdS at ~80 °K are shown in Fig. 1. Several comparisons can be drawn from these data. The upper two traces are for the $y(xz)x$ scattering geometry with the magnetic field parallel to the optic axis $\hat{z}$. The magnetic field $\vec{H}$ is then perpendicular to the scattering plane which contains the wave-vector transfer $\vec{q}$; i.e., $\vec{q}\cdot\vec{H}=0$. The frequency shift of the spin-flip scattering is $g_e\mu_B H/\hbar$ and from the data for the 5×10^{17}-cm^{-3} sample, we measure a splitting of 7.85 cm^{-1} in a field of 89 kOe. This corresponds to a conduction-electron g value for CdS of $g_e = 1.86 \pm 0.03$. This may be compared with values of 1.76 determined from Raman scattering and 1.795 determined from fluorescence for *bound electrons* in CdS by Thomas and Hopfield[2] in fields of ~ 30 kOe. Of the several possible sources of the difference in g_e, the magnetic field dependence of g_e can be eliminated, since an increasing field tends to depress rather than to increase the g value.[5] Experimental errors account for an estimated 2%, leaving approximately a 2% difference in g values between mobile conduction electrons and bound electrons in CdS. While a difference in g_e between mobile electrons and bound electrons is not surprising, it is expected to be quite small for shallow donors, and the bound-electron values[2] have become the accepted ones for CdS.

While the same value of g_e is obtained for the 4×10^{19}-cm^{-3} sample as for the 5×10^{17}-cm^{-3} sample. within experimental error, several differences do exist in their spin-flip Raman spectra. Most apparent is the much broader linewidth of the 4×10^{19}-cm^{-3} spectrum. The linewidth of the higher-concentration sample is ~ 8 cm^{-1}, much greater than the $\lesssim 0.2$ cm^{-1} ascribed to the 5×10^{17}-cm^{-3} sample. Qualitatively, this variation in linewidth with n_e resembles that observed over a much narrower range of n_e in InSb by Slusher *et al.*[3] They found that the spin-flip linewidth increased from 5 to 30 cm^{-1} when n_e was increased from 1×10^{16} to 6×10^{16} cm^{-3}. Notice, however, that our CdS samples with carrier concentrations up to 1000 times greater give comparable linewidths to these for $n_e = 10^{16}$ cm^{-3} in InSb.

Another important difference between the two CdS samples represented in Fig. 1 is the variation of Raman-scattered intensity with n_e. The scattering efficiencies were measured relative to that of the 992-cm^{-1} line of liquid benzene, for which the absolute scattering cross section has been reported.[6] A sample of liquid benzene was inserted in place of the semiconductor samples, and the 992-cm^{-1} Raman line was observed. The integrated intensity of the 992-cm^{-1} benzene line is ~ 5 times greater than that of the spin-flip line from the 4×10^{19}-cm^{-3} CdS sample when proper account is taken of absorption in the latter. Because of the large width of the spin-flip line, this implies a ratio of ~ 100:1 in the peak cross sections in favor of the benzene line. For the 5×10^{17}-cm^{-3} CdS sample the integrated intensity observed is, surprisingly, only about a factor of 2.5 less than the benzene line. Because the spin-flip linewidth in this sample is $\lesssim 0.2\ \mathrm{cm}^{-1}$, the peak Raman efficiency is at least as great as that of the benzene line, which can easily be made to produce stimulated Raman scattering (SRS). Thus the 5×10^{17}-cm^{-3} CdS spin flip is an excellent candidate for a magnetically tunable SRS source in the visible region of the spectrum. The observed spontaneous peak Raman efficiency implies an SRS threshold intensity of less than $500\ \mathrm{MW/cm}^2$ per centimeter of path length. (See Ref. 7 for the relevant equations.)

