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Sharp-Line Photoluminescence in $ZnSiP_2$

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We have studied the photoluminescence spectra of $ZnSiP_2$. Time-resolved spectra, time decays of different spectral components, and excitation-intensity dependence studies were performed at various temperatures between 1.8 and 250 °K. We observe a series of sharp emission lines (half-width ~ 1 meV) which we attribute to phonon-assisted processes of an unidentified transition involving impurities or defects. Superimposed on this series is a featureless broad emission band. At energies above this series of lines, several other independent sharp lines are observed. Some of the latter are strongly enhanced as the temperature increases from 1.8 to 35 °K. These results are discussed and compared with somewhat similar spectra of GaP.

I. INTRODUCTION

Interest has risen recently in ternary semiconducting compounds of the group II-IV-V. Although these compounds are expected to have properties analogous to III-V compounds, they are clearly a step towards more complexity. The possibility of interesting physics and the potential of these compounds for devices make them attractive materials for intensive studies.

We report here the photoluminescence studies of $ZnSiP_2$ crystals. At 1.8 °K, we observe many sharp lines (half-width ~ 1 meV) at wavelengths greater than 6000 Å. These sharp lines merge into a rather broad band peaking at 6400 Å. Another broad emission band is also observed at ~ 7100 Å. We have studied these spectra in detail, including investigation of the temperature dependence between 1.8 and 250 °K, time-resolved spectra (TRS) at various temperatures, as well as the time decay of several spectral components. We describe and analyze these results in this paper.

General discussions of II-IV-V compounds have been published by several authors.[1-3] For $ZnSiP_2$ in particular, band-edge absorption has been studied by Goryunova *et al.*[4] for temperatures greater than 77 °K. These authors reported a steep absorption edge at ~ 6300 Å (~ 2.0 eV) where the absorption coefficient rose to values greater than 10^3 cm^{-1}. However, preliminary absorption measurements by Shaklee[5] on our samples, which have high resistivity, show an absorption edge at wavelengths less than ≈ 5400 Å (> 2.3 eV). Cathodoluminescence spectra for $T > 77$ °K were reported by Alekperova *et al.*[6] for samples of different dopings. These spectra all showed rather broad bands at wavelengths longer than 7000 Å. Some of the bands contained weak secondary maxima separated from each other in energy by ≈ 0.03 eV. This was attributed to participation of phonons of energy 0.03 eV. The present work, to the best of our knowledge, is the first study of photoluminescence in $ZnSiP_2$.[7,8] We have observed the first sharp-line emission spectrum in this material. Sharp lines were not obtained by previous authors,[6] who worked with electron beam excitation and samples at temperatures above 77 °K. However, Shay *et al.*[9] in this laboratory have obtained spectra similar to ours using electron beam excitation with samples at temperatures between 10 and 50 °K.

II. CRYSTAL DATA

The samples were grown with no intentional doping by a vapor transport technique using $ZnCl_2$. They were irregular in shape but showed several facets about 2×3 mm in size, which were used for the photoluminescence studies. The x-ray measurements indicated that the crystals have chalcopyrite structure. No measurements on Hall mobilities, etc., are available on these samples at present. The room-temperature resistivity was high (~ 10^7 Ω cm) in sample 20 on which most measurements were made. This high resistivity is probably due to a high degree of compensation, which might be a result of having Zn on Si sites, and vice versa.

III. EXPERIMENTAL TECHNIQUES

Luminescence was excited either by a 1-W cw argon ion laser, or by a pulsed argon ion laser capable of delivering up to 40 W (peak power) in a pulse of 3-μsec half-width with a repetition rate of up to 30 pulses/sec. The samples were mounted in a Janis immersion Dewar for 1.8 °K and in a Janis supervaritemp Dewar for studies above 5 °K. They were immersed in liquid He in the former and were in the atmosphere of the vapor in the latter. The emitted light was analyzed by a Spex 1400 double spectrometer and detected by an EMI 9558 S-20 photomultiplier. No polarization studies were made. A synchronous detection system including a lock-in amplifier was used with the cw argon laser. A box-car integrator was used with the pulsed argon laser. Time-resolved spectra (TRS) were obtained by fixing the amplifier gate at a given delay and scanning the spectrometer, while the time decay measurements were obtained by fixing the spectrometer at a given wavelength and scanning the gate.

IV. EXPERIMENTAL RESULTS

We divide this section into several subsections. We first describe the spectra at 1.8 °K and then describe their temperature dependence. Finally, we describe the TRS and the time decay measurements at various temperatures.[10]

A. 1.8 °K Spectra

In Fig. 1 we show the photoluminescence spectra as obtained using the cw Ar^+ laser for two $ZnSiP_2$ samples grown in different batches. The most striking features of the spectra are the sharp lines, numbered 1, 2, 3, ..., which appear to merge into

