STRAIN-INDUCED SPLITTING AND POLARIZATION OF EXCITONS DUE TO EXCHANGE INTERACTION

O. Akimoto and H. Hasegawa
Department of Physics, Kyoto University, Kyoto, Japan
(Received 18 March 1968)

Recently, Koda and Langer reported a strain-induced splitting and polarization of exciton lines in the wurtzite type II-VI crystals, ZnO, CdS, and CdSe.[1] They observed that, at the particular geometry where an external stress $\vec{P}$ is applied perpendicularly to the c axis of these crystals and the k vector of the incident light is parallel to the c axis, the A and B exciton lines (according to Thomas' notation[2]) split into two components which are completely polarized with the electric vectors $\vec{E}$ parallel and perpendicular, respectively, to the direction of the stress. Both A and B excitons observed in this geometry have been assigned to belong to the two-dimensional irreducible representation Γ_5 of the C_{6v} group,[3] and may be expected from a symmetry consideration alone to split into two components $\Gamma_{5\parallel}$ and $\Gamma_{5\perp}$ by the uniaxial stress $\vec{P}\perp c$, each being allowed for the lights with the two types of polarization $\vec{E}\parallel\vec{P}$ and $\vec{E}\perp\vec{P}$, respectively. However, such a simple consideration fails to give a satisfactory interpretation of the observed effect, as pointed out by the above authors, since within a framework of the one-electron band scheme and the usual deformation-potential theory a static strain cannot split the Kramers degeneracy of any orbitally quenched one-electron band. Hence the two-particle nature of the exciton states should play an essential role for the above phenomena. We report in this Letter that the exchange interaction between spins of the electron and the hole that compose the exciton is the plausible answer to the above question raised in Koda's experimental results.

To substantiate our assertion we show first a more explicit reason of the failure of the usual one-electron band scheme to account for the phenomena. Let us write the exciton wave function according to Elliott[4] as direct products of the conduction- and valence-band spinors with the following convention:

$$\Psi_A = \psi_C \psi_A^K, \quad \Psi_B = \psi_C \psi_B^K, \text{ etc.,} \tag{1}$$

where $\psi_A, \psi_B, \cdots, \psi_C$ represent the two-component spinor Bloch states (ordinarily at $\vec{k}=0$) of the valence bands $A, B,$ etc., and the conduction band C, respectively. For the valence-band states the superscript K is labeled to indicate the time-reversal conjugate because of the holes. Envelope functions of the exciton relative motion do not matter in the above expressions as far as direct allowed excitons are concerned. If we use the deformation potential theory to calculate the perturbation energy of the above excitons caused by a strain, we must solve a secular equation which is set up on the basis of the above direct-product spinors. It is then easy to show that without extra mixings caused by some other interactions between the electron and the hole, the resulting secular matrix itself is a direct product, such as $1\times$[one-electron deformation potential matrix], giving rise to no splitting. We therefore consider a mixing of the elementary exciton states in Eq. (1) due to an exchange interaction between the electron and hole spins and discuss its combined effect with the strain perturbation to lead to a splitting.

In our present example of the wurtzite crystals the relevant valence-band states are the Γ_9 and the upper Γ_7 states of the irreducible representation of the double C_{6v} group, which stem from a single spin-mixed atomic p-like level according to Hopfield's quasicubic interpretation.[3] (The other Γ_7 will be ignored for the reason of a large energy separation.) The valence-band one-electron wave function may then be written as

$$\psi(\Gamma_9) = [\psi_1\alpha, \psi_{-1}\beta], \tag{2a}$$

$$\psi(\Gamma_7)_{\text{upper}} = [a\psi_0\alpha + b\psi_1\beta, -b\psi_{-1}\alpha - a\psi_0\beta], \tag{2b}$$

where ψ_m ($m = 1, 0, -1$) are the three orbital functions with the z component of the angular momentum parallel to the c axis being equal to $1, 0, -1$, respectively, and α and β are the spin functions. The coefficients a, b in Eq. (2b) can be determined from the two parameters of the quasicubic model, i.e., the spin-orbit and the trigonal field parameters.[3]

We decompose the wave functions expressed in the direct-product forms as Eq. (1) into irreducible components corresponding to the representation Γ_5^A, Γ_6, Γ_1, Γ_2, and Γ_5^B (A and B denoting the Γ_9- and Γ_7-associated excitons hereafter) and calculate matrix elements of the exchange and strain Hamiltonians between these decomposed exciton states. The exchange coupling in the exciton is treated according to Elliott.[4] Nonvanishing off-diagonal matrix elements are then found to arise in the following combinations (all others vanish).

