clusions for the small spectral range considered. Multiple reflections could be also included in the same framework.

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Hot Excitons in Highly Excited CdS

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Hot exciton distributions, as much as 30°K in excess of the He ambient, are observed in optically pumped CdS. The effective exciton temperature is determined by analyzing the luminescence line shape for E_x-2LO recombination of free excitons. The exciton state is found to remain a viable excitation up to the maximum pump intensity of 10^7 W/cm^2, with the only observed response to the increasing pump power being a rise in effective exciton temperature.

We report observations of excitation-induced heating of the free-exciton bath in optically pumped CdS platelets. For pulsed excitations of $\sim 10^7$ W/cm^2 (N_2 laser, $\sim 10^{26}$ photons/cm^2 sec) the exciton bath achieves a temperature in excess of 30°K while the crystal temperature is observed to rise less than 10°K above the He ambient. These observations have been made by detailed analysis of the experimental E_x-2LO line shape. By defining an effective exciton temperature, different from the background lattice temperature, the theory of Segall and Mahan[1] for phonon-assisted free-exciton recombination can be applied to fit the experimental spectra over the entire range of pump intensities investigated. While the overall luminescence spectrum is strongly modified in the highly excited crystal,[2,3] the E_x-2LO line continues to provide a means of probing the free exciton system.[4]

For the entire range of excitation ($> 10^3$) the total exciton population is found to vary linearly with pump power. Accordingly exciton-exciton interactions, or exciton–free-carrier interactions, do not significantly influence the dynamics of the exciton system; the exciton state appears to remain a viable excitation of the crystal. This observation is significant in view of recent speculation concerning the nature of interacting excitons in highly excited semiconductors.[5,6] In particular we find no evidence for an excitonic condensation. Conversely, the only observed response to increasing pump power is the rise in exciton temperature.

The measurements were made on CdS platelets maintained at 2°K by immersion in liquid helium. A pulsed (~ 10 nsec) nitrogen laser with 100 kW peak power at $\lambda = 3371$ Å ($E = 3.68$ eV) was used to excite the crystals. A duty factor of $\sim 10^{-6}$ insured that average heating of the crystal by the pump was negligible. Transient heating was ruled out by monitoring the I_1 bound-exciton line. The ratio of no-phonon component to the phonon wing of this line has been shown to decrease quite rapidly with increasing lattice temperature (exponentially above 10°K).[7] Thus as the lattice temperature increases the no-phonon component of this line falls off much faster than linearly. Over the range of pump intensities investigated here the no-phonon component of this line was found to increase linearly with pump power. We conclude, therefore, that the lattice (crystal average) temperature in the exciting volume remains <10°K during the excitation pulse.[8] Recent studies of the optical properties of CdS at high excitation intensities also support this conclusion.[9]

The contribution of a thermal-equilibrium exciton distribution to the line shape of the E_x-2LO luminescence line was first reported by Gross, Permogorov, and Razbirin[4] for the case where the excitons were in thermal equilibrium with the crystal at 77°K. Segall and Mahan[1] have analyzed this phonon-assisted exciton recombination process for equilibrium systems at temperature T. They have shown that

$$I(E) \propto (E - E_0)^{1/2} \exp[(E_0 - E)/kT] \text{ for } E \gtrsim E_0, \quad (1)$$

$$I(E) = 0 \text{ for } E < E_0,$$

where E = photon energy, $E_0 = E_x - 2E_{LO}$, E_{LO} = LO phonon energy, and T corresponds to the equilibrium temperature of the crystal. We have applied this model to our experiment by setting T in Eq. (1) equal to T_x, the exciton temperature, which is taken different from the lattice temperature. Thus we take the line shape function to reflect the two factors[4] which determine the free-exciton distribution: a density of states factor, $(E - E_0)^{1/2}$, and a Maxwell-Boltzman distribution, $\exp[(E_0 - E)/kT_x]$, of the excitons over this manifold of states.

