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Photoluminescence at High Exciton Densities in CdS[†]

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This report is concerned with exciton interactions in CdS at 4.2 °K in a range of concentrations where exciton densities are very large ($\sim 10^{19}/\text{cm}^3$) and the independent-particle description of the exciton is no longer valid. The exciton interactions are studied by monitoring the photoluminescence emission from this compound when excited by intense laser radiation. The exciton-emission spectra of CdS were studied as a function of excitation power in the region of the M band (4904 Å). As the laser power is increased from 100 kW/cm^2 to 8 MW/cm^2, several new emission bands appear on the long-wavelength side of the M band shifted by several meV from the M band. Both of these new bands show a superlinear dependence on laser power. Several theories for the behavior of high-density exciton systems are examined, and it is shown that the formation and subsequent decay of an excitonic molecule can consistently explain the observed photoluminescence behavior. We deduce a molecular binding energy of 3–4 meV for the excitonic molecule in CdS.

I. INTRODUCTION

The history of the bound electron-hole pair in solids dates from the 1930's with the preliminary work of Frenkel[1] and Wannier.[2] It is only in more recent times, however, that the concept of the exciton has been effectively used to explain and understand the interactions of electron-hole pairs in solids. The work of Dutton[3] and Thomas and Hopfield[4] on the optical properties of excitons in CdS provided the first coherent understanding of the band structure and excitonic energy levels in this II-VI compound. Their work utilized the conventional photoexcitation sources capable of producing exciton concentrations of the order of $10^{15}/\text{cm}^3$. This density corresponds to an exciton separation of ~1000 Å and an exciton-exciton collision frequency, $\langle f \rangle = \langle v \rangle R^2 \eta_{\text{ex}} \sim 10^8/\text{sec}$, where $\langle v \rangle$ is the thermal velocity at 4.2 °K, $R = 28$ Å is the Bohr radius of the exciton, and η_{ex} is the exciton concentration. The measured exciton lifetime of 0.5 nsec[5] in CdS shows that at these concentrations excitons rarely meet and that the treatment[3,4] of the exciton system as a dilute gas of noninteracting particles is completely justified.

As the density of excitons is increased from the low-density value discussed above, new features appear in the photoluminescence spectra of several II-VI compounds that cannot be explained by noninteracting-particle theories. Magde,[6] Magde and Mahr,[7] and, earlier, Benoit à la Guillaume *et al.*[8] reported the observation of a new emission band in the photoluminescence spectra of CdS, CdSe, and ZnO at He temperatures. The new band, referred to as the M band, appeared in CdS for laser powers at 3471 Å, greater than 1 kW/cm^2. Assuming an absorption constant of 10^5 cm^{-1} for CdS, we can calculate the photon density on the sample as $F = \frac{1}{2} I_0 \kappa / \hbar\omega$, where κ is the absorption constant and we have assumed 50% reflectivity from the surface of CdS. For $I_0 = 1$ kW/cm^2, we find $F = 10^{26}/\text{cm}^3\,\text{sec}$. For an exciton lifetime of 0.5 nsec this gives a steady-state concentration (steady state is valid since the laser pulse width is much greater than the lifetime) of $5 \times 10^{16}/\text{cm}^3$. This gives an average separation of 270 Å for the excitons. The average collision frequency $\langle f \rangle$ can be calculated as previously and we find $\langle f \rangle = 0.5 \times 10^{10}\ \text{sec}^{-1}$. We can summarize the situation for an intermediate concentration of excitons by the following picture. The separation of the individual excitons is sufficiently large so that the electron-hole interaction will not appreciably be modified by couplings between individual excitons. We also note that the average interaction time between excitons is now comparable with the lifetime of the exciton itself. Thus, it is not unreasonable to expect evidence of processes involving exciton-exciton collisions. This was observed by Magde and Mahr.[7] They found that the new emission band in CdS, CdSe, and ZnO was red shifted by approximately the binding energy of a free exciton. Thus, the new band was envisioned as arising from a free-exciton–free-exciton scattering process in which one exciton gains an energy equal to the excitonic binding energy and is excited to the conduction band and the other exciton loses an amount of energy equal to the binding energy and emerges as a luminescent photon.

