agreement between theory and experiment is seen to be good in spite of the simplicity of the model.

The effects described above will appear to a greater or lesser degree in essentially all bound hole or electron states which are orbitally degenerate. Their importance in specific cases can be determined either experimentally or through calculation of the coupling strengths. Only in the third example above—the bound exciton—does experiment confirm unambiguously the existence of a dynamic Jahn-Teller effect and provide a direct measure of its strength. In the second example the coupling to excited vibronic states can be tested experimentally through further Raman studies of other systems. The extent of the Jahn-Teller contribution to the reduction factors and g factors of specific acceptor states is not known at present because of the incomplete nature of our understanding of "shallow" acceptor states and because of a very similar reduction effect generated by the local strain field around the impurity atom. This strain contribution will be discussed in a later communication.

It is a pleasure to acknowledge the help of A. Onton in relating theory and experiment and of Jane van W. Morgan and J. C. Slonczewski in numerous discussions of theory.

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EXCITON-EXCITON INTERACTION IN CdS, CdSe, AND ZnO†

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An extra luminescence band is observed in CdS, CdSe, and ZnO under intense illumination by laser light. It is suggested that the additional luminescence arises from a particular exciton-exciton interaction process common to these semiconducting compounds.

This paper reports the appearance of an extra luminescence band in CdS, CdSe, and ZnO under intense illumination by (laser) light pulses. The spectral position of the new bands in the three substances, at approximately twice exciton binding energy away from the band gap, and their appearance under conditions of excitation favoring high exciton densities suggest that we observe the result of a particular exciton-exciton interaction in which one of the excitons (which gains energy) scatters into a higher excited exciton state or into the dissociation state, while the other exciton (conserving momentum and energy) scatters from an excitonlike state of the "exciton-polariton"[1] to a photonlike state. In the photonlike state (which is not coupled to phonons) the "exciton-polariton"[1] is free to propagate through the crystal to emerge as a "luminescence" photon.

Exciton-exciton interactions giving rise to stable entities, biexcitons or excitonic molecules, were observed in Si,[2] Ge,[3] and CuCl.[4] In anthracene, certain photoconductivity results[5] have been explained[6] in terms of collision ionization, a scattering process in which two excitons are destroyed to create one state within the electron-hole continuum. The particular type of exciton-exciton interaction suggested by our experiments was first tentatively proposed as one of two alternatives (biexcitons being the other) by Benoit à la Guillaume, Debever, and Salvan[7] to explain extra luminescence seen in a particular type of CdS wafer after strong electron-beam excitation. A theoretical prediction of such a process was made by Keldysh and Kozlov.[8]

The results to be presented suggest that this particular exciton scattering is operative in various sample types of three typical II-VI compounds. We submit therefore that this process is a common and major exciton interaction process in such semiconductors.

Single crystals of CdS, CdSe, and ZnO were photoexcited, mostly at 1.8°K, with pulses of 25 nsec duration from laser sources (the second harmonic of ruby or neodymium lasers or the radiation from a laser-pumped tunable organic dye laser). The frequency of the incident radiation was chosen to fall into the band-to-band transition region or, alternatively, into the free-exciton band region. The results were independent of the frequency of the exciting light. The samples, mounted at an angle of 30° to the direction of the incident laser beam, were immersed in liquid helium. Luminescence emitted from the front surface of each sample was observed at 90° by a monochromator and photomultiplier. Each signal pulse was displayed, along with a monitor of exciting pulse intensity, on a dual-beam oscilloscope and photographed. The wavelength range over which luminescence occurred was mapped point by point. The maximum resolution was 1 Å. The lowest excitation levels reported were limited by shot noise.

Conventional luminescence measurements were also performed on all samples using continuous Hg-arc excitation. These served three purposes: First, they served as reference spectra for the laser-excited results. Second, measurements could be made at high resolution to identify fine structure (such as the splitting of the well-known I_2 multiplet in CdS) as a test of excessive impurity content and sample strain. Third, such results were used in comparison with published data for sample identification.[9]

Results for a typical CdS platelet are shown in Fig. 1. The lowest curve shows, on a displaced intensity scale, the continuously recorded, conventional photoluminescence. At relatively low laser-intensity levels of 2 kW cm^{-2} a luminescent spectrum was obtained which agreed in its main features with the one obtained by Hg excitation of the same sample. We are confident, then, that at low light levels no artifacts are introduced by laser excitation of luminescence. Increasing the level of laser excitation to 12 and 40 kW cm^{-2} produces a growth of the low-level features I_1, I_2, and I_1–LO. In addition an extra band of luminescence, M, grows larger and larger. The existence of M was clearly established through additional measurements at a variety of incident intensity levels in the range 2-100 kW cm^{-2}. It was also determined that the peak luminescence value of M grows at a rate faster than linear, whereas the peak value of

