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# Polarized Edge Emission of SiC

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The photoluminescence of some relatively pure hexagonal SiC crystals (polytype 6*H*) includes a strongly polarized edge emission. Two distinct patterns of edge emission lines have been found, but never in the same crystal. In either type, the edge emission includes several narrow lines (half-width $\sim kT/4$ at 77°K) and a number of wider bands spaced at regular energy intervals of 0.03 ev, suggestive of a vibrational interaction. Some lines, found in the 77°K edge emission spectrum, vanish at 4°K. Mechanisms for producing polarized light are discussed, and it is concluded that the most probable luminescence centers are donor-acceptor pairs. The two types of spectra may be attributed to two different pairs. Intrinsic recombination radiation was looked for but not found.

## 1. INTRODUCTION

The term "edge emission" is often used[1] to describe certain narrow-band components of the photoluminescence of relatively pure phosphor crystals (e.g., ZnS, CdS, ZnO). The photon energy in edge emission is only slightly less than the energy gap of the material, and very often there are several lines with a regular spacing between them, suggesting that the radiative transitions may be accompanied by phonon emission. A good example is the edge emission of CdS, which consists of two parts, a blue edge emission which may be due to exciton[2] decay, and a green edge emission attributed to hole-electron recombination at a sulfur vacancy.[3] Both parts are polarized.[4]

The present paper gives photoluminescence spectra that are typical of a number of relatively pure SiC crystals, which have a very extensive and complex polarized edge emission. Such edge emission has not previously been observed either in the electroluminescence[5] or in the photoluminescence[6] of SiC. Our use of the descriptive term "edge emission" does not imply a knowledge of the luminescence mechanism, nor that a single mechanism can account for the various edge emissions reported in different materials. In fact, there are significant differences between the edge emissions of SiC and CdS, as will be pointed out later.

We now consider the question of polarization. Recently, a number of authors have reported the polarized photoluminescence of single crystal materials. Much work has been done on cubic crystals, using polarized exciting light,[7] and this method has been applied also to anisotropic crystals.[8] However, we shall describe polarized luminescence found with *unpolarized* exciting light. The light does not excite the luminescence center directly, but creates hole-electron pairs, which later recombine at a center, and the polarization is determined entirely by the recombination process. For anisotropic crystals, several mechanisms have been suggested to explain such polarization, and they will be discussed in the next section.

In SiC we observe a polarization of the entire spectrum, with a particularly strong polarization of the edge emission. Peaks separated by only $10^{-3}$ ev show very different degrees of polarization. Thus, a meaningful measurement requires high resolution and simultaneous measurement of the degree of polarization.

We have found two kinds of edge emission in SiC, which we shall call type $X$ and type $Y$. Each type is easily recognized by its pattern of 15 or 20 emission lines, and all the edge emission spectra we have measured can be classified as type $X$ or type $Y$, with no mixtures. The two types of crystals do not appear to have any significant polytype differences,[9] so the $X$ and $Y$ spectra are believed to be due to different impurities. Nevertheless, as we shall point out in detail in Sec. 10, the $X$ and $Y$ luminescence patterns have much in common, including the same regular 0.03-ev "vibrational" structure.

It will be shown that the SiC edge emission is *not* intrinsic recombination radiation, but must occur at a luminescence center. The nature of the center has not yet been determined; the present evidence seems to favor donor-acceptor pairs. A calculation of the polarization of light emitted by donor-acceptor pairs will be given in the following paper.[10]

## 2. MECHANISMS FOR THE POLARIZATION OF LUMINESCENCE

Consider an anisotropic crystal in which ultraviolet light creates excess holes and electrons. Photons may be emitted when the holes and electrons recombine, the

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[1] F. Kröger and H. J. G. Meyer, Physica **20**, 1149 (1954); J. J. Hopfield, J. Phys. Chem. Solids **10**, 110 (1959).

[2] R. J. Collins and J. J. Hopfield, Bull. Am. Phys. Soc. **4**, 323 (1959); G. Diemer and A. J. Van der Houven van Oordt, Physica **24**, 707 (1958).

[3] R. J. Collins, J. Appl. Phys. **30**, 1135 (1959); Lambe, Klick, and Dexter, Phys. Rev. **103**, 1715 (1956).

[4] D. Dutton, J. Phys. Chem. Solids **6**, 101 (1948); Bancie-Grillot *et al.*, Compt. rend. **248**, 86 (1959).

[5] Lyle Patrick and W. J. Choyke, J. Appl. Phys. **30**, 236 (1959).

[6] J. A. Lely and F. A. Kröger, *Semiconductors and Phosphors* (Interscience Publishers, Inc., New York, 1958), p. 514.

[7] P. P. Feofilov, J. phys. radium **17**, 656 (1956).

[8] A. Lempicki, Phys. Rev. Letters **2**, 155 (1959).

[9] For information on polytypism in SiC, see R. S. Mitchell, Z. Krist. **109**, 1 (1957); or A. R. Verma, *Crystal Growth and Dislocations* (Butterworths Scientific Publications, London, 1953), Chap. 7.

[10] Lyle Patrick, Phys. Rev. **117**, 1439 (1960), following paper.

recombination taking place either directly or through localized luminescence centers. The selection rules which govern the polarization of the emitted photons depend on symmetry properties of the wave functions which represent the state of the system before and after the radiative transition. These symmetry properties may, in turn, depend on (a) the symmetry properties of the valence and conduction bands; (b) the symmetry of the crystal field at a luminescence center; or (c) the symmetry properties of a luminescence center itself.

(a) Polarization of the intrinsic recombination radiation should depend on the band structure of the crystal, but does not seem to have been observed. However, the symmetry properties of valence and conduction bands may determine the symmetry properties of excitons,[11] and Hopfield[12] has attributed the polarized exciton *absorption* structure in ZnO to symmetry properties of the valence bands. He has also suggested[13] that band symmetry determines the polarization of the green edge emission of CdS, in which case the recombination is thought to take place through a shallow recombination level. Birman has postulated[14] that the band structure is significant in transitions involving electrons trapped at deep levels.