The least explored and most interesting region of the exciton system is the high-density phase. By high density we mean that the average separation between excitons is comparable to the linear extent of the exciton. For CdS we saw that the exciton radius was 28 Å. Using the requirement that the particle separation is 28 Å we can calculate, by the method used in the intermediate case, the laser power required to generate this density and find $I_0 = 900$ kW/cm^2. This corresponds to a particle density of 5×10^{19}/cm^3. The average interaction time is now about 10^{-12} sec. For the high-density exciton phase we see that (i) each exciton suffers many (~ 500) collisions within its lifetime, and (ii) the exciton separation is so small that it is not unreasonable to expect the electron-hole interaction to be modified or changed completely. The precise manner in which the electron-hole interaction is changed at high concentrations has been the subject of much controversy.

Mott[9] suggested that as the density of excitons is increased, the electron-hole interaction is screened by a Fermi–Thomas interaction and, finally, excitons cease to exist. A number of investigators have reported anomalous behavior in the properties of semiconductors at high exciton (or impurity) concentrations, most prominently in Ge,[10–13] Te,[14] InP,[15] CdS,[16] which they ascribe to a Mott-type transition from an insulating to a conducting state. This supra-Mott-density phase has recently become the focus of particular attention in Ge[10–13] since the first observation of such a phase as electron-hole drops.[17]

The second proposed modification of the electron-hole interaction is the creation of a bound exciton-exciton pair, the so-called excitonic molecule. It is assumed that a weak attractive potential exists between a pair of free excitons. At sufficiently high exciton concentrations the two free excitons will bind to form a single molecule consisting of two electrons and two holes in a H_2-like configuration. The appearance of new emission bands in the photoluminescence spectra of Si[18] and CuCl,[19] CuBr,[20] CuI,[21] and, very recently, CdS[22] have been attributed to the formation of excitonic molecules. Stimulated emission has also been observed from the excitonic molecule.[23] Calculations[24,25] of the binding energy, based on the formal analogy to the H_2 molecule, yield differing results but are in qualitative agreement with the measured values in Si and CuCl. These calculations predict binding energies for the CdS excitonic molecule that are between 0.3 and 3.0 meV.

A third suggestion for the exciton interaction at high densities was made by Moskalenko[26] and Casella.[27] They pointed out that the exciton, since it is composed of two fermions, should obey Bose–Einstein (BE) statistics. In particular for sufficiently low temperatures and sufficiently high concentrations, the excitonic system should undergo a BE condensation to a state of zero momentum. For a given temperature T, the critical density for BE condensation is given by Moskalenko as

$$\eta_c = 2.61\,(MkT/2\pi\hbar^2)^{3/2}\,, \qquad (1)$$

where M is the mass $(m_e + m_h)$ of the boson and k is Boltzmann's constant. BE condensation in CdSe has been reported.[28]

In the foregoing sections we have shown that the question of how a system of excitons behaves at high concentration is quite complicated in some cases and poorly understood in other cases. The situation can be characterized by two basic questions that have yet to be answered for the high-density exciton system in CdS. First, do excitons continue to exist even when their density is greater than the Mott density? Second, if excitons do continue to exist, what is the form of the interaction between them? Is it attractive or is it repulsive? If it is attractive, is it strong enough to bind two or more excitons into a stable complex? For CdS the situation is doubly confusing. First, there exist several different, and in some cases orthogonal, theories of the electron-hole interaction and the exciton-exciton interaction at high densities. Second, there are few experimental investigations of the high-density phase of this semiconductor to provide a basis for discrimination among the proposed theories. The intent of the present experiment was to investigate the properties of the high-density exciton phase in CdS at He temperatures with the hope of providing new information that would allow one to construct a coherent picture of the high-density interactions. We have chosen to study the exciton interactions by monitoring the low-temperature exciton photoluminescence. There are several compelling reasons for this choice: (i) The optical properties of semiconductors in the region of the band gap are largely determined by excitons and their interactions. (ii) The low-density spectra are known and well understood so that the appearance of new features at high densities can be readily identified. (iii) Such studies have been extremely useful in the past for identifying new phenomenon at higher exciton concentrations.