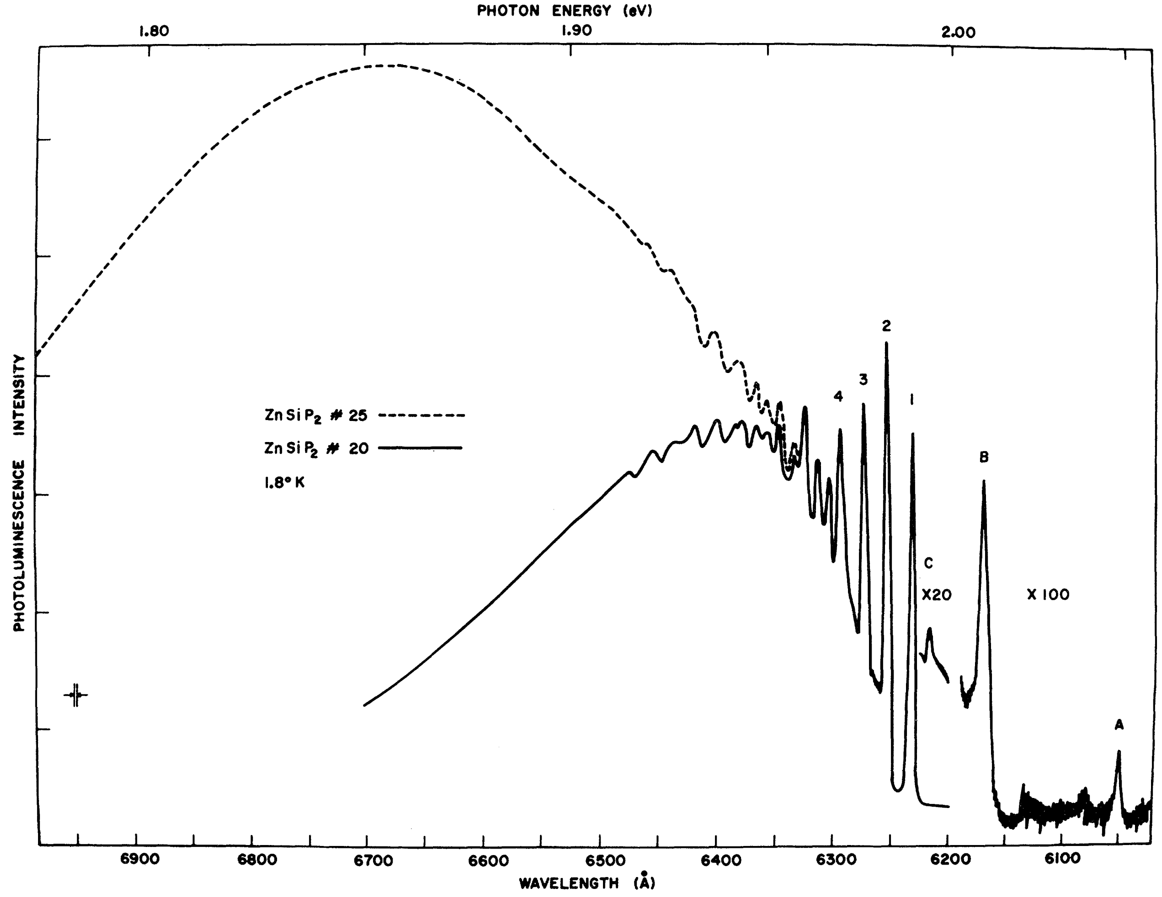

FIG. 1. Photoluminescence spectrum at 1.8 °K of two $ZnSiP_2$ crystals excited by the cw Ar^+ laser. The sharp lines numbered 1, 2, ... were identical in the two samples but the lines lettered *A*, *B*, ... were strong in sample 20 only. Instrumental resolution was ≈ 1.8 Å.

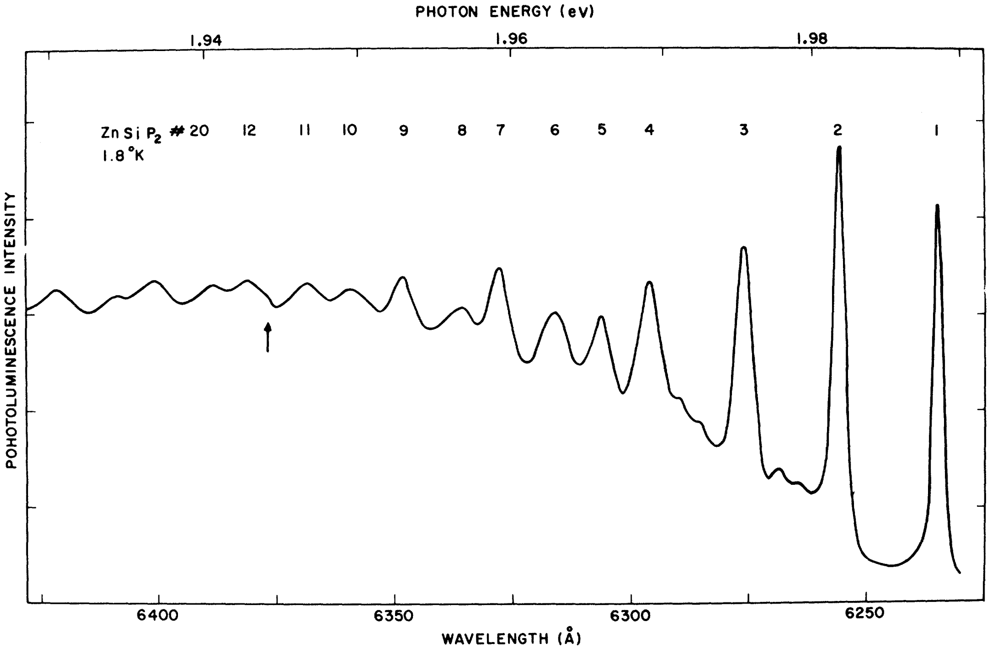

FIG. 2. High-resolution photoluminescence spectrum at 1.8 °K of the numbered sharp lines in $ZnSiP_2$ sample 20. Energies of the peaks are given in Table I. Resolution was 0.6 Å.

a broad long-wavelength maximum. Identical "numbered" lines were found in these two samples as well as in two others. However, the broad maximum occurred at different wavelengths in different samples. Sample 28 showed no sharp lines at all, only a broad band at longer wavelengths than those mentioned above (at ≃ 6800 Å). In this paper, we shall concentrate on one of these samples, namely, sample 20, the one in Fig. 1 with broad maximum near 6400 Å (1.94 eV).

