

## Polarization of the Luminescence of Donor-Acceptor Pairs

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The polarization is calculated for donor-acceptor pair luminescence in SiC. Certain degrees of polarization depend only on the axial directions of the donor-acceptor pairs, thus permitting one to identify emission by such centers in SiC, or in other uniaxial crystals with tetrahedral bonds. A comparison with experiment is inconclusive because of insufficient resolution. The Prener-Williams conclusion about nearest-neighbor donor-acceptor pairs are discussed.

### INTRODUCTION

THE previous paper<sup>1</sup> (CHP) reported a strongly polarized edge emission in the photoluminescence of SiC single crystals. It was shown that the edge emission is not an intrinsic property of the pure crystal, but depends on some activating impurities not yet identified. The luminescence centers suggested as most probable were iron group elements and donor-acceptor pairs (DA pairs). The present paper will consider the polarization properties of DA pair emission, and will show that certain degrees of polarization can be used to distinguish between DA pairs and the iron group elements. These degrees of polarization depend only on the bond directions, which are possible axial directions of the DA pairs. Thus, they should also be found in DA edge luminescence in other uniaxial single crystals which have tetrahedral bonding, e.g., ZnS and CdS.

It is suggested that DA pairs may contribute not only to edge luminescence, but also, through multiphonon emission, to broad band emission at energies far from the absorption edge.

### THE LUMINESCENCE CENTER

We consider only nearest neighbor DA pairs, at substitutional positions in the lattice. Including atoms to which the DA pair is bonded, the DA luminescence center in SiC may be represented by whichever is the more stable of the two configurations, 3Si-A-D-3C or 3Si-D-A-3C.

One point of view is to consider the DA pair as a dipole imbedded in the lattice; D is positive, A negative. The dipole has shallow trapping levels for either holes or electrons.<sup>2</sup> After trapping a carrier, the center attracts the carrier of opposite sign, for which the trapping level is now somewhat deeper.

Another point of view is to consider the DA pair as a heteronuclear diatomic molecule (with an even number of electrons). Bonding reduces the symmetry of the "molecule" from  $C_{\infty v}$  to  $C_{3v}$ .

The axis of the DA pair lies along one of the tetrahedral bond directions, but in a uniaxial crystal the

tetrahedra are elongated or contracted in the direction of the crystal  $c$  axis. Centers with the DA axis along the  $c$  axis will be called  $c$  centers. The others, oriented along the three still equivalent tetrahedral directions, will be called  $t$  centers. The distortion of the tetrahedra may have several effects significant for the luminescence:

- (a) a difference in wavelength of the  $c$  and  $t$  emission,
- (b) a difference in the distribution of DA pairs between  $c$  and  $t$  sites during crystal growth,
- (c) a difference between  $c$  and  $t$  centers in their capture cross sections for holes and electrons.

A closer examination shows that the  $t$  centers do not have the full  $C_{3v}$  symmetry because one of the three Si bonds and one of the three C bonds lie along the crystal axis, and so are not equivalent to the other Si and C bonds. The symmetry of the  $t$  center is reduced to  $C_s$ , the only symmetry element being a plane, parallel to the  $c$  axis, which contains the DA axis and the 2 bonds which lie along the  $c$  axis.

Another point to notice is that although the symmetry for  $c$  centers is always  $C_{3v}$ , the 3 Si atoms may or may not coincide with the 3 C atoms when viewed along the crystal axis. In SiC, polytype 6H, the order of occupied sites in the (0001) planes is given by the sequence  $ABCACB\cdots$ <sup>3</sup> for either Si atoms or C atoms. When both Si and C atoms are considered simultaneously, the sequence of sites may be written  $AABBCAACCCBB\cdots$ . A DA pair lying along the  $c$  axis fills two similar sites and may be represented by underlining 2 similar neighboring letters in the above sequence of letters. The 3 C or 3 Si atoms bonded to the DA pair then fall into sites represented by letters neighboring the underlining pair. These will be bracketed. Examples of the two kinds of  $c$  sites for DA pairs are the following,

$$AABBC(C)\underline{AA}(C)CBB\cdots \quad (1)$$

$$AAB(B)\underline{CC}(A)ACCBB\cdots, \quad (2)$$

in which the bracketed letters are similar in (1), representing similar orientation of the 3 Si and 3 C atoms about the crystal axis; and dissimilar in (2), representing a 60° relative orientation about the axis.