The scattering cross section *per electron* in our CdS samples is of some interest for purposes of comparison with the value of $1.05\times10^{-29}\ \mathrm{cm}^2\,\mathrm{sr}^{-1}$ per molecule[6] reported for benzene. However, for reasons indicated below these numbers are difficult to estimate accurately. In general, not all of the carriers can contribute to the spin-flip scattering. Only states separated by $\Delta s = 1$ which lie, respectively, above and below the Fermi surface are connected by the scattering process. The calculation of the density of available final states for a system where the Landau and spin levels are well defined is a straightforward, but tedious process, but is necessary if one wants to obtain a correct relation between the observed scattered intensity and the cross section per particle. Thus far this relation has been worked out only for the simplest cases[8,9] which do not correspond to the situation in our experiments. In all of our samples the collision time τ, as determined by both Hall measurements and by the linewidth of the plasmon line observed in Raman scattering[4], is small (10^{-14}–10^{-13} sec). Thus even at fields up to 100 kOe, $\omega_c\tau < 1$ and the Landau levels are quite smeared out. For this reason, we estimate the effective number of electrons which may participate in the spin-flip scattering to be of order $n_e(\hbar\omega_s/E_F)$. For $\omega_s \approx 8\ \mathrm{cm}^{-1}$, the effective numbers are $3.6\times10^{16}\ \mathrm{cm}^{-3}$ for the $n_e = 5\times10^{17}$-cm^{-3} sample, and $1.5\times10^{17}\ \mathrm{cm}^{-3}$ for the $n_e = 4\times10^{19}$-cm^{-3} sample. Together with the above information on total scattering efficiencies, these numbers would imply a cross section *per particle* of $8\times10^{-25}\ \mathrm{cm}^2\,\mathrm{sr}^{-1}$ for the $n_e = 5\times10^{17}$-cm^{-3} sample and $2\times10^{-26}\ \mathrm{cm}^2\,\mathrm{sr}^{-1}$ for the 4×10^{19}-cm^{-3} sample. However, when effects of absorption of the 5145-Å laser light are properly included, one finds the cross section per particle for the 4×10^{19}-cm^{-3} sample to be $\sim 1\times10^{-25}\ \mathrm{cm}^2\,\mathrm{sr}^{-1}$; while the value for the 5×10^{17}-cm^{-3} sample is essentially that given above. This strange variation of scattering cross section with carrier concentration is similar to that reported for InSb,[3] and has no theoretical explanation at present.

Not all aspects of the spin-flip scattering in CdS are different for different values of n_e. The scattering selection rules for both samples were identical and are as follows: Spin-flip scattering could be observed only for the Raman tensor elements α_{ij} when $i\neq j$ and either $\hat{i}\parallel\hat{H}$ or $\hat{j}\parallel\hat{H}$. We found no variation in these selection rules or in the scattering efficiency when the direction of $\hat{H}$ was changed from $\hat{H}\parallel\hat{Z}$ to $\hat{H}\parallel\hat{X}$ by rotating the sample. This is in striking contrast to the behavior observed for the spin-flip scattering from bound electrons in CdS. Thomas and Hopfield[2] found that the scattering intensity decreased by a factor of at least 300 when the angle between $\hat{H}$ and the c axis was decreased from 90° to 0°, for $\hat{q}\parallel\hat{Z}$. The strongest scattering they observed was for $\hat{H}\perp\hat{Z}$, $\hat{q}\parallel\hat{Z}$. For $\hat{H}\parallel\hat{Z}$, the scattering for $\hat{q}\perp\hat{Z}$ was found to be more than three times stronger than for $\hat{q}\parallel\hat{Z}$ (the latter is described as not detectable.[2]) The selection rules for spin-flip scattering from a substitutional point defect with the environmental symmetry of C_{3v} have been worked out by Hopfield and Thomas[2] and found to agree with their observations.

