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SPLITTING OF EXCITON LINES IN WURTZITE-TYPE II-VI CRYSTALS BY UNIAXIAL STRESS*

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Usually the effects of uniaxial stress on exciton lines of semiconductors are considered to be mainly determined by the change of the one-electron energy band structure by the external stress. Energy shifts and splittings of exciton lines are related to the change of energy gaps, effective masses, and degeneracies of the energy bands involved in the exciton state, leading to an interpretation in terms of the deformation potential theory based on the one-electron energy band scheme.[1] In this Letter, however, we report strain-induced splitting of exciton lines observed in the wurtzite-type II-VI crystals, ZnO, CdS, and CdSe, which cannot be accounted for by such a simple deformation-potential theory. The basic features of the experimental results are presented here along with brief discussions on the possible interpretation of the phenomena.

The uniaxial stress measurements have been made on the reflection spectra of oriented samples of ZnO, CdS, and CdSe single crystals at 1.8°K. The force exerted on a parallelepiped sample was generated by a hydraulic system, the details of which will be described elsewhere, and changes of the reflection spectra (for an angle of incidence of about 5°) were measured photographically during uniaxial compression of the sample by a 2-m Bausch and Lomb grating spectrograph with an inverse dispersion of 4 Å/mm. Although measurements have been made for several orientations of the stress relative to the crystallographic axes of the sample, splittings of the exciton lines to be reported here were observed only at the particular geometry where the external uniaxial stress $\vec{P}$ is applied perpendicularly to the C axis and the k vector of the incident light is parallel to the C axis ($\vec{P} \perp C$ and $\vec{k} \parallel C$). For all other geometries, including the case of $\vec{P} \perp C$ and $\vec{k} \perp C$, exciton lines simply shifted in energy but no splitting was observed.

Figure 1 shows the change of the reflection spectra on the (0001) plane of ZnO crystal during uniaxial compression in this particular geometry. A double structure exists initially

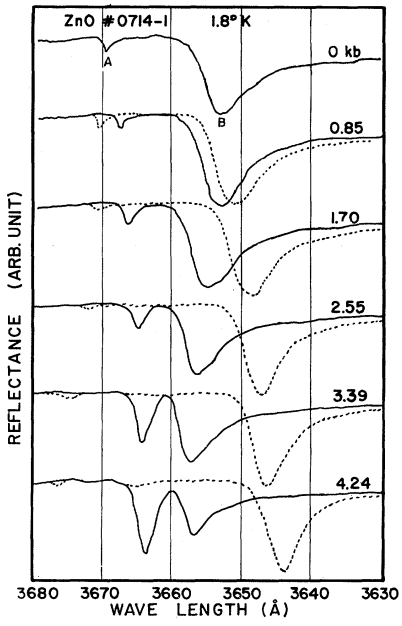

FIG. 1. The change of the reflection spectra of ZnO for $\vec{P} \perp C$ and $\vec{k} \parallel C$. Solid and broken lines indicate the components polarized with $\vec{E} \parallel \vec{P}$ and $\vec{E} \perp \vec{P}$, respectively

in this spectrum at $P=0$. It corresponds to the A and B exciton lines according to Thomas's notation.[2] By applying uniaxial stress along the direction perpendicular to the C axis, both of these lines were found to split, as seen in Fig. 1, into two components which are completely polarized with the electric vectors $\vec{E}$ parallel and perpendicular, respectively, to the direction of the stress. In the A exciton, the higher energy component is polarized with $\vec{E} \parallel \vec{P}$; while in the B exciton, polarization of the split components is reversed with the components of $\vec{E} \perp \vec{P}$ at the higher energy side. The relative intensities of these split components are also changed remarkably during compression. In both the A and B excitons, intensities of the higher energy components are increased with increasing stress accompanied by a simultaneous decrease of the intensities of the lower energy components.

When the k vector of the incident light is perpendicular to the C axis ($\vec{P} \perp C$ and $\vec{k} \perp C$), both lines seem to shift without splitting. However, the A and B excitons in ZnO are strongly polarized along the direction perpendicular to the C axis, and in this geometry, these selection rules allow us to observe only the components polarized with $\vec{E} \parallel \vec{P}$. In fact, the energy shifts and intensity changes of these lines observed in this geometry are exactly the same as those of the split components of $\vec{E} \parallel \vec{P}$ in the geometry of $\vec{P} \perp C$ and $\vec{k} \parallel C$. Measurements have also been made by bending thin platelet ZnO crystals, having the $(10\bar{1}0)$ plane as the surface, with the C axis as the bending axis. Change of the reflection spectra observed at the concave side, where the lattice is compressed in the direction perpendicular to the C axis, are qualitatively the same as observed under the uniaxial stress in the geometry of $\vec{P} \perp C$ and $\vec{k} \perp C$. At the convex side (elongation side), the A exciton shifts oppositely to lower energy with decreasing intensity, while the B exciton shifts to higher energy with increasing intensity. Although we cannot observe in this geometry the other split components of $\vec{E} \perp \vec{P}$ which are expected to exist, one may conclude from these results that, when the lattice is uniaxially elongated in the direction perpendicular to the C axis, the senses of polarization of the split components are reversed with the higher energy components again increasing in their intensities.