II. EXPERIMENTAL APPARATUS

The apparatus used to measure the emission spectra of CdS was of conventional design. A rotating Q-switched ruby laser was used in conjunction with an ADP(ammonium dihydrogen phosphate) second-harmonic generator to produce a 2 MW/cm^2, 26-nsec pulse of 3471-Å radiation. The second harmonic was separated from the fundamental by use of a $CuSO_4$-liquid filter cell. The reproducibility of the second harmonic was ± 10% as measured by a ballistic thermopile. In order to provide a controlled and reproducible attenuation of the 3471-Å laser radiation, a liquid absorption cell filled with a calibrated mixture of $NiSO_4$ in H_2O was used. The laser radiation is passed through the cell to the sample cryostat. The photoluminescence was analyzed with a grating monochromator having a linear dispersion of 33 Å/mm. For most experiments the spectral resolution used was 0.8 Å. The monochromator was calibrated using several known lines from an argon-ion laser. The output from the monochromator was viewed with a photomultiplier. Normalization was provided by viewing the 3471-Å beam with a second photomultiplier. Both signals were then fed to a 551 Tektronix oscilloscope. The CdS samples were single-crystal platelets, $2\times4\times0.1$ mm thick grown by a vapor-transport method using ultrahigh-purity CdS by the Eagle-Picher Co. The samples were mounted, nonoriented, and cooled by immersion to 4.2 °K. The crystal platelets were used as received; no surface treatment was attempted. About six laser shots were fired for each wavelength setting of the analyzing monochromator. The total scatter of the results as well as the average value was recorded. As used later in Fig. 1 the vertical length of the hash mark with each data point represents the scatter limits of the individual results.

III. EXPERIMENTAL RESULTS

Figure 1 shows the photoluminescence from CdS at 4.2 °K for several excitation powers. Curve *a* shows the emission observed when a conventional low-power (200 W) Hg arc is used as the source of the exciting radiation. The I_1 and I_2 bound-exciton lines plus a phonon replica of I_1 are clearly seen. Curves *b*–*g* show the emission spectra observed with laser excitation at 3471 Å. The relative laser