While our results reveal no dependence upon the direction of $\hat{H}$ relative to the crystal axes, we do find that the angle between $\hat{H}$ and $\hat{q}$ is important. The bottom trace in Fig. 1 shows the spectrum for the 5×10^{17}-cm^{-3} sample taken for $\hat{H}\parallel\hat{Z}$ with $\hat{q}$ at 45° to $\hat{H}$. If we assume that the flat background scattering (which is real and presumably due to nonmagnetic single-particle scattering) is $\hat{q}$ independent, we conclude that the 45° scattering intensity is weaker by about a factor of 8 than for $\hat{q}\perp\hat{H}\parallel\hat{Z}$. Also, we note that the 45° spectrum is about $1\ \mathrm{cm}^{-1}$ broader than the $\hat{q}\perp\hat{H}$ spectrum.

In addition to the expected and observed invariance of the selection rules to changes in n_e, other similarities were observed. In particular, no strong dependence of the scattering efficiency upon laser frequency was observed. At 2 °K for example, laser wavelengths of 4765, 4880, and 5145 Å were used in CdS samples with n_e between 1×10^{16} and $4\times10^{19}\ \mathrm{cm}^{-3}$. Even accounting for the wavelength variation in transparency of the sample this result is quite different from the bound-electron scattering in CdS where the cross section was observed to fall[2] by a factor of 130 in going from 4880 to 4965 Å. The latter behavior is ascribed to a strong resonance effect which accidentally occurs between the I_2 bound-exciton energy and the 4880-Å argon-laser frequency.[2]

Finally, we mention the magnetic field dependence of the scattering efficiency. The spin-flip spectra for the 4×10^{19}-cm^{-3} sample at various magnetic fields shown in Fig. 2 were not taken with identical gain. When properly analyzed these spectra show that the integrated intensity increases with increasing field in a roughly linear manner. The 5×10^{17}-cm^{-3} sample, on the other hand, revealed a less than linear field dependence to the intensity (nearly field independent).

An increase in spin-flip scattering efficiency with field was also observed in InSb,[3] over a limited field range (between 26 and 52 kOe). While several theoretical predictions[8,9] have been given for the magnetic field dependence of the scattered intensity (some of which account for the complications of the Landau ladder relative to the Fermi surface), none have been able to account completely for the previous or present experimental observations.

In none of our experiments on either CdS or ZnSe were we able to observe Landau-level scattering. As mentioned above, the collision time (without spin flip) is so short in CdS[4] that the Landau-level structure is expected to be smeared out. On the other hand, there has recently been reported the observation of well-resolved cyclotron resonance in lower concentration (5×10^{14} cm^{-3}) n-CdS.[10] Another contributing factor to our failure to observe Landau levels may be the geometrical selection rule given by Blum.[11] He has noted that for $\hat{q} \perp \hat{H}$, the Landau-level scattering is heavily screened and should be much stronger for $\hat{q} \parallel \hat{H}$. Unfortunately, our experimental geometry did not allow study of the $\hat{q} \parallel \hat{H}$ condition.

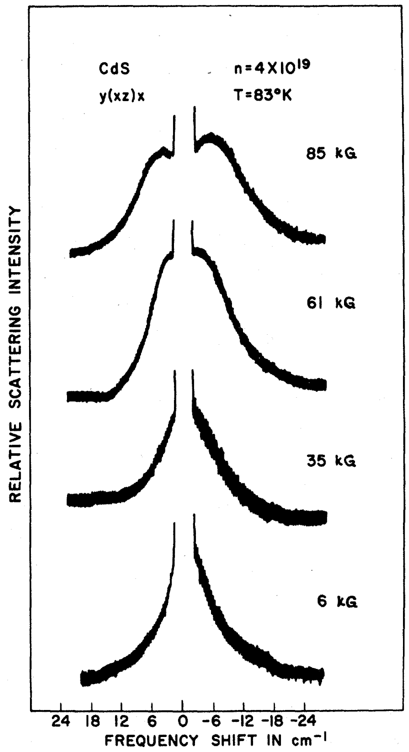

FIG. 2. Spin-flip spectra of In-doped CdS having $n=4\times10^{19}$ cm^{-3}. Data are shown as a function of applied field. The traces shown were recorded with different gains; the gain for 6 kOe is 10 times that for 85 kOe and 3 times that for 35 and 61 kOe. Instrumental width is ~ 2 cm^{-1}.