$$\mathcal{H}_{\text{exchange}}:\ \Gamma_{5x}{}^{A}-\Gamma_{5x}{}^{B},\ \Gamma_{5y}{}^{A}-\Gamma_{5y}{}^{B},$$

$$\mathcal{H}_{\text{strain}}:\ \Gamma_{5x}{}^{A}-\Gamma_{5x}{}^{B},\ \Gamma_{5y}{}^{A}-\Gamma_{5y}{}^{B},$$

$$\Gamma_{1}-\Gamma_{6-},\ \Gamma_{2}-\Gamma_{6+}.$$

Here the uniaxial strain is assumed to be applied in the x direction perpendicular to the c axis. The components Γ_{5x}, Γ_{5y}, and Γ_1 are allowed for the x-, y-, and z-polarized light, respectively, and the components Γ_6 and Γ_2 are forbidden. The magnitude of the off-diagonal element between $\Gamma_{5x}{}^{A}$ and $\Gamma_{5x}{}^{B}$ is different from that between $\Gamma_{5y}{}^{A}$ and $\Gamma_{5y}{}^{B}$ due to the presence of both the exchange and strain terms, and consequently Γ_5's split. It may be noted that neither of the exchange nor strain alone can generate this splitting.

Solving the secular equation, we obtain the following expression for energy levels:

$$E=E_0\pm\tfrac{1}{2}(\Delta\pm\delta), \tag{3}$$

where δ is the magnitude of the splitting, which is of the same value for the Γ_9- and Γ_7-associated excitons, and Δ is the difference between the centers of gravity of the split levels in each of the two excitons. (See Fig. 1.) To first order of the applied strain s the quantities δ and Δ are of the form

$$\delta=\frac{4\gamma|F(0)^2\Omega}{\Delta_0}|JD_u s|, \tag{4}$$

$$\Delta=\Delta_0-(1-\gamma)\left\{1-4\gamma\left(\frac{J|F(0)|^2\Omega}{\Delta_0}\right)^2\right\}^{1/2}D_u s, \tag{5}$$

where we put

$$\gamma\equiv b^2=1-a^2, \tag{6}$$

and J is the exchange integral between Wannier functions, $F(0)$ the amplitude of exciton envelope at the origin, Ω the unit cell volume, D_u the appropriate shear-deformation-potential constant, and Δ_0 the level difference at zero strain.

Since the off-diagonal elements between Γ_{5x} and Γ_{5y} vanish, the split components are completely polarized with E vectors in the x or y direction, according to the following rule: When $JD_u s>0$, the outer two levels are x polarized (parallel to strain) and the inner two are y polarized (perpendicular to strain), and when $JD_u s<0$, the above polarization is just reversed. This rule is independent of the energy ordering of Γ_9 and Γ_7 valence bands. In order to explain the observed polarization in ZnO and CdS spectra, the sign $JD_u>0$ (for the case $s<0$, i.e., compression) is favorable. This is reasonable in view of the consideration that J is the direct exchange ($J>0$) between Wannier functions, and that in other similar crystals, e.g., CdTe, D_u is positive.[5]

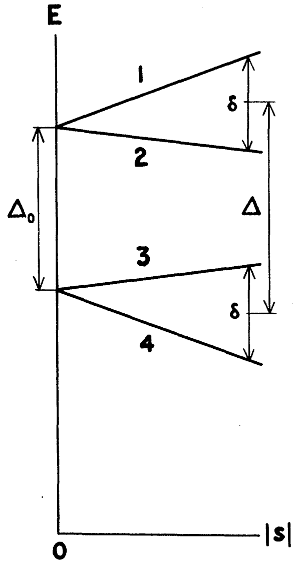

FIG. 1. Splitting of the Γ_5 exciton levels. The outer two lines 1 and 4 and the inner two lines 2 and 3 represent the split levels which are polarized perpendicular and parallel, respectively, to a uniaxial stress $\vec{P}\perp c$, when $JD_u s<0$.

The experimental results show the following tendencies as to δ and Δ: The coefficient of $|s|$ in δ decreases and the coefficient of $|s|$ in Δ increases in order of ZnO, CdS, and CdSe. Our results can be checked to agree with these experimental tendencies by considering the following three points:

(1) The factor γ decreases in order of ZnO, CdS, and CdSe (about 5:3:2) in accordance with increasing of the ratio of the spin-orbit parameter to the trigonal field parameter.

(2) The factor $|F(0)|^2$ decreases in the same order in accordance with decreasing of the exciton locality.

