Zeeman Effect of Bound Excitons in Gallium Phosphide

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The Zeeman effect of the recombination radiation from bound exciton complexes in GaP was investigated as function of direction of the magnetic field in the crystal. Cubic anisotropy was observed in the Zeeman pattern. This was analyzed using an effective spin Hamiltonian for the bound holes; numerical values of the constants in the spin Hamiltonian and g values of the electrons were determined from the data.

1. INTRODUCTION

IN the preceding paper,[1] three sharp lines called A, B, and C in the optical spectrum of GaP were described. On the basis of the evidence discussed there, which is further strengthened by the analysis of the anisotropy of the Zeeman effect presented below, the following centers are assumed to be responsible for these lines.

Line C arises from the recombination of an indirect exciton bound to a neutral donor; it has an energy of 2.3101 eV while the free exciton has an energy of about 2.315±0.005 eV and the indirect band gap is about 2.325±0.005 eV at 0°K. The two electrons (from the X_1 band edge) of the complex are in orbital singlet states and their spins are paired off. Lines A and B arise from an exciton bound to an ionized donor. They have energies of 2.3177 and 2.3168 eV, respectively. Since the center is tightly bound, its electron must be derived from a conduction band minimum lying above the band edge, probably the [000] minimum.

The Zeeman effect of lines B and C shows anisotropy when the direction of the magnetic field relative to the crystal axes is changed. In this paper we account for this anisotropy in terms of the anisotropy of the magnetic properties of the holes, and we determine from the data the values of the spin Hamiltonian parameters of the holes and the g values of the electrons.

2. THE SPIN HAMILTONIAN OF THE HOLE

A hole bound to an impurity center in a cubic crystal can have a fourfold or a twofold degeneracy.[2] The ground state is expected to be fourfold degenerate, and so its magnetic behavior can be described by a spin Hamiltonian with spin $J=\frac{3}{2}$.

$$\mathcal{H}=\beta[K\mathbf{J}\cdot\mathbf{H}+L(J_x^3H_x+J_y^3H_y+J_z^3H_z)], \quad (1)$$

where β is the Bohr magneton, x, y, z refer to the cube axes, and K and L are constants. That (1) is the most general linear Zeeman Hamiltonian for $J=\frac{3}{2}$ in cubic symmetry was shown by Luttinger[3] and other authors. The first term is isotropic, the second term, in L, is not.

The constants K and L have no simple relation to fundamental band structure constants. The effective mass Hamiltonian of a free hole depends on five such constants[3]; it is given by

$$\mathcal{H}_f=\frac{1}{m}[(\gamma_1+\tfrac{5}{2}\gamma_2)\mathbf{k}'^2-\gamma_2(k_x'^2J_x^2+\text{c.p.}) -2\gamma_3(\{k_x'k_y'\}\{J_xJ_y\}+\text{c.p.})] +\beta[\kappa\mathbf{J}\cdot\mathbf{H}+q(J_x^3H_x+\text{c.p.})], \quad (2)$$

where $\mathbf{k}'=\mathbf{k}+e\mathbf{A}/\hbar c$ and $\mathbf{A}$ is the vector potential of $\mathbf{H}$. The constants γ_1, γ_2, γ_3 characterize the orbital motion. The term proportional to the magnetic field depends on an apparent spin moment which is determined by the constants κ and q. The constant q would vanish in the absence of spin-orbit coupling and so it is much smaller than κ; a typical value is $q\sim10^{-3}\kappa$ for germanium.[4] The constants κ and q contribute explicitly to the Zeeman splitting of a hole (free or bound), but the orbital degeneracy of the acceptor state results in an orbital magnetic moment which also contributes to the splitting. The situation is similar to that of a free atom in an orbitally degenerate state: The last two terms of Eq. (2) correspond to the magnetic interaction of the spin moment, the first three terms give contributions analogous to the interaction of an orbital moment, and the effective Hamiltonian, Eq. (1), describes the resulting anomalous Zeeman effect with the constants K and L corresponding to the Landé g factor.

Two conclusions can now be drawn. First, the values of K and L are expected to differ in different complexes, since the orbital contribution is determined by the particular state of binding. Second, the ratio L/K is expected to be appreciable even though q/κ may be negligible; this is because the anisotropy in the effective mass, which is not negligible, is reflected through the orbital motion in the anisotropy of the total effective moment.