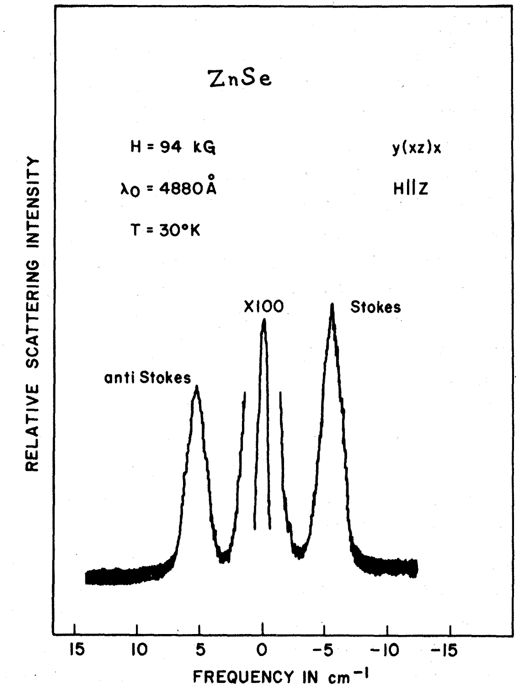

FIG. 3. Spin-flip spectrum of ZnSe. Excitation is approximately 80 mW at 4880 Å. Sample temperature is 30 °K. Scattering geometry is $y(xz)x$ with $H=94$ kG parallel to $\hat{z}$ and $\hat{q} \perp \hat{H}$. This In-doped sample has a room-temperature carrier concentration $n=5\times10^{17}$ cm^{-3}.

C. ZnSe Results

The observation of spin-flip scattering in ZnSe was confined to a single sample which was In doped to a level of $\sim 10^{19}$ In/cm^3 and had an estimated room-temperature carrier concentration of $n_e = 5\times10^{17}$ cm^{-3}. Other ZnSe samples having higher carrier concentrations (up to 10^{19} cm^{-3}) exhibited no observable spin-flip scattering. In Fig. 3, we show the spectrum obtained in the $y(xz)x$ geometry with $\hat{H} \parallel \hat{Z}$ and $\hat{q} \perp \hat{H}$ at 30 °K in a field of 94 kOe. The conduction-electron g factor implied by the 5.2-cm^{-1} wave-number shift is 1.18 ± 0.03. No other published value for g_e is available, although Kurik[12] has quoted an unpublished observation of 1.14. The spin-flip linewidth in our ZnSe sample is ~ 1.5 cm^{-1} in excess of the instrumental width. Despite the fact that ZnSe is cubic, the same selection rules apply to ZnSe as described above for hexagonal CdS. The integrated intensity for the spin-flip scattering in ZnSe is about a factor of two greater than for the 5×10^{17}-cm^{-3} CdS sample. One striking difference was noted, however, between ZnSe and CdS: Whereas in CdS no appreciable dependence of scattering efficiency upon laser frequency was observed, we found that in ZnSe, no spin-flip scattering could be observed with 5145-Å laser excitation, but the strong scattering shown in Fig. 3 could be excited with 4880-Å light. We note, however, that a similar frequency dependence was *not* observed for the nonmagnetic single-particle scattering which appears as a flat background in Fig. 3. This scattering was of comparable intensity for both laser frequencies.

III. DISCUSSION

Theories of spin-flip-scattering linewidth, scattering intensity, and field- and carrier-concentration dependence are far from complete, especially for the II-VI semiconductors, but some comparison of our results to the present partial theories is in order here.