Figure 2 shows a high-resolution spectrum of the sharp lines, with energies listed in Table I. Note that lines 1, 2, 3, and 4 are very nearly equally spaced and become broader as one goes toward longer wavelengths. Line 5 is narrower than either line 4 or 6 but broader than line 1. The lines beyond line 6 appear to merge together and the spectrum gives the appearance of several doublets spaced one from another by an energy equal to that between the first and the second sharp lines. The resemblance of this spectrum to that reported[11–13] for Cd-O impurity complexes in GaP is very striking.

The dependence of the spectrum on excitation intensity (I_{ex}) was studied in detail by varying the intensity of the cw argon laser over four orders of magnitude using neutral density filters. It was found that the relative magnitudes of the sharp lines and the spectral shape remained constant with no significant shift within our experimental error. In order to go to still higher excitation intensities, the pulsed argon laser was used. The results are shown in Fig. 3. We notice first of all that as I_{ex} is increased the sharp lines seem to broaden and the background under the first few lines seems to increase. The sharp lines decrease in strength relative to the broad maximum at

TABLE I. Energy positions of various emission lines at 1.8 °K and their interpretations in terms of phonon-assisted transitions. X_1 and X_2 correspond to the two phonon energies involved.

Photoluminescence line (1.8 °K)	$h\nu$ (eV)	Assignment	
A	2.0494		
B	2.0103		
C	1.9953		
1	1.9904	E_0	
2	1.9837	$E_0 - X_1$	
3	1.9772	$E_0 - 2X_1$	
4	1.9709	$E_0 - 3X_1$	
5	1.9677		$E_0 - X_2$
6	1.9646	$E_0 - 4X_1$	
7	1.9609		$E_0 - X_2 - X_1$
8	1.9579	$E_0 - 5X_1$	
9	1.9547		$E_0 - X_2 - 2X_1$
10	1.9512	$E_0 - 6X_1$	
11	1.9484		$E_0 - X_2 - 3X_1$
12	1.9446	$E_0 - 7X_1$	
13	1.9426		$E_0 - X_2 - 4X_1$
14	1.9387	$E_0 - 8X_1$	

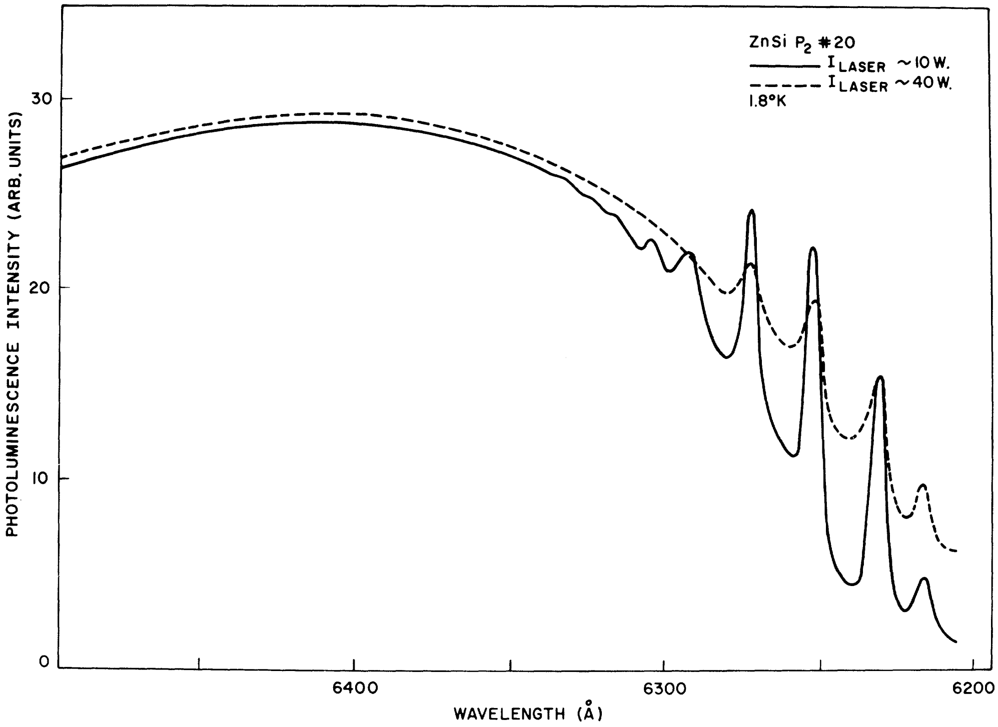

FIG. 3. Photoluminescence spectra at 1.8 °K for several excitation intensities using the pulsed Ar$^+$ laser. Highest power density at the sample was ~ 10^5 W/cm^2. The two spectra have been normalized so as to show about the same amplitude at the 6400-Å broad maximum.