Splittings have been also observed in the A and B exciton lines of CdS in the same geometry of $\vec{P} \perp C$ and $\vec{k} \parallel C$. In CdS, the A and B exciton lines shift as a whole nonlinearly toward lower and higher energies, respectively, as observed by Lowe, Cardona, and Pollak.[3] Although the magnitude of splittings is smaller than those in ZnO, splittings of these lines show qualitiative behavior similar to those in ZnO with regard to the polarization and the relative intensity changes of the split components. Measurements on CdSe revealed that the A exciton in CdSe is also split in the same geometry. The splitting is much smaller in magnitude than those observed in ZnO and CdS, and the split components have polarizations opposite to those of the splittings of the A excitons in ZnO and CdS. There was no observable splitting in the B exciton in CdSe within the experimental accuracy. In Fig. 2, the splittings observed in the A and B excitons in ZnO, CdS, and CdSe are plotted against applied pressure. Experimental points shown in Fig. 2 do not correspond to the exact exciton energies, but were taken for convenience at the unique characteristic positions of the structure, in most runs at their reflection minima. In the plots of ZnO and CdS, shown in Fig. 2(a) and 2(b), energy shifts of sharp emission lines are also plotted. There is no observable splitting in these emission lines.

As for the explanation of these splittings, one would not expect any splitting to occur within a framework of the simple one-electron en-

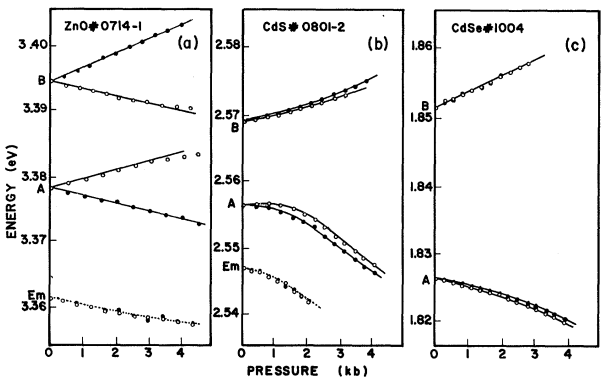

FIG. 2. Splitting of the A and B exciton lines in ZnO, CdS, and CdSe. Open and closed circles represent the experimental positions of the split components polarized with $\vec{E} \parallel \vec{P}$ and $\vec{E} \perp \vec{P}$, respectively. Shifts of emission lines in ZnO and CdS are shown by the broken lines. (Definition of the A and B lines in ZnO indicated follows Thomas, Ref. 2.)

ergy-band scheme, since any energy band in the wurtzite crystal does not have orbital degeneracy. Consequently, one has to seek the sources of this type of the splitting in the particular symmetric property of the exciton itself. According to Hopfield,[4] the symmetries of the A and B exciton states which we are observing in the geometry of $\vec{E} \perp C$ belong to the irreducible representation of Γ_5 of the C_{6v} group which is isomorphous with the Γ-point symmetry of the wurtzite lattice. Since this Γ_5 state is a two-dimensional representation of the single group, one can expect, at least group theoretically, that each of these doubly degenerate exciton states may decompose into two one-dimensional states as the symmetry reduces from C_{6v} to C_{2v} by the uniaxial distortion of the lattice along the direction perpendicular to the C axis. Since these one-dimensional representations correspond to dipole oscillators oriented parallel and perpendicular to the direction of stress, respectively, it will be natural to ascribe the observed split components to these dipole oscillators which are decomposed from the Γ_5 exciton state.

When the k vector of the incident light is not parallel to the C axis, the decomposition of these Γ_5 states occurs, even without external stress, into the transverse and longitudinal states as discussed by Hopfield and Thomas.[5] This transverse-longitudinal exciton splitting is caused by the long-range Coulomb interaction associated with the polarization field of the exciton itself and is strongly dependent on the direction of the k vector of the incident light. For the k vector oriented along the C axis, there occurs no transverse-longitudinal exciton splitting. The resulting degeneracy of the Γ_5 state will than be removed by the Stark effect due to the uniaxial deformation of the lattice. We believe the qualitative picture mentioned above explains what is happening in the deformed wurtzite crystals observed here. However, the degeneracy of the Γ_5 exciton state is not an orbital one but essentially comes from the two-particle nature of the exciton state. Hence, in order to step further into a more quantitative understanding of this effect, we shall have to deal with this problem by explicitly taking account of the exciton symmetry including the electron and hole spins. We noticed that there is an evident tendency for the magnitude of the splitting to become larger as the spin-orbit interaction in the valence bands becomes smaller in the sequence CdSe, CdS, and ZnO. Then the existence of the nearby exciton states having different symmetry might be responsible for the mixing of these states by the external strain thereby giving rise to the splitting of the Γ_5 state. Calculations are now in progress along this line by taking the two-particle exciton Hamiltonian into account in the deformation-potential theory for the wurtzite structure.

