TABLE II. Values of the lattice mobilities and the β's.

	Band 1	Band 2	Band 3
μ_L (in $\mathrm{cm}^2/\mathrm{V\,sec}$)	3900	195	1365
β	0.001	0.0001	0.0003

is due to lattice vibrations and ionized impurities. As a result lattice mobilities were calculated to be 3900, 195, and 1365 $\mathrm{cm}^2/\mathrm{V\,sec}$ for the light-hole band, the heavy-hole band, and the split-off band, respectively. Lattice scattering was seen to predominate over ionized-impurity scattering. For the best fit of the theoretical magnetoresistance to the experimental points, values of the ratios of the lattice hole mobilities and β's were found which are not too different from those calculated from theory. (Mobilities for the limit of zero magnetic field were used). Since our measured value of the Hall mobility in this diamond at room temperature is 1300 $\mathrm{cm}^2/\mathrm{V\,sec}$, the conductivity mobility calculated above is about right. Thus, the consistency of the results gives support to some of the assumptions used in the theory, in particular to Rauch's assignment[11] of the effective masses and his value for the spin-orbit splitting. Explanation of the longitudinal magnetoresistances, however, would require modification of the theoretical model.

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Luminescence Excitation Spectra of $ZnSiP_2$ at 2 °K

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We have studied the low-temperature luminescence excitation spectra of the chalcopyrite semiconductor $ZnSiP_2$ by using a cw dye laser. Our results confirm the earlier identification of the sharp emission lines as phonon replicas, but show that the highest-energy emission line in the series is *not* the no-phonon line. Our results also show that $ZnSiP_2$ is most likely an indirect-band-gap material and that the low-energy phonon involved in the emission and absorption spectra is indeed a local mode.

I. INTRODUCTION

The luminescence spectra of the chalcopyrite semiconductor $ZnSiP_2$ have been investigated in detail in the past.[1,2] The 2 °K luminescence spectrum of $ZnSiP_2$ is dominated by a series of equally spaced sharp lines. These emission lines have been identified as phonon replicas of a no-phonon line[1,2] and the nature of the center giving rise to this emission has been investigated by Zeeman studies.[3]

We have studied the luminescence excitation (LE) spectra of $ZnSiP_2$ at low temperatures. In the LE spectra one measures the intensity variation of an emission line as a function of the wavelength of the exciting light. The spectra thus obtained give essentially the same information as the absorption spectra in the same spectral range. We present here the results of these studies on $ZnSiP_2$. These results confirm the identification of the sharp emission lines as phonon replicas but show that the no-phonon line is *not* the highest-energy emission line in the series, as assumed earlier. The results also show that the phonon involved is indeed a local mode. Finally, the results lead us to the conclusion that the lowest-energy band gap in $ZnSiP_2$ is most likely indirect.

II. EXPERIMENTAL TECHNIQUES

The excitation source used in these experiments was a Rhodamine 6G cw dye laser,[4] pumped with a 1-W argon laser. A motor-driven grating enabled us to scan the dye-laser wavelength in either direction from ~ 5700 to 6400 Å. A recently proposed output coupling scheme[5] was used to reduce the fluorescence background of the dye to an acceptable level and to obtain a beam whose direction is independent of wavelength. The linewidth of the dye laser was $\lesssim 0.3$ Å and the useful output power was typically 10–15 mW. The sample was immersed in liquid helium, pumped to 1.8 °K. The photoluminescence of the sample was dispersed by a double spectrometer and detected by a photomultiplier. The LE spectra were obtained by setting the spectrometer at the wavelength of one of the sharp emission lines and scanning the dye laser over the desired wavelength range.

The crystals used in this work were grown by Buehler and Wernick by using a vapor-transport technique. A description of this technique has been given previously.[6]

III. EXPERIMENTAL RESULTS AND DISCUSSION

The left-hand side of Fig. 1 shows a part of the 2 °K luminescence spectrum of $ZnSiP_2$ excited by the dye laser at 5850 Å. This is identical to the spectrum obtained earlier by using an argon laser as the excitation source.[2] The right-hand side of Fig. 1 shows the corresponding LE spectrum obtained by setting the spectrometer at peak No. 1 and scanning the dye laser. The LE spectra obtained with the spectrometer set at peaks 2, 3, 4, and 5 are *identical* to the one shown in Fig. 1.