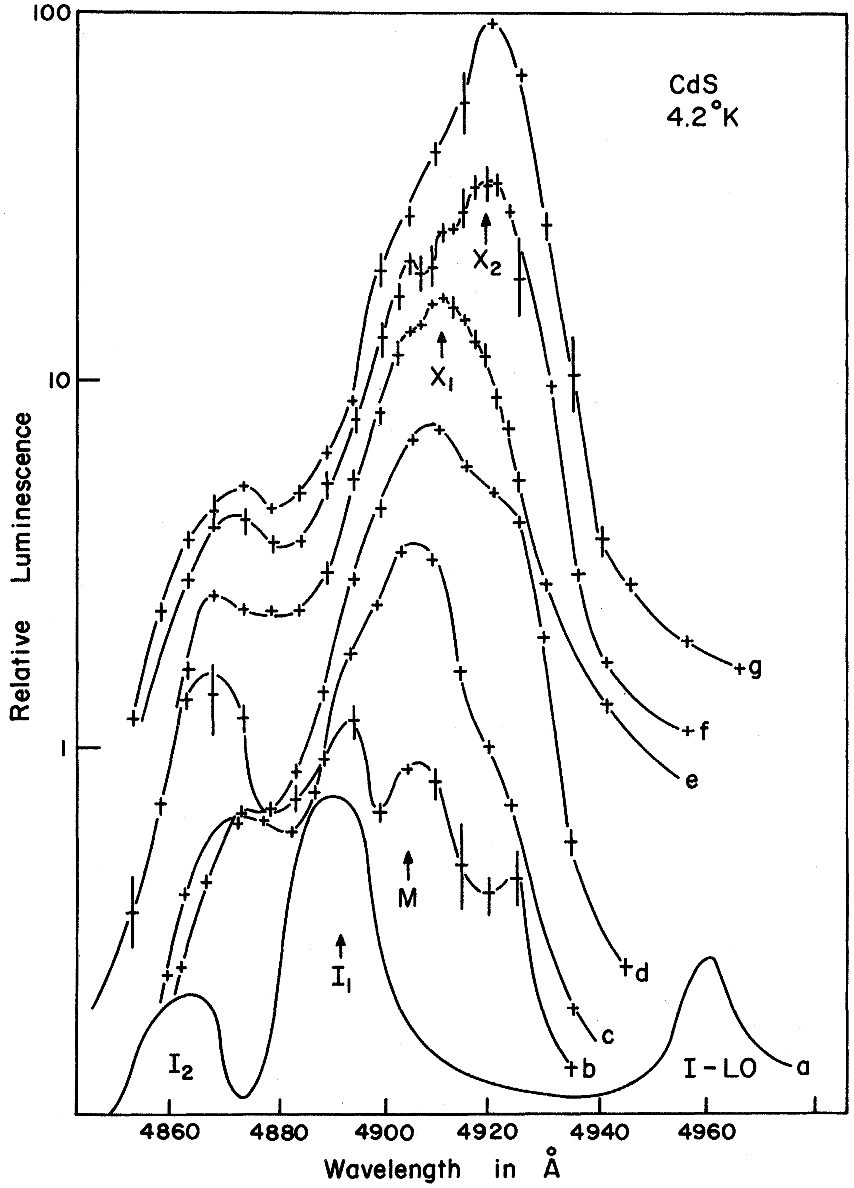

FIG. 1. Photoluminescence from CdS at 4.2 °K for various excitation powers. Curve *a*: Hg-arc excitation, resolution ~4 Å. Curves *b*–*g*, 3471-Å laser excitation, resolution 0.8 Å with powers as follows: *b*: 24 kW/cm^2, *c*: 180 kW/cm^2, *d*: 380 kW/cm^2, *e*: 700 kW/cm^2, *f*: 1200 kW/cm^2, *g*: 2000 kW/cm^2.

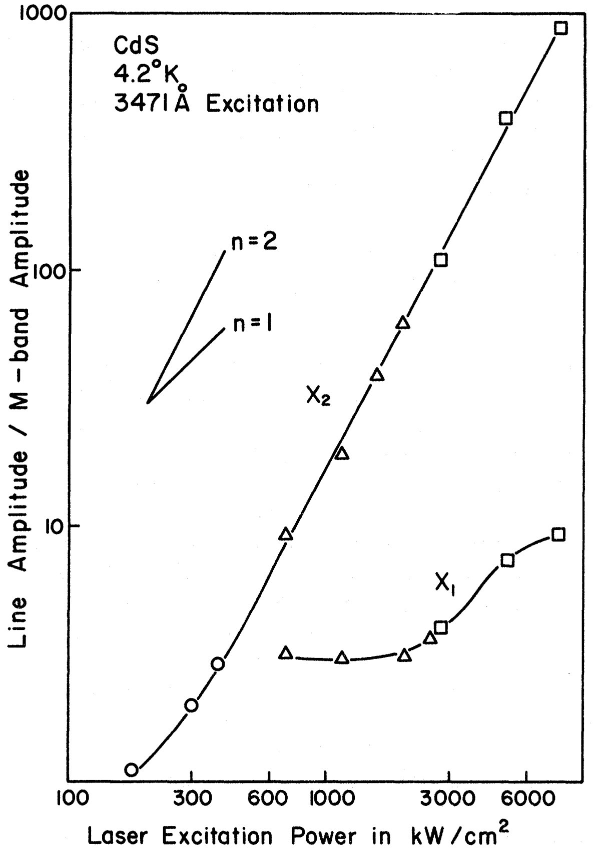

FIG. 2. X_1 and X_2 peak amplitudes normalized to M peak amplitude as a function of laser excitation power. Circles, triangles, and squares denote data from different experimental runs.

powers are accurate to ± 10%. The absolute powers are accurate to a factor of 2. At the lowest intensity of 24 kW/cm^2 we see that the I_1-, I_2-, and M-band emissions are all of comparable intensity, in agreement with the earlier results of Magde[6] and Magde and Mahr.[7] As the excitation power is increased to 380 kW/cm^2 (curve *d*) a new emission band emerges on the long-wavelength side of the M band. As the excitation power is increased further, from 700 kW/cm^2 (curve *e*) to 2 MW/cm^2 (curve *g*), the emission to the low-energy side of M is seen to be composed of two new emission lines, one at 4910 Å designated X_1 and one at 4920 Å designated X_2. At lower powers X_2 grows faster than quadratic and then begins to saturate for powers above 400 kW/cm^2. M shows a similar behavior, increasing as $P^{1.6}$ (P is the laser excitation power) at intermediate powers and beginning to saturate for powers above 400 kW/cm^2.

