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Reflection Spectra of $CdCl_2$–$CdBr_2$ Mixed Crystals in the Region of Band Gap Excitons

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Reflection spectra have been measured on $CdCl_2$–$CdBr_2$ mixed crystals in the region of band gap excitons using the cleaved surfaces. It is found that both the persistence and the amalgamation types of the spectral behavior upon making mixture can occur in this system. The behavior is interpreted in terms of the exciton transitions at the Γ point from halogen p-like valence bands to a cadmium s-like conduction band: The amalgamation-type behavior comes from an admixture of the p_z-state wave function to the Γ_4^- valence states, and the persistence-type behavior is ascribed to the p_x- and p_y-like character of the Γ_5^- and Γ_6^- valence states.

§1. Introduction

The compounds $CdCl_2$ and $CdBr_2$ are ionic layered materials, bonding being strong between atoms within a particular layer and weak between layers. They have a crystal structure which belongs to the D_{3d}^5 space group with one molecule per primitive cell. There is still little information on their optical properties and no theoretical calculation of their electronic energy band structure. Because these compounds are highly anisotropic, an evaporated film is inadequate for studying their optical properties, although several reports[1] on fundamental absorption spectra of the evaporated film were published. We reported in a previous paper[2] the reflection spectra of single crystals of these compounds. These spectra were composed of several exciton bands near the optical gap and characteristic sharp lines lying in the deep interband energy region. The low lying spectral structures were associated with the halogen p-state spin-orbit interaction under the influence of a strong crystal field parallel to the c axis.

In the present work, the low lying exciton spectra were measured on $CdCl_2$–$CdBr_2$ mixed crystals using the cleaved surfaces. The purpose is to investigate how the crystal field contributes to the exciton transitions in the mixed system and to obtain some information about the upper valence band structure of $CdCl_2$ and $CdBr_2$.

§2. Experimental

Single crystals of $CdCl_2$–$CdBr_2$ mixtures could be grown from the melt over the whole range of their composition by the Stockbarger technique. A mixture of appropriate amount of reagent grade powders of $CdCl_2 \cdot 5/2\ H_2O$ and $CdBr_2 \cdot 4H_2O$ was dehydrated by heating in vacuum and then was melt and sealed into an evacuated cylindrical quartz ampoule to grow a single crystal.

The crystal was cleaved in air along the c plane immediately before the mounting in the sample chamber, and the chamber was then quickly evacuated. The cleaving of $CdCl_2$-rich crystals (which were highly hygroscopic) was done at a temperature of about 100°C to keep the cleaved surface clean.

Nearly normal incidence ($\sim 5°$) reflection spectra of the cleaved surfaces were measured in the photon energy region 4.0–7.1 eV by means of a double-beam, single-lock-in-detection method. (Details of this method will be reported elsewhere.) The light source was a 200 W deuterium lamp and the monochromator was of 40 cm Seya-Namioka type. The measurements were performed at liquid nitrogen temperature (LNT) in vacuum of about 3×10^{-7} Torr.

The compositions of the samples were determined (after the measurements) by measuring intensities of absorption at 6.45 eV due to Br^--ion in the aqueous solutions of the samples. The compositions of the samples were different from those of the corresponding mixed powders by less than 5% in the concentration-ratio of the two constituents.

