Zeeman Effect of Bound Excitons in II-IV-V_2 Chalcopyrite Semiconductors

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We present an analysis of the Zeeman effect of bound excitons in II-IV-V_2 chalcopyrite semiconductors and compare our results with those in wurtzite semiconductors like CdS. We also present experimental data on Zeeman studies of sharp luminescence lines in $ZnSiP_2$ and identify the most prominent emission line in the spectrum as due to an exciton bound to an ionized or isoelectronic impurity.

We present an analysis of the Zeeman effect of the three simplest kinds of bound excitons in II-IV-V_2 chalcopyrite semiconductors[1] and apply this analysis to determine the origin of the sharp luminescence lines in $ZnSiP_2$.[2,3]

These ternary semiconductors belong to the point group D_{2d} (or $\bar{4}2m$).[4] From electroreflectance measurements, Shay *et al.*[5] have concluded that $CdSnP_2$, $ZnSiAs_2$, and $CdSiAs_2$ are direct band-gap materials whose fundamental band gaps (at Γ) are derived from the $\Gamma_5 \rightarrow \Gamma_1$ transitions[6] in the corresponding zinc-blende materials. In Fig. 1, we show the band structure (at Γ) for chalcopyrites[5] and compare it with the band structures in zinc-blende and wurtzite semiconductors. We will assume this band structure of chalcopyrite semiconductors for the present discussions. The point we wish to emphasize here is that the ordering of the valence bands is different from that in a wurtzite semiconductor like CdS. From Fig. 1, we can see that the symmetry of the top (or A) valence band in a chalcopyrite crystal is similar to the symmetry of the B valence band in a wurtzite crystal. Therefore the Zeeman effect of a bound exciton containing a hole from the A valence band in a chalcopyrite crystal will be similar to that of a bound exciton containing a hole from the B valence band in CdS.

Thomas and Hopfield[7] have analyzed the Zeeman effect of bound excitons containing holes from A as well as B valence bands in CdS. With assumptions similar to those made by Thomas and Hopfield,[7] and considering holes from only the top (or A) valence band, the Zeeman effects of bound excitons in a chalcopyrite crystal are as shown in Fig. 2. We have considered three cases: (i) an exciton bound to a neutral donor $\oplus - - +$, (ii) an exciton bound to a neutral acceptor $\ominus + + -$, and (iii) an exciton bound to an ionized or isoelectronic[8] impurity $I - +$. Here $\oplus$ represents an ionized donor, $\ominus$ an ionized acceptor, I an ionized or isoelectronic impurity, $-$ an electron, and $+$ a hole from the top valence band. The figures are self-explanatory, but we wish to point out the following features:
(a) For an exciton bound to a neutral impurity,

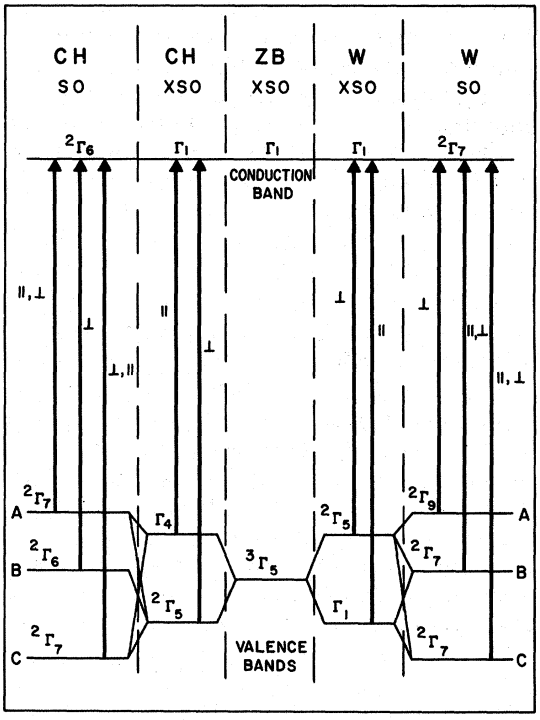

FIG. 1. Schematic diagram of band structure at Γ in chalcopyrite (CH) and wurtzite (W) crystals derived from the $\Gamma_5 \rightarrow \Gamma_1$ transitions in the corresponding zinc-blende (ZB) crystals. SO and XSO mean, respectively, with and without spin-orbit coupling. Selection rules are indicated for light polarized parallel ($\parallel$) and perpendicular ($\perp$) to the c axis. Superscripts on representation labels Γ indicate degeneracy. Chalcopyrite band structure from Ref. 5.