3. LINE C

The upper level has two electrons in orbital singlets and with antiparallel spins, and a hole (see Fig. 2, preceding paper). It has the spin Hamiltonian given

[1] D. G. Thomas, M. Gershenzon, and J. J. Hopfield, preceding paper, Phys. Rev. **131**, 2397 (1963).
[2] D. Schechter, J. Phys. Chem. Solids, **23**, 237 (1962).
[3] J. M. Luttinger, Phys. Rev. **102**, 1030 (1956).
[4] This is an old estimate by W. Kohn (unpublished).

by (1). The lower level, an orbital singlet in cubic symmetry with a spin of $\frac{1}{2}$, has an isotropic g factor. Thus, the anisotropy in the Zeeman spectrum is due to the hole in the upper level.

The anisotropy in the levels of the Hamiltonian (1) has already been given by Bleaney.[5] Before discussing its application to line C, we shall give his result, using a slightly different notation.

Let $\pm\frac{3}{2}g_0\beta H$ and $\pm\frac{1}{2}g_i\beta H$ (g_0 and g_i are positive) denote the position of the two outer and two inner levels for an arbitrary direction of the field. While g_0 and g_i depend on direction, the sum of the squares, $9g_0^2+g_i^2$, does not. This follows from the fact that $9g_0^2+g_i^2$ is proportional to the magnetic susceptibility of the bound hole which, in cubic symmetry, must reduce to a scalar. We define two quantities, M and ϵ, through

$$10M^2=9g_0^2+g_i^2,$$
$$M^2(1+(8/3)\epsilon)=g_0(001)g_i(001),$$

where $g_0(001)$ is the g_0 value for the field in the [001] direction. M is an average g value and ϵ characterizes the departure from spherical symmetry; it lies within the range $-\frac{3}{8}$ to $+\frac{1}{4}$, the two extremes corresponding to the vanishing of $g_i(001)$ or $g_i(111)$, respectively. The g values for an arbitrary direction λ of the field, are given in terms of M and ϵ by

$$9g_0^2=M^2\{5+4[1+15\epsilon(1+\epsilon)\times(\lambda_x^2\lambda_y^2+\lambda_y^2\lambda_z^2+\lambda_z^2\lambda_x^2-\tfrac{1}{5})-\epsilon^2]^{1/2}\}, \quad (3a)$$

$$g_i^2=M^2\{5-4[1+15\epsilon(1+\epsilon)\times(\lambda_x^2\lambda_y^2+\lambda_y^2\lambda_z^2+\lambda_z^2\lambda_x^2-\tfrac{1}{5})-\epsilon^2]^{1/2}\}. \quad (3b)$$

The extreme values of g_0 and g_i occur along the [001] and [111] directions and, for a field lying in the plane of these two directions, the position of the levels varies monotonically between these two directions.

The values of the Zeeman splittings determine M^2 and ϵ uniquely, but for a given M^2 and ϵ there is an eightfold ambiguity in the values of K and L. This is because there are eight possible ways of ordering (in energy) the four states: The levels with positive energy can have the m_J values of $\frac{3}{2}$ and $\frac{1}{2}$; $\frac{1}{2}$ and $\frac{3}{2}$; $\frac{3}{2}$ and $-\frac{1}{2}$; $-\frac{1}{2}$ and $\frac{3}{2}$; and the four other combinations with opposite m_J. To decide which of these occurs in GaP we use the selection rules for electric dipole transitions which are shown on Fig. 2 of the preceding paper. Six lines are predicted; the experimental results are plotted in Fig. 1. They show only four lines. The outer lines are polarized with $\mathbf{E}\perp\mathbf{H}$ while the inner lines are not strongly polarized. As discussed in the preceding paper,[1] we assume that the two inner lines are actually two pairs of lines which nearly coincide and are not resolved. Further, it is known that the spin-orbit coupling in GaP is small so that the electron g value must be close to 2. When this fact and the selection rules are taken into account it is seen that of the eight possible cases for the upper level, only one is consistent with the data: namely, the level $m_J=\frac{3}{2}$ has the highest Zeeman energy and next to it is the level $m_J=\frac{1}{2}$. This is the ordering that would occur if L were zero and it corresponds to relatively small values of $|L/K|$. The relation between M^2, ϵ, and K, L for this case is

$$M^2=K^2+(41/10)KL+(73/16)L^2,$$
$$\epsilon=-(\tfrac{3}{5}KL+\tfrac{3}{2}L^2).$$