The most striking feature of the data is the approximate mirror symmetry between the emission and the LE spectra. Such a symmetry was first observed in[7,8] ZnTe and subsequently in GaP doped with Cd : O or Zn : O.[9,10] The existence of such a symmetry confirms the earlier interpretation[1,2] of the emission lines as phonon replicas of a no-phonon line. The fact that there is no overlap between the emission and the LE spectra shows that the highest-energy emission line in the series (No. 1) is not the no-phonon line, as assumed earlier.[1,2] The nonoverlap of the emission and the LE spectra is the most interesting feature of the data. We will consider it in detail later in this paper.

Another interesting feature of the data is that the low-energy phonon in the luminescence spectrum has an energy of $X_1 = 6.5$ meV, whereas in the LE spectrum it has an energy of $X_1' = 5.3$ meV. This difference in phonon energies in the absorption and emission processes is characteristic[9] of local modes and confirms the earlier suggestion regarding the nature of this phonon. The fact that this difference is rather large (≈ 20%) indicates that the presence of an exciton significantly reduces the restoring force constant.

We return now to the question of the nonoverlap of the emission and the LE spectra. This observa-

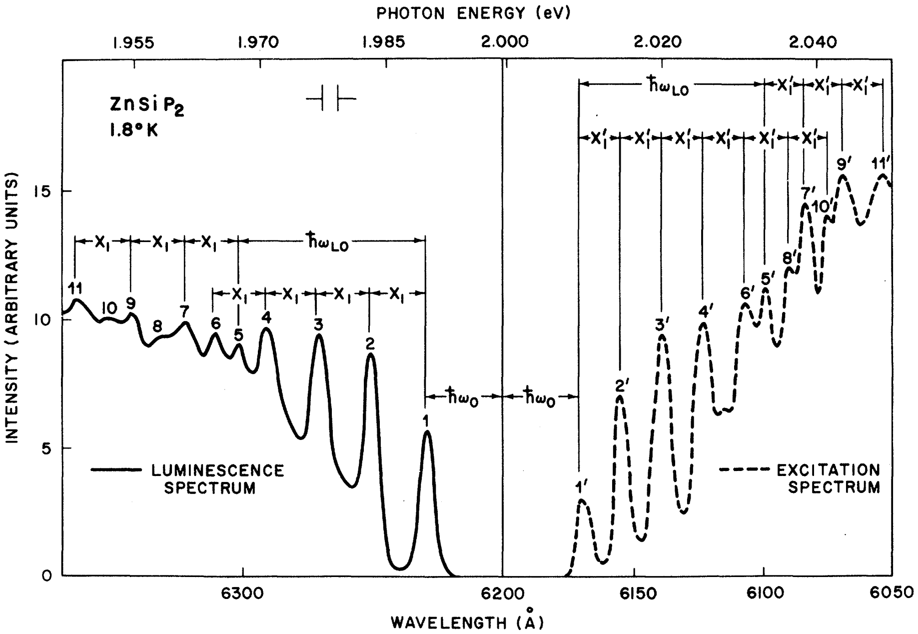

FIG. 1. Luminescence and LE spectra of $ZnSiP_2$ at 1.8 °K. The luminescence spectrum (left-hand side) was obtained by exciting with the dye laser at 5850 Å and scanning the spectrometer. The LE spectrum (right-hand side) was obtained by setting the spectrometer at 6230 Å (line 1) and scanning the dye laser. The excitation spectra for spectrometer set at lines 2, 3, 4, and 5 are identical to the one shown here. The excitation spectrum is normalized for constant excitation intensity: $\hbar\omega_0 = 9.3 \pm 0.2$ meV, $X_1 = 6.5 \pm 0.2$ meV, $X_1' = 5.3 \pm 0.3$ meV, $\omega_{LO} = 22.7 \pm 0.2$ meV.

tion is in contrast with those in ZnTe[7,8] and Cd : O-doped GaP[9,10] in which sharp lines were observed, but is qualitatively similar to the observation in Zn : O-doped GaP[9] in which no sharp lines were observed. There are two possible explanations for the nonoverlap in the two spectra: (i) There is a Franck-Condon-type shift[11] between the absorption and emission spectra, or (ii) the center under consideration cannot absorb or emit light without the help of a phonon, whose energy is $\hbar\omega_0$ in Fig. 1. Let us consider these two possibilities in detail.