Since the basic quantity measured here is the conduction-electron g factor, we shall begin with it. Roth *et al.*[13] have given an equation relating effective mass m^*, spin-orbit splitting Δ, and effective g factor g_e, for III-V semiconductors. In the zero-field limit, the measurements on the InSb[3] g factor give good agreement with Roth's value (to within a few percent). Kurik[12] has stated that for the II-VI semiconductors, the appropriate relation is

$$g_e = 2\left[1-\left(\frac{m_e}{m^*}-1\right)\left(\frac{\Delta}{3E_g+\Delta}\right)\right] , \qquad (1)$$

where E_g is the energy gap. Using 0.07 eV, 2.57 eV, and 0.18 for Δ, E_g, and m^*/m_e, respectively, for CdS, we obtain $g_e^{\text{calc}} = 1.92$. For ZnSe with 0.45 eV, 2.79 eV, and 0.17 for Δ, E_g, and m^*/m_e, respectively, we obtain $g_e^{\text{calc}} = 1.50$. These values are not in very good agreement with our results for ZnSe.[14] The g_e value for CdS is so close to 2 that this material offers no real test of the validity of the algebraic form of Eq. (1). It appears that Kurik's statement[12] that the above equation provides good agreement for the II-VI compounds is in error.

Let us now turn briefly to a consideration of the scattering intensities. Several theoretical papers have appeared in recent years treating the problem of inelastic light scattering from conduction electrons in magnetic fields.

The most complete treatment is that of Blum,[11] who discusses several inelastic light-scattering processes from mobile carriers in magnetic fields and who refers to all of the earlier work in this field. His results for the spin-flip scattering are equivalent to those given originally by Yafet.[8] The result for a single particle is approximately

$$\frac{d\sigma}{d\Omega} \approx \left(\frac{\hbar\omega_0}{E_g}\right)^2 \left(\frac{e^2}{m_s c^2}\right)^2 \text{ cm}^2/\text{sr} , \qquad (2)$$

where m_s is the effective spin mass (given by $e/g_{\text{eff}}\mu_B c$). Note that this simple form predicts no magnetic field dependence for the scattering cross section. For CdS with 5145-Å excitation, $\hbar\omega_0/E_g = 0.94$ and $m_s \approx m_e$, giving 6.9×10^{-26} cm^2/sr. For ZnSe with 4880-Å excitation, $\hbar\omega_0/E_g \approx 0.91$ and $m_s \approx 1.5 m_e$, giving 2.8×10^{-26} cm^2/sr. These values are in order-of-magnitude agreement with the observations on ZnSe and CdS.

This agreement should not be taken too seriously in view of the fact that the cross section per particle does not bear a simple relation to the observed scattering intensity because more than one Landau level lies beneath the Fermi surface in all these experiments. Wherrett and Harper[9] have analyzed in detail the concentration and magnetic field dependence of the spin-flip scattering in the extreme quantum limit (zero temperature with the Fermi energy lying near the $n=0$ spin-split Landau levels). This is the only case treated in detail and does not correspond directly to our experimental situation. However, Wherrett and Harper[9] find that while there is some nonmonotonic variation in scattering efficiency as the Fermi energy increases to include more and more Landau levels, its order of magnitude is the same when the number of such levels is small.

One should also note that Eq. (2) omits consideration of resonant-enhancement effects to the scattering cross section. This is another reason why the above-cited argument with Eq. (2) should not be taken too seriously. While a detailed study of resonance effects in spin-flip scattering will not be given here,[15] we should mention that our results suggest that for CdS, resonance enhancement exists for both 4880- and 5145-Å excitation (for which the enhancements are approximately equal); whereas for ZnSe only the 4880-Å exhibits resonance enhancement (the 5145-Å photons lying too far below the relevant exciton levels in energy).