The peak amplitudes of X_1 and X_2, normalized to the amplitude of the M band are shown in Fig. 2 as a function of laser power. X_2/M is seen to vary as P^n with $n=2$ over a range of powers from 200 kW/cm^2 to 8 MW/cm^2. The results for X_1/M are not consistent and suggest a power-law dependence with n between 0 and 1.

Using mildly focused beams, excitation powers between 2 and 8 MW/cm^2 were obtained. The observed photoluminescence at these powers continued the trends of Fig. 2. At the highest powers used in the experiment, 8 MW/cm^2, we observed a series of emissions at 4910, 4917, 4924, and 4930 Å. At these powers, samples were destroyed frequently.

IV. INTERPRETATION OF RESULTS

In this section we wish to return to the question of the behavior of the exciton system at high exciton concentrations. To put the problem in perspective we shall review some of the more important results of Sec. III. At low laser excitation powers the photoluminescence spectra of CdS is dominated by the M-band emission at 4904 Å. At higher powers at least two new emission lines appear at lower energies, X_1 at 4910 Å and X_2 at 4920 Å. The first point to emphasize is that these are new lines and not merely energy shifted versions of lines that are present in the low-intensity spectra. Such line shifting as a function of excitation power has been reported in silicon,[29] InP,[14,15] and CdS.[30] In the case of X_2, the line can be followed as the excitation power is changed by nearly two orders of magnitude. The second point we wish to emphasize is that of the dependence of the line amplitude on excitation power. At the lower laser intensities, I_1 and I_2 were linear in the laser power P, M was superlinear, and X_2 was superquadratic. For sufficiently high powers all lines saturate or begin to saturate. When the line amplitudes of X_1 and X_2 were normalized to the amplitude of the M band and were plotted against laser power, we found that X_1/M was approximately constant over the small dynamic range that we could accurately follow it. For X_2, we found that X_2/M was quadratic in the laser power over nearly two orders of magnitude of laser powers.

It is most important to recognize that conclusions, to follow below, do not depend on the special exponent of a power law. What is used in the following is the fact that some lines rise *more* than linear in laser power (whereas I_1 and I_2 luminescence *does* rise linearly), and X_1/M rises linearly and X_2/M quadratically in laser power.

These comments are in order for two reasons: (i) The mode structure of Q-switched ruby lasers is notoriously bad. The local mode behavior is nonuniform in space and time and changes from shot to shot. (ii) The penetration depth of the radiation is very small, about 10^{-5} cm; luminescence is emitted from regions exposed to very different levels of laser power.

Because the phenomena reported here depend on the absolute value of the laser power, any inhomogeneity due to local mode structure or nonuniform penetration of the exciting radiation tends to smear out spectral features. The observed spectra will be the superposition of the spectra of several laser levels. Also, the power-law dependence of the spectral features will be affected by the inhomogeneous illumination. We feel, however, that superlinear behavior or the particular X_1/M or X_2/M peak ratio cannot be "produced" by inhomogeneities alone; these features are, then, typical of the material involved.

To summarize then: Any theory or model that seeks to explain the above phenomenon must successfully account for (i) the appearance of new emission bands rather than shifted emission bands, and (ii) the superlinear power dependences of all the high-excitation power lines and in particular the observation that $X_1 \propto M$ and $X_2 \propto P^2 M$. We shall now consider some of the proposed theories of the behavior of a high-density system of excitons as outlined in Sec. I. We shall show that most of these theories are inconsistent with our present results.

The first proposed theory we shall consider is that of a Bose-Einstein condensation (BEC) of excitons at high exciton concentrations. Calculations for the expected emission from the condensate, whether this emission is spontaneous[31] or stimulated,[32] predict shifts of the emission frequency that increase with increasing density of the condensate. The luminescence intensity should simply be proportional to the number of excitons in the condensate. Hence neither of our explicit observations are explained from the viewpoint of BEC. Nor is one implicit observation explained either. The BEC should be abrupt. Once the critical density is reached every additional exciton enters the condensate. In our experiments no abrupt transition in the photoluminescence behavior is seen. For these reasons we rule out the possibility of a BEC.