6400 Å. This is not due to a heating effect since the lines do not shift with increasing intensity.

B. Temperature Dependence

As the temperature is increased above 2 °K, the numbered series of sharp lines (Fig. 2) changes very little up to ≃ 35 °K. (Temperature dependence of the "lettered" series is discussed in Sec. IV E.) Above 35 °K the numbered lines broaden noticeably and are barely seen at 50 °K, as seen in Fig. 4. All the sharp lines shift by about 7 Å toward longer wavelengths as the temperature is increased from 2 to 50 °K.

As the sample temperature is raised above 50 °K the spectrum shows only a broad band at 6400 Å, which grows smaller with increasing temperature and finally disappears above ≃ 100 °K. Another broad band with a maximum located in the infrared near 7100 Å arises at temperatures above 80 °K. As the temperature is raised, this band becomes equal to and then larger than the 6400-Å band and persists up to ≃ 250 °K. Figure 5 is a plot of the peak emission intensities of the two broad bands as a function of $1/T$. Activation energies of ~ 70 and ~ 110 meV can be inferred from these plots for the 6400- and 7100-Å peaks, respectively.

C. Time-Resolved Spectra (TRS)

Figure 6 shows TRS of sample 20 at 1.8 °K at several delay times indicated on the figure. Note that the background emission under the sharp lines changes noticeably near the high-energy end of the spectrum as the delay is increased. A similar behavior is observed at temperatures up to 50 °K. TRS were also studied at 77 °K, when only the broad-band peaking at 6400 Å could be seen, as shown in Fig. 7. Note that this band shifts to longer wavelengths as the delay time is increased.

D. Time Decay Measurements

These measurements were performed only at 1.8 °K.[14] The time decay of the luminescence at several wavelengths is shown in Fig. 8. These spectra were taken with laser intensity, such that the first peak had very little or no background under it while the successive lower-energy peaks had increasing amount of background under them. In Fig. 8, one can see that the decay curve of the first peak is almost completely exponential, whereas those of peaks 2 and 3 are exponential only at longer times. A time constant can be de-

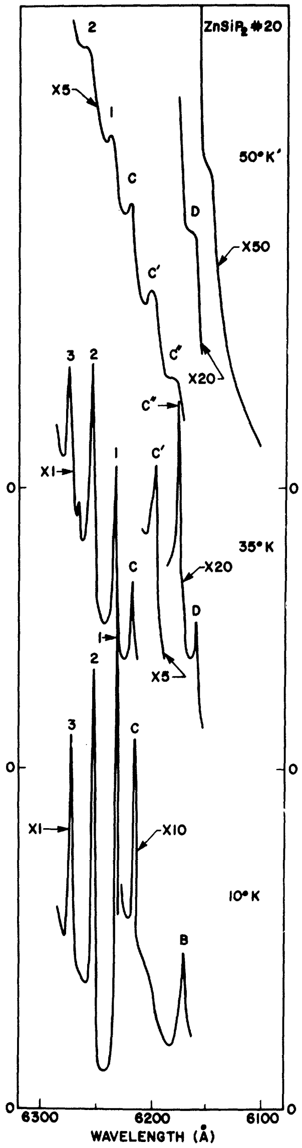

FIG. 4. Temperature dependence of the photoluminescence spectrum. Spectra are given for 10, 35, and 50 °K showing the weakening of the numbered sharp lines as well as the intriguing variation of the lettered lines. Note that the zero levels are offset.

termined from each exponential. We note that they are equal within experimental uncertainty. The other two decay curves in Fig. 8 show the time dependence of the emission at the broad peak and at the long-wavelength half-intensity point. Notice that these decay curves cannot be fit well to an exponential even at longer times.

E. Higher-Energy Lines

At energies above those of the numbered system of lines three other lines are also present in sample 20 (Fig. 1), whereas in sample 25 they are absent. Line A completely vanishes at 10 °K whereas lines B and C show a marked enhancement. Further rise in temperature increases the strength of these lines to a point where C becomes comparable to line 1 at 35 °K. An absolute increase of a factor of 40 was measured for line C from 1.8 to 35 °K. Line B, however, only increases up to ~ 20 °K and is only hinted as a shoulder of a new line (C'') at 35 °K as shown in Fig. 4.

Above 10 °K three new lines (C', C'', and D) emerge. C' is 6.5 meV above C, and C'' is 6.5 meV above C'. The third line D is 5.7 meV above C''. Spectra at 10 and 35 °K are shown in Fig. 4.

The lettered lines and the numbered lines have a different dependence on excitation intensity. For instance, at 1.8 °K line 1 is ~ 200 times stronger than line C at low excitation intensities (Fig. 1), but at much higher excitation intensities these lines become comparable. This, however, is not due to sample heating since the lines C', C'', and D do not appear.