§3. Experimental Results

In Fig. 1 are shown the outlines of the reflection spectra of the $CdCl_2$–$CdBr_2$ mixed system. Optical gap energies determined by transmission measurements are also indicated by arrows in the figure. The spectra of the pure compounds are well resolved as compared with those observed in evaporated films,[1] and agree with the previous measurement.[2] The doublet structure marked X_1 and X_2 comes essentially from the halogen p-state spin-orbit coupling; the weak structures X_1' and X_2' are assumed to be due to $n=2$ excitons; the additional structure X originates in the crystal-field splitting of the halogen p-states.[2] By making mixed crystals of the two compounds, a characteristic change is caused in the doublet structure. The low energy component X_1 of the $CdCl_2$-rich mixtures, which appears as a prominent peak in pure $CdCl_2$, decreases in intensity with increasing addition of $CdBr_2$ and disappears at 39 mol% addition (persistence type). Similar change is also observed for the $CdBr_2$-rich mixtures: The X_1 structure appearing as a prominent peak in pure $CdBr_2$ disappears at 61 mol% addition of $CdCl_2$. On the other hand, the high energy component X_2 of the doublet is maintained without big change in intensity throughout the full range of composition (amalgamation type). These behaviors of the doublet structure are different from the halogen-doublet behaviors observed in many isotropic mixed systems of halogen-substituted binary metal-halides; in these systems, both components of the doublet behave in pairs as a persistence type (alkali halides[3]) or as an amalgamation type (silver halides,[4] cuprous halides[5]). It is noted in Fig. 1 that the structures X of pure $CdCl_2$ and $CdBr_2$ amalgamate into a single structure in the mixtures; a pair-like bebavior is observed between X and X_2.

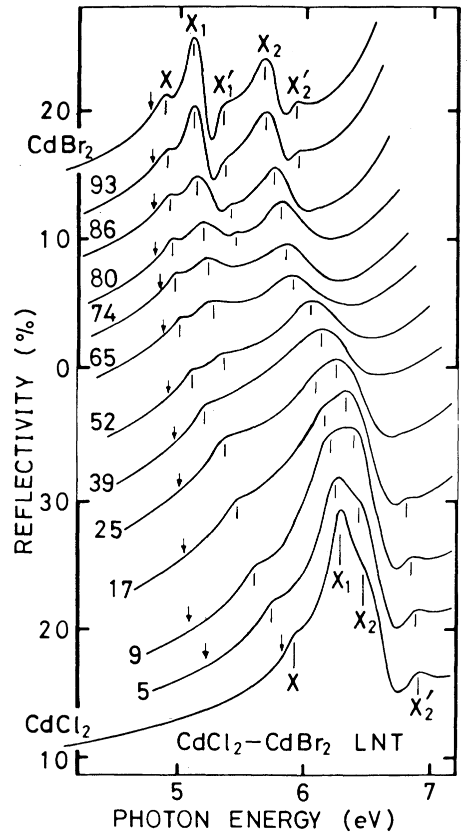

Fig. 1. The outlines of the nearly normal incidence reflection spectra of the cleaved surfaces of $CdCl_2$–$CdBr_2$ mixed crystals measured at liquid nitrogen temperature in the region of band gap excitons. These spectra are all shown in the same linear scale of reflectivity with their baselines shifted; in the figure, the scale of reflectivity is shown only for the pure materials in the ordinate: $CdCl_2$-lower part, $CdBr_2$-upper part. The numbers put at the left end of each spectrum denote the concentration of $CdBr_2$ in the samples in mole percent. The arrows put at low energies indicate the positions of the optical gap energies determined by transmission measurements.

In Fig. 2 the energy positions of the spectral structures and the optical gap energies are plotted against the concentration. The energy position of X_2 shifts almost linearly with the change of the concentration throughout the full range of composition. The structure X shows a quadratical change in energy against the change in the concentration. As for the persistence-type structures, only linear changes of the energy positions are observed. Almost no change in the doublet separation between X_1 and X_2 is observed for $CdCl_2$. For $CdBr_2$, the doublet separation between X_1 and X_2 increases with increasing content of $CdCl_2$. The energy positions of X_1 of the $CdBr_2$-rich mixtures lie along the straight line connecting the energy position of X_1 of pure $CdBr_2$ and

