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Abstract

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THE STARK EFFECT ON EXCITON LEVELS OF CADMIUM SULFIDE CRYSTAL

There have as yet been no direct experiments observing the motion of an exciton through the crystal lattice. However, there exist a number of ideas and experiments showing that exciton motion can be demonstrated indirectly. Examples of such experiments are the recently observed phenomena of magnetic-field inversion in the spectrum of exciton absorption of CdS crystals (1) and the observation of the fine structure of exciton lines in CdS (2). Especially important and convincing for demonstrating exciton motion is the discovery of the effect of magnetic-field inversion in CdS. This phenomenon is closely connected with the appearance of an electric field arising as a consequence of exciton motion in a magnetic field (1). The resulting electric field should also directly affect the exciton levels, producing the Stark effect. This Stark effect may manifest itself in experiments with magnetic-field inversion, complicating the observed phenomenon. Therefore it seemed to us very important and interesting to investigate the ordinary Stark effect on exciton lines in a CdS crystal in an external electric field, in the absence of a magnetic field. To our knowledge, the Stark effect on exciton levels of CdS has until now remained unknown.

The study of the Stark effect on exciton lines of CdS is also of interest from another standpoint. A characteristic and fundamental property of the exciton, besides its motion, is its large size. It is precisely the fact that the exciton is an excitation encompassing simultaneously a large number of cells of the crystal that distinguishes it from other formations in the crystal. The Stark effect may provide evidence in favor of the large size of the exciton, since it is known (3) that the action of an electric field is the greater, the higher the degree of excitation of the exciton states in the crystal.

Proceeding from these considerations, we undertook a study of the Stark effect on the exciton lines of the absorption spectrum of a CdS crystal at a temperature of 4.2° K.* The investigations were carried out on very thin single crystals, with thickness from tenths of a micron to ten microns, which made it possible to observe clearly the exciton lines (4), in which the absorption is very large. As a result of the investigations it was possible to establish the following.

First series of lines (Γ_9—Γ_7) (6,5,2)

1. **The direction of the electric field F coincides with the direction of the optical axis of the crystal $C(F \parallel C)$.**

a) $E \parallel C$. The lines corresponding to exciton states with high excitation are most sensitive to the electric field. Already at electric-field strengths of tens of volts per cen-

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* It is, of course, of great interest to study the influence of the electric field separately on the lines of transverse excitons and separately on the lines of longitudinal excitons (2). At the present stage of our work we did not set ourselves such a task, but restricted ourselves to elucidating the general features of the Stark effect phenomenon, postponing these more delicate experiments to our further investigations.

- becomes noticeable: there is some broadening of the exciton lines $n = 4$ and $n = 3$ and their shift into the violet region of the spectrum. As is seen from Fig. 1a, b, the shift of the line $n = 4$ is considerably greater than that of $n = 3$. A further increase in the electric field leads to broadening and to a shift toward shorter wavelengths also of the line $n = 2$. At the same time, no shift of the line $n = 1$ was noticeable even in fields of 10-15 kV/cm. Further, splitting of the lines $n = 2$ and $n = 3$ was found. On the line $n = 1$, no splitting was observed for any of the fields used.

The clearest picture of the Stark effect is observed on the line $n = 2$. In fields of about 100 V/cm, a noticeable shift to the red side begins for the "satellite" ($\lambda 4814.8$ Å) of the line $n = 2$ ($\lambda 4813.2$ Å) (Fig. 1b). Following the shift of the "satellite," as the field is increased, the line $n = 2$ itself splits (Fig. 1c). The long-wavelength component of the line $n = 2$ is almost not displaced and remains, with increasing field, near the initial position of the line $\lambda 4813.2$ Å. Conversely, the short-wavelength component is strongly displaced toward the violet side of the spectrum as the field increases. Both the "satellite" and the short-wavelength component of the line $n = 2$, which are extremely weak for $E \parallel C$ and for normal incidence of light on the plane of the crystal, are sharply enhanced in the extraordinary ray when the crystal is rotated about an axis perpendicular to the optical axis, whereas the long-wavelength component of the line $n = 2$ is then somewhat weakened.