A second proposal is that at sufficiently high exciton densities the system undergoes a Mott-type transition. Although the exact character of this new phase is somewhat unclear, there are several current ideas. In one case the excitons are assumed to be totally ionized and behave as a plasma of free electrons and holes. The new emission could then result from either direct or phonon-assisted electron-hole recombination across the band gap. No combination of band gap and available phonon energies is capable of reproducing the emission energies of X_1 and X_2. It the band gap were a function of exciton density, decreasing with increasing exciton concentration, it would be possible to fit the observed energies of X_1 and X_2 at one value of the energy gap. However, as the exciton density in the sample was varied the value of the energy gap would also change giving rise to a continually shifting emission line.[30] This is not consistent with our observation that the new emission occurs at a fixed wavelength. In either case the intensity of the luminescence again would be proportional to the number of excitons in the plasma phase. In the second case it is assumed that the new supra-Mott phase consists of liquid drops of a condensed exciton gas.[17,33] This model could predict a discrete shift in the energy of the emission spectra. The energy shift would just be equal to the energy the exciton lost in going over to the liquid phase from the gas phase, i.e., the heat of vaporization for the excitonic liquid. Simple calculations by Ashkinadze *et al.*[29] for the liquid-drop model show that the emission intensity should be proportional to the number of condensed excitons. Thus we see that both versions of the plasma model fail to explain all of our observations in a consistent way. We now turn to the final model that we will consider, that of the formation of molecular excitons.

In this model we assume two excitons interact via an attractive potential to form a bound exciton-exciton complex of two electrons and two holes in an H_2-like configuration. The energy of this new state is lower than the energy of two free excitons by an amount equal to the binding energy B of the molecule. The initial formation of the molecule requires two excitons and hence is quadratic in the laser power. The molecular exciton model has had good success in explaining the appearance of new superlinear emission bands in silicon[18] and CuCl,[19] and recently in CdS.[22] With this motivation we now wish to show how the present experimental results can be explained in a consistent way by the application of the excitonic molecule model. We shall deal with the X_1 emission first.

Figure 3 shows the proposed model for the X_1 emission band. Also shown in the same figure is the exciton-exciton scattering process that is responsible for the M-band emission. We shall review briefly the M process to provide a background and motivation for what is to follow. In exciton-exciton scattering an exciton of energy A_1 collides inelastically with another exciton of energy A_1. One exciton is scattered into the conduction band gaining an energy equal to B_f, the binding energy of the free exciton. The second exciton is scattered down to the photonlike section of the dispersion curve and appears as a luminescence photon. The energy of the M-band photon is just given by

$$h\nu_m = E_g - 2B_f , \tag{2}$$

where E_g is the energy of the gap. Since the process depends on the interaction of two particles the luminescence intensity will be quadratic in the par-

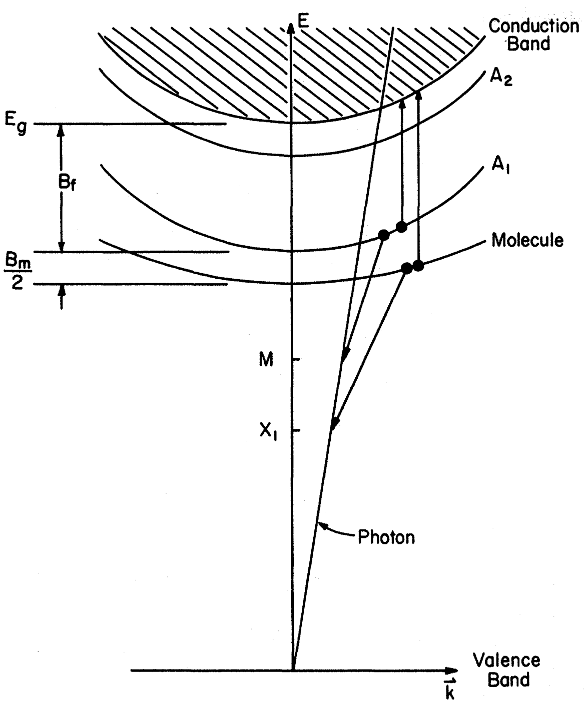

FIG. 3. Model for X_1 emission. Energy per particle has been plotted for convenience.

ticle density and hence quadratic in the excitation power. Now let us consider the X_1 emission line.