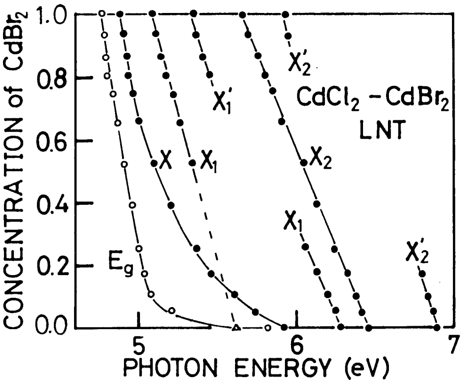

Fig. 2. The plot of the energy positions of the spectral structures and the optical gaps shown in Fig. 1 against the concentration of $CdBr_2$. The point marked △ at the bottom of the figure indicates the energy position of the absorption band due to Br^--ion in Br^--doped $CdCl_2$.

the point △ at the bottom of the figure, the energy position of the absorption band due to Br^--ion in $CdBr_2$-doped $CdCl_2$. The optical gap energy E_g shows a rapid rise in the $CdCl_2$-rich region.

§4. Discussion

As mentioned in §1 no energy band calculation is still available for $CdCl_2$ and $CdBr_2$. In a zero-order band picture, upper valence bands of these compounds will be of predomi nant halogen *p*-like character, while the lowest conduction band will be of cadmium *s*-like character. In the upper valence bands, is there a possibility of a certain admixture of cadmium *d*-state wave functions (if it is not parity-forbidden) because of relatively shallow atomic energy levels of the cadmium 4*d* electrons. Such an admixture would reduce the spin-orbit energy in the valence bands as it is in the cases of silver halides[4)] and cuprous halides.[5)] In $CdCl_2$ and $CdBr_2$, however, the doublet separations between the structures X_1 and X_2 are comparable with the atomic spin-orbit coupling energies of the constituent free halogen ions.[2)] The valence bands associated with these structures will therefore have no substantial admixture of the cadmium *d*-state wave functions.

According to group-theoretical arguments, the Γ and Z points in the Brillouin zone can have representations of halogen *p*-like character in which the *d*-admixture is parity-forbidden. They are one-dimensional Γ_2^- and Z_2^- of p_z-like character and two-dimensional Γ_3^- and Z_3^- of p_x- and p_y-like character, in the single group. Energy band structures of layered materials reported for PbI_2[6)] and CdI_2,[7-8)] both of which crystallize in the CdI_2 structure, have a common feature along the k_z axis ($\Gamma - A$) in the Brillouin zone: The top of the halogen *p*-like valence bands along this axis is located at the Γ point, at which the energy level of the Γ_2^- state lies above that of the Γ_3^- state. This would be also the case in $CdCl_2$ and $CdBr_2$ because of the same symmetry properties of the critical points along the k_z axis ($\Gamma - Z$).

When the spin-orbit interaction of the halogen *p*-states is introduced, the Γ_3^- state splits into a two-dimensional Γ_4^- state and two one-dimensional Γ_5^- and Γ_6^- states which are degenerate by time-reversal symmetry, and the Γ_2^- state goes into a Γ_4^- state.* The Γ_4^- state coming from Γ_3^-, which will be denoted as Γ_4^{3-} state, is of predominant p_x- and p_y-like character with a small admixture of the p_z-like wave function, whereas the Γ_4^- state coming from Γ_2^-, which will be denoted as Γ_4^{2-} state, is of predominant p_z-like character with a small fraction of p_x- and p_y-like character. The Γ_5^- and Γ_6^- states, which will be denoted as Γ_5^-, Γ_6^- states, are of pure p_x- and p_y-like character. On the other hand the cadmium *s*-like conduction band at the Γ point is of Γ_1^+ symmetry in the single group and of Γ_4^+ symmetry in the double group. Therefore, three excitons formed at the Γ point from the halogen *p*-like valence bands and the cadmium *s*-like conduction band are visible for the light with the electric vector $\boldsymbol{E}$ perpendicular to the *c* axis ($\boldsymbol{E} \perp c$). The observed structures X, X_1 and X_2 shown in Fig. 1 are attributable to these excitons. It is to be noted that the previous assignment[2)] for these structures is essentially the same as the present one, when the previous excitation model is translated into the band model.