Finally, some discussion of our results in comparison with the scattering observation in the narrow-gap semiconductor InSb is in order. Slusher *et al.*[3] noted an increase in linewidth with increasing n_e in InSb. This increase can probably be accounted for in terms of the nonparabolicity of the conduction band in InSb. Such an effect is probably *not* the cause of the n_e-dependent broadening in CdS because in going from the 5×10^{17}-cm^{-3} to the 4×10^{19}-cm^{-3} samples, the value of k_F increases by less than a factor of 5, while the linewidth increases by a factor of $\gtrsim 40$. If one takes the parameter of nonparabolicity in the two-band model to be $\gamma \sim (E_F/E_g)$, we find $\gamma \sim 0.005$ and ~ 0.10 for the 5×10^{17} and 4×10^{19} samples in CdS. This compares to 0.12 for 5×10^{16} InSb. A crude estimate of the spin-flip linewidth due to nonparabolicity can be made as follows: If ν_1 is the spin splitting at $q=0$ and ν_2 at $q=q_F$, then we might expect

$$|\nu_1-\nu_2|/\nu_1 \sim E_F/E_g .$$

The spread $|\nu_1-\nu_2|$ is then the nonparabolicity-induced linewidth $\delta\nu_{\rm NP}$. Using the above numbers (and assuming $H = 100$ kOe) for the semiconductors in question, we find

$$\delta\nu_{\rm NP} \sim (0.10\times 8)\ {\rm cm}^{-1} \quad \text{for } 4\times 10^{19}\ \text{CdS}$$

$$\sim (0.005\times 8)\ {\rm cm}^{-1} \quad \text{for } 5\times 10^{17}\ \text{CdS}$$

$$\sim (0.12\times 150)\ {\rm cm}^{-1} \ \text{for } 5\times 10^{16}\ \text{InSb}\ .$$

Thus for the InSb, the $\delta\nu_{\rm NP} \sim 18$ cm^{-1} suggests that the nonparabolicity accounts for most of the observed linewidth.[3] The spin-flip linewidth in the 4×10^{19}-cm^{-3} CdS sample does not appear, from the calculation sketched above, to be due to nonparabolicity. We estimate the lifetime contribution below using expressions derived by Yafet.[16]

The spin lifetime τ_s is related to the collision lifetime τ by the equation

$$\tau/\tau_s \approx (\delta g)^2 (m^*/m)(kT/E_g)^2\ , \qquad (3)$$

where $\delta g = 2 - g = 0.2$ in CdS, $m^* = 0.16 m_e$, and for degenerate samples like ours, kT is replaced by E_F, the Fermi energy. τ for our 4×10^{19}-cm^{-3} CdS samples is known from Hall measurements and Raman plasmon linewidths[4] to be $\lesssim 6\times 10^{-14}$ sec. E_F is $\sim 0.1 E_g$ and thus τ/τ_s is estimated from (3) to be $\sim 10^{-5}$. However, the observed ratio is $\sim 10^{-2}$, and thus this estimate of spin lifetime suggests that our observed linewidth is not lifetime dominated. Unfortunately, the only spin lifetimes directly measured in systems similar to ours are for very low-concentration dopants.

Yafet (private communication) has suggested that a more accurate estimate of $|\nu_1 - \nu_2|$ than that given above can be obtained from the q^4 contribution in $g_{\rm eff}(n, q)$. Since the $q_F \simeq 10^6$ cm^{-1} in the 4×10^{19}-cm^{-3} sample is not very much greater than the q transfer in our visible-light-scattering experiments, this effect may well account for the large observed width of the spin-flip line.

An even more interesting difference between our results in CdS and ZnSe and those in the InSb lies in the polarization selection rules. As discussed earlier, the selection rules we observe are precisely those expected for a free-carrier spin-flip scattering, viz., α_{xz}, $\alpha_{yz} \neq 0$; α_{xx}, α_{zz}, α_{yy}, and $\alpha_{xy} \approx 0$, where $\hat{z}$ is the direction of $\hat{H}$. The observed ratios α_{xz}/α_{xy}, etc., are ≥ 100. In contrast, the spin-scattering selection rules in InSb have recently been studied by Patel and Yang,[17] who find that *all* Raman tensor elements are observed. One possible source of the anomalous selection rules is the scattering from collective modes[18] (charge-density fluctuations of the electron gas at this spin frequency). Such scattering will give rise to a diagonal Raman tensor α_{ii}. Even adding this mechanism to the single-particle spin flip leaves unaccounted for the α_{xy} found in InSb. Moreover, it remains a puzzle why these anomalous effects are not seen in the II-VI compounds we have studied.

