

in the injection efficiency for electrons as compared to holes can be attributed to the difference in their mobilities. With this relatively simple model we have been able to quantitatively describe the essential features of the experimental results for low light energies.

Based on a simple interpretation of the results obtained so far the generation efficiency could be expected to be unity for energies greater than u_G . However, the data presented by Tabak and Warter² for $\lambda=4000$ and 4300 Å (Figs. 1 and 6 in their paper) show a rather striking kink at about $E=10^4$ V/cm from roughly linear to square-root dependence on the field which clearly indicates that the generation efficiency is not unity and is field dependent at these light energies. Actually in comparing the data of Pai and Ing¹ and Tabak and Warter² for high-energy light we are faced with a conflict. The data for $\lambda=4500$ Å in Fig. 8 of the former's paper shows the log of the pulse height to be proportional to \sqrt{E} in the high-field region but the latter's data for $\lambda=4300$ Å indicate

the peak photocurrent to be directly proportional to \sqrt{E} in the same region.

At this point we can only speculate on the processes involved for light energies near the effective band gap u_G and greater. This will be an interesting area for further investigation. The exact relevance of the effective band gap u_G in our model and how it may be related to the activation energy involved in the expression for the mobility is an interesting question. We feel that the distinction between the photoinjection process and the photogeneration process will be useful in further investigation of the photodischarge process.

ACKNOWLEDGMENTS

I would like to express my thanks for the stimulating discussions and critical comments by my colleagues here, I. P. Batra, W. D. Gill, K. K. Kanazawa, R. M. Macfarlane, B. H. Schechtman, and B. D. Silverman. The support given by E. Kay has been most helpful in this work.

- ¹ D. M. Pai and S. W. Ing, Jr., Phys. Rev. **173**, 729 (1968).
- ² M. D. Tabak and P. J. Warter, Jr., Phys. Rev. **173**, 899 (1968).
- ³ J. Frenkel, Phys. Rev. **54**, 647 (1938).
- ⁴ A. Many, J. Phys. Chem. Solids **26**, 575 (1965).
- ⁵ I. T. Johansen, J. Appl. Phys. **37**, 499 (1966).
- ⁶ H. Hirose and Y. Wada, Jap. J. Appl. Phys. **4**, 639 (1965).
- ⁷ C. A. Mead, Phys. Rev. **128**, 2088 (1962).
- ⁸ T. E. Hartman, J. C. Blair, and R. Bauer, J. Appl. Phys. **37**, 2468 (1966).
- ⁹ G. A. Dussel and R. H. Bube, J. Appl. Phys. **37**, 2797 (1966).

- ¹⁰ J. G. Simmons, Phys. Rev. **155**, 657 (1967).
- ¹¹ A. K. Jonscher, Thin Solid Films **1**, 213 (1967).
- ¹² J. L. Hartke, J. Appl. Phys. **39**, 4871 (1968).
- ¹³ Frederick Seitz, *The Modern Theory of Solids* (McGraw-Hill, New York, 1940), p. 161.
- ¹⁴ Charles Kittel, *Introduction to Solid State Physics*, 2nd ed. (Wiley, New York, 1956), p. 358.
- ¹⁵ W. E. Spear, Proc. Phys. Soc. (London) **76**, 826 (1960).
- ¹⁶ J. M. Caywood and C. A. Mead, Appl. Phys. Letters **15**, 14 (1969).

Phosphorus Clusters in ZnSe†

R. K. WATTS AND W. C. HOLTON

Texas Instruments Incorporated, Dallas, Texas 75222

(Received 13 July 1970)

The electron paramagnetic resonance of a center consisting of four phosphorus ions in ZnSe is reported. The paramagnetism is localized primarily on one phosphorus, and a smaller superhyperfine interaction with the other three is observed. The observed spin Hamiltonian parameters are $g_{||}=1.997$, $g_{\perp}=2.034$, $A_{||}=591\times 10^{-4}$ cm⁻¹, $A_{\perp}=445\times 10^{-4}$ cm⁻¹, $K_{||}=19.0\times 10^{-4}$ cm⁻¹, $K_{\perp}<2.5\times 10^{-4}$ cm⁻¹. The center has trigonal symmetry with a $\langle 111 \rangle$ axis, and the phosphorus ions are located at the points of a regular tetrahedron.