(b) For luminescence centers in which the initial and final states of the transitions are both localized states of a single atom, the symmetry that determines the polarization is that of the crystal field at the site of the atom. The elements of chief interest here are those with unfilled inner shells. There has been little work on polarized *emission*, but the kind of result to be expected can be seen from the very extensive work on *absorption* of polarized light by these elements in anisotropic crystalline surroundings of various symmetries.[15] The $4f$ shell of the rare earths is usually well enough shielded from the lattice to give narrow absorption or emission[16] lines. The energy levels may sometimes be correlated with those of the free atom. On the other hand, the $3d$ shell of iron group atoms is usually not well shielded from the lattice. The absorption or emission line widths of iron group atoms show considerable variation, depending both on the atom and on the crystal lattice.[15]

(c) Finally, luminescence centers consisting of two or more atoms (or defects) have symmetry elements of their own which may determine the polarization. For example, a donor-acceptor pair in an uniaxial crystal has an axis which may or may not lie along the crystal axis. The energy and polarization of a photon emitted by such a center then depend on the relative orientation of the two axes. Prener and Williams[17] have suggested that nearest neighbor donor-acceptor pairs may give rise to edge emission.

## 3. DESCRIPTION OF SAMPLES

The blue edge emission of $X$- and $Y$-type crystals is not apparent to the eye because both types also have a green emission which is moderately efficient at 77°K (perhaps about one percent). The room temperature luminescence is an extremely weak orange. Although $X$ and $Y$ samples appear similar to the eye under photoluminescence, they may be distinguished by their thermoluminescence, which is green for $X$-type, and orange for $Y$-type. This observation suggests that the trap depth is greater in $Y$ samples, the trapped carriers being thermally released at a higher temperature.

### A. Growth Conditions

All samples were prepared in a high-temperature laboratory furnace. A full description of the equipment and procedure may be found elsewhere.[18] Most samples which exhibit edge emission were prepared from DuPont "Solar Cell" silicon and purified powdered carbon at temperature ranging from 2500°C to 2650°C. In comparison with crystals which do not show edge emission, these crystals are relatively pure, and are grown at relatively high temperatures. Both $X$- and $Y$-type crystals have been grown in either hydrogen or argon atmospheres. As a rule, crystals prepared in argon have a faint green tinge (thought to be due to nitrogen), while those grown in hydrogen are slightly gray. The factors in crystal growth which differentiate $X$ and $Y$ samples have not yet been identified.

### B. Impurities

Spectrographic analyses of the samples with edge emission indicate the presence of Fe and, at times, Al and Ag at levels of the order of $10^{17}$ atoms/cm$^3$. Nitrogen may be present at about the same level. Other impurities likely to be present, although at a level too low to be detected, are those commonly found in commercial SiC, *viz.*, Ti, V, Mn, Ni, Cu, and perhaps Mg and Ca. Rare earth impurities have not been reported in SiC and are probably not to be expected because of their large covalent radii (about 40% larger than that of Si).[19] It has not yet been possible to find a significant difference in impurity content to distinguish $X$- and $Y$-type crystals.

When a SiC crystal grows in an atmosphere containing both donors and acceptors, there is a tendency for the crystal to incorporate them in equal numbers.[20]

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[11] G. Dresselhaus, J. Phys. Chem. Solids **1**, 14 (1956).

[12] J. J. Hopfield, Bull. Am. Phys. Soc. 4, 154 (1959).

[13] J. J. Hopfield, Bull. Am. Phys. Soc. **3**, 409 (1958).

[14] J. L. Birman, Phys. Rev. Letters **2**, 157 (1959).

[15] E. Fick and G. Joos, in the *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1957), Vol. XXVIII, p. 205, give references to the work of Hellwege and others.

[16] S. P. Keller and G. D. Pettit, J. Chem. Phys. **30**, 434 (1959).

[17] J. S. Prener and F. E. Williams, Phys. Rev. **101**, 1427 (1956).

[18] D. R. Hamilton, J. Electrochem. Soc. **105**, 735 (1958); D. R. Hamilton, *Proceedings of the Conference on SiC* (Pergamon Press, Inc., New York, 1959).

[19] Therald Moeller, *Inorganic Chemistry* (John Wiley & Sons, Inc., New York, 1952), p. 135.

[20] R. L. Longini and R. F. Greene, Phys. Rev. **102**, 992 (1956); F. A. Kröger and H. J. Vink, Physica **20**. 950 (1954).

There is a further tendency for the ionized donors and acceptors to associate because of their Coulomb attraction.[21] The SiC samples used in this experiment remained at a high temperature long enough for such association to take place. A rough calculation of the association in SiC, done in the manner of the Prener-Williams calculation[21] for ZnS, indicates that there should be a significant degree of association in our samples.

### C. Polytype

The crystal structure has been determined for a number of samples, by x ray and optical means, and is found to be predominately $6H$ polytype for both $X$- and $Y$-type crystals. Traces of $15R$ polytype are found in both $X$-type and $Y$-type crystals. The edge emission spectra, however, appear to be completely $X$-type or completely $Y$-type, with no mixtures, and this purity of spectral type seems to be a property of the crystal as a whole, being independent of the part of the crystal excited by the ultraviolet light. Hence we find no correlation of spectral type and polytype.

Thus, although $X$ and $Y$ samples differ in their edge emission and in their thermoluminescence, it has not been possible to find a difference in their growth conditions, probable impurities, or polytypes.

