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Abstract

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FREE AND BOUND EXCITONS IN A CADMIUM SULFIDE CRYSTAL AND AN OPTICAL ANALOG OF THE MÖSSBAUER EFFECT

Already in the very first works ($^{1-3}$) on the study of the structure of the fundamental absorption edge of a cadmium sulfide crystal at 4.2° K, the existence of two characteristic groups of lines was discovered.

The first group has a very large absorption coefficient and lies in the wavelength interval $\lambda\lambda$ 4857—4600 Å. This group of lines was already interpreted by us at that time as an exciton spectrum. A number of subsequent studies gave convincing evidence of the exciton origin of the lines. These lines are associated with excitons freely moving in the CdS crystal lattice.

The second group of considerably narrower absorption lines is situated on the long-wavelength side of the first, in the wavelength interval $\lambda\lambda$ 4889—4857 Å. The absorption coefficient in these lines is several orders of magnitude smaller than in the exciton lines. The variability of the lines of this group did not allow us to associate them with free excitons in the CdS lattice, and we put forward the suggestion that the occurrence of these lines is connected with impurity centers and defects in the crystal (^{2}). It was possible to think that the spectrum of fine lines belongs to "impurity excitons" (^{2}), formed in the vicinity of a lattice defect (^{3}), with an energy smaller than that of free excitons. We considered them similar to the α- and β-excitons in alkali-halide crystals considered by Seitz (^{4}). Ideas about the role of lattice defects in exciton excitation were further developed in the works of Bassani and Inchospe (^{5}), Lampert (^{6}), and Haynes (^{7}), who proposed the formation of complexes involving an impurity center and an exciton.

In a series of experimental works ($^{2,3,8-10}$) on the absorption and emission spectra of a CdS crystal, we studied a number of properties of the fine lines and attempted to clarify the role of defects in their formation. The further development of our investigations in this direction is the work whose results are set forth below.

1. Careful investigations established a substantial difference between the exciton and the fine lines of the CdS spectrum. Experiments showed that

Fig. 1. Absorption spectra (a) and resonance-emission spectra (b) of "bound" excitons in a CdS crystal

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Fig. 4. Effect of illumination of the crystal on various fine absorption lines in a CdS crystal

Figure 2: Fig. 4. Effect of illumination of the crystal on various fine absorption lines in a CdS crystal

there is no shift of the fine emission lines relative to the absorption lines (to an accuracy of 10^{-5} eV), i.e., they are resonant (see Fig. 1a, b).

On the contrary, the lines of free excitons in emission, polarized in the same way as the corresponding absorption lines*, show an obvious shift to the long-wavelength side relative to the absorption lines, depending on the principal quantum number n (^{12}). Thus, in the series (Γ_9—Γ_7) (^{10,11}), the shift is 0.1 Å for $n = 1$; 1.8 Å for $n = 2$, and 2.2 Å for $n = 3$ (see Fig. 2a, b). On the emission line $n = 1$ we succeeded in observing the same fine structure in emission as in absorption (^{11}), associated with longitudinal and transverse excitons, but shifted by 0.1 Å.

We believe that the shifts of the exciton emission lines relative to absorption lines may be associated with the recoil effect for a free exciton (^{13}). The absence of such a shift for the fine lines confirms that the excitons here are bound to heavy formations in the lattice—to impurity centers.

Fig. 1. Absorption spectra (a) and resonance-emission spectra (b) of "bound" excitons in a CdS crystal

Fig. 4. Effect of illumination of the crystal on various fine absorption lines in a CdS crystal. Spectrum of the crystals: a—illuminated from the region $\lambda\lambda$ 4000—6500 Å; b—the same crystal without illumination; c—the same crystal, illuminated from the region $\lambda\lambda$ 0.7—2 μ; d—an unilluminated crystal; e—a crystal illuminated from the region $\lambda\lambda$ 4000—4800 Å; f—the same crystal without illumination.