According to a qualitative picture proposed above, the splitting observed in the A and B exciton lines of the wurtzite II-VI crystals are explained as being caused by the decomposition of the degenerate Γ_5 states belonging to to the C_{6v} wurtzite symmetry group. However, as discussed by Thomas and Hopfield,[6] a weakly bound exciton at a substitutional impurity or defect will possess energy states with practically the same symmetries and degeneracies as an intrinsic exciton does. Then an analogous argument will also apply to the weakly bound extrinsic exciton lines regarding their behavior under the uniaxial strain, and one cannot eliminate the possibility of the extrinsic nature of the A line in ZnO as proposed by Park et al.[7] simply because of the splitting observed in this line. However, if the A line is due to a bound B exciton at some simple lattice defect, one might expect to observe the similar splitting pattern for the A line as that of the original B exciton. Actually, we observed that the splitting occurs with opposite polarization compared with the splitting of the B exciton line. The situation will become more complicated if one postulates a more complicated nature of the lattice defect. We shall not make further speculation at present about the recent controversy on the interpretation of the exciton lines in ZnO until we arrive at a more thorough understanding of the phenomena.

Finally, another possible contribution to the splitting may also evolve by taking into account the off-Γ-point transitions; namely, the exciton state might be affected by the k-linear terms existing in the Γ_7 conduction and valence bands. According to Mahan and Hopfield,[8] the magnitude of these effects is normally quite small, but they might play some role when the lattice is uniaxially distorted. A more detailed experimental account of the uniaxial stress measurements on the wurtzite-type II-VI crystals and a more quantitative theoretical treatment which is now in progress will be published

shortly.

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BOUNDARY SCATTERING IN SUPERCONDUCTORS*

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Boundary scattering in gallium single crystals produces little shift of the superconducting critical temperature T_c consistent with the assumption of specular reflection of quasiparticles at the sample boundary.

This paper reports the results of an investigation of the effect on T_c of reducing the mean free path (mfp) in 99.9999% pure gallium single crystals by means of boundary scattering. The purpose of this investigation was to observe the so-called "mfp" effect first noted by Lynton, Serin, and Zucker.[1] This effect, a consistently observed reduction of T_c with reduction of mfp by the addition of impurities, was explained theoretically as the result of averaging the anisotropic pairing interaction present in real superconductors.[2]

21 single-crystal plates of gallium with thickness ranging from 25 to 250 μ were used in this investigation. The crystals were divided into three approximately equal groups with the crystals of each group having one of the principal axes of gallium perpendicular to the surface of the thin plate. Shifts in critical temperature were measured in reference to bulk single crystals of identical purity using the change in mutual inductance of a pair of coils containing the sample as an indication of the phase transition. Previous experiments[3] had shown that the critical temperatures of the plates could be determined to at least $\pm 10^{-4}$ °K using this technique. Further details of the experimental procedure and sample making are given in Ref. 3.

The experimental results are shown in Fig. 1, where the shift in T_c of the thin plates from the T_c of bulk gallium samples is plotted versus $1/d$, where d is the sample thickness. One can see that for samples of all orientations, the shift in T_c is negligible. The data gave the best least-squares fit to a function of the form $\Delta T_c = A/d + B$ and it was found that $A = (-0.28 \pm 0.059) \times 10^{-6}$ °K cm and $B = (0.10 \pm 0.04) \times 10^{-3}$ °K. The constant term B is of the order of the scatter in the data and only represents the slight uncertainty in the measurement of T_c. Associating the A term with the mfp effect, we find that this shift of T_c with specimen thickness, when converted to ΔT_c versus mfp,[4] is much smaller than that reported earlier for the mfp effect.[1,2] In fact, the shift of T_c may be zero within the uncertainty of the data. This apparent lack of a mfp effect is surprising since the Fermi velocity of gallium is typically[5] 6×10^7 cm/sec, so that scattering from the boundaries of a film 25 μ thick will take place every 5×10^{-11} sec. The lifetime of superconducting pairs has been calculated[6] and measured[7] to be of the order of 4×10^{-8} sec; hence many thousand collisions should occur during the typical pair lifetime and anisotropy averaging should be complete.

When the results shown in Fig. 1 were found,