## 4. OPTICAL EQUIPMENT

Holes and electrons were created in the SiC crystal ($E_G \approx 3.0$ ev at 77°K) by illuminating it with ultraviolet light from an H6 high-pressure mercury lamp, filtered to exclude photons of energy less than 3.1 ev. The crystal luminescence was then passed through HN-22 Polaroid to a model No. 83 Perkin-Elmer monochromator with a dense flint prism. Filters were used to exclude the ultraviolet exciting light. The monochromator was calibrated against a Cenco spectrum tube containing argon. The reproducibility and the highest resolution obtained were both about $10^{-3}$ ev. The detector was an RCA 1P28 photomultiplier in a vacuum jacket cooled by liquid nitrogen. Photon counting equipment was used in order to obtain high sensitivity.[22] The relative sensitivity of the complete optical system, as a function of photon energy, was obtained by calibration against a tungsten ribbon lamp, whose color temperature was measured, and whose emissivity was taken from the literature. This was done for two angular positions of the Polaroid in order to correct for any polarization of the light by the optical system itself.

## 5. EXPERIMENTAL PROCEDURES

The SiC samples used in this experiment were all (0001) platelets. For light propagated along the crystal axis, the electric vector is always perpendicular to the axis, and no polarization is observed. Hence, the crystals were turned edge-on to the monochromator entrance slit, in order to observe light with the propagation vector perpendicular to the $c$ axis. In this case, the Polaroid is able to separate emission components which have their electric vectors perpendicular or parallel to the $c$ axis. These two components are quite different, but the spectrum of the perpendicular component was found to be identical with that of the light propagated along the $c$ axis, indicating that we are observing electric dipole rather than magnetic dipole radiation.[23]

The crystal was oriented by maximizing the polarization ratio at a strongly parallel polarized emission peak. Parts of the crystal were covered with Aquadag to reduce the possibility of light getting into the monochromator after one or more reflections at crystal surfaces. In spite of these precautions, it is thought that most measurements include something like five percent of the light with the "wrong" polarization.

The temperature of 77°K is certain because the measurements were made with the sample immersed in liquid nitrogen. However, the 4°K measurements were

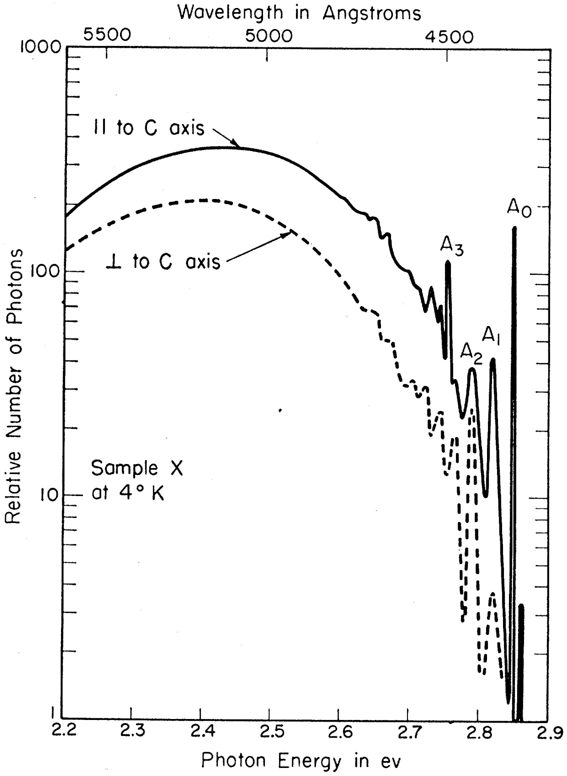

FIG. 1. Photoluminescence of Sample $X$ at 4°K, showing the broad green band ($P=+0.23$), and some of the edge emission structure. The regular 0.03-ev spacing of the edge emission lines suggests a vibrational interaction. The final state of the transition is considered to be a vibrational level of the ground state, the subscript on $A$ indicating the level number.

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[21] J. S. Prener and F. E. Williams, Phys. Rev. **101**, 1427 (1956); Howard Reiss, J. Chem. Phys. **25**, 400 (1956).

[22] G. A. Morton, RCA Rev. **10**, 525 (1949); Boeschoten, Milatz, and Smit, Physica **20**, 139 (1954).

[23] Sayre, Sancier, and Freed, J. Chem. Phys. **23**, 2060 (1955).

made with the sample attached by silicone vacuum grease to a copper block cooled by liquid helium. The crystal temperature was not measured, and it is called 4°K merely for convenience. The actual temperature must have been somewhat higher, as the crystal was continuously illuminated with about 0.1 watt of ultraviolet light; a good thermal contact is necessary to realize a temperature *near* 4°K. However, no spectral change of the luminescence was observed on reducing the exciting light intensity to one-third of its usual value.

The following variations in experimental conditions were found to have no effect on the luminescence spectrum.

(a) The *spectrum* of the uv exciting light was changed by using various filters.

(b) The *intensity* of the uv exciting light was varied over a range of about ten, by using neutral filters.

(c) The crystal surface was ground off to make sure that the edge emission was a property of the entire crystal.

### 6. EXPERIMENTAL RESULTS—*X* CRYSTALS

We now present the 4°K and 77°K spectra of Sample *X*, which is one of a group of crystals with a characteristic pattern of edge emission lines which we call the type *X* spectrum.

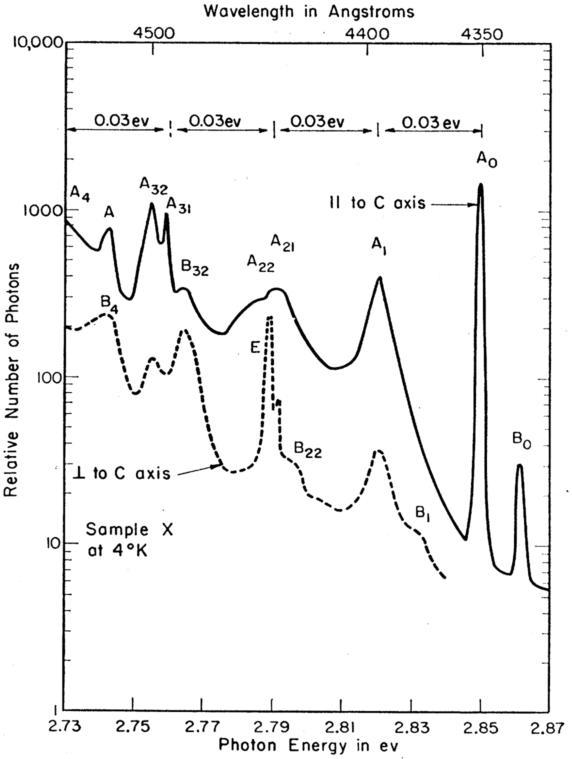

FIG. 2. The edge emission of Sample *X* at 4°K. The 0.03-ev vibrational spacing is indicated above the drawing. In the notation used here, the first subscript indicates the vibrational level, and the second subscript indicates component parts of complex peaks.