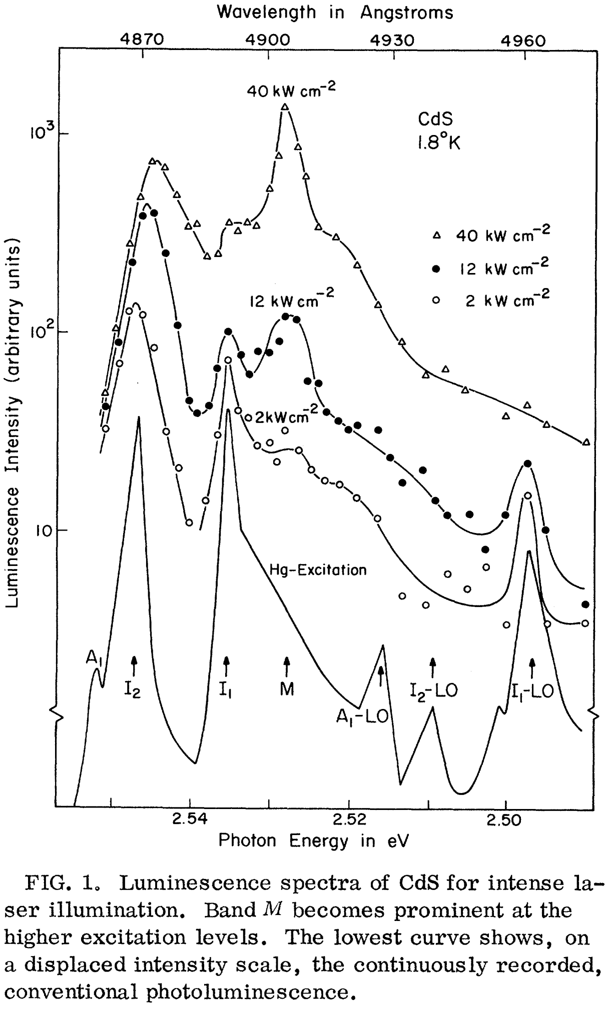

FIG. 1. Luminescence spectra of CdS for intense laser illumination. Band M becomes prominent at the higher excitation levels. The lowest curve shows, on a displaced intensity scale, the continuously recorded, conventional photoluminescence.

I_2 grows nearly linearly at first but begins to saturate near 80 kW cm^{-2}. Luminescence band M was observed in all samples[9] investigated (platelets, "chunks" of single crystals); it was identical at 1.8 and 4°K and was found to be still present, although broadened, at 20°K.

A similar band M was found in CdSe at 1.811 eV and in ZnO at 3.324 eV. In CdSe saturation of conventional luminescence structure (other than M) was observed at excitation levels around 1000 kW cm^{-2}. In ZnO no such behavior was observed even at 3000 kW cm^{-2}. In ZnO as well as CdSe the directly observed peak value of M rose more steeply than linear with excitation intensity.

All prominent emission structure (including M) was found to be preferentially polarized perpendicular to the c axis in the three compounds. This establishes a relationship to the A-type[10] exciton. The incident light intensities at which band M becomes "prominent" are similar (but sample dependent to a factor of 3 or 5) in CdS and CdSe and about an order of magnitude higher in ZnO.

At excitation levels higher than shown in Fig. 1 but below the threshold for detectable crystal damage, further changes in the luminescence spectra of CdS and CdSe were observed. The cause of these changes and their relation to M is not presently understood.

The most striking feature of the new luminescent band M is illustrated in Fig. 2. Here the normalized energy schemes of excitons, their phonon replicas, bound excitons, and band edges are plotted for CdS, CdSe, and ZnO.[10] The energy levels are adjusted such that the band edges A_∞ coincide and the scales are adjusted so that the free-exciton energies A_1 also coincide for the three substances. As shown, the luminescent band M is at almost the same relative position in all three substances. Furthermore the peak position of M is shifted to lower photon energies by an amount which lies between the binding energy $(A_\infty - A_1) = \mathrm{B.E.}$ and the energy difference $(A_2 - A_1)$ between the $n=2$ and $n=1$ exciton state. No other such correlation of the position of M with bound-exciton emission lines or phonon-shifted free- or bound-exciton emission lines is observed for all three substances.