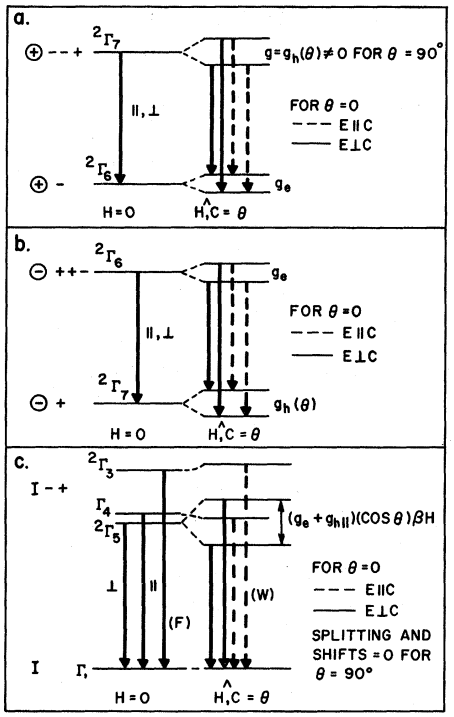

FIG. 2. Schematic representation of energy levels of three kinds of bound excitons in a chalcopyrite crystal. For a general direction of H, all lines observable in both polarizations. Special selection rules for $\theta=0$ are indicated. (a) Exciton bound to a neutral donor, (b) exciton bound to a neutral acceptor, and (c) exciton bound to an ionized or isoelectronic impurity. F indicates forbidden, W indicates weak transitions.

there is only one emission line in the absence of magnetic field. This line is allowed for both $E\parallel C$ and $E\perp C$ but the ratio $(r=I_{\parallel}/I_{\perp})$ of parallel to perpendicular intensities will vary from one material to another and can be calculated by using the quasicubic model.[9] When a magnetic field is applied, this emission line will split into four components, all of which will be allowed for both polarizations for a general direction of magnetic field. (b) From symmetry arguments, one can prove that neither g_e nor g_h vanishes for $H\perp C$. Therefore, there will be finite splittings of the excited and ground states of an exciton bound to a neutral impurity for $H\perp C$. (c) For $I-+$, there will be two emission lines (one in each polarization) for $H=0$. The $\Gamma_3\rightarrow\Gamma_1$ transition is forbidden for $H=0$. The relative splittings of the three levels depend on the material. (d) For $H\neq 0$, the Γ_5 level of the $I-+$ complex splits into a doublet whose separation varies linearly with magnetic field. The Γ_3 and Γ_4 levels will be mixed and will shift away from each other nonlinearly. The exact nature of the shift will depend on the zero-field Γ_3-Γ_4 splitting. $\Gamma_3\rightarrow\Gamma_1$ transition will be allowed but weak, so that only three emission lines may be observed. From symmetry arguments one can show that the splitting of Γ_5 and the shifts of Γ_3 and Γ_4 will vanish for $H\perp C$.

With this brief description of the expected Zeeman patterns in chalcopyrites, we turn our attention to $ZnSiP_2$. The 2 °K luminescence spectrum of $ZnSiP_2$ is dominated by a series of equally spaced sharp lines, called the "numbered lines" in Ref. 3. (See Fig. 1 of Ref. 3.) We concentrate on line 1 because the other numbered lines are phonon replicas of line 1.[3] The application of magnetic field to the sample broadens and then splits line 1 into a triplet as shown in Fig. 3(b). The separation between the outer two components of the triplet increases linearly with H, as shown in the insert in Fig. 3. When the temperature is reduced to 2 °K, the triplet collapses into a single line as shown in Fig. 3(c).