The energy separation between the emission peak 1 and LE peak 1′ is = 18.6 meV, whereas $2X_1+X_1'$ = 18.3 meV. Since these two values are equal within the experimental accuracy, it is tempting to ascribe the separation between 1 and 1′ to a Franck-Condon shift. According to this model (Fig. 2), the LE peak 1′, for example, is due to the absorption from the $v=0$ vibrational state in the ground state to the $v'=1$ vibrational state in the excited state, the emission peak 1 is due to transition $v'=0$ to $v=2$, and the transitions $v'=0$ to $v=0$ or 1 are not observed because of reduced overlap in the wave functions. However, one can calculate the intensity of transition $v'\rightarrow v$, and the result for the special case in which $v'=0$ (corresponding to the emission at $kT \ll \hbar\omega$) is given by[12,13]

$$I_{0v}=\frac{e^{-S}S^v}{v!}\ , \tag{1}$$

where

$$S=\frac{\omega\Delta^2}{2\hbar}\ . \tag{2}$$

I_{0v} is essentially the overlap integral between the wave functions of the zeroth vibrational level in the excited state and the vth vibrational level in the ground state. S is a coupling-strength parameter; the larger the S, the stronger the coupling. ω is the frequency of the local mode and Δ is the displacement in configurational coordinate space, as shown in Fig. 2. From these equations and the fact that the intensities of lines 1 and 2 are comparable, one can see that the missing lines in the series ($0\rightarrow 1$ and $0\rightarrow 0$) should also have intensities comparable to those of lines 1 and 2. Since this does not agree with experimental observations,[14] we must reject this model.

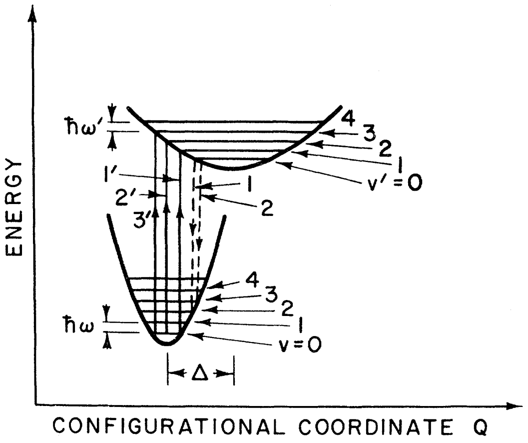

FIG. 2. Configurational coordinate model for 0 °K. The solid (dashed) vertical lines represent absorption (emission) and their numbers correspond to those in Fig. 1.

Another possible explanation, also based on the Franck-Condon principle, is the one proposed for GaP doped with Zn : O.[9] It is assumed in this model that there are *two* phonons (with energies $\hbar\omega_1=X_1$ and $\hbar\omega_2=\hbar\omega_0$ in Fig. 1) and the zero-phonon line is halfway between lines 1 and 1′. If v_1 and v_2 (v_1' and v_2') represent the vibrational quantum numbers for phonon 1 and phonon 2, respectively, in the ground (excited) state, then line 1 is due to transition $v_1'v_2'\rightarrow v_1v_2$, where $v_1'=v_2'=v_1=0$ and $v_2=1$. Line 2 is due to $0\,0\rightarrow 2\,1$ and so on. The transition $0\,0\rightarrow 0\,0$, which would be expected midway between line 1 and 1′, is not observed because of nonoverlap in the wave functions. Such a model might be reasonable for Zn : O-doped GaP, in which no sharp lines are observed. However, we believe that we can rule out this model for $ZnSiP_2$ by once again considering the relative intensities. For this complicated model, one can calculate the intensity I_n of an n-phonon satellite following the analysis given by Toyozawa.[12] Considering once again the special case of 0 °K, the intensity of an n-phonon satellite in the luminescence spectrum is given by[13]

$$I_n=e^{-S}\,\frac{S^n}{n!}\ , \tag{3}$$

where

$$\begin{aligned} S&=S_1+S_2\\ &=\frac{\omega_1\Delta_1^2}{2\hbar}+\frac{\omega_2\Delta_2^2}{2\hbar}\ ,\\ n&=n_1+n_2\ . \end{aligned}$$