(3) The level difference Δ_0 is about the same value for ZnO and CdS, and is larger to some extent for CdSe, as seen from the data of Koda and Langer.

The agreement of our results with the qualitative feature of the observation confirms that the splitting and polarization reported by Koda and Langer is a combined effect between the electron-hole exchange interaction and the strain. At the same time, it seems to support the intrinsic nature of the A line in ZnO contrary to the proposal by Park *et al.*,[6] although the extrinsic nature cannot entirely be eliminated.

Finally, we can make a rough estimation of the exchange integral J for ZnO. Using the values $a_B = 14$ Å (Thomas[2]), $D_u \sim 2$ eV (guess), $\Delta_0 \sim 0.015$ eV, $\gamma \sim 1$ and $\Omega \sim 50$ Å^3, one gets roughly $\delta \sim 3J|s|$ eV. Comparing this with the experimental data using a compliance constant $\sim 10^{-3}$ kbar^{-1}, one gets $J \sim 1$ eV. The present study suggests that this type of strain-induced effect measurement provides a useful tool for determining the exchange integral acting in excitons.[7]

---

[1] T. Koda and D. W. Langer, Phys. Rev. Letters 20, 50 (1958).

[2] D. G. Thomas, J. Phys. Chem. Solids 15, 86 (1960).

[3] J. J. Hopfield, J. Phys. Chem. Solids 15, 97 (1960).

[4] R. J. Elliott, in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Plenum Press, New York, 1963), p. 269.

[5] D. G. Thomas, J. Appl. Phys. Suppl. 32, 2298 (1961).

[6] Y. S. Park, C. W. Litton, T. C. Collins, and D. C. Reynolds, Phys. Rev. 143, 512 (1966).

[7] The importance of the exchange coupling in excitons in alkali halides has recently been pointed out by Y. Onodera and Y. Toyozawa, J. Phys. Soc. Japan 22, 833 (1967).

COMMENTS ON "STANDING SPIN-WAVE RESONANCE IN 'FLASH-EVAPORATED' PERMALLOY FILMS"

P. E. Tannenwald and R. Weber
Lincoln Laboratory,* Massachusetts Institute of Technology, Lexington, Massachusetts 02173

(Received 8 January 1968)

We wish to point out that it is not possible to conclude, on the basis of evidence presented, that "flash-evaporated" Permalloy films[1] will be of particular value in studying fundamental physical interactions of basic importance to magnetism in bulk material by means of spin-wave resonance (SWR). Specifically, we question the validity of a number of points made by the author of that Letter:

(1) Films made in the same vacuum give widely different results; e.g., curves a and b of Fig. 2 of Ref. 1 yield (by reading the slopes from the graph) $A/M = 1.08 \times 10^{-9}$ G cm^2 and $A/M = 0.88 \times 10^{-9}$ G cm^2, respectively.

(2) The g value of Permalloy is 2.07-2.14 as measured in bulk[2] and 2.08 ± 0.01 as measured in previous SWR experiments,[3] and not ~2.01.

(3) A/M for the stated Permalloy composition is not $\sim 1 \times 10^{-9}$ G cm^2 as stated in the caption of Fig. 2, nor $\sim 0.95 \times 10^{-9}$ G cm^2 as stated in the text, but is $(1.12 \pm 0.03) \times 10^{-9}$ G cm^2 (Ref. 3).

(4) The fact that even modes are so strongly excited for films of these thicknesses (Fig. 1; and Fig. 2, especially film b) at this microwave frequency indicates that the films are probably not magnetically uniform—contrary to the stated advantages of these flash-evaporated films. An additional disturbing feature of the SWR spectrum displayed in Fig. 1 is that there is not present the expected type of amplitude alternation between the odd and even modes. In uniform films of thickness less than a skin depth, the even modes should be so weakly excited that they are substantially smaller than adjacent odd peaks. This failure is indicative of a layered film structure, with different layers having different magnetic characteristics.

(5) In addition to the preceding difficulties, so far only relatively thin films have been flash-evaporated (up to 2200 Å in the text). It is possible that practical difficulties could arise with respect to uniformity and gradients in making the hundreds of flashed layers to obtain thicker films. Until it is demonstrated that good quality, thicker films can be fabricated by this method, thereby providing the possibility of exciting many more SWR peaks than is possible with the present films, some of the proposed experiments (temperature dependence of the exchange constant, the exchange coupling between multilayered films, and the magnon-phonon interaction) could not be carried out in a meaningful fashion. Furthermore, these measurements have already been done, with regularly evaporated films, in experiments where many more SWR peaks were excited.[3-6]