The "immobility" of bound excitons is indicated by the extraordinary narrowness of the fine lines in comparison with the lines of a freely moving exciton. The latter circumstance was noted in the interesting work of Haynes (^{7}), devoted to the spectrum of silicon. Another indication that the narrow lines in CdS are not associated with a freely moving exciton is provided by the study of the Zeeman effect (^{10}), which did not reveal an inversion effect for them. The fact

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* Near the exciton emission line λ 4825.5 Å, $n = 1$ of the series $(\Gamma_7$—$\Gamma_7)_1$, an emission line λ 4828.0 Å is observed, polarized with $E \perp C$.

Fig. 2. Shift of the emission lines $n = 2$ and $n = 3$ of the $(\Gamma_9 - \Gamma_7)$ series of free excitons relative to the absorption lines

Figure 3: Fig. 2. Shift of the emission lines $n = 2$ and $n = 3$ of the $(\Gamma_9 - \Gamma_7)$ series of free excitons relative to the absorption lines

that the fine lines belong to bound excitons is supported by the circumstance that the excitation maximum of the luminescence of the fine lines coincides with the absorption lines of free excitons.

Fig. 2. Shift of the emission lines $n = 2$ and $n = 3$ of the $(\Gamma_9 - \Gamma_7)$ series of free excitons relative to the absorption lines.

2. In the CdS spectrum one observes yet another characteristic phenomenon, which argues in favor of the existence in the crystal of centers associated with excitons. Fine emission lines, resonant with the absorption lines and being the principal ones, are accompanied on the long-wavelength side by a series of equidistant lines ([9], [14]), the spacing between which is equal to the energy of a longitudinal optical phonon. These lines are formed with the simultaneous emission of a photon and n phonons $(n = 0, 1, 2 \ldots)$, i.e., an exchange of energy occurs between the bound exciton and the optical branches of the lattice vibrations.

In addition to this phenomenon, we found that such exchange can occur not only with the optical but also with the acoustic branches of the lattice vibrations. Interaction with acoustic phonons is detected both in the emission spectrum and in the absorption spectrum of the CdS crystal.

As is seen from Fig. 3a, the absorption line $\lambda 4888.6$ Å, of width 0.5 Å, is accompanied on the short-wavelength side by a considerably weaker band with a maximum at $\lambda 4887.0$ Å, of width 5 Å, with a characteristic intensity distribution.

A similar pattern is observed in emission. The fine emission line $\lambda 4888.6$ Å, resonantly coincident with the absorption line, is accompanied on the long-wavelength side by a weaker band with a maximum at $\lambda 4890.2$ Å* (see Fig. 3b), mirror-symmetric to the absorption band and having the same width. The center of this mirror-symmetric pattern (Fig. 3c) is the line $\lambda 4888.6$ Å. We associate the origin of the symmetrically located emission and absorption bands with phonons of the acoustic branch.

Further, we found that this “acoustic band” is repeated in the emission spectrum with the frequency of the optical phonon, accompanying the repetition of the principal line $\lambda 4888.6$ Å.

Thus, in our experiments an interesting fact is observed: a mirror-symmetric pattern of absorption and emission bands accompanies—

* In some crystals, against the background of this emission band, a second

Fig. 3

Figure 4: Fig. 3

maximum is observed at $\lambda 4893.5$ Å.

is a strong narrow line* of the phononless transition, which is the center of a symmetric pattern. This phenomenon is unusual for a luminescence spectrum. In the spectra of absorption and luminescence bands that obey the well-known experimental law of mirror symmetry of Levshin (15), narrow lines of the phononless transition are not observed. As is known, Levshin’ s law was substantiated for an impurity center in a crystal in theoretical studies by Pekar, Krivoglaz (16), and Lax (17). Further work by Trifonov (18) showed that in the case of weak coupling of the center to the lattice (the case of small Stokes losses), at the center of the mirror-symmetric pattern of

Fig. 3. Mirror symmetry of the absorption and emission bands near the line λ 4888.6 Å. *a* –microphotogram of the absorption spectrum, *b* –microphotogram of the emission spectrum, *v* –superposed microphotograms of the absorption and emission spectra

absorption and luminescence a narrow line of the phononless transition may be observed, the more intense the smaller the Stokes losses. Our experiments, which revealed this line, thus confirm Trifonov’ s theory.