Figure 3 illustrates the energies of the three valence states Γ_4^{2-}, Γ_4^{3-} and Γ_5^-, Γ_6^- (lower

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* The subscripts of the Γ notation for the extra representations are those of BRADLEY C. J. and CRACKNELL A. P., *The Mathematical Theory of Symmetry in Solids* (Clarendon Press, Oxford, 1972) p. 430.

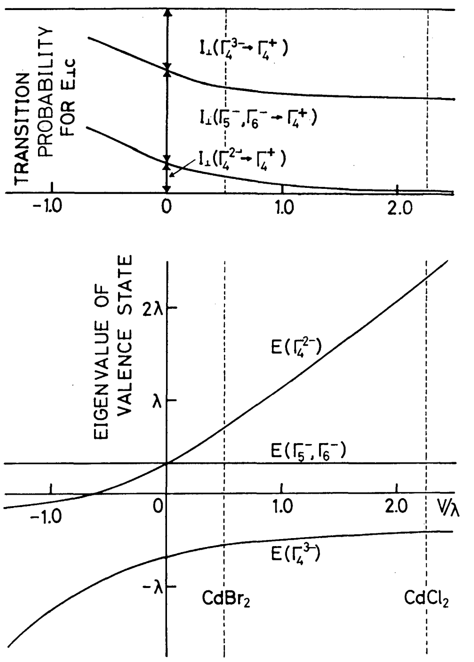

Fig. 3. The model for upper valence bands of $CdCl_2$ and $CdBr_2$ at the Γ point. The lower part shows the eigenvalue of halogen p-like valence states as a function of V/λ, the ratio of the crystal-field parameter V describing the energy separation between the Γ_2^- state of p_z-like character and the Γ_3^- state of p_x-, p_y-like character to the halogen p-state spin-orbit coupling energy λ. The upper part indicates the variation of the probability of the direct optical transition from these valence states to the cadmium s-like conduction state for $\boldsymbol{E}\perp\boldsymbol{c}$ as a function of V/λ. The dashed lines mark the experimental situation.

half) and the probabilities of the interband optical transitions from these states to the conduction state Γ_4^+ for $\boldsymbol{E}\perp\boldsymbol{c}$ (upper half), as a function of the normalized crystal-field parameter V/λ. The letter V is the crystal-field parameter describing the energy separation between the valence states Γ_2^- and Γ_3^-, and λ (>0) is the halogen p-state spin-orbit coupling energy. The explicit forms of the eigenvalues and the eigenfunctions of the valence states are given in Appendix. When both the exchange interaction between electron and hole and the contribution of the hole mass to the reduced mass of exciton are not taken into account, the ratio of the oscillator strengths for $\boldsymbol{E}\perp\boldsymbol{c}$ of the excitons associated with the interband edges $\Gamma_4^{2-}-\Gamma_4^+$, $\Gamma_4^{3-}-\Gamma_4^+$ and Γ_5^-, $\Gamma_6^- -\Gamma_4^+$ are proportional to that of the corresponding interband optical transition probabilities shown in Fig. 3. The V-dependence of the energies of the Γ_4^{2-} and the Γ_4^{3-} states comes essentially from the interaction of the p_z orbital with crystal field. The dashed lines mark the experimental situations of pure $CdCl_2$ and $CdBr_2$ determined from the relative energy positions of the spectral structures X, X_1 and X_2. In both compounds, the ratio of the interband optical transition probabilities determined by the dashed lines agrees well with an approximate estimate of the intensity ratio of the corresponding spectral structures. The electron-hole exchange interaction seems to be very weak and the hole mass is expected to be much larger than the electron mass.