INTRODUCTION

The association of two or more atoms of the same kind in a compound semiconductor has been observed in several cases. Six fluorines can surround an iron in CdTe.¹ Four noble metals associate with an interstitial rare earth in CdTe² and ZnSe.³ Rare-earth and 3d transition-metal fluoride molecules can be incorporated in ZnS.⁴ Centers consisting of three associated lithiums have been observed in GaP,⁵ and of two associated silicons in GaAs.⁶ This paper reports

observation by electron paramagnetic resonance of a cluster of four phosphorus ions in ZnSe.

EXPERIMENTAL PROCEDURES

ZnSe powder was compounded by allowing molten 6N pure zinc to react with a flowing stream of H₂Se gas. The powder produced was then sublimed in vacuum to a higher-density mass of more uniform stoichiometry. A small amount of phosphorus dopant was added, and single crystals were grown in a sealed ampoule by a gradient-freeze technique.⁷ The volatility

of phosphorus made such a growth method necessary. The details of this procedure may be found in Ref. 7.

Single crystals of sphalerite structure were cleaved from the boules and mounted against the lower end of a light pipe inside the microwave cavity with a {110} cleavage face parallel to the plane of rotation of the dc magnetic field. All measurements were made with a superheterodyne X-band spectrometer with the sample usually at 77°K. The light pipe of Infrasil quartz extends along the axis of the erect TE_{101} right circular cylindrical cavity, allowing the sample to be illuminated while the electron paramagnetic resonance (EPR) signal is monitored. Illumination is provided by a 1.5-kW BH6 mercury-arc lamp and a prism monochromator.

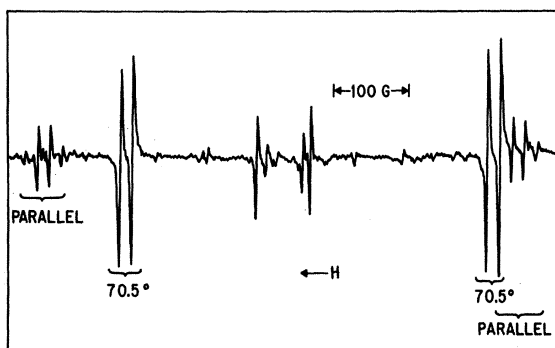


FIG. 1. These spectra are observed at 9.4 GHz and 77°K with the magnetic field along a $\langle 111 \rangle$ direction. The resonances from centers whose symmetry axes are parallel to the magnetic field are marked "parallel" and those due to centers whose axes are the other three $\langle 111 \rangle$ directions, making an angle of 70.5° with the field, are marked "70.5°." Resonances at the center of the figure are of unknown origin.

PARAMAGNETIC RESONANCE SPECTRA

With the sample at 77°K the spectra shown in Fig. 1 are observed near $g=2$. The signal intensity increases upon irradiation of the sample with light of wavelength less than 0.50 μ . Light of wavelength longer than 0.55 μ quenches the resonances lightly. The small unmarked resonances at the center of the figure are of unknown origin (but are probably due to phosphorus) and will not be discussed; when the magnetic field is rotated these lines split but do not mingle with lines due to the center of interest here. A weak spectrum of Mn^{2+} is also seen in Fig. 1.

The doubling of the spectrum (two groups marked parallel and two marked 70.5°) evident in Fig. 1 is due to a large hyperfine interaction with a single 100% abundant isotope with nuclear spin $I=\frac{1}{2}$. The spectrum has $\langle 111 \rangle$ axial symmetry. When the magnetic field is parallel to $\langle 111 \rangle$ it is along the axis of one-fourth of the centers and makes an angle of 70.5° with the axes of three-fourths of the centers. Superimposed on the large hyperfine splitting is a

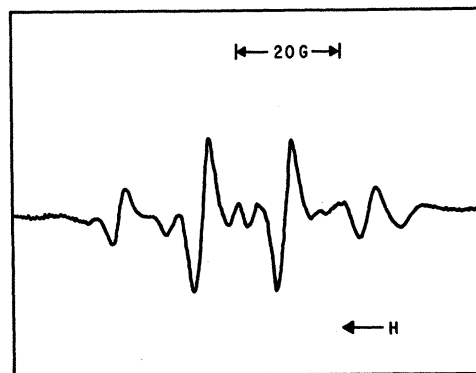


FIG. 2. High-field group of the "parallel" spectrum of Fig. 1 is shown in more detail. The intensities of the four main lines are in the ratios 1:3:3:1.

smaller superhyperfine interaction which splits each component of the parallel spectrum into four lines and each component of the 70.5° spectrum into two lines, the magnitude of the splitting between adjacent lines being the same in the two cases.