Here n_1 and n_2 are the numbers of phonon-1 and phonon-2 processes, respectively. For the moment let us consider $n_1=0$. Then the intensities of the zero-, one-, and two-phonon-2 processes will be in the ratio $1:S_2:\frac{1}{2}S_2^2$. Experimentally, the ratio of a one-phonon to a no-phonon process is >20 in an excitation spectrum and >100 in an emission spectrum. Therefore, $S_2>20$ in this model and the two-phonon-2 processes will be expected to be ~10 times stronger than the one-phonon-2 process. No such line is observed experimentally. Moreover, Toyozawa[12] has shown that for $S\gtrsim 5$ electron-phonon coupling is very strong and no distinct phonon structure will be observed. Thus our experimental data cannot be explained on the basis of the Franck-Condon principle.

We therefore believe that the second possibility mentioned earlier applies to our case; i.e., the center under consideration cannot absorb or emit light without the help of a phonon of energy $\hbar\omega_0$ in Fig. 1. Thus the no-phonon line is either not allowed or very weakly allowed and is not observable. Emission line 1 is due to the emission of a photon and a phonon, whereas the LE line 1′ is due to the absorption of a photon and the *emission* of one phonon. The other lines (2, 3, ... and 2′, 3′, ...) are replicas of lines 1 and 1′ by local modes of energies X_1 and X_1' and the LO phonon. Thus, if E_0 is the energy of the no-phonon line, the emission peaks would occur at $E_0 - \hbar\omega_0 - nX_1 - m\hbar\omega_{LO}$ and the LE peaks at $E_0 + \hbar\omega_0 + nX_1' + m\hbar\omega_{LO}$, where n and m are zero or integers. From the data we deduce $E_0 = 1.9997$ eV and $\hbar\omega_0 = 9.3$ meV.

This energy of 9.3 meV is considerably smaller than the energy of the smallest phonon (13 meV) observed in Raman scattering.[2,15] Therefore the 9.3-meV phonon appears to be a large k-vector phonon. This leads us to the conclusion that $ZnSiP_2$ is most likely an indirect-band-gap material. The 9.3-meV phonon would then be required in the absorption and emission processes to conserve momentum.

Since the phonon energies for large $\vec{k}$ are not known for $ZnSiP_2$, it is not possible to compare the value of 9.3 meV with phonon energies at critical points. However, a rough comparison may be obtained as follows. c/a in $ZnSiP_2$ is approximately twice as large as in GaP so that the $(0, 0, \pm 2\pi/a)$ point in GaP is expected to map[16] into (0, 0, 0) in $ZnSiP_2$ and the $(0, 0, \pm\pi/a)$ point in GaP becomes a zone-edge point in $ZnSiP_2$. From Raman-scattering studies, Kaminow *et al.*[15] found that a low-frequency zone-center phonon in $ZnSiP_2$ has an energy close to the zone-edge TA-phonon energy in GaP.[17] Therefore one might expect a zone-edge TA phonon in $ZnSiP_2$ to have an energy equal to the TA-phonon energy in GaP at the point $(0, 0, \pm\pi/a)$. This energy[17] (10.8 meV) does agree reasonably well with the energy $\hbar\omega_0 = 9.3$ meV obtained earlier.

It should be mentioned here that the concept of folding the Brillouin zone,[16] which we applied to the phonons, can be equally well applied to the electronic band structure. Such folding or mapping would lead to direct energy band gaps in a chalcopyrite corresponding to indirect gaps in its binary analog. These have been called "pseudodirect" band gaps.[18] One might expect the lowest band gap in $ZnSiP_2$ to be pseudodirect. However, our results indicate that the lowest band gap of $ZnSiP_2$ is indirect, as we have seen above.