Hence there are two kinds of  $c$  luminescence centers

<sup>1</sup> Choyke, Hamilton, and Patrick, Phys. Rev. **117**, 1430 (1960), preceding paper.

<sup>2</sup> J. S. Prener and F. E. Williams, Phys. Rev. **101**, 1427 (1956).

<sup>3</sup> See reference 9 of CHP.

TABLE I. Selection rules for  $C_{3v}$  symmetry.

Final state	Initial state		
	$A_1$	$A_2$	$E$
$A_1$	$\pi$	0	$\sigma$
$A_2$	0	$\pi$	$\sigma$
$E$	$\sigma$	$\sigma$	$\pi, \sigma$

in the  $6H$  polytype. This may lead to a doubling of the spectral lines or bands belonging to the  $c$  centers. A prediction of relative intensities cannot be made; the three factors listed above in discussing the differences between  $c$  and  $t$  centers are also significant here.

### SELECTION RULES

Group theory may be used to derive selection rules<sup>4</sup> for electric dipole transitions within the DA center. For a center with point group symmetry  $C_{3v}$ , and an even number of electrons, the wave functions must belong to one of three irreducible representations,<sup>5</sup> two of which are one-dimensional (designated by  $A_1$  and  $A_2$ ), and the third two-dimensional ( $E$ ). The selection rules for electric dipole transitions between two states depend only on the representations,  $A_1$ ,  $A_2$ , or  $E$ , to which those states belong, and are given in Table I. The symbols  $\pi$  and  $\sigma$  mean that the transition is allowed, with radiation polarized parallel ( $\pi$ ) or perpendicular ( $\sigma$ ) to the axis of the DA pair. Except for a transition between two states belonging to the representation  $E$ , all allowed transitions are fully polarized ( $\pi$  or  $\sigma$  but not both). Only the fully polarized transitions will be considered in our example in the next section.

Group theory correlation tables<sup>6</sup> show that the twofold degeneracy of the  $E$  state will be lifted by a reduction of symmetry to  $C_s$ , such as occurs for the  $t$  centers. Instead of an  $E-A_1$  transition, with  $\sigma$  polarization, there are now two transitions. Selection rules for  $C_s$  symmetry show that both transitions are polarized, one perpendicular and one parallel to the symmetry plane. The transition polarized perpendicular to the symmetry plane is also perpendicular to the crystal axis. For the transition parallel to the symmetry plane, however, the degree of polarization cannot be calculated, since it is not isotropic in the plane, the axial direction of the DA pair being a special direction in that plane. Because of this indefiniteness, only  $C_{3v}$  symmetry will be considered in comparing calculated and experimental degrees of polarization. It is not known whether or not the lifting of the degeneracy is great enough to be observed experimentally.

<sup>4</sup> R. S. Mulliken, Phys. Rev. 43, 279 (1933).

<sup>5</sup> Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), p. 384.

<sup>6</sup> Wilson, Decius, and Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955), p. 334.

### A SPECIFIC EXAMPLE

We do not know what states to postulate for the DA pair, with  $C_{3v}$  symmetry, but for the sake of definiteness we shall consider the specific example of Fig. 1 in which we specify only the representation to which the state belongs. The ground state is assumed to be of type  $A_1$ , which is the type corresponding to zero angular momentum. The excited states are chosen to give one  $\pi$  oscillator and one  $\sigma$  oscillator. With  $\pi$  and  $\sigma$  oscillators at  $c$  and  $t$  sites, this simple model gives four oscillators which may be designated  $\pi_c$ ,  $\sigma_c$ ,  $\pi_t$ , and  $\sigma_t$ .

