Photoexcited hot electrons and excitons in CdSe at 2 °K

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A study of the radiative recombination from the free carriers and the free excitons in CdSe reveals that the free carriers as well as the free excitons are "hot." When the lattice is at $\simeq 2$ °K, the exciton and the free-carrier temperatures are, respectively, ~ 25 °K and ~ 140 °K at the highest intensity used in these experiments, $\simeq 4\times 10^6$ W/cm^2. The results on electron heating can be quantitatively explained by a theory based on polar-optical scattering as the dominant energy-loss mechanism for the electrons. Thus the dynamics of the electron heating is well understood but that of excitons is not.

I. INTRODUCTION

Excitation of a semiconductor with a laser of photon energy much greater than the energy band gap results in the generation of electrons with considerable excess energy. These electrons rapidly lose their excess energy, mainly by interacting with optical phonons and other electrons and holes present in the semiconductor. If the photoexcitation is sufficiently intense, the process described above would lead to a large nonequilibrium population of the optical phonons and also to electron-hole gas whose temperature is higher than that of the lattice. Observations of such photoexcited hot electrons[1] and hot longitudinal-optical (LO) phonons[2] were reported earlier for the case of GaAs. Observation of photoexcited hot excitons has been reported for CdS.[3] Hot electrons