Figure 2 shows more clearly one of the groups of the parallel spectrum. The strong lines have relative intensities 1:3:3:1, indicating a superhyperfine interaction with three equivalent 100% abundant isotope nuclear spins $\frac{1}{2}$. The two weak satellites about each of the four main lines are 14% as intense as the main line. These may be due to a superhyperfine interaction with three equivalent selenium nuclei. Since Se^{77} with nuclear spin $\frac{1}{2}$ is 7.50% abundant, the satellites should be 11.2% as intense as the main line, if they are due to Se.

We shall assume that the four nuclei which produce the prominent interactions discussed above are phosphorus. P^{31} is the only naturally occurring isotope and the nuclear spin is $\frac{1}{2}$. It is possible that some other ion with spin $\frac{1}{2}$ and a singly naturally occurring isotope, not intentionally added to the melt, is present in the observed center, but because of the strength of the resonance signal we consider this possibility remote. The spin Hamiltonian describing the resonance of one of the centers is written

$$\mathcal{H} = g_{||}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{||}I_z S_z + A_{\perp}(I_x S_x + I_y S_y) + \sum_{i=1}^3 \mathbf{I}^i \cdot \mathbf{K}^i \cdot \mathbf{S}. \quad (1)$$

TABLE I. Observed parameters.

$g_{ } = 1.997 \pm 0.001$
$g_{\perp} = 2.034 \pm 0.003$
$A_{ } = (591 \pm 4) \times 10^{-4} \text{ cm}^{-1}$
$A_{\perp} = (445 \pm 7) \times 10^{-4} \text{ cm}^{-1}$
$K_{ } = (19.0 \pm 0.5) \times 10^{-4} \text{ cm}^{-1}$
$K_{\perp} < 2.5 \times 10^{-4} \text{ cm}^{-1}$

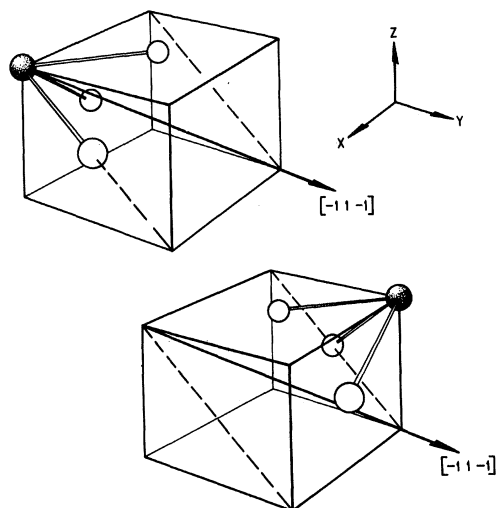


FIG. 3. Centers with symmetry axes $[111]$ (upper) and $[111]$ (lower). The tetrahedra are shown inscribed in cubes for clarity. The x , y , z axes are $\langle 100 \rangle$ directions. The dark ball represents the phosphorus on which the paramagnetism largely resides.

$A_{||}$ and A_{\perp} describe the large P^{31} hyperfine interaction. The axis of \vec{g} and \vec{A} is $\langle 111 \rangle$. \vec{K} describes the superhyperfine interaction with the other three P^{31} nuclei. The axis of \vec{K}^i is a $\langle 110 \rangle$ direction, and K_{\perp} is small, leading to the doublet structure of the 70.5° spectrum. $S=I=I^i=\frac{1}{2}$. The Se hyperfine structure is not sufficiently prominent to warrant analysis. The values of the parameters are given in Table I. If $K_{\perp}^i=0$ then when the magnetic field is parallel to $[111]$ the angle between the field and the three $\langle 110 \rangle$ axes of the \vec{K} 's is 35.3° for the centers whose symmetry axes are $[111]$, leading to the observed four-line pattern with splitting, $K^i=K_{||}\cos(35.3^\circ)$. For the other centers, as for example, those whose symmetry axis is $[111]$ (see Fig. 3), the angles between the field and the axes of the three \vec{K} 's are 90° , 90° , and 35.3° , leading to a two-line pattern with splitting $K^i=K_{||}\cos(35.3^\circ)$ also.