F. Surface Raman Scattering

Since the appearance of the spectrum (Fig. 1) suggests presence of phonons, surface Raman

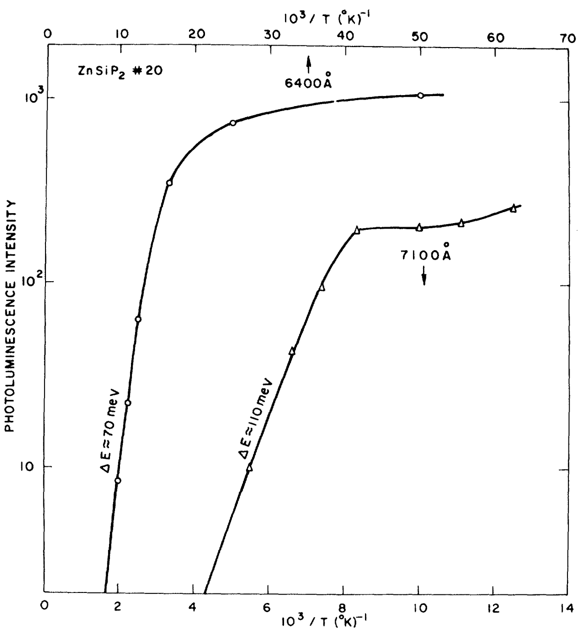

FIG. 5. Graph of the peak emission intensities versus $1/T$ for the two broad bands with maxima near 6400 and 7100 Å. The numbers shown give activation energies derived for exponential variation with temperature.

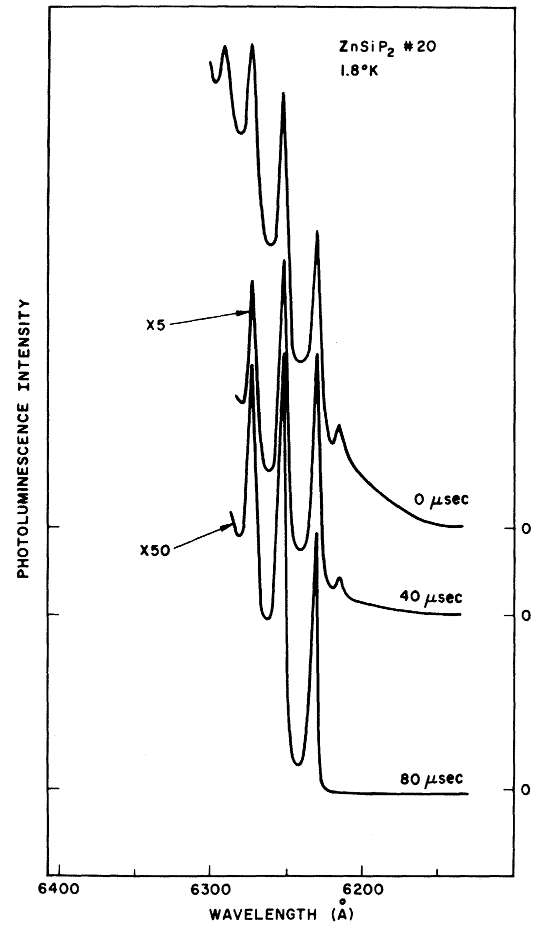

FIG. 6. TRS at 1.8 °K for several delay times after the exciting laser pulse. Note the change in the background under the sharp lines at the high-energy end of the spectrum. The zero levels of the spectra are offset.

scattering experiments were performed at 300 °K on our sample 20 using the cw argon laser. A typical spectrum is shown in Fig. 9. It shows five Raman active phonons with frequencies indicated in the figure. A more comprehensive study of Raman effect by the transmission technique has been carried out by Kaminow,[15] who has observed at least three more phonon modes in addition to the ones reported here.

V. DISCUSSION

We divide the discussion into several subsections. We first show that the most prominent feature of the spectrum, the series of sharp lines labeled 1, 2, ... can be explained in terms of two phonons. Next, we show that there are in fact two emission bands superposed on each other in the observed red emission. We then show that the lines marked A, B, C, ... are independent of the lines 1, 2, 3, ...

A. Numbered Lines

Consider the sharp lines 1, 2, 3, ... of the photoluminescence spectrum as indicated in Fig. 2 and Table I. Note that the energy separations between peaks 1, 2, 3, 4, 6, 8, 10, ... are the same: 6.5 ± 0.2 meV. Lines in this series are seen to be successively broader. This indicates that these peaks are due to transitions accompanied by emission of one or more phonons of energy $X_1 = 6.5$ meV, possibly a local mode at this small energy. This phonon interpretation is supported by our time decay measurements (Fig. 8) which show that the peaks 1, 2, and 3 have identical decay times. The zero-phonon transition appears to be at energy $E_0 = 1.990$ eV (line 1).[16] See Table I. Now, line 5 is seperated from E_0 by an energy $X_2 = 22.7 \pm 0.3$ meV, which corresponds in energy to the mode $h\nu_3$ as obtained from Raman scattering (Table II). Thus line 5 is attributed to phonon-assisted recombination with emission of one phonon of energy X_2, which is evidently a lattice mode.

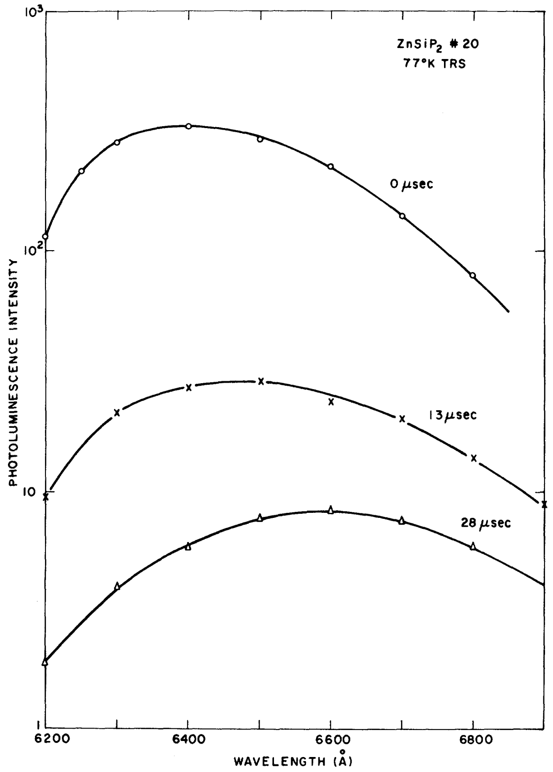

FIG. 7. TRS at 77 °K for several delay times. Note the shift of the broad band toward longer wavelengths at the longer delay times. The curves are not offset in this figure.