We propose that the X_1 emission arises from recombination radiation emitted from a bound excitonic molecule in CdS. The process we envision is as follows: Two free excitons of energy A_1 each interact via an attractive potential and form a bound excitonic molecule with a binding energy of B_m. The excess energy is carried away by crystal phonons. The excitonic molecule then undergoes radiative decay by an Auger process. One exciton is excited into the conduction band gaining an energy equal to $\frac{1}{2}B_m + B_f$. The other exciton loses an equal amount of energy and is deexcited to the photonlike section of the dispersion curve and emerges as a luminescent photon. The energy of this emitted photon is given by,

$$h\nu_{X_1} = E_g - 2(\tfrac{1}{2}B_m + B_f) \; . \qquad (3)$$

The dynamics of the exciton-exciton scattering and the molecular-decay processes are the same. Therefore, we would expect the X_1 luminescence to be quadratic in the excitation power, or more importantly, we would expect the X_1 luminescence to be directly proportional to the M-band luminescence. The energy difference of the two emissions can be calculated by taking the difference between Eqs. (2) and (3). We find

$$\Delta h\nu \equiv h\nu_M - h\nu_{X_1} = B_m \; . \qquad (4)$$

From Fig. 1 we see that $\Delta h\nu$ is equal to 3 meV. Therefore, we find $B_m = 3$ meV.

We can compare this result with theoretical calculations.[24,25] The important parameter is σ, the ratio of effective electron-to-hole mass of the electron. With σ about 0.15 and the binding energy of the A exciton about 30 meV a prediction of about 2–3 meV results from the various calculations. The situation is complicated by the fact that CdS has an anisotropic hole mass. It is therefore premature to calculate an exact prediction; the order-of-magnitude agreement is encouraging, however. A more recent experiment[22] in CdS suggests an experimental value of 5.4 meV for the binding energy. To summarize, the molecular-recombination model can explain the presence of the new emission band at X_1 and it can account for the linear dependence of X_1 intensity on M intensity. We will now consider the X_2 emission.

The important observation regarding the X_2 band is that the ratio of the X_2-line amplitude to the M-line amplitude is proportional to the square of the laser excitation power. Since the binding of two excitons to form a molecule is a process that should be proportional to the square of the number of excitons present, the above observation suggests that the X_2 luminescence is emitted by a process involving the interaction of two excitonic molecules. We would envision this interaction as

$$\text{molecule} + \text{molecule} \rightarrow X_2 \; .$$

For the mechanism of the interaction we propose the molecular analog of the M-band interaction for free excitons. That is, we suggest that the X_2-band luminescence comes from an inelastic scattering process involving two excitonic molecules. The proposed process is shown in Fig. 4 and discussed in the following. Two excitonic molecules, each with energy $2(E_g - B_f - \frac{1}{2}B_m)$, inelastically collide. As a result of the collision both molecules become unbound: one exciton is scattered into the conduction band, two excitons are scattered to the A_1 band, and the final exciton is scattered to the photonlike part of the dispersion curve and emerges as a luminescence photon. The energy of the emitted photon is approximately given by

$$h\nu_{X_2} = E_g - 2B_f - 2B_m \; . \qquad (5)$$

Recall for the M band, that

$$h\nu_M = E_g - 2B_f \; .$$

We see that the energy shift of X_2 from M, other parameters being unchanged, is just

$$\Delta E = h\nu_M - h\nu_{X_2} = 2B_m \; .$$

Experimentally we find that $\Delta E = 8$ meV so that we deduce a value of 4 meV for the binding energy of the molecule. We see that this value of the molecular