The phonon-assisted recombination line has been extensively studied for low-intensity excitation[1,4,10] and we have extended these measurements to higher pumping powers. For high excitation intensities new luminescence features appear which have been related to exciton-exciton and free-carrier–exciton interactions.[2,3] However, the line due to free-exciton recombination, assisted by emission of two LO phonons, is still clearly resolved. In Fig. 1 we illustrate typical line shapes for this emission at various pump powers. The open circles correspond to the original data. A theoretical fit to these data using Eq. (1) is shown as solid lines. In fitting the data there are two parameters: E_0 and kT_x. A single value of E_0, taken at the emission peak for the lowest pump intensity, is used to fit all the results.[11] The effective exciton temperature T_x is then the only parameter varied in the calculation of the theoretical curves in Fig. 1. Some measure of the accuracy of this fitting procedure can be obtained by noting that at the highest pump intensity the value of kT_x that best fits the tail of the emission also gives the position of the peak, which has shifted ~1 meV to higher energy. The use of a single value of E_0 to fit the data over the entire range of pump powers indicates that the exciton binding energy is not changing as a result of the increased density of excitons, within the resolution of our fitting procedure.

Exciton temperatures determined from the fitting procedure described for Fig. 1 are plotted as a function of pump intensity in Fig. 2(a). The exciton temperature shows a rather weak dependence on pump intensity, and the data suggest a relationship of the form $T \propto P^{1/3}$, as indicated by the solid line. Further insight into the dynamics of the exciton system can be gained by investigating the variation of the total E_x-2LO emission. In Fig. 2(b) the integrated emission, which is directly proportional to the total number of excitons, is shown to vary linearly with pumping power, over the range investigated. We conclude from this result that there is no significant change in the exciton lifetime as a result of the large density of excitons.

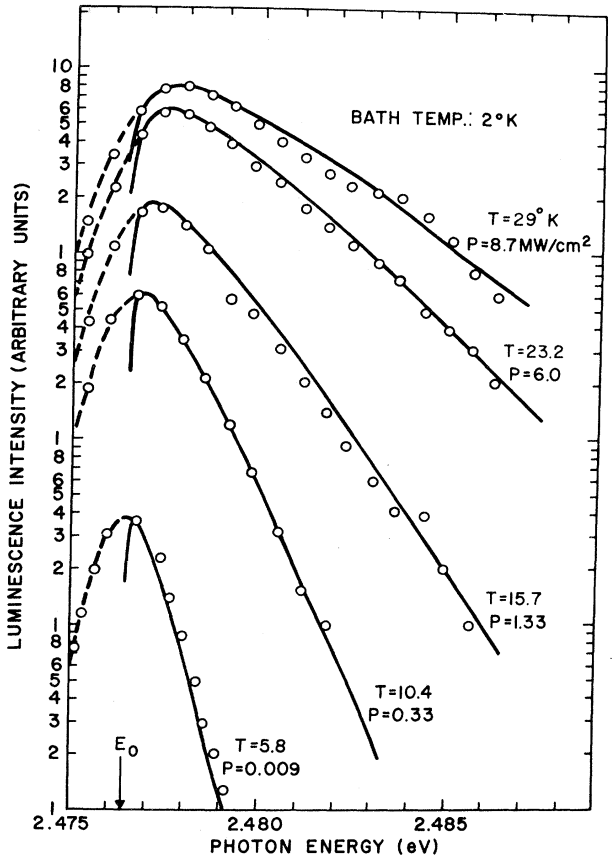

FIG. 1. Emission line shape for 2LO-phonon-assisted recombination of free excitons in CdS. The open circles correspond to original data obtained by subtracting out background luminescence. The solid curves correspond to a theoretical fit to the data using Eq. (1) of the text. The dashed curve indicates how the emission falls off for $E < E_0$. No attempt has been made to take account of broadening in fitting the data.