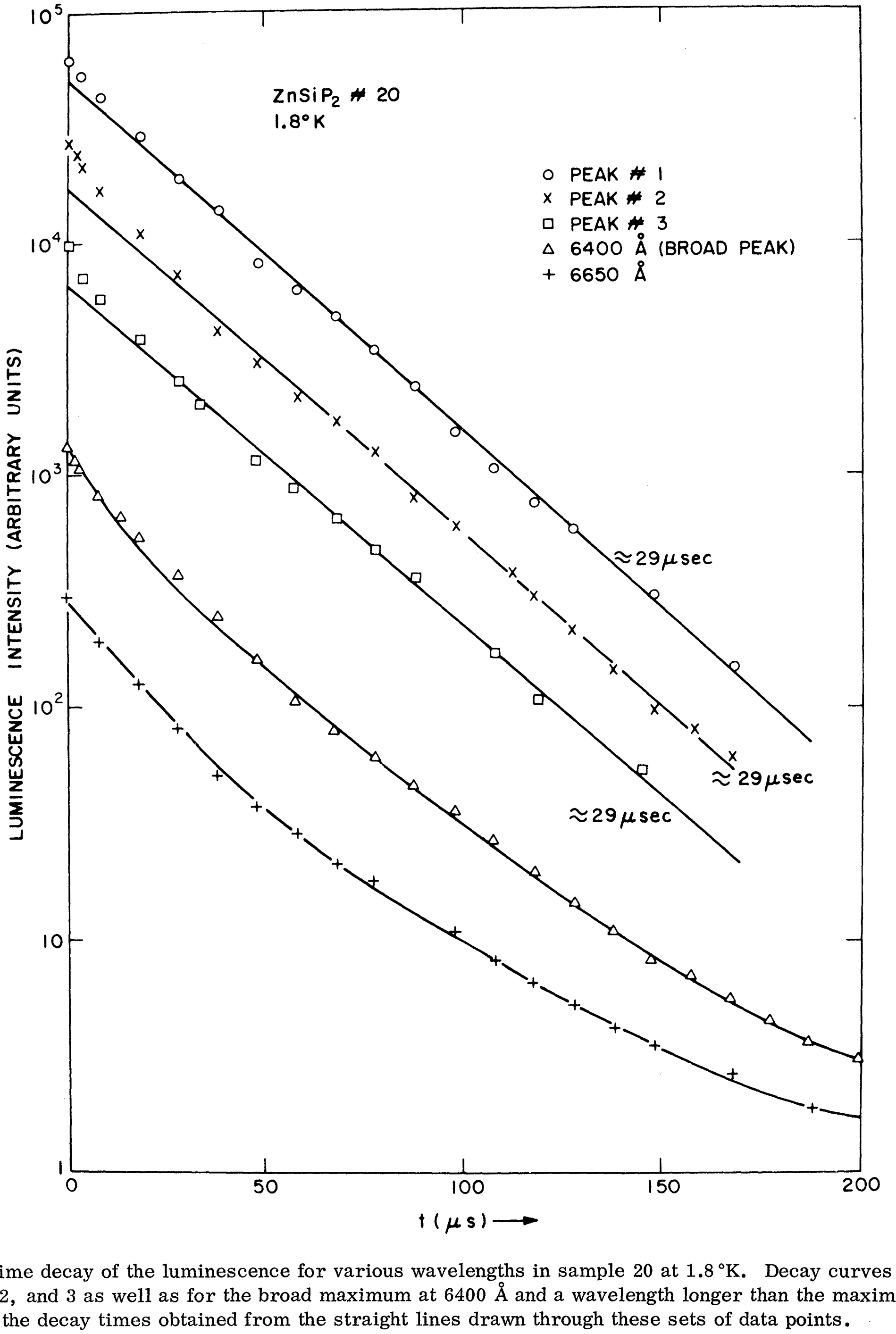

FIG. 8. Time decay of the luminescence for various wavelengths in sample 20 at 1.8 °K. Decay curves are shown for peaks 1, 2, and 3 as well as for the broad maximum at 6400 Å and a wavelength longer than the maximum. The numbers are the decay times obtained from the straight lines drawn through these sets of data points.

Lines 7, 9, 11, ... then are due to multiphonon-assisted processes involving one X_2 phonon and one or more X_1 phonons, as indicated in Table I. There is a small shoulder near 1.944 eV where one would expect transitions with emission of two phonons of energy X_2 (arrow in Fig. 2). The spectrum clearly indicates strong electron-phonon coupling, which suggests predominance of short-range forces at impurities or defects.