Now let us try to interprete the behaviors of the spectral structures of the mixtures on the basis of this assignment. When a small amount of $CdBr_2$ is added to $CdCl_2$, particular Cl^- ions are replaced by Br^- ions. This gives rise to the change in the halogen p-like valence bands. Because these ions are situated in a strong electric field parallel to the c axis, the p_z orbitals of these ions may strongly interact with the field, and the energy difference between the bromine and the chlorine p_z orbitals may be smeared out. Therefore the bromine p_z orbital may be able to serve as a substitute for the chlorine p_z orbital in the mixture. As a result, the bromine p-state wave functions contribute to the Γ_4^{2-} and Γ_4^{3-} valence states of chlorine p-like character through the admixture of the p_z-state wave functions. This contribution may become remarkable with increasing addition of $CdBr_2$ in $CdCl_2$, and the amalgamation-type behavior of the structures X and X_2 upon making mixture is favorably accounted for by the continuous change of these valence states from chlorine p-like to bromine p-like character.

The persistence-type behavior of the structure X_1 can be explained by associating the structure with the Γ_5^-, Γ_6^- valence states. The interaction of the p_x and p_y orbitals with the crystal field is expected to be very weak compared with that of the p_z orbital. Therefore, each of the Br^- and Cl^- ions may persist its p_x- and p_y-orbital energy in the mixed crystal. Thus the Γ_5^-, Γ_6^- valence states, being of pure p_x- and p_y-like character, may be split as two valence states corresponding to the two different halogen ions in the mixed crystal. This gives rise to the persistence-type behavior of the structure X_1 upon making mixture. The absorption band due to Br^--ion in Br^--doped $CdCl_2$ is of worth mentioning. As shown in Fig. 2, the energy position of this band (which is marked △ in the figure) lies on the extension of the plot of the energy position for the X_1 structure of $CdBr_2$-rich mixtures. The shape of this band is Gaussian around the band maximum and follows Urbach's rule in the low energy tail region.[9)] These facts suggest a continuous change of the exciton mechanism from the band exciton (of pure $CdBr_2$ formed at the Γ point from the bromine p_x- and p_y-like valence band of Γ_5^-, Γ_6^- symmetry and the cadmium s-like conduction band of Γ_4^+ symmetry) to the localized exciton (of bromine p_x- and p_y-like character at the doped Br^--ion).

In isotropic materials, there have been many experimental studies on the behavior of the spectral structures upon making mixture, and a unifying theoretical expression has been given in ref. 10 by which both the persistence and the amalgamation types of the behavior can be described. In this expression the parameter Δ/T is used, where Δ is the energy difference of the two individual components of the mixture and T stands for the width of the energy band. (For example, in the case of a halogen-substituted binary metal-halide, the energy difference of the p-orbitals between the two halogens may be taken as the value of Δ and the width of the halogen p-like valence band as the value of T.) When Δ/T is large, the energy band is split as two bands in the mixed crystal. Each band gives rise to its own spectral structure of persistence type. Conversely, when Δ/T is small, the two individual energy bands merge into a single band, giving rise to a single spectral structure of amalgamation type. Various situations realized in the actual mixed crystals of isotropic materials have been successfully interpreted in terms of this expression.

The corresponding interpretation of the spectral behavior upon making mixture would be more complicated in anisotropic materials. In fact, both the persistence and the amalgamation types of the behavior are seen in the $CdCl_2$–$CdBr_2$ mixed system. If the expression mentioned above is applied to the present system, the structure X_1 corresponds to a large value of Δ/T and the structures X and X_2 to a small value of Δ/T. In other words, the value of the band-width parameter T is small for X_1 and large for X and X_2; the parameter T is no longer of single-valued. This may be understood as follows: Because the crystal field interacts more strongly with the p_z orbitals of the halogen ions than with the p_x and p_y orbitals of the same ions, the width of the valence bands to which the p_z orbitals can contribute is larger than that of the valence bands to which the p_x and p_y orbitals can contribute; this gives rise to a two-valued character of the band-width parameter T; the admixture of the p_z-state wave functions to the Γ_4^{2-} and Γ_4^{3-} valence states brings about a large value of T for X and X_2, whereas the pure p_x^- and p_y-like character of the Γ_5^-, Γ_6^- valence states a small value of T for X_1.