Excitation of CdS by the 3371-Å line of the N_2 laser results in electron-hole pairs with more than 1 eV excess kinetic energy. Much of this energy is dissipated to the lattice via the emission of LO phonons. However, near the bottom of the band the electron-hole pairs can interact efficiently only with acoustical phonons, or with the electron-hole system (excitons, free carriers, etc.). It appears that electron-hole pairs near the bottom of the band rapidly form excitons which then reach a steady state out of equilibrium with the crystal. Thus the exciton system is

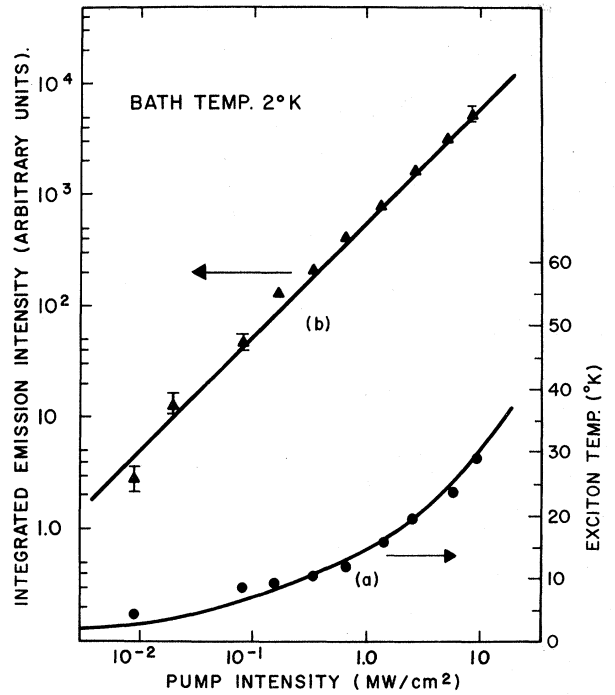

FIG. 2. (a) Exciton temperature as a function of excitation intensity. The solid curve indicates a $P^{1/3}$ dependence of T_x on pumping power. (b) Integrated emission due to E_x-2LO recombination process. These data were obtained by measuring the total area under the experimental curves in Fig. 1, replotted on a linear scale. The solid line corresponds to a linear dependence of integrated emission on pump intensity.

temporarily storing part of the excess energy due to the 3371-Å pump. There must, indeed, be many such nonequilibrium sinks of energy since the crystal does not exhibit the 100°K temperature rise that a specific-heat calculation would predict for the incident power.

The applicability of a theory that ignores exciton interactions to fit the experimental results described here is surprising. At an excitation intensity of 10^7 W/cm^2, penetrating 10^{-4} cm into the crystal, an equilibrium density of excitons of $\sim 10^{20}$ cm^{-3} should result for an exciton lifetime of $\sim 10^{-10}$ sec. At such large densities exciton wave functions would begin to overlap and screening effects would be expected to affect the exciton binding energy. However, we find that the luminescence due to phonon-assisted recombination of free excitons in fact persists up to these highest pump intensities, with no evidence of a change in binding energy. Since the total number of excitons generated remains proportional to the pump intensity, there is no evidence that a significant fraction of the excitation can be decaying through a separate state such as the excitonic condensate observed in Ge and Si,[6] and recently suggested for CdSe by Akopyan, Gross, and Razbirin.[5,12] From the foregoing discussion it would appear that even for pump intensities of 10^7 W/cm^2 it is not possible to saturate the pumped region of the crystal with excitons.

The detailed dynamics of the exciton system responsible for the results described here is not well understood. However, it is possible to draw several general inferences: The exciton state remains a viable excitation of the crystal. There is no evidence for a change in binding energy or for the formation of a condensed state. The exciton system can be maintained in a steady state with a temperature greater than the average temperature of the crystal.

The authors would like to acknowledge helpful discussions with J. J. Hopfield and P. A. Wolff.

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[12]We have conducted measurements in CdSe similar to those reported here for CdS and have found essentially the same results for each material with no evidence for a condensate.