Two weak peaks located near 1.98 eV between lines 2 and 3 (Fig. 2) have replicas between lines 3 and 4, with the latter separated from the former

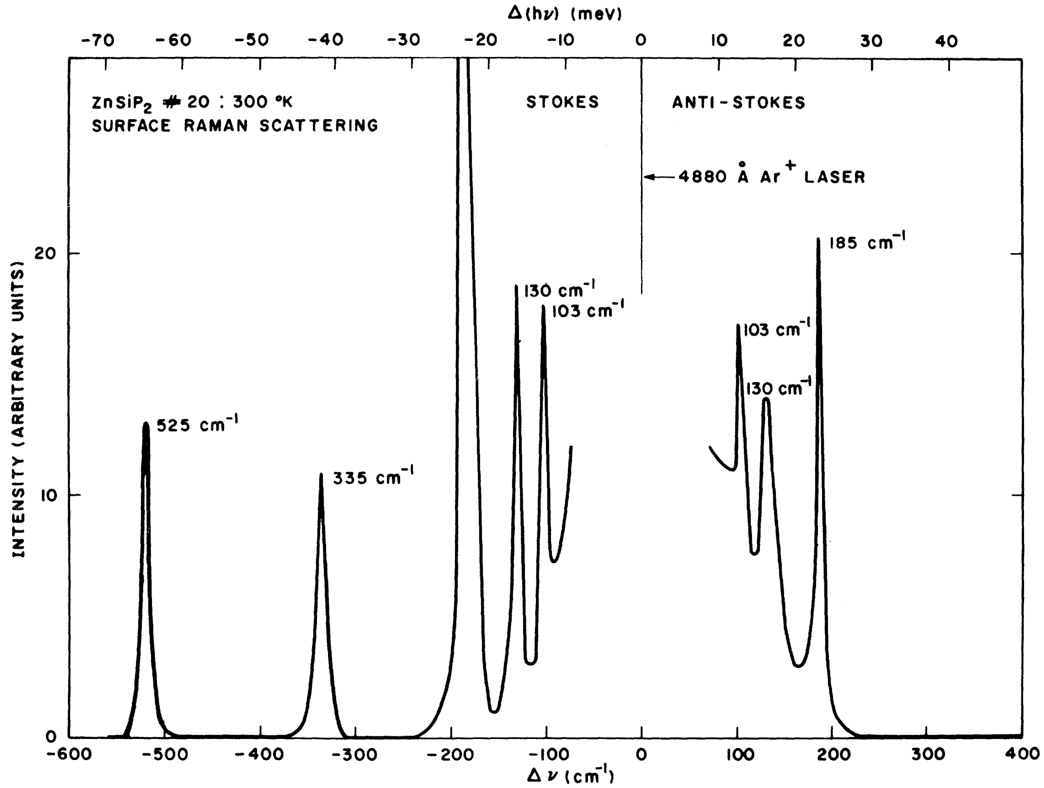

FIG. 9. Raman spectrum of light scattered off a $ZnSiP_2$ surface at 300 °K using the cw Ar^+ laser source at 4880 Å. Frequencies of the observed modes are listed in Table II.

by the energy $X_1 = 6.5$ meV. The origin of these weak structures is unknown.

B. Evidence That Red Emission Is Composed of Two Overlapping Bands

Notice from Fig. 1 that although the numbered sharp lines are identical in samples 20 and 25, the maxima of the spectra occur at different wavelengths. Another sample (sample 28, not shown in Fig. 1) shows no sharp lines but only a broad band peaking at ~ 6800 Å. These observations suggest that a broad featureless band (hereafter called band II), due to a process different from that giving rise to the sharp lines, may be present in approximately the same spectral range as the sharp lines discussed in Sec. V A. (The envelope of the sharp lines and its phonon replicas will be referred to as band I.)

Further evidence for the presence of two overlapping bands is the "cutting off" of the "background" at short wavelengths in TRS for long delay times as shown in Fig. 6 at 1.8 °K. Similar behavior in TRS is also observed at higher temperatures. Furthermore, as we noted before (Fig. 3), the *relative* intensities of line 1, say, and the maximum of the emission band change as I_{ex} is varied. Finally, the most striking evidence for the existence of the emission band II is the shift observed in TRS at 77 °K as shown in Fig. 7. Such a shift is qualitatively similar to what one would expect for a broad emission band due to distant donor-acceptor pairs involving Coulomb energy. However, such an interpretation is ruled out in our case by the fact that the time decay curves for different wavelengths of band II are not sufficiently different. We believe that this shift is a result of the dominance of the emission band II over band I at longer times. No noticeable shift is observed below 50 °K, which may be explained by the slower decay of band I at these temperatures, as suggest-

TABLE II. Energies of various phonons as obtained from surface Raman scattering.

Raman modes	meV	cm $^{-1}$
$h\nu_1$	12.6 ± 0.2	103 ± 2
$h\nu_2$	16.2 ± 0.2	130 ± 2
$h\nu_3$	23.0 ± 0.2	185 ± 2
$h\nu_4$	41.6 ± 0.2	335 ± 2
$h\nu_5$	65.1 ± 0.2	525 ± 2

ed by the TRS measurements.