DISCUSSION

The resonance is evidently due to a center comprised of four phosphorus ions located at the points of a regular tetrahedron, oriented as shown in Fig. 3. The paramagnetism is largely concentrated on one of these. Unfortunately, there seem to be few other conclusions which can be safely drawn. The com-

ponents of the hyperfine tensor can be written (in G)

$$A_{||}=a\alpha^2+2b\beta^2, \quad A_{\perp}=a\alpha^2-b\beta^2, \quad (2)$$

where

$$a=8\pi|\psi_s(0)|^2\mu/3I, \quad b=2\langle r^{-3} \rangle_p\mu/5I. \quad (3)$$

α^2 and β^2 are the densities in the phosphorus $3s$ and $3p$ orbitals. $|\psi_s(0)|^2$ is the $3s$ orbital density at the nucleus, and $\langle r^{-3} \rangle_p$ is the expected value of r^{-3} for an electron in the $3p$ orbital. μ is the nuclear magnetic moment of P^{31} . If core polarization is ignored and a and b are known, then α^2 and β^2 can be calculated from the observed values of $A_{||}$ and A_{\perp} .

Hartree-Fock values^{8,9} of $|\psi_s(0)|^2$ and $\langle r^{-3} \rangle_p$ for the free ions P^- , P^0 , and P^+ have been plotted versus charge state and extrapolated to obtain values of a and b for the range of charge states P^{2-} to P^{4+} . For the experimentally observed hyperfine parameters, β^2/α^2 (the ratio of p to s occupation) varies from 2.7 for P^{4+} to 6.4 for P^{2-} ; and $\alpha^2+\beta^2$ (the total density on this phosphorus) varies from 0.35 for P^{4+} to 1.2 for P^{2-} . Thus the density is largely concentrated in the p orbital. The g factors are those expected for the p^5 configuration in a trigonal field.¹⁰ The p^5 configuration results for P^{2-} , assuming that the $3s$ electrons are not promoted to the p shell.

It is not possible to infer from the data the lattice position occupied by the tetrahedron of four phosphorus ions. There are four positions in the lattice where such tetrahedra occur: The nearest neighbors of each substitutional site and the four common ions about each interstitial site. All of these sites have three seleniums nearby which would be equivalent when the magnetic field is parallel to a $\langle 111 \rangle$ direction. It seems most likely that phosphorus would substitute for the four zincs about one of the two interstices, one phosphorus having (approximately) the $(3s)^2(3p^5)$ configuration and the others, $(3s)^2$. Thus the complex $[P^{2-}_{Zn2+}, 3P^{3+}_{Zn2+}]^-$ has one excess negative charge. It is interesting to note that the P_4O_6 , P_4O_{10} , and P_4S_{10} molecules have the same structure¹¹ as the complex and its immediate neighbors would have at this site. A compensating defect along the trigonal symmetry axis could make the phosphorus on which the paramagnetism resides inequivalent to the other three.

ACKNOWLEDGMENT

We thank R. D. Stinedurf for growing the ZnSe crystals.

[†] Research supported in part by the Air Force Office of Scientific Research under Contract No. F44620-67-C-0073.

¹ L. C. Kravitz and W. W. Piper, Phys. Rev. **146**, 322 (1966).

² R. K. Watts and W. C. Holton, Phys. Rev. **173**, 417 (1968).

³ J. D. Kingsley and M. Aven, Phys. Rev. **155**, 235 (1967).

⁴ D. Kahng, Appl. Phys. Letters **13**, 210 (1968).

⁵ R. S. Title and T. S. Plaskett, Appl. Phys. Letters **14**, 76 (1969).

⁶ W. G. Spitzer and W. Allred, J. Appl. Phys. **39**, 4999 (1968).

⁷ W. C. Holton, R. K. Watts, and R. D. Stinedurf, J. Crystal Growth **6**, 97 (1969).

⁸ E. Clementi, IBM J. Res. Develop. **9**, 2 (1965).

⁹ C. Froese, J. Chem. Phys. **45**, 1417 (1966).

¹⁰ W. C. Holton, A. R. Reinberg, R. K. Watts, and M. de Wit, J. Luminescence **1**, 2, 583 (1970); R. K. Watts, W. C. Holton, M. de Wit, and A. R. Reinberg, Phys. Rev. B (to be published).

¹¹ A. F. Wells, *Structural Inorganic Chemistry* (Oxford U. P., London, 1967), pp. 645 and 657.