IV. CONCLUSION

The spin-flip Raman scattering from conduction electrons has been extended into the visible (and potentially into the ultraviolet) region of the spectrum by studying the wide-band-gap semiconductors CdS and ZnSe. We have obtained accurate values for the conduction-electron g values in both materials and have observed anomalously broad linewidth in heavily doped CdS. The observed polarization selection rules are those expected for a free-carrier spin-flip process and are quite different from those found from free-carrier scattering in InSb as well as from bound-electron scattering in CdS. The scattering efficiencies we observe are quite high, suggesting the real possibility of achieving a magnetically tunable spin-flip Raman laser which operates in the visible (or in the uv using ZnS or ZnO). Observed dependence of the scattering intensity on carrier concentration and magnetic fields indicates the need for more theoretical work in this area.

ACKNOWLEDGMENTS

We thank P. A. Wolff, C. K. N. Patel, and Y. Yafet for helpful discussions and H. L. Carter and D. H. Olson for technical assistance.

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[1] See, for example, P. A. Fleury and R. Loudon, Phys. Rev. 166, 514 (1968), and references therein.

[2] D. G. Thomas and J. J. Hopfield, Phys. Rev. 175, 1021 (1968).

[3] R. E. Slusher, C. K. N. Patel, and P. A. Fleury, Phys. Rev. Letters 18, 77 (1967); C. K. N. Patel and R. E. Slusher, Phys. Rev. 167, 413 (1968); 177, 1200 (1969).

[4] J. F. Scott, R. C. C. Leite, T. C. Damen, and Jagdeep Shah, Phys. Rev. B 1, 4330 (1970).

[5] B. Lax, J. G. Mavroides, H. J. Zeiger, and R. J. Keyes, Phys. Rev. 122, 31 (1961).

[6] J. G. Skinner and W. G. Nilsen, J. Opt. Soc. Am. 58, 113 (1968).

[7] See, for example, R. H. Pantell and H. E. Puthoff, *Fundamentals of Quantum Electronics* (Wiley, New York, 1969), pp. 235–264. Stimulated spin-flip scattering has recently been seen in InSb; C. K. N. Patel and E. D. Shaw, Phys. Rev. Letters 24, 451 (1970).

[8] Y. Yafet, Phys. Rev. 152, 858 (1966); G. B. Wright, P. L. Kelley, and S. H. Groves, in *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer, Berlin, 1969), p. 335.

[9] B. S. Wherrett and P. G. Harper, Phys. Rev. 183, 692 (1969).

[10] K. J. Button, B. Lax, and D. R. Cohn, Phys. Rev. Letters 23, 375 (1970).

[11] F. A. Blum, Phys. Rev. B 1, 1125 (1970).

[12] M. V. Kurik, Soviet Phys. Semicond. 3, 1056 (1970). We note that Kurik's equation differs from that of Roth *et al.* in an insignificant way unless $\Delta \approx E_g$.

[13] L. M. Roth, B. Lax, and S. Zwerdling, Phys. Rev. 114, 90 (1959).

[14] The values for E_g, Δ, and m^*/m_e used here are taken from *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (Wiley, New York, 1967).

[15] T. C. Damen (private communication).

[16] Y. Yafet, Solid State Phys. 14, 1 (1963).

[17] C. K. N. Patel and K. H. Yang (unpublished).

[18] F. A. Blum, Phys. Rev. Letters 23, 73 (1969).