In view of these data, what can we say about the

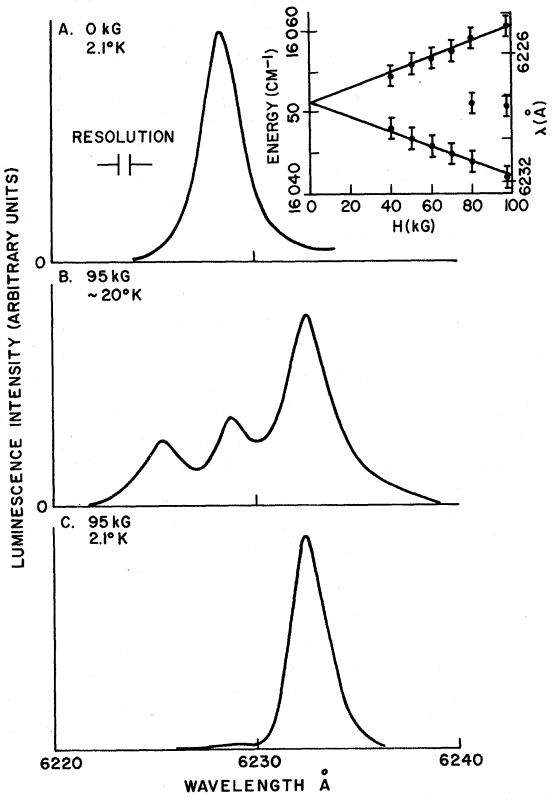

FIG. 3. Zeeman splitting of line 1 in photoluminescence spectrum of $ZnSiP_2$ No. 20. (a) $H=0$, $T=2.1$ °K, (b) $H=95$ kG, $T\approx 20$ °K, and (c) $H=95$ kG, $T=2.1$ °K. Intensity scales are linear. The insert shows peak energies of the three components of the triplet as a function of H. The points are experimental, the solid lines are calculated using $E\pm=E_0\pm\frac{1}{2}(g_e+g_h)\beta H$ with $g_e+g_h=4$. The large error bars are a result of the large width of the emission line.

origin of line 1? Recent electroreflectance measurements by Shay *et al.*[10] indicate that the fundamental band gap in $ZnSiP_2$ is either indirect or pseudodirect.[5] In either case, the details of the theoretical analysis presented above (such as the selection rules and the angular dependencies) will not apply directly to $ZnSiP_2$. However, if we assume a "simplified $ZnSiP_2$" model analogous to the "simplified GaP" model of Thomas *et al.*,[11] the *splittings* of bound excitons in $ZnSiP_2$ will be expected to be similar to those discussed above. Using this assumption, we can identify the center responsible for line 1 as an exciton bound to an ionized or isoelectronic impurity by the following reasoning: (i) We see a triplet in magnetic field. This is consistent with $I-+$.[12] For an exciton bound to a neutral impurity, a quartet is expected for arbitrary θ; a triplet is expected only at specific values of θ when the splitting of the excited state equals that of the ground state. We observe a triplet in more than one sample, with different values of θ. This rules out an exciton bound to a neutral impurity. (ii) When the temperature is lowered to 2 °K, an exciton bound to a neutral impurity is expected to give rise to two emission lines of approximately equal intensities. Instead we find that a single emission line dominates [Fig. 3(c)]. The ratio of intensities of the lowest to the middle component is ~40. This behavior is completely consistent with $I-+$,[13] but not with an exciton bound to a neutral impurity. (iii) The linear variation (with H) of the outer two components of the triplet and the slight shift of the central component are also consistent with $I-+$.

This identification of line 1 as due to an exciton bound to an ionized or isoelectronic impurity should be considered tentative until a detailed comparison is made between the theory and experiments regarding the selection rules and angular dependences. An incomplete knowledge of the band structure of $ZnSiP_2$ and the smallness of the available samples prevent such a comparison at the present time.

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[1]For a recent review, see N. A. Goryunova, *Proceedings of the Ninth International Conference on the Physics of Semiconductors, Moscow*, 1968 (Nauka, Leningrad 1968), p. 1198.

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[5]J. L. Shay, E. Buehler, and J. H. Wernick, Phys. Rev. Letters 24, 1301 (1970); Phys. Rev. B 2, 4104 (1970). See also *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Mass.*, 1970, edited by S. P. Keller, J. C. Hansel, and F. Stern (U.S. AEC, Oak Ridge, Tenn., 1971), p. 589; Phys. Rev. B 3, 2004 (1971). For $CdSiAs_2$ and $CdGeAs_2$, see J. L. Shay and E. Buehler, *ibid.* 3, 2598 (1971).

[6]The notation is from G. F. Koster, J. O. Kimmock, R. G. Wheeler, and H. Statz, *Properties of Thirty Two Point Groups* (MIT Press, Cambridge, Mass., 1963).

[7]D. G. Thomas and J. J. Hopfield, Phys. Rev. 128, 2135 (1962).

[8]See, for example, D. G. Thomas and J. J. Hopfield, Phys. Rev. 150, 680 (1966); also R. A. Faulkner and J. J. Hopfield, in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum, New York, 1968), p. 218.

[9]J. J. Hopfield, J. Phys. Chem. Solids 15, 97 (1960). Extension of the quasicubic model to ternary chalcopyrite crystals is discussed by J. E. Rowe and J. L. Shay, Phys. Rev. B 3, 451 (1971).

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[11]D. G. Thomas, M. Gershenzon, and J. J. Hopfield, Phys. Rev. 131, 2397 (1963).

[12]The fourth component is made allowed by the magnetic field but is expected to be weak. Also, the Boltzmann factor $e^{-\Delta E/kT}$ works against it.

[13]The observed ratio corresponds to $T \approx 3.7$ °K while the nominal helium bath temperature was 2.1 °K. The difference may be due to local sample heating.