An analogous picture, no less distinct, is also observed on the line $n = 3$ ($\lambda 4805.8$ Å). As the electric field is increased, already at fields of several tens of volts per centimeter, a rather broadened and weak line splits off from the long-wavelength edge of the line $n = 3$, which then rapidly shifts to the red side of the spectrum (Fig. 1b). The behavior of this line in an electric field is analogous to the behavior of the "satellite" of the line $n = 2$, and therefore it may be assumed that this line is a "satellite" of the line $n = 3$, which is difficult to observe in the absence of an external electric field because of its weakness

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

and its close position to the line $n = 3$. In an electric field, the "satellite," apparently increasing in intensity, moves away from the line and therefore becomes noticeable.

Following the splitting-off of the "satellite," with a further increase in the field, from the short-wavelength edge of the line $n = 3$ ($\lambda 4805.8$ Å), apparently, another line splits off, which shifts to the violet side of the spectrum as the field increases. The third line remaining from $n = 3$ also shifts somewhat to the violet side as the field increases (Fig. 1c). It should be emphasized that the splitting-off of the "satellite" and of the short-wavelength component of the line $n = 3$ occurs at considerably smaller fields than for the line $n = 2$.

No splittings of the line $n = 4$ ($\lambda 4803.5$ Å) were observed, since this line is extremely weak and rapidly broadens with increasing electric field F.

Fig. 1. Stark effect on the exciton series of absorption lines $\Gamma_9 - \Gamma_7$ in the spectrum of CdS in polarized light. The crystal is rotated about an axis perpendicular to the optical axis.
$E\widehat{C} = 45^\circ$. Field orientation $F \parallel C$ ($T = 4.2^\circ$K). $a - F = 0$, $b - F = 600$ V/cm, $c - F = 5500$ V/cm

Fig. 2. Stark effect on the line $n = 2$ of the series $\Gamma_9 - \Gamma_7$. Polarization $E \perp C$. Field orientation $F \parallel C$. $a - F = 0$, $b - F = 500$ V/cm

Fig. 3. Stark effect on the line $n = 2$ of the series $\Gamma_9 - \Gamma_7$ in polarized light. The crystal is rotated about an axis perpendicular to the optical axis. $E\widehat{C} = 45^\circ$. Field orientation $F \perp C$. $a - F = 0$, $b - F = 2500$ V/cm

Fig. 4. Stark effect on the line $n = 2$ of the series $\Gamma_7 - \Gamma_7$ for $E \parallel C$ and $E \perp C$. Field orientation $F \parallel C$ and $F \perp C$. $a - F = 0$, $b - F = 500$ V/cm

* The quoted numerical values of the field strengths were determined only from the difference of potentials and the distance between the electrodes. These values do not give the actual magnitude and distribution of the field acting in the crystal, but are only certain average values. In this work, exact measurement of the field inside the crystal by means of probes was not carried out.

Fig. 1

Fig. 2

Fig. 4

Fig. 4

Figure 3: Fig. 4

Fig. 3

Figure 4: Fig. 3

Fig. 3

b) $E \perp C$. With light polarization $E \perp C$, the lines of the $\Gamma_9 - \Gamma_7$ series are considerably broader and stronger than for $E \parallel C$, and therefore extremely thin crystals are required for their study. The investigation of crystals with thicknesses of tenths of a micron showed that, as in the case $E \parallel C$, even in fields of 10-15 kV/cm no influence of the electric field on the line $n = 1$ is noticeable. On the other hand, already in fields of hundreds of volts per centimeter, the appearance, in place of the line $n = 2$, of two lines of approximately equal intensity becomes noticeable (Fig. 2). These lines move apart with a further increase of the field F. The long-wavelength one of these lines should apparently be identified with the "satellite" of the line $n = 2$, and the short-wavelength one with the short-wavelength component of the line $n = 2$ observed for $E \parallel C$. This observation, together with the experiments described for $E \parallel C$, shows that both the "satellite" of the line $n = 2$ and the short-wavelength component of the line $n = 2$ are apparently polarized in an electric field with $E \perp C$, whereas the long-wavelength component of the line $n = 2$, absent in the field for $E \perp C$, is apparently polarized in $E \parallel C$.