Thus we have found broad-band emission in about the same energy range as the sharp-line luminescence, with the latter involving well-defined phonon energies. The presence of two such features in a given energy range is strikingly similar to results reported previously for GaP doped with Cd and O.[11–13] That material showed a series of sharp luminescence lines due to phonon-assisted recombination of excitons bound to Cd-O nearest-neighbor pairs. A broad emission band was found also in the same energy range due to transitions of electrons from Cd-O complexes to distant Cd acceptors, a type of pair transition lacking Coulomb interaction. Although this GaP spectrum is similar to our spectrum for $ZnSiP_2$, other characteristics are different. We find that at 1.8 °K the sharp lines and broad band have comparable decay times in contrast with results for GaP which show quite different decay times for the two processes. At high intensities our sharp lines are weak relative to the broad-band emission, which is opposite from the intensity dependence of the two processes in GaP.

C. Higher-Energy Lines

We have seen in Sec. IV that the lettered lines may be absent from samples in which the numbered lines are very prominent. These two systems also have completely different intensity and temperature dependences. We conclude therefore that these two systems are not related.

The highest-energy line A is already absent at 10 °K when B and C are increasing in intensity. Therefore A is not an excited state related to B or C. It seems that a very shallow center must be involved in whatever transition is responsible for A.[17]

Line B has a more interesting temperature behavior. As the temperature increases from 2 to 20 °K, line B increases in intensity. With a further increase in temperature line B decreases, which indicates also a rather shallow center. Line B cannot be due to an excited state of the center responsible for C since C continues to increase in intensity above 20 °K. It seems therefore that the three lines A, B, and C are not related.

Lines C, C', and C'' (Fig. 4) have an energy spacing equal (under our experimental uncertainty) to the local mode involved in the numbered lines. Hence it is rather tempting to relate these lines through this local mode. Let us suppose first that C'' is the lowest-order (in phonon cooperation) emission band, say the zero-phonon line, and that C' and C are its phonon replicas. However, the cutoff of this series at energies below C cannot be understood. It is also impossible for C' and C'' to be anti-Stokes components of C because no Stokes components are observed. One might suggest that C and C'' are the Stokes and anti-Stokes components of C' which is almost forbidden, and the local mode, if not entirely symmetric, could significantly induce the transition. If coupling with the local mode is not too strong, the higher-order processes might be negligible and not observable. This would explain the data at 35 °K. However, C and C' have a rather different temperature dependence, peak C' being absent at lower temperatures. We leave therefore this intriguing point as an open question until more samples showing the C, C', and C'' lines are available.

Line D, observed only around 35 °K, is 5.7 meV higher than C'' and does not seem to be related to any other line.

It is perhaps worth noting that an increase in absolute intensity of relatively sharp lines with increasing temperature has been observed in bound exciton complexes for which the $J=1$ state is a forbidden transition and the $J=2$ state is allowed.[18] The $J=2$ transition increases in strength with increasing temperature as this state becomes populated. In the present case, however, B, C, C', and C'', which increase in intensity with increasing temperature, did not show any related lower-energy line. Their temperature dependence may thus be simply due to kinetic effects as carriers thermally released from shallower centers become available for recombination through the processes responsible for these transitions.

VI. SUMMARY AND CONCLUSIONS

We have presented evidence to show that the red emission of $ZnSiP_2$ is made up of emission due to two different processes. The first process gives rise to the most striking feature of the spectrum, i.e., the numbered series of sharp lines. These sharp lines have been explained as phonon replicas of a no-phonon line (presumably line 1). Of the two phonons involved X_2 ($\simeq 23$ meV) is a lattice mode whereas X_1 ($\simeq 6.5$ meV) is perhaps a local mode. The dominance of phonon-assisted transitions suggests that an impurity with a short-range potential is involved. The second process making up the red emission gives rise to a rather broad featureless emission band (band II). At low temperatures, the emission is dominated by the numbered sharp lines at all times. At 77 °K, band II seems to dominate at longer times. We have pointed out the similarity of our results with Cd-O doped GaP. However, no definite conclusions about the processes involved in $ZnSiP_2$ can be made until materials technology improves to the extent that some impurity control is possible.

Finally, we have pointed out the puzzling and most interesting behavior of the lettered series of lines. A more detailed study of these remains to be made.

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[14] Time decay measurements at higher temperatures are reported in Ref. 9.

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[16] It is possible that the zero-phonon line is forbidden and hence much weaker than its phonon replicas. The zero-phonon line may even be completely absent. However, since no higher-energy line related to the numbered lines is observed, we tentatively assign line 1 to be the zero-phonon line.

[17] This suggests the possibility of a band gap at energies slightly above 2.05 eV. If such an energy gap indeed exists, it would appear to be indirect in view of the low absorption coefficient ($< 10\ cm^{-1}$) obtained by Shaklee (Ref. 5). The high resistivity of these samples should preclude any Burstein effect.

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Hall Angle of a Normal Current Flowing through the Core of a Vortex*

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A calculation, based on the microscopic theory of superconductivity, is made of the Hall angle of a normal current flowing through the core of a single vortex. The magnetic vector potential is assumed uniform throughout the core region and the moments of the current are taken with the electric field. The ratio of these two quantities yields the tangent of the Hall angle. In agreement with a prediction of Bardeen, we find $\tan\alpha = (e\tau/mc)H_{\text{eff}}$, where τ is the relaxation time of the electrons, and the effective magnetic field H_{eff} is in part due to the depression in the order parameter at the core of the vortex and in part to the actual magnetic field in the core of the vortex. For niobium, H_{eff} is very nearly equal to H_{c2}. At 0 °K for niobium, our theory is valid for l/ξ ranging from ∞ to about 10, where l is the mean free path and ξ the coherence length.