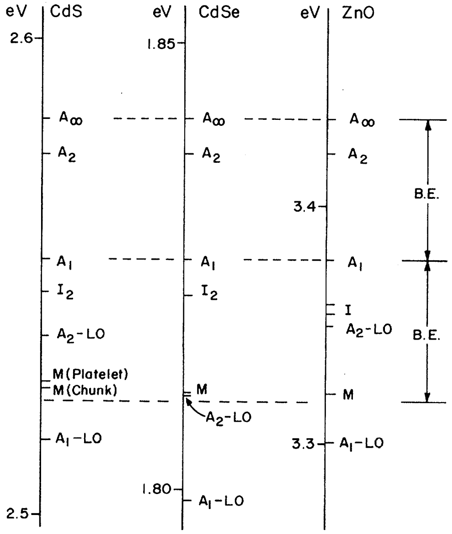

FIG. 2. Normalized, relative energy scheme of excitons, bound excitons, phonon replicas of excitons and bound excitons, and band gaps for CdS, CdSe, and ZnO. The relative peak position of the additional luminescence band M is as indicated in the three compounds.

We stress this point because a great variety[11] of mechanisms involving such features have been advanced, tentatively, in the past to explain unusual luminescence under high excitation in one or another semiconducting compound. While each suggestion does explain certain isolated results, none explains the systematic effect noted here. Nor can the extra structure be connected with an overall increase in sample temperature. A large temperature increase is unlikely in view of the fact that the I_2 band remains stronger than the I_1 band as the excitation level increases.[12] The final possibility, that normally weak transitions involving excited states of bound excitons,[13] near neighbor pairs,[14] or completely new bound excitons, not previously reported, are somehow enhanced at high excitation levels, is difficult to rule out definitively. Again we suggest that the similarity in spectral position and in intensity level required to observe the effect in three different compounds, and in individual samples of widely different impurity content,[9] favors an explanation in terms of an intrinsic effect.

The main experimental results, namely, the relative position of band M and the fact that luminescence is observed, can, however, be explained with the model shown in Fig. 3. Two excitons situated, for example, at energy and momentum values like a, a', can be scattered into two new states, conserving momentum and energy over all. One exciton is scattered to a higher excited state of the exciton (A_2, A_3, etc.) (as near b' in Fig. 3) or the ionization state A_∞. The other exciton which is "excitonlike"[1] near a will be scattered to a mainly "photonlike"[1] exciton state near b. This photonlike exciton will traverse the crystal unattenuated (because

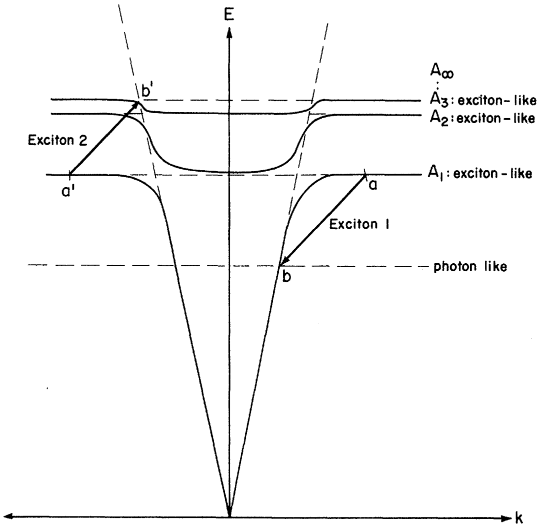

FIG. 3. "Exciton-polariton" dispersion curve showing the kinematics of interaction of two excitons at *a* and *a'* such that final states near *b* and *b'* result. Photon *b* is observed in the experiment.

the exciton-phonon coupling is negligible near *b*) to leave as a "luminescence" photon of energy $\hbar\omega_b$. All initial states from various regions of the A_1 "excitonlike" branch of Fig. 3 can participate in the scattering and all final states conserving total momentum and energy, with one exciton in A_2, A_3, etc. or A_∞ and the other exciton near $\hbar\omega_b$, are allowed. The shape of the luminescence band M around $\hbar\omega_b$ is then determined by the distribution of excitons over initial states, the availability of final states, and the relative strength of the transition moments involved.

In the process of interaction between two excitons a stable entity, a biexciton, may be formed and subsequently decay into two different exciton states. The temperature independence of M (at 1.8 and 4°K identical results were observed, while at 20°K a somewhat broadened band M was still prominent at comparable excitation levels) suggests that no stable biexcitons form at 1.8°K in CdS. A repulsive interaction potential exists then, due to the fact that at increasing densities excitons will come so close to each other that their internal makeup of electrons and holes will become noticeable. The Coulombic interaction between the subparticles determines the scattering strength. No calculation is available for the scattering process discussed here and depicted in Fig. 3.[15]

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[9] CdS and CdSe samples were purchased from the Eagle Picher Company. Two types of CdS samples were investigated: Thin platelets showed intense I_1 and I_2 bound-exciton lines. "Chunks," cleaved from ultrahigh-purity single crystals, showed no I_1 line. CdSe samples were cleaved from single crystals and showed the analog of the I_2 line. The ZnO single crystal, supplied by 3M Corporation, showed a series of three bound-exciton lines at 3.345, 3.341, and 3.326 eV under conventional excitation.

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