Finally, the question arises as to why this bound exciton in $ZnSiP_2$, which couples so strongly to local modes, would need the assistance of a phonon to emit or absorb light. A partial answer to this emerges when one realizes that the ability to emit light without phonon assistance depends on the magnitude of the electron wave function at $k = 0$, whereas the strength of phonon coupling [S in Eq.(2)] depends on the difference in the charge distributions in the ground and excited states.[12] Since these two quantities are not necessarily related, it is possible to have strong phonon coupling but negligible luminescence without phonon assistance. Nevertheless, most known bound excitons in indirect semiconductors do emit light, however weakly, without phonon assistance and it is somewhat surprising that the no-phonon transition of this bound exciton in $ZnSiP_2$ is so weak as to be nonobservable. It would therefore be of interest to verify the interpretation given above by some independent means.

Another point of interest would be an analysis of the nature of the local mode observed in these spectra. The local-mode energy (~6 meV) is about half the smallest zone-center-phonon energy observed in Raman scattering.[2,15] It would be interesting to investigate the origin of this local mode.

IV. SUMMARY AND CONCLUSIONS

Our results on the LE spectra show an approximate mirror symmetry with the luminescence spectra. It is somewhat surprising that a material in its early stages of development would show such sharp and well-defined emission and absorption spectra. An analysis of the spectra confirms the earlier assignment of the emission lines as due to phonon replicas, but the zero-phonon line is not at 1.9904 eV, as assumed earlier, but at 1.9997 eV. The data show that $ZnSiP_2$ is most likely an indirect-band-gap material. The results point out the usefulness of a cw dye laser in obtaining high-resolution high-sensitivity excitation spectra in semiconductors.

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[13] These results are exactly valid only for $\omega = \omega'$. However, we expect the change to be small in our case because $\omega \approx \omega'$. Also, the ratio of intensities of any two lines would still be given by these equations.

[14] At 2 °K, the ratio of the intensity of line 1 to that of a higher-energy line (*c* in Ref. 2) is >100. A large number of higher-energy lines, approximately a factor of 2–5 less than line 1, do appear at $T > 15$ °K. These are presumably due to transitions from higher vibrational levels in the excited state to the various vibrational levels in the ground state [Jagdeep Shah (unpublished)].

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Gamma-Ray Compton Profiles of Diamond, Silicon, and Germanium

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160-keV γ rays were used to measure the Compton profiles of diamond, silicon, and germanium single crystals in five crystallographic directions (⟨100⟩, ⟨110⟩, ⟨111⟩, ⟨112⟩, and ⟨221⟩). The data are analyzed so as to obtain the differences in the profiles in the various directions for each material. A direct comparison of the data is made with band calculations for Si which suggests that the differences in the profiles can provide a sensitive test of band calculations. Interesting comparisons between the three materials are made by normalizing the data to equal electron density for the outer valence electrons. In addition to providing information on the three materials studied, this work demonstrates that systematic studies of families of solid-state systems by Compton scattering can be a very powerful experimental technique.

I. INTRODUCTION

Compton scattering of photons as a tool for studying electron momentum distributions[1–7] has received renewed interest in the past several years, but measurements have been restricted to materials with low photoelectric absorption at the x-ray energies used (17 keV). Recent work[8,9] has shown that this restriction is no longer necessary when a high-energy γ-ray source is used in conjunction with a Ge(Li) detector.

In this paper we wish to report a systematic study of the Compton profiles of the isostructural elements diamond, silicon, and germanium. From the data, we are able to determine for each material the anisotropy of the electron momentum distributions between the ⟨100⟩ and the ⟨110⟩, ⟨111⟩, ⟨112⟩, and ⟨221⟩ crystallographic directions. We compare our Si and Ge results with the positron-annihilation data of Erskine and McGervey[10] and find there is basic agreement between the two studies. In comparing our results with the published x-ray Compton profiles of diamond,[6] we find agreement, but for Si there is disagreement.[11]

Our Si results agree with the theoretical calculation of Stroud and Ehrenreich.[12] However, it appears that the pair of directions they used to calculate the anisotropy is not the set most sensitive to the details of the wave function. Thus their conclusion that momentum profiles are not a sensitive test of band calculations may be incorrect.

Considering that diamond is an insulator with only 1*s* electrons in its core and Ge is a semiconductor with 3*d* electrons in its core and Si is in between, the Compton profiles for the valence electrons of all three elements are remarkably similar when compared at equal electron densities. This similarity suggests that to first order the wave function for the bonding electrons in the three ma-