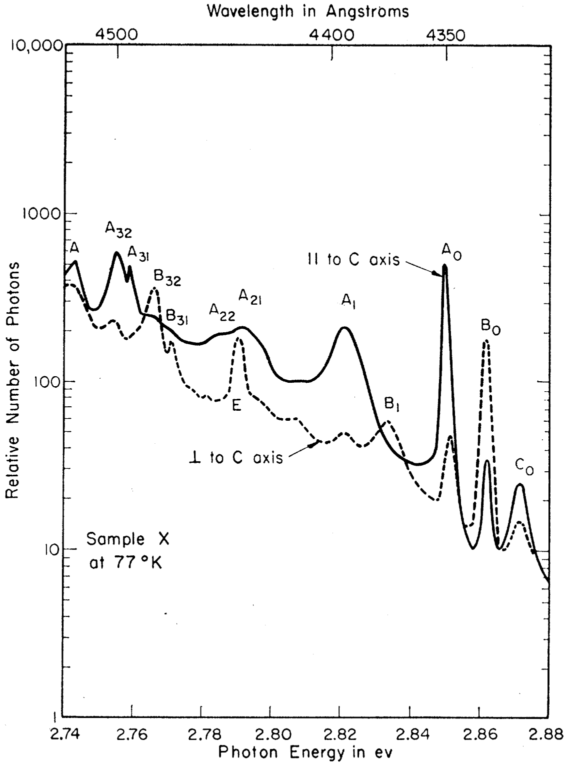

FIG. 3. The edge emission of Sample *X* at 77°K. At this higher temperature, the *B* lines are much stronger, and are polarized perpendicular to the *c* axis. A third narrow but weak peak, $C_0$, is also present.

The first four figures show the photoluminescence of Sample *X*: at 4°K in broad outline (Fig. 1), then the edge emission at 4°K and 77°K in greater detail (Figs. 2 and 3), and finally, in greatest detail, the narrow peaks at the high-energy end.

The results are presented in semilog graphs because of the wide range of intensities. In these graphs, the light polarized parallel to the *c* axis is always shown by a solid line, and light polarized perpendicular to the *c* axis by a dotted line.

The degree of polarization is defined by

$$P \equiv (I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp}),$$

where $I_{\parallel}$ and $I_{\perp}$ denote intensities of light with electric vector parallel and perpendicular to the *c* axis of the crystal. Thus, $P$ ranges from $+1$, for light polarized parallel to the axis, to $-1$ for light polarized perpendicular to the axis, and is zero for unpolarized light.

A large energy range is shown in Fig. 1 so that one can see the relative strengths of the edge emission and the broad green peak (maximum ~2.4 ev). However, much of the fine detail in the edge emission cannot be seen on this energy scale. At lower energies than shown here, the relative number of photons continues to fall, as does the degree of polarization. At 2.4 ev, $P=+0.23$. The edge emission lines marked $A_0$, $A_1$, $A_2$, and $A_3$ are spaced at intervals of approximately 0.03 ev, thus suggesting a vibrational interaction. The notation is chosen to suggest, in the subscript, the vibrational level of the final state. $A_0$ is assumed to be a transition to the zero vibrational level because it is very narrow.

Figure 2 shows the edge emission in greater detail. The peaks $A_2$ and $A_3$ are observed to be compound, and a second subscript is used to number their component peaks. Because of the increasing complexity at lower photon energies, it is impossible to be sure of the correct subscript assignment beyond $A_3$. There is a peak at 2.73 ev, which one can call $A_4$, maintaining the regular 0.03-ev spacing, but there is a peak between $A_{32}$ and $A_4$ which might be a component of either $A_3$ or $A_4$. It is called $A$ (no subscript). There is a considerable amount of structure at energies smaller than those shown in Fig. 2, but it is less distinct, and the vibrational spacing is no longer recognizable. Below 2.6 ev, the spectrum becomes quite smooth.

A second *narrow* peak is marked $B_0$ in Fig. 2. The $A_0-B_0$ spacing is 0.012 ev, and this interval is found elsewhere, e.g., between $A_{32}$ and $B_{32}$.

In the relatively weak perpendicular spectrum, peaks may appear because of a misorientation of the sample, as explained in Sec. 5. Where the perpendicular intensity is less than 10% of the parallel intensity, one must be cautious in interpreting perpendicular peaks which coincide with parallel peaks. Hence, the presence of $A_1$ in perpendicular polarization is somewhat doubtful. The peak $E$ is a narrow doublet which does not appear to fit into the pattern of $A$ and $B$ peaks.

The spectrum at 77°K is shown in Fig. 3. There is no significant displacement in energy of the peaks between 4°K and 77°K. The 77°K peaks are somewhat broader, and they do not stand out as strongly above the background. The spectrum of $B$ peaks is more pronounced at 77°K, and it is possible to find a $B$ peak at 0.012 ev from each $A$ peak, although $B_{21}$ and $B_{22}$ are too weak to show in Fig. 3. A third *narrow* peak, $C_0$, is now observed at 2.873 ev and a weak $C_1$ is barely observable at 2.843 ev. (It is not shown in Fig. 3.) It appears that all the structure, except peak $E$, can be derived from the primary peaks $A_0$, $B_0$, and $C_0$ by vibrational interaction and by a splitting into component peaks.