The investigation of the Stark effect on the lines $n = 3$ and $n = 4$ for $E \perp C$ has so far proved impossible, since these lines were observed indistinctly in the polarization $E \perp C$.

2. Direction of the electric field F perpendicular to the optical axis of the crystal C ($F \perp C$).

This case was investigated in our experiments insufficiently completely. As preliminary experiments show, for $F \perp C$ essentially the same phenomena are observed as for $F \parallel C$. No action of the field on the line $n = 1$ was observed. In the region of the line $n = 2$, for $E \parallel C$, just as in the case $F \parallel C$, three absorption lines were observed in the electric field. The features of the orientation $F \perp C$ are apparently a somewhat different ratio of the intensities of these three lines and a somewhat different mutual spacing between them (Fig. 3). In addition, indications of a complex structure are found in the long-wavelength component of the line $n = 2$.

The study of the Stark effect on the lines $n = 3$ and $n = 4$ proved very difficult because of the indistinctness of the observed pattern in the region of these lines in crystals in which the electric field F was oriented perpendicular to the optical axis C.

Second series of lines $(\Gamma_7 - \Gamma_7)$

The first line of this series, $n = 1$ (λ4826.5 Å), does not split or shift in fields up to 10–15 kV/cm*. The second line, $n = 2$ (λ4785 Å), for any orientation of F and C, independently of the polarization of the light, splits into two components of approximately equal intensity (Fig. 4), and with increasing field the short-wavelength component of the line $n = 2$ shifts toward the violet side of the spectrum, while the long-wavelength component shifts toward the red. On the line $n = 3$ (λ4777.5 Å) the Stark effect could not be observed, since this line is extremely weak.

No observations of the Stark effect were carried out on the lines of the third series $\Gamma_7 - \Gamma_7$.

Summarizing the results obtained, it may first of all be noted that the very fact of observing the Stark effect in very small fields ([3]) (tens of volts per centimeter) confirms that in the CdS crystal the exciton dimensions are large and increase as the frequencies of the lines (the quantum numbers n) in the spectrum ([5,7]), belonging to one and the same series, increase. The stronger Stark effect on lines corresponding to states with high exciton excitation is in good agreement with the increase of the diamagnetic shift in the Zeeman effect for the CdS absorption lines as the

* In one of the CdS crystals we noticed, in fields of about 10 kV/cm, a certain shift of the long-wavelength edge of the line $n = 1$ toward the red. This phenomenon requires further study.

their quantum numbers n ([8,5]). The results of our experiments on the Stark effect are also in good agreement with the recent works of Birman ([9]), Lempicki ([10]), and Thomas and Hopfield ([6]) on the structure of the valence band and the exciton spectrum of the CdS crystal.

From the study of the Stark effect it follows that, apparently, the "satellites" of the lines $n = 2$ and $n = 3$ are considerably enhanced in the field. This fact indicates that these lines are forbidden in the CdS spectrum, since in the absence of an electric field they are very weak. If this is so, then the behavior of the "satellite" lines in an external electric field is of interest to compare with their behavior in a magnetic field ([5]), where they are also enhanced. Indeed, their enhancement in the latter case may be caused by the electric field arising from the motion of the exciton in the magnetic field ([1]). Then the enhancement of the "satellite" lines in a magnetic field may be regarded as evidence in favor of the motion of excitons through the lattice of the CdS crystal.

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Note: Figure translations are in progress. See original paper for figures.