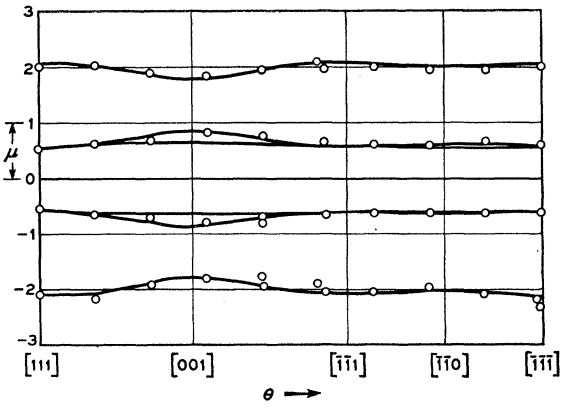

FIG. 1. Zeeman splitting of line C as a function of direction at 4.2°K. The field is in the $(1\bar{1}0)$ plane, $H=31$ kG; $\mu=0.1293$ meV. The circles are the experimental points; the curves are the result of the theory, Eq. (3). The inner lines were assumed to coincide when the field is in the [111] direction.

According to this model, the outer lines of C, produced by the transitions $(J,m_J)=(\frac{3}{2},\pm\frac{1}{2})$ to $(\frac{1}{2},\mp\frac{1}{2})$ are polarized $\mathbf{E}\perp\mathbf{H}$, have a relative intensity of 1 and are separated by $g\beta H$ where $g=(g_e+g_i)$. The two inner lines produced by the transitions $(\frac{3}{2},\pm\frac{3}{2})$ to $(\frac{1}{2}\pm\frac{1}{2})$, are polarized $\mathbf{E}\perp\mathbf{H}$, have a relative intensity of 3, and a g value $g=|3g_0-g_e|$. The other two inner lines arise from the transitions $(\frac{3}{2},\mp\frac{1}{2})$ to $(\frac{1}{2},\mp\frac{1}{2})$, are polarized $\mathbf{E}\|\mathbf{H}$, have a relative intensity of 2, and a g value $g=g_e-g_i$. We must verify that the assumption of near coincidence of the inner lines is consistent with the anisotropy of g_0 and g_i. To do this we assume that the coincidence is exact for the field in the [111] direction and use the measured splittings in this direction to determine g_e, g_0, and g_i. We find $g_e=1.92$; $g_i=1.09$; $g_0=0.92$; from which $M^2=0.881$ and $\epsilon=-0.087$. With these values of M^2 and ϵ the values of g_0 and g_i were calculated, using Eq. (3), for other directions of the field. The resulting six lines are plotted in Fig. 1. The maximum divergence of the inner pairs occurs in the [001] direction, but because the anisotropy is only moderate the line separation is still within our experimental resolution. The assumption of coincidence for the [111] direction is actually somewhat extreme and in the absence of more knowledge we may assume the coincidence to occur midway between the [001] and

[5] B. Bleaney, Proc. Phys. Soc. (London) **73**, 939 (1959).

[111] directions. We find, in this case,

$$g_e=1.89\pm0.10,$$
$$g_i=1.12\pm0.10,$$
$$g_0=0.93\pm0.04.$$

The limits of error have been estimated by assessing an experimental accuracy of $\pm6\%$ for the inner lines and $\pm3\%$ for the outer ones. For the parameters ϵ, L, K we find

$$\epsilon=-0.10\pm0.04,$$
$$K=0.65\pm0.07,$$
$$L=0.15\pm0.05.$$

4. LINES *A* AND *B*

These lines are assumed[1] to arise from a direct exciton at the center of the zone, bound to an ionized donor. The angular momenta of the electron and hole, $j=\frac{1}{2}$ and $j=\frac{3}{2}$, combine to form states with total angular momentum $J=1$ and $J=2$, which are split by the Coulomb interaction. (The $j=\frac{1}{2}$ hole state will also make a small contribution to the $J=1$ level; this is discussed at the end of this section.) Theoretically the state with the greatest multiplicity is expected to be lowest, and this is in agreement with experiment. The $J=2$ level is split further by the cubic field. We describe the magnetic levels of this complex by a spin Hamiltonian which is the sum of a crystalline field term $\mathcal{H}^{(c)}$ and a Zeeman term $\mathcal{H}^{(z)}$:

$$\mathcal{H}=\mathcal{H}^{(c)}+\mathcal{H}^{(z)}, \tag{4}$$
$$\mathcal{H}^{(c)}=-a\mathbf{J}\cdot\mathbf{S}-b(J_x^3S_x+J_y^3S_y+J_z^3S_z), \tag{5a}$$
$$\mathcal{H}^{(z)}=\beta[K\mathbf{J}\cdot\mathbf{H}+L(J_x^3H_x+J_y^3H_y+J_z^3H_z)+g_e\mathbf{S}\cdot\mathbf{H}]. \tag{5b}$$

Here **J** is the "spin" of the hole, **S** that of the electron, and g_e is the isotropic g factor of the electron. The values of K, L, and g_e are, of course, not expected to coincide with those in the previous section.