The primary peaks, $A_0$, $B_0$, and $C_0$, are shown on an expanded energy scale in Fig. 4 at 4°K and 77°K. The half-width of $A_0$ in parallel polarization is shown to be $\sim kT/4$ at 77°K. In perpendicular polarization, $A_0$ is displaced 0.001 ev toward higher energy. At 4°K, the perpendicularly polarized displaced peak is barely observable, being largely hidden by the undisplaced peak marked doubtful (?) because of the possibility of sample misorientation. At 2.85 ev, values of $P$ are at least $+0.85$ for both 4°K and 77°K. This is a polarization ratio of more than twelve to one.

The peaks $B_0$ and $C_0$ appear to be somewhat wider than $A_0$, but they were too weak to measure the line shape accurately with the narrow monochromator slits used for the measurement of $A_0$. The peak $B_0$ reverses polarization, going from $P=+0.3$ at 4°K to $P=-0.67$ at 77°K. Peak $C_0$ is not observed at 4°K, and is too weak at 77°K to yield an accurate value of $P$.

Correlated with the relatively strong perpendicular peak $B_0$ at 77°K is the observation that other $B$ peaks are also more prominent at 77°K, and are most easily observed in the perpendicular direction. It appears that the degrees of polarization of $A_0$ and $B_0$ may be repeated in other $A$ and $B$ peaks, but the resolution of the broad peaks is not good enough to be certain of this.

At 77°K, the double peak $A_{31}A_{32}$ is repeated in the $B$ spectrum (Fig. 3), with the usual $AB$ displacement of 0.012 ev (the $B_{31}B_{32}$ separation is identical with that of $A_{31}A_{32}$). However, at 4°K (Fig. 2), one observes that $B_{31}$ is no longer present, although $A_{31}$ is still strong.

All the 77°K peaks shown in Sample $X$ (and no others) can be observed in any one of a group of type $X$ crystals, not all taken from the same furnace lot. The fact that all peaks appear together suggests that only a single luminescent center is present.

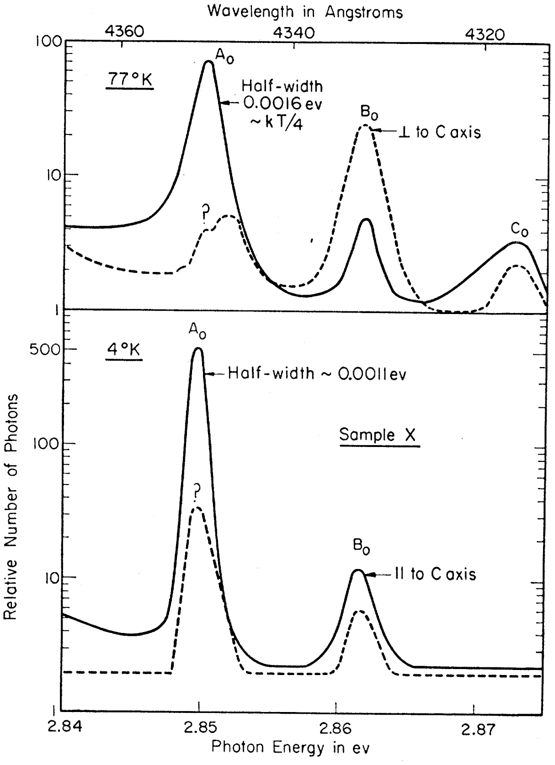

FIG. 4. The narrow lines of Sample $X$ on an expanded energy scale, showing their temperature dependence. $A_0$ is observed to be a double peak, with different maxima for the two polarization directions. The small half-width of $A_0$ at 77°K ($\sim kT/4$) is very significant. Note the reversal of the polarization of $B_0$ and the vanishing of $C_0$ at 4°K. Values of $P$ at 77°K are $+0.85$ at 2.850 ev, and $-0.67$ at 2.862 ev, corresponding to polarization ratios of 12 to 1 parallel, and 5 to 1 perpendicular, respectively.

Thus, although the $X$ spectrum is complex, it is possible to arrange most of the peaks in series associated with the narrow primary peaks $A_0$ and $B_0$; each series is characterized, in first approximation, by a vibrational spacing of 0.03 ev. The 4°K spectrum is made up primarily of the $A$ series peaks, whereas both $A$ and $B$ series peaks are prominent at 77°K.

### 7. DISCUSSION OF TYPE $X$ SPECTRA

The initial state for a photon-emitting transition is assumed to reach its lowest vibrational level before the relatively slow electronic transition takes place. The sharpest lines, labeled $A_0$, $B_0$ and $C_0$, are thought to be due to transitions to the lowest vibrational level of the final state. To explain three such lines, three excited electron states are required. These may be three excited state of a single luminescence center, but such possibilities as transitions at three nonequivalent lattice sites must also be considered. Peaks with subscripts other than zero are regarded as being transitions to higher vibrational levels of the ground state, the lowest level being reached subsequently by phonon emission.

The vibrational spacing of 0.03 ev is quite different from the energies of longitudinal optical (0.12 ev) or transverse optical (0.095 ev) phonons in SiC.[24] In this respect, the vibrational structure is unlike that commonly found in edge emission.[1] If the 0.03-ev spacing is attributed to a SiC phonon, it could possibly be a short wavelength transverse acoustic phonon, as may be seen by scaling up the known energies of Si and Ge phonons.[25] The 0.03-ev spacing may, however, be attributed to a vibrational quantum of the luminescence center itself.

One cannot exclude the possibility that the SiC optical phonons are also involved in our edge emission spectrum. For example, the energy difference between peaks $A_{32}$ and $A_0$ is 0.095 ev, the energy of a transverse optical phonon. However, the optical phonons alone do not suffice to explain the complex structure observed.

Details of the structure of peaks with nonzero subscripts will be useful when a more specific model of the luminescence center is available. For the present, however, attention will be focused on the sharp peaks $A_0$, $B_0$, and $C_0$. Regarding these as *only three* peaks is probably an oversimplification. Figure 4 shows that the parallel and perpendicular $A_0$ peaks do not coincide, which probably indicates two independent transitions. Similarly, two independent transitions provide the simplest explanation of the temperature dependence of the polarization of peak $B_0$, with the assumption that one dominates at 77°K, the other at 4°K. The disappearance of peak $B_{31}$ at 4°K can then be correlated with the disappearance of one of the two components of $B_0$. The peak $C_0$ is too weak to measure accurately enough for any further analysis.

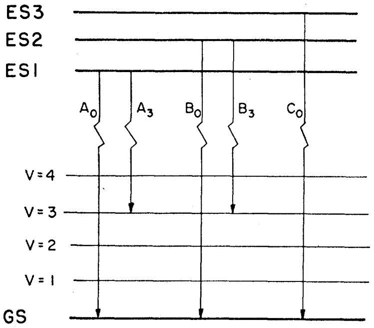

FIG. 5. A simple energy-level diagram of the kind which might be used to analyze the type $X$ spectrum. This diagram applies if there is a single luminescence center with three excited states. Several possible transitions are indicated. The transitions are considered to be from the zero vibrational level of one of the three excited states, to a vibrational level of the ground state.

The separation of the peaks $A_0-B_0$ is about $2kT$ at 77°K, and that of $B_0-C_0$ is about the same. Thus, their relative intensities appear reasonable on the assumption that there is a single luminescence center with three excited states in thermal equilibrium. At 4°K, however, one might expect not only the disappearance of $C_0$, but of $B_0$ also. It was suggested that one component does disappear. The other component is weak at 4°K, but does not disappear, and so may possibly belong to a different luminescence center.

For the sake of illustration, we have drawn an energy level diagram in Fig. 5, in which we consider the case of a single luminescence center with three excited states. Some of the possible transitions are indicated by the vertical lines. To account for the observed doubling of the peaks, one could postulate, for example, that the luminescence center may occupy two slightly different lattice sites.

### 8. PROBABLE LUMINESCENCE CENTERS

The small half-width, $kT/4$, of $A_0$ at 77°K enables us immediately to rule out intrinsic recombination radiation, for which, in SiC, a half-width of 3.5 $kT$ has been calculated.[26]

Similarly, we can rule out luminescence resulting from capture of a free hole or a free electron. Here the half-width is a function of the dependence of capture cross section on carrier energy, but can scarcely be as small as $kT/4$.

The possibility of exciton decay luminescence was excluded by a measurement of the absorption spectrum, which showed nothing that could be attributed to exciton absorption. (The experimental uncertainty in the absorption coefficient is not more than 10 cm$^{-1}$ at 2.85 ev, which is the energy of the emission line $A_0$.)[27]

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[24] W. J. Choyke and Lyle Patrick, Phys. Rev. **105**, 1721 (1957). See also the infrared measurements given in reference 6, or by Spitzer, Kleinman, and Walsh, Phys. Rev. **113**, 127 (1959).

[25] B. N. Brockhouse, Phys. Rev. Letters **2**, 256 (1959).

[26] See Sec. 5D of reference 5.

[27] We have recently made some better measurements of the absorption edge of 6H SiC. These measurements show a dependence on photon energy, at low absorption coefficients, which is of the kind recently found in Ge and Si, and which has been attributed to exciton absorption in which a phonon is simultaneously

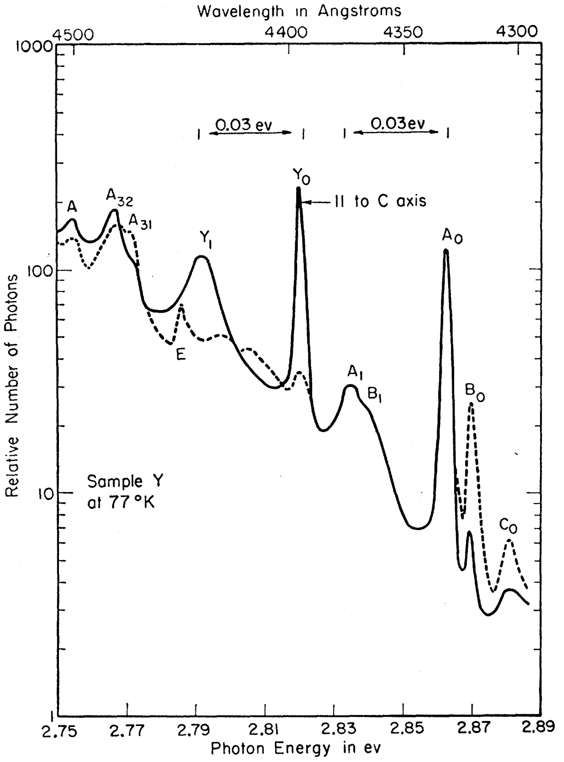

FIG. 6. The edge emission of Sample *Y* at 77°K. The peaks $A_0$, $B_0$, and $C_0$ differ from those of Sample *X* in energy, energy intervals, and relative intensities. $Y_0$ and $Y_1$ are the first two lines of a series which is observed in all *Y* samples.

Thus, of the three types of mechanisms for the production of polarized luminescence considered in Sec. 2, it is possible to rule out those in the first category, which depend on the symmetry of the conduction or valence bands.

We conclude that the optical transitions occur within a luminescence center which can bind both hole and electron in an excited state. The simple acceptors and donors of columns III and V cannot do this, but rare earths and iron group elements can. Rare earths will not be considered because they are not likely to be present. (See Sec. 3B.) On the other hand, several iron group elements are commonly found in SiC.

The spectra of iron group elements depend strongly on their surroundings. Some interesting examples of Mn *absorption* spectra have been reported by Gielessen.[28] For Mn in $MnCl_2 \cdot 4H_2O$, the spectrum includes a group of narrow absorption lines and several groups of broader lines, with a regular energy separation between groups. Allowing for the differences between absorption and emission spectra, one can see that Mn in SiC could possibly give rise to the kind of emission spectra we have observed. On the other hand, fine structure in iron group spectra is most often observed when the element is part of a complex.[15]

Of the third kind of polarized luminescence source described in Sec. 2, we shall consider only donor-acceptor pairs, shown in Sec. 3B to be very probable in our SiC samples.

Of all the possible sources of polarized edge emission, we conclude that iron group atoms and donor-acceptor pairs are the most probable. A further discussion of these two possibilities will be given after the type *Y* spectra have been considered.

## 9. EXPERIMENTAL RESULTS—*Y* CRYSTALS

We now present parts of the 77°K and 4°K spectra of Sample *Y*, which is one of a group of crystals with a characteristic pattern of edge emission lines which we call the type *Y* spectrum.

Sample *Y*, like Sample *X*, has a broad, polarized, green emission band in which no fine structure has been found. The degree of polarization at the 2.4-ev maximum is $P=+0.23$ at 77°K, and $P=+0.28$ at 4°K. As in Sample *X*, there is no dividing line between the blue edge emission and the green band. The resolution simply becomes increasingly poorer as one goes away from the edge.

The edge emission, which differs considerably from that of Sample *X*, is shown in Fig. 6. The perpendicular spectrum is omitted in one interval in which it is very close to the parallel spectrum. At 77°K, there are three narrow peaks, $A_0$, $B_0$, and $C_0$, with many of the characteristics of the corresponding peaks in Sample *X*, but differing from the *X* peaks in energy, energy intervals, and relative intensities, as shown in Table I. The $B_0$ and $C_0$ peaks disappear at 4°K.

At 2.82 ev, Sample *Y* has an additional narrow line (half-width $\sim kT/4$ at 77°K), which is very intense and strongly polarized at both 4°K and 77°K. Through vibrational interaction it gives rise to a new series of peaks marked $Y_0$, $Y_1$, etc. More peaks in this series are shown in Fig. 7 at 4°K. One observes a great similarity between the *A* and *Y* series of peaks. The energy spacing is 0.03 ev in both, as in the *A* series of Sample *X*. However, there are no extra peaks associated with $Y_0$ in the way that $B_0$ and $C_0$ are associated with $A_0$.

TABLE I. Comparison of narrow lines in *X* and *Y* spectra at 77°K.

| Line | Energy (in ev) *X* | *Y* | Relative intensity (as % of $A_{0\parallel}$) *X* | *Y* |
|---|---|---|---|---|
| $A_{0\parallel}$ | 2.850 | 2.862 | 100 | 100 |
| $A_{0\perp}$ | 2.851 | 2.863 | 11 | 97 |
| $B_{0\parallel}$ | 2.862 | 2.869 | 8 | 5 |
| $B_{0\perp}$ | | | 40 | 22 |
| $C_{0\parallel}$ | 2.872 | 2.881 | 5 | 3 |
| $C_{0\perp}$ | | | 3 | 5 |

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emitted or absorbed. As a result of these measurements we can state that the energy gap of 6H SiC at 77°K is somewhat larger than we reported in reference 24. Any luminescence resulting from the decay of these excitons would be found at a higher energy than the edge emission reported here.

[28] J. Gielessen, Ann. Physik 22, 537 (1935). See Fig. 2.

## 10. COMPARISON OF $X$ AND $Y$ SPECTRA

Figure 8 shows the energies of the most prominent peaks in both samples $X$ and $Y$. The peaks can be grouped into five series, each associated with a narrow primary peak, $A_0$ or $B_0$ in $X$, and $A_0$, $B_0$, or $Y_0$ in $Y$. The $C_0$ peaks are too weak to give rise to a similar $C$ series, although $C_1$ has been observed. The energy intervals between corresponding peaks in all series are substantially identical. Relative intensities of corresponding peaks vary somewhat from one series to another, but similarities can be found. For example, peaks with first subscript two are relatively weak in all series. They are sometimes barely observable, sometimes completely hidden by nearby peaks. Most of the missing lines in Fig. 8 are those of subscript two peaks. The polarization in a given series tends to be like that of the primary peak (subscript zero). For example, at 77°K, in Sample $Y$, the $A$ peaks are weakly polarized, like $A_0$, and the $Y$ peaks are strongly polarized, like $Y_0$.

The $B$ lines disappear at 4°K in Sample $Y$, and are weak in Sample $X$, thus behaving like the primary $B_0$ peaks. The disappearance of $B_0$ and $C_0$ in $Y$ suggests that these peaks arise from higher excited states which are depopulated at 4°K. $A_0$ is considered to be due to transitions from the lowest excited state. Whether or not a different interpretation is necessary for $X$ samples, because of the failure of $B_0$ to disappear completely at 4°K, is not known. More 4°K measurements are needed, with the temperature uncertainty eliminated by immersion of the sample in liquid helium.

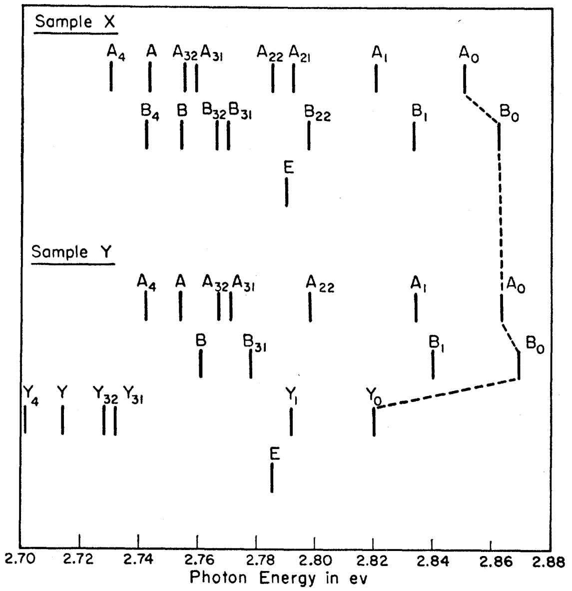

FIG. 8. Prominent lines in both $X$ and $Y$ samples. The energy intervals are identical in each of the five series ($A$ and $B$ series in $X$ samples, $A$, $B$, and $Y$ series in $Y$ samples). The series as a whole are displaced in energy, as indicated by the dotted line connecting the peaks with subscript zero. The lines missing in some series are either weak or are not detected because of strong nearby peaks. Those with subscript two are relatively weak in all series.

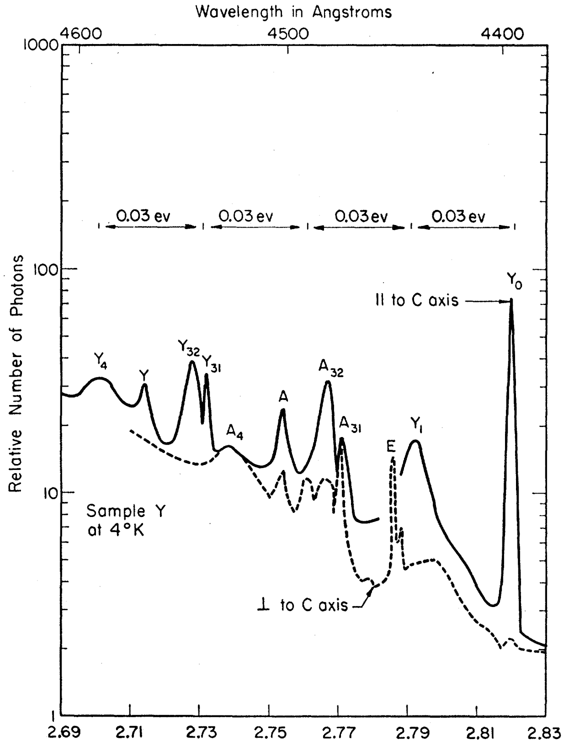

FIG. 7. Sample $Y$ at 4°K, in a somewhat lower energy interval, chosen to display the similarities in structure of the four $Y$ peaks at the left, and the corresponding $A$ peaks in the center. Off the scale at the right, $A_0$ and $A_1$ are still intense at 4°K, but $B_0$ and $C_0$ have vanished.

The fact that, in Sample $Y$, the peaks $A_0$ and $Y_0$ remain approximately equal in intensity at 4°K, indicates that these peaks result from transitions at two distinct centers, possibly due to two kinds of lattice sites for the center.

The spectra thus suggest one independent center in $X$ samples, two in $Y$ samples. In view of the similarities in the series of Fig. 8, it might be more satisfying to attribute the three series, $A$ in $X$ samples, and $A$ and $Y$ in $Y$ samples, to (a) three luminescence centers, or (b) three lattice sites, instead of to two luminescence centers, one of which has two lattice sites. However, (a) seems to be ruled out by the fact that, in all $Y$ samples examined, the ratio of $A_0$ and $Y_0$ intensities was the same; and (b) seems to be ruled out by the occurrence of both $X$ and $Y$ spectra in the same polytype.

Figure 8 also shows the double peak $E$, which appears in all samples, but does not fit into the patterns discussed above. Nor is its energy shift in going from $X$ to $Y$ samples related to that of any of the primary peaks $A_0$, $B_0$, or $C_0$. The width of $E$ is more strongly temperature dependent than that of the other peaks, but at 77°K the half-width is barely $kT$, although $E$ is known to be a double peak from the 4°K measurements. Hence, it is doubtful if it can be attributed to transitions involving free electrons or free holes. Intrinsic recombination radiation can be ruled out because of the width, and also because of the energy shift.

The intensity progression in the edge emission of SiC is quite different from that of the green edge emission of CdS, in which the intensity steadily decreases with increasing number of phonons, until the edge emission is no longer observable.[3] No such decrease is observed in SiC; hence, it is conceivable that the same luminescence center is responsible for both the blue edge emission and the broad green band. Presumably, the green emission would be accompanied by the emission of a large number of phonons. In all samples examined, the 2.4-ev band has been found if, and only if, edge emission is present (either $X$ or $Y$ type).

## 11. THE LUMINESCENCE CENTERS

In Sec. 8, it was concluded that the most probable centers were donor-acceptor pairs or iron group impurities. If the differences in $X$ and $Y$ spectra are to be attributed to different impurities, as suggested in Sec. 10, the donor-acceptor hypothesis is favored; the similarities of the $X$ and $Y$ spectra are more easily reconciled with the change of only part of the luminescence center than they are with the substitution of a totally different center.

Two other reasons for favoring donor-acceptor pairs are:

(1) In the following paper,[10] the calculated polarization of the radiation of donor-acceptor pairs is shown to be *consistent* with that found experimentally, although a decisive comparison cannot be made. The presence of several kinds of donor-acceptor sites is also noted.

(2) The narrow peaks are within a fifth of an electron volt of the energy gap of SiC. This is expected for donor-acceptor pairs, but would have to be considered accidental for iron group atoms.

## 12. SUMMARY

Two distinct types of polarized edge emission spectra have been found in relatively pure single crystals of SiC. Both types of spectra have narrow lines ($\sim kT/4$ at 77°K), ascribed to phonon-free transitions, and a large number of broader peaks, ascribed to the same electronic transitions, but going to an excited vibrational level of the ground state. Both types of spectra have a polarized broad green band which may possibly be attributed to the same luminescence centers, with the emission of many phonons.

The two types of spectra have never been found in the same crystal, but have been found in the same polytype ($6H$), and are therefore attributed to hole-electron recombination at different, but unknown, impurities. A number of single impurity centers have been ruled out, and, at present, donor-acceptor pairs are considered the most probable luminescence centers. It is hoped that further work will lead to identification of the centers.

## ACKNOWLEDGMENTS

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