The appearance in luminescence of a narrow unshifted line, coinciding in frequency with a narrow line in absorption, must be regarded as an analogue of the Mössbauer effect in optics. As is known, in the region of γ-quanta an unshifted narrow emission line (and a narrow absorption line) is obtained as a result of transfer of the momentum of the γ-quantum to the entire lattice as a whole, when the vibrational states of the lattice are not excited. In the optical region of the spectrum, in the case of impurity centers, recoil effects may be neglected because of their smallness. Our experiments show that processes occur in the crystal in which electron-vibrational transitions are absent and a narrow line is obtained in absorption and a narrow unshifted line in emission, as in the Mössbauer effect. At the same time the general features of the phenomenon, as noted above, fit within the framework of Trifonov’ s theory (18).

As follows from the theoretical works mentioned above, a mirror pattern of absorption and luminescence is characteristic of an impurity center. This argues in favor of the fact that the group of fine lines in the CdS spectrum indeed belongs to excitons bound to impurity centers.

3. In the spectrum of fine lines we discovered one more interesting phenomenon. It turned out that the intensity of many absorption lines, when observed in a spectrally narrow beam of light $\Delta\lambda = 4840$–4900 Å, depends strongly on additional illumination of the crystal. According to their behavior under illumination of the crystal by light of different frequencies,

the fine lines can be divided into several groups.

* The line λ 4888.6 Å is considerably more intense than the mirror-symmetric bands around it, both in absorption and in emission. In Fig. 3 a, b, v, the ratio of the intensities of the line and of the bands is strongly distorted during microphotometry of the spectrograms, so that the intensities of the line and of the bands turned out to be almost equal.

1. λ 4866.2; λ 4862.8; λ 4860.5; λ 4858.4 Å. These absorption lines, clearly observed under ordinary illumination of the crystal with unfiltered light, are completely absent when it is illuminated through a monochromator with a spectrally narrow beam of light $\Delta\lambda$ (Fig. 4b). With simultaneous illumination of the crystal by visible light λλ 4000–6500 Å, these lines appear in the spectrum and are very strong (Fig. 4a). Simultaneous infrared illumination (λλ 0.7–2 μ) somewhat reduces the absorption intensity of these lines.
2. λ 4866.7 Å. When the crystal is illuminated in the region $\Delta\lambda$, the line is weak (see Fig. 4e). Simultaneous illumination of the crystal from the intrinsic absorption band (λλ 4000–4800 Å) almost completely destroys the line λ 4866.7 Å, whereas infrared illumination (λλ 0.7–2 μ) sharply enhances it (Fig. 4c).
3. λ 4888.6; λ 4864.0; λ 4868.0 Å. These lines, as a rule, are observed distinctly under ordinary illumination of the crystal with unfiltered light. When illuminated through a monochromator in the region $\Delta\lambda$, the lines λ 4888.6 and λ 4864.0 Å are observed distinctly, while the line λ 4868.0 Å is absent (Fig. 4e). Simultaneous illumination from the region of the intrinsic absorption band (λλ 4000–4800 Å) causes a noticeable enhancement of the first two lines (λ 4888.6 Å, λ 4864.0 Å) and the appearance of the third (λ 4868.0 Å) (Fig. 4d). Simultaneous illumination with infrared light (λλ 0.7–2.0 μ) has little effect on the lines.
4. λ 4865.4 Å; λ 4862.7 Å. In a spectrally narrow beam of light $\Delta\lambda$, these lines are observed rather distinctly. Simultaneous illumination with infrared light (λλ 0.7–2.0 μ) enhances them.

In all cases the illumination effects disappeared as soon as the illumination was switched off. At the same time, the effect of enhancement or weakening of the lines has no noticeable inertia or saturation in time when observed directly by eye through the spectrograph. The reproducibility of the phenomena did not depend on the number of experiments performed.

Experiments on the influence of additional illumination on the absorption of narrow lines also testify in favor of the fact that these lines belong to excitons bound to impurity centers. The energy of a bound exciton may differ depending on whether the impurity center is ionized or neutral. This should lead to the appearance of one or another fine line. Additional excitation of the crystal by light can substantially change the concentration of ionized and nonionized centers and lead to enhancement or weakening of the corresponding lines.

The study of the different influence of illuminations will apparently help to reveal the nature of the centers and the positions of their energy levels.

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