The electron and hole belong to representations Γ_6 and Γ_8. The decomposition of the direct product, $\Gamma_6\times\Gamma_8=\Gamma_4+\Gamma_3+\Gamma_5$ shows that the $J=2$ level is split into Γ_3 and Γ_5; this splitting arises from the second term of $\mathcal{H}^{(c)}$. The energy levels of $\mathcal{H}^{(c)}$ are found to be

$$E(\Gamma_4)=(5/4)a+(41/16)b,$$
$$E(\Gamma_5)=-\tfrac{3}{4}a-(15/16)b,$$
$$E(\Gamma_5)=-\tfrac{3}{4}a-(39/16)b.$$

The experimental data on the anisotropy of lines A and B are shown on Fig. 2. The Zeeman splitting of line A is isotropic, which was to be expected from the isotropy of the magnetic susceptibility, while line B has a slight anisotropy. We have obtained the Zeeman levels of the Hamiltonian Eq. (4) for the two most important directions of the magnetic field, [001] and [111], but as the expressions are rather lengthy we shall not give them here. Our experimental accuracy warrants keeping only the terms linear in H and these are easy to obtain. We go on to discuss the determination of the five constants of Eq. (4) from the data.

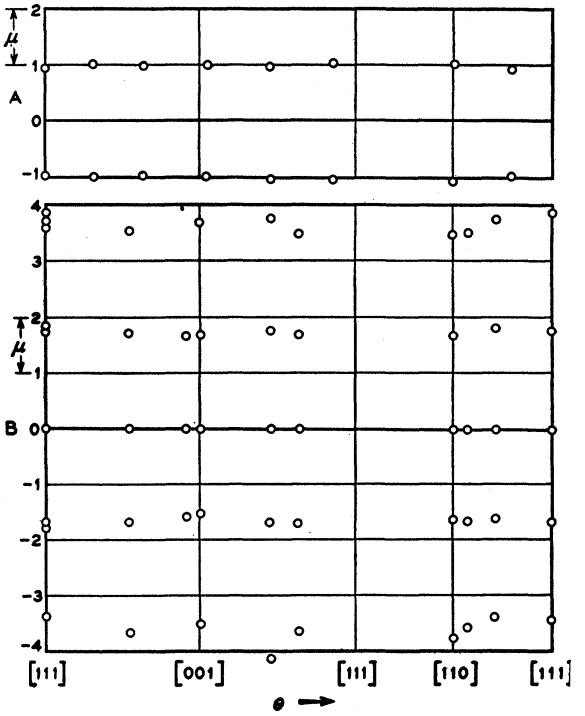

FIG. 2. Zeeman splitting of lines A and B as function of field direction at 4.2°K. The field is in the $(1\bar{1}0)$ plane, $H=31$ kG; $\mu=0.1306$ meV. The outer components of line B are weak and broad (see Fig. 3) and their positions could not be determined with good accuracy. They were disregarded in the interpretation of the data.

The separation between the $J=1$ and the $J=2$ levels, measured at zero field, is 9.0×10^{-4} eV. We were not able to resolve the levels Γ_3 and Γ_5 at zero field. Examination of the wave functions shows that when [001] is taken as the quantization axis the $m_J=0$ state belongs to the Γ_3 level, but when [111] is the quantization axis, $m_J=0$ belongs to Γ_5. Hence, a shift of $\frac{3}{2}b$ in the central line of the B group should occur as the field is rotated from the [001] to the [111] direction. We did not detect this shift but the measured separation between the central lines of A and B had, as a function of angle, a scatter of 0.5×10^{-4} eV. Thus, a maximum value of $|b|\sim0.35\times10^{-4}$ eV is compatible with our data. A possible cause for our inability to measure b is the presence of stray strains in the sample. A typical width of a Zeeman line is indicated on the trace shown in Fig. 3.