PHYSICAL REVIEW B VOLUME 3, NUMBER 6 15 MARCH 1971

Phonon Conductivity of Ge in the Temperature Range 2-1000 °K*

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(Received 22 July 1970)

The contributions of transverse and longitudinal phonons toward thermal conductivity of undoped Ge have been investigated, both in high- as well as low-temperature regions. Four-phonon processes are also included in the determination of the combined relaxation time τ_c and hence the phonon conductivity. The group velocity of respective phonons in the conductivity integral is obtained on the basis of $\vec{q} = (\omega/\vec{v})(1+\alpha\omega^2)$, where the parameter α is determined from the experimentally obtained dispersion curves for the different acoustic branches in the region $0-\frac{1}{2}q_{\max}$ and $\frac{1}{2}q_{\max}-q_{\max}$. It is observed that the transverse phonons in general make a major contribution toward thermal conductivity in the entire temperature range.

I. INTRODUCTION

Recently Hamilton and Parrott[1] have used a variational treatment to calculate the thermal resistance of Ge in the temperature range 5–300 °K, and have shown that the major contribution toward thermal conductivity is due to transverse phonons. The contribution of transverse phonons on the basis of the variational treatment varies from 80 to 90%. Because the variational treatment gives the nearest approximation to the correct answer, it is desirable to investigate how far one can explain the phonon conductivity results on the basis of transverse phonons alone in the framework of the relaxation-time approach. The calculations of phonon conductivity of Ge due to transverse phonons have been performed in the temperature range 2–1000 °K, both in the presence and absence of four-phonon processes, which play an important role at high temperatures. For the above calculations we have used Holland's[2] model for transverse phonons and appropriate expressions for the different phonon-phonon-scattering relaxation times for the different temperature ranges.

Since the phonon conductivity results of Ge in the temperature range 2–1000 °K cannot be explained on the basis of transverse phonons alone, the aim of the present paper is to investigate the contribution of transverse phonons in the presence of longitudinal phonons as well as four-phonon processes. Holland has not considered the contribution of four-phonon processes in his calculations. Previously Holland replaced v_g/v_p^2 by $1/v_p$, which is a crude approximation. We have used an empirical relation $\vec{q} = (\omega/\vec{v})(1+\alpha\omega^2)$ in order to calculate v_g/v_p^2 for the conductivity integrals. The present approach of calculating v_g/v_p^2 is considered to be quite realistic. Analytical expressions for the various conductivity integrals under different approximations are also obtained. These analytical expressions are quite useful in obtaining the approximate values of the phonon-phonon scattering strenghts which are treated as adjustable parameters.

II. PHONON CONDUCTIVITY DUE TO TRANSVERSE PHONONS

The integral formulation of thermal conductivity as originally suggested by Callaway[3] is divided into two parts[2] according to the two modes of lattice thermal conduction. It leads to

$$\kappa = \kappa_T + \kappa_L \,. \tag{1}$$

The conductivity due to transverse mode κ_T is further divided[2] into two parts on the basis of angular frequency ranges of transverse phonons,

$$\begin{aligned}\kappa_T &= \kappa_{T1} + \kappa_{T2} \\ &= \frac{2}{3}\frac{k_B}{2\pi^2}\left(\frac{k_B T}{\hbar}\right)^3 \left((v_{T1})^{-1}_{0<\omega<\omega_1} \right. \\ &\quad \times \int_0^{\theta_1/T} \frac{x^4 e^x/(e^x-1)^2}{\tau_B^{-1} + \tau_{pt}^{-1} + B_T \omega T^4}\, dx + (v_{T2})^{-1}_{\omega_1<\omega<\omega_2} \\ &\quad \left. \times \int_{\theta_1/T}^{\theta_2/T} \frac{x^4 e^x/(e^x-1)^2}{\tau_B^{-1} + \tau_{pt}^{-1} + B_{TU}[\omega^2/\sinh(\hbar\omega/k_B T)]}\, dx \right) .\end{aligned} \tag{2}$$

In these integrals which refer to the isotropic case, the phonon velocity (v_{T1} or v_{T2}) of the trans-