The degree of polarization  $P \equiv (P_{11} - P_{\perp}) / (P_{11} + P_{\perp})$  refers to the crystal axis. As the  $c$  centers lie along the  $c$  axis, the resulting polarization can be given immediately by  $P = +1$  for  $\pi_c$  and  $P = -1$  for  $\sigma_c$ . For the  $t$  centers, the three vectors representing their directions must be projected onto directions parallel and perpendicular to the crystal axis. Squaring and adding components to get intensities, one finds  $P = -0.6$  for  $\pi_t$  (a polarization ratio of 4 to 1, predominantly perpendicular to the  $c$  axis), and  $P = +0.23$  for  $\sigma_t$  (a ratio of 1.6 to 1, predominantly parallel to the axis). Assuming fully polarized transitions (valid for a nondegenerate ground state), it is the two numbers  $P = -0.6$  and  $P = +0.23$  that are characteristic of DA luminescence, since they are characteristic of the nonaxial bond directions; whereas, for single atom impurities, the only axis fixing the polarization direction is the crystal axis, (neglecting a possible Jahn-Teller distortion).

### COMPARISON WITH EXPERIMENTAL DATA

In comparing the polarization predictions of the DA model with experiment, it is sufficient to consider, in the experimental data, only those peaks with subscript zero. A different subscript simply means that a certain number of phonons are also emitted in the transition. As an example of how the experimental data may be interpreted, the four oscillators  $\pi_c$ ,  $\sigma_c$ ,  $\pi_t$ ,  $\sigma_t$  of Fig. 1 will be used to fit the two unresolved double peaks  $A_0$  and  $B_0$  (the weak peak  $C_0$  being disregarded).

In the 77°K data of Fig. 4 in CHP, the values of  $P$  are such that only one assignment of the four oscillators to the four peaks is possible. That assignment is given by  $A_0 = \pi_c + \pi_t$  and  $B_0 = \sigma_c + \sigma_t$ , with the weaker peaks in  $A_0$  and  $B_0$  both being ascribed to  $t$  oscillators. Since

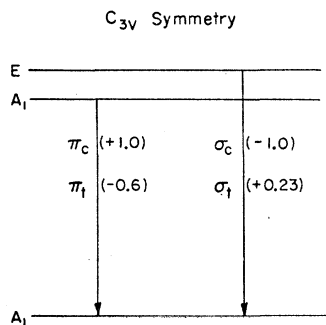


FIG. 1. An energy-level diagram for a DA luminescence center with excited states of  $A_1$  and  $E$  symmetry, and a ground state of  $A_1$  symmetry. The calculated degrees of polarization for electric dipole radiation are indicated for both  $c$  and  $t$  centers. The degrees of polarization of the  $t$  centers,  $P = -0.6$  and  $P = +0.23$ , are characteristic of DA luminescence.

these weak peaks are not resolvable, one cannot find the values of  $P$  characteristic of the DA model. On our model, the splitting between  $c$  and  $t$  levels due to tetrahedral distortion (observable only for the  $\pi$  oscillators) is  $10^{-3}$  eV, the separation between the two  $A_0$  peaks. The polarization ratios exclude the possibility that either  $A_0$  or  $B_0$  is made up of  $t$  oscillators alone, hence that the  $c$ ,  $t$  splitting is the larger interval  $A_0 - B_0$ . In spite of the small splitting, it appears that most radiative transitions occur at  $c$  sites.

The extra peak marked  $Y_0$  in the  $Y$  samples may be assigned to  $\pi_c$  at the second kind of  $c$  center expected in  $6H$  polytype. This is consistent with the observation that  $Y_0$  is fully polarized. The reason why the second site should be important in  $Y$  samples but not in  $X$  samples is not evident, since both are predominantly  $6H$  polytype.

With the above assignment of oscillators it is possible to account for the change in sign of the polarization of  $B_0$  (Fig. 4 of CHP) in going from  $77^\circ\text{K}$  to  $4^\circ\text{K}$ , by saying that the oscillator  $\sigma_c$  predominates at  $77^\circ\text{K}$ , but that  $\sigma_t$  predominates at  $4^\circ\text{K}$ . The experimental value of  $P = +0.3$  at  $4^\circ\text{K}$  does not agree very well with the expected value of  $P = +0.23$ , but it may be within experimental error.

To account for the weak peak  $C_0$  it is necessary to postulate a third excited state. In addition, there are differences between  $X$  and  $Y$  spectra that are not yet explained.