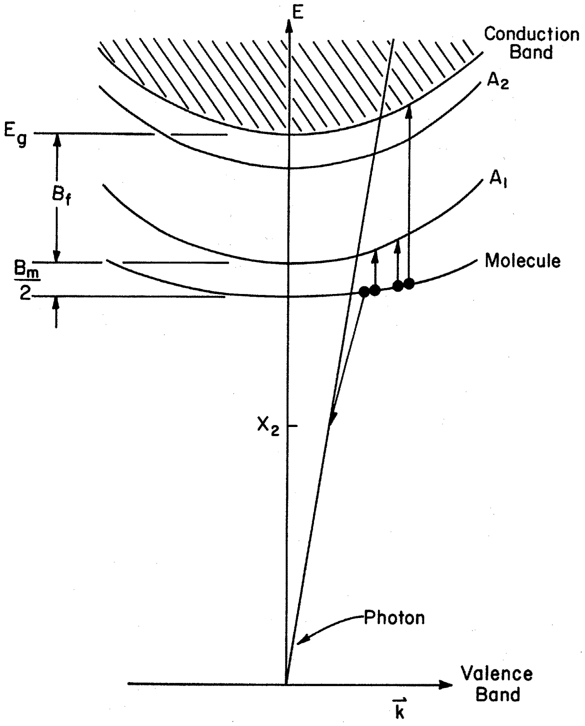

FIG. 4. Model for X_2 emission. Energy per particle has been plotted for convenience.

binding energy agrees favorably with the value of 3 meV calculated for the X_1 emission band. This agreement obviously supplies a portion of the motivation and support for the above model for X_2. Both values are also within the range of predictions of models of excitonic molecules.

At excitation levels of 8 MW/cm^2 or higher, evenly spaced lines were seen at 4910, 4917, 4924, and 4930 Å. It is quite possible that at these power levels stimulated emission[34] occurred in these lines. Further investigation of the luminescent behavior of CdS at these high excitation levels is certainly necessary.

V. SUMMARY

We would like to summarize our experimental findings and attempt to answer some of the questions posed at the end of Sec. I by proposing the following explanation for the behavior of a high-density system of excitons at low temperatures. At the lowest concentrations, the excitonic system behaves as a dilute gas of noninteracting particles, as was discussed earlier, and the luminescence behavior is dominated by direct recombination processes and trapping processes. As the concentration is increased, exciton encounters are more frequent. However, since the cross section for M-band scattering is larger than the cross section for competing processes, the M-band emission dominates the long-wavelength photoluminescence spectra. As the exciton concentration is increased to its highest value of the present experiment (10^{19}/cm^3), the rate of formation of excitonic molecules increases because of the increased frequency of encounters between free excitons. These excitonic molecules can then undergo an inelastic scattering process analogous to the exciton-exciton scattering process responsible for the M band. The rate for the molecular scattering process now exceeds the rate for M-band scattering and the X_2 luminescence dominates the emission spectrum. The molecules can also undergo a radiative-decay process. These two processes account for the observed X_1 and X_2 emission and predict a binding energy for the excitonic molecule in CdS of 3–4 meV.

There are several points we wish to emphasize in the above model that bear directly on the questions posed in Sec. I. (i) At even the highest densities a bound state of the electron hole still exists.[16] It is a moot point whether the single exciton itself exists at the highest densities, however. (ii) The interaction between excitons at high densities is attractive rather than repulsive. (iii) The attractive potential is sufficient to bind the excitons into a binary molecular form.

After the completion of this work results were published of the photoluminescence of CdSe at high exciton densities by Bille *et al.*[35] Results very similar to those found in CdS at comparable power levels were obtained.

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Dispersion Curves and Elastic Constants of Graphite

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Lattice vibrations of the hexagonal graphite crystal are analyzed using two-body carbon-carbon interaction potentials. The potential parameters are obtained from estimates of the long-wavelength frequencies of graphite and a knowledge of the nitrogen-nitrogen potential parameters. The dispersion relations along high-symmetry directions are calculated showing excellent agreement with the experimental observations along $\langle 00\xi \rangle$. The elastic constants of graphite are also calculated and compared with the available experimental data. There is general agreement between the theoretical calculations and the experimental observations.

I. INTRODUCTION

The lattice dynamics of graphite have been discussed by several authors using few-parameter Born–von Karman models.[1–6] The unknown parameters of the models are fitted to the experimental data such as specific heat[7] and the measurements of phonon dispersion relations.[8] The graphite structure assumed in lattice-dynamical calculations corresponds to the hexagonal crystal structure where sheets of carbon atoms are stacked on one another and held by van der Waals forces. The forces in the sheets are due to the strong covalent forces. This structure is highly anisotropic in properties such as thermal expansion and elasticity.[7]

In this paper we intend to analyze the lattice vibrations of graphite in the hexagonal crystal structure. The lattice-dynamical model employed will be the usual Born–von Karman model in which significant interactions between carbon atoms are represented by finite-value force constants. However, our approach will be different from previous attempts in the use of analytical potentials for car-