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Appendix

Because the primitive cell of $CdCl_2$ and $CdBr_2$, which contains two halogen atoms and one cadmium atom, can be taken to have inversion symmetry with respect to the cadmium atom, it is convenient to describe the halogen p-like valence states in terms of the symmetrical and the antisymmetrical orbitals of the form

$$p_{i\mp}=(p_{iA}\mp p_{iB})/\sqrt{2} \quad i=x, y, z, \qquad (\text{A}\cdot 1)$$

where p_{iA} and p_{iB} represent p_i orbitals on the two halogen atoms distingwished by the atomic sites named A and B in the primitive cell. The symmetrical orbitals p_{x-}, p_{y-} and p_{z-} can mix with cadmium d orbitals at every k point in the Brillouin zone. For the antisymmetrical orbitals p_{x+}, p_{y+} and p_{z+}, such a mixing is parity-forbidden at the Γ and Z points owing to inversion symmetry. Thus the valence states Γ_4^{2-}, Γ_4^{3-} and Γ_5^-, Γ_6^- are only composed of these antisymmetrical orbitals. Simple calculation shows that the eigenvalues of the three valence states are given by

$$E(\Gamma_4^{2-})=\frac{1}{2}\left[-\frac{\lambda}{3}+V+\sqrt{\lambda^2+\frac{2}{3}\lambda V+V^2}\right],$$
$$E(\Gamma_4^{3-})=\frac{1}{2}\left[-\frac{\lambda}{3}+V-\sqrt{\lambda^2+\frac{2}{3}\lambda V+V^2}\right],$$
$$E(\Gamma_5^-,\Gamma_6^-)=\frac{\lambda}{3}. \qquad (\mathrm{A}\cdot 2)$$

The corresponding eigenfunctions have the form

$$\Gamma_4^{2-}\begin{cases} \mathrm{i}u_0\!\downarrow \cos\theta-\mathrm{i}u_{-1}\!\uparrow \sin\theta, \\ -\mathrm{i}u_0\!\uparrow \cos\theta+\mathrm{i}u_1\!\downarrow \sin\theta, \end{cases}$$
$$\Gamma_4^{3-}\begin{cases} u_0\!\downarrow \sin\theta+u_{-1}\!\uparrow \cos\theta, \\ -u_0\!\uparrow \sin\theta-u_1\!\downarrow \cos\theta, \end{cases}$$
$$\Gamma_5^- \quad \frac{1}{\sqrt{2}}(u_{-1}\!\downarrow-\mathrm{i}u_1\!\uparrow),$$
$$\Gamma_6^- \quad \frac{1}{\sqrt{2}}(\mathrm{i}u_{-1}\!\downarrow-u_1\!\uparrow), \qquad (\mathrm{A}\cdot 3)$$

where

$$u_0=p_{z+},$$
$$u_{-1}=\frac{1}{\sqrt{2}}(p_{x+}-\mathrm{i}p_{y+}),$$
$$u_1=-\frac{1}{\sqrt{2}}(p_{x+}+\mathrm{i}p_{y+}), \qquad (\mathrm{A}\cdot 4)$$

and

$$\tan 2\theta=\frac{2\sqrt{2}\lambda}{\lambda+3V}. \qquad (\mathrm{A}\cdot 5)$$

The arrows ↑ and ↓ indicate the up- and the down-spin wave functions respectively. The probabilities of the $\boldsymbol{E}\perp\boldsymbol{c}$ optical transitions from these valence states to the cadmium s-like Γ_4^+ conduction state are given by

$$I_\perp(\Gamma_4^{2-}-\Gamma_4^+)=\sin^2\theta,$$
$$I_\perp(\Gamma_4^{3-}-\Gamma_4^+)=\cos^2\theta,$$
$$I_\perp(\Gamma_5^-,\Gamma_6^- -\Gamma_4^+)=1. \qquad (\mathrm{A}\cdot 6)$$

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