The values of K, L, and g_e are obtained from the splitting of the $J=1$ level and from the splittings of the $J=2$ level for the two directions [001] and [111]

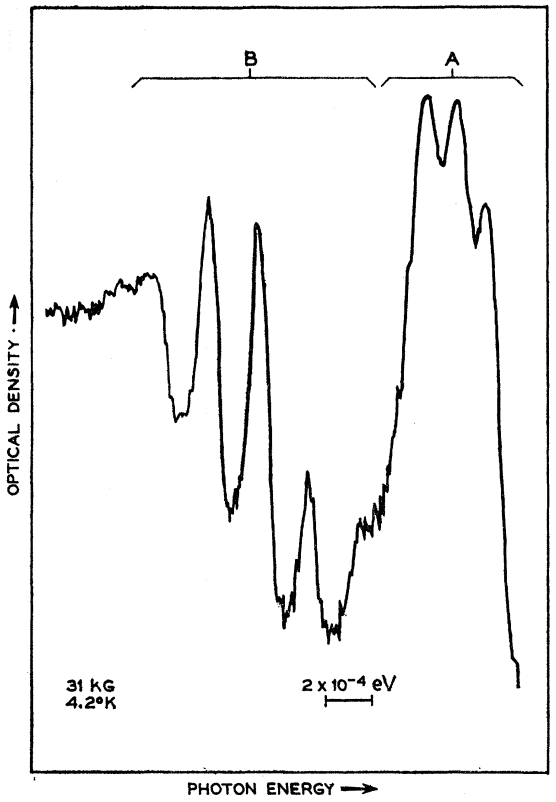

FIG. 3. Microphotometer trace of the Zeeman components of lines A and B at 31 kG and 4.2°K. Notice that the two outer components of line B are weak and broad; they correspond to the highly forbidden $\Delta J=2$, $\Delta m_J=\pm 2$ transitions.

of the field. We find

$$K=0.77\pm 0.16,$$
$$L=0.11\pm 0.07,$$
$$g_e=2.02\pm 0.12.$$

The limits of error were estimated by assuming a $\pm 5\%$ accuracy for the splittings of line A and a $\pm 3\%$ accuracy for those of line B.

The assumption that only the $j=\frac{3}{2}$ hole contributes to the wave function of the $J=1$ level is not strictly speaking valid. The spin-orbit splitting of the valence band is[6] 0.128 eV which is small compared to the binding energy of the center so that an appreciable admixture of the $j=\frac{1}{2}$ state in the wave function of Γ_4 could be expected. However, our assumption is that it is the electron which is tightly bound, while the binding of the hole is weak. In this case, the $j=\frac{1}{2}$ hole component in the wave function will be small, but finite. To take this admixture into account would introduce additional parameters in the theory; the Zeeman energy of the hole is not diagonal in j and the analysis becomes complicated. It is still possible to define the constants K and L for the $J=2$ state since only the $j=\frac{3}{2}$ hole contributes to it. The value of L is then the same as that obtained above but K and g_e cannot be determined separately; only $3K+g_e$ is given by the splitting of the $J=2$ state alone.

We have estimated that a change of 10% in the deduced value of g_e can result from an admixture of a few percent of the $j=\frac{1}{2}$ hole state. For this reason the electron g value deduced from lines A and B is *not* the g value at the higher (presumably Γ) band edge. On the other hand, the g value deduced from line C is the average g at the band edge X. We are trying to make a theoretical estimate of these g values.

5. DISCUSSION

The following two comments can be made concerning the values of b, K, and L:

(a) The j-j coupling of the electron and hole arises from the Coulomb interaction; since this is isotropic, the constant b must be a result of the anisotropy of the hole wave function. This anisotropy is roughly measured by the ratio L/K which, for line B, is $\sim 1/7$. The experimental uncertainty quoted above indicated $|b/a|\lesssim\frac{1}{10}$. The smallness of b is, therefore, physically reasonable.

(b) The values of K and L are expected to be sensitive to the state of binding of the hole. The values which we found for the two centers are not very different. This similarity is consistent with our models for the two centers because in both, the wave function of the hole must be fairly extended. If the extensions are comparable the proportions of s and d envelope functions will be similar, which will lead to similar values for K and for L.

More quantitative discussion must await calculations of bound exciton wave functions which are lacking at present.

[6] J. W. Hodby (to be published). We thank Dr. Hodby for communicating his results before publication.