It is apparent that an adequate comparison of theory and experiment requires either better resolution in the experimental data, or a better theory to predict quantitatively the energy levels of a DA center. However, the experimental results appear to be consistent with those expected for DA pairs.

#### THE PRENER-WILLIAMS MODEL

For ZnS and similar phosphors, Prener and Williams<sup>7</sup> have suggested that DA pairs, as nearest neighbors, may account for the edge luminescence, and that donor acceptor pairs, as second or third nearest neighbors (designated here as  $D \cdots A$  pairs) may account for the broad band luminescence at energies considerably less than the energy gap. Their estimates<sup>8</sup> indicate that the number of DA pairs will normally exceed the number of  $D \cdots A$  pairs for ZnS. Similar calculations show that DA pairs should also predominate for SiC. Whether DA or  $D \cdots A$  luminescence predominates depends not only on the relative numbers of centers present, but on their radiative recombination cross sections for holes and electrons, and cannot easily be predicted. Therefore, as a possible means of distinguishing these centers, it is worth while considering the polarization of radiation from  $D \cdots A$  centers also.

The fundamental reason for the polarization of the edge emission in SiC, according to our interpretation, is the differentiation of  $c$  and  $t$  sites for DA pairs. Both  $\pi$  and  $\sigma$  oscillators would emit unpolarized light if the  $c$  and  $t$  sites could not be distinguished in any way. With this in mind, we consider the situation for  $D \cdots A$  pairs. For second or third nearest neighbors, there are a large number of possible axial directions. Furthermore, these directions are not those of the tetrahedral bonds, and so they are not as strongly differentiated by the tetrahedral distortion as are the  $c$ ,  $t$  directions of the DA axes. It therefore seems unlikely that  $D \cdots A$  luminescence will be strongly polarized.

Experimentally, a close correlation between edge luminescence and the broad peak at 2.4 eV was found in all samples examined by CHP. This correlation can be explained by attributing the 2.4-eV peak to the DA pairs which emit the edge luminescence, or to  $D \cdots A$  pairs, which must also be present. However, for the broad 2.4-eV peak at  $4^\circ\text{K}$ , the light polarized parallel to the  $c$  axis exceeded that perpendicular to the axis by 1.6 in Sample  $X$ , and by 1.8 in Sample  $Y$ . This is the preferred polarization direction of the edge emission, and the stronger polarization in Sample  $Y$  can be correlated with the fact that there is an additional series of lines in the edge emission of that sample which are fully polarized parallel to the  $c$  axis. This polarization suggests that the broad 2.4-eV peak should also be attributed, at least in part, to DA pairs. In this case, one would conclude that in most DA transitions a large number of phonons are emitted (less than  $10^{-3}$  of the light appears in the narrow peaks  $A_0$ ,  $B_0$ , and  $C_0$  of Sample  $X$  at  $77^\circ\text{K}$ ).

In other phosphors activated by DA pairs, it is conceivable that the proportion of edge emission may be considerably less than in SiC. Thus, one should not exclude the possibility that a phosphor may be activated by DA pairs (as nearest neighbors), even if no edge emission is observed.

#### SUMMARY

Nearest neighbor DA pairs in a SiC lattice will have their axes along the tetrahedral bond directions. The small tetrahedral distortion is sufficient to differentiate two kinds of DA sites, called  $c$  and  $t$  sites, and hole-electron recombination at these sites will result in polarized edge emission. The polarization ratios of the  $t$  center luminescence, if observable experimentally, should serve to identify this kind of edge emission.

The strongly polarized edge emission found by CHP is probably due to DA pairs, but the fact that certain peaks ( $A_0$  and  $B_0$ ) are unresolved double peaks makes it impossible to find the characteristic polarization ratios of DA luminescence. It is suggested that DA pairs may also contribute to emission bands far from the absorption edge, with the simultaneous emission of a large number of phonons.

<sup>7</sup> J. S. Prener and F. E. Williams, J. phys. radium 17, 667 (1956); J. Chem. Phys. 25, 361 (1956).

<sup>8</sup> J. S. Prener and F. E. Williams, Phys. Rev. 101, 1427 (1956); J. S. Prener, J. Chem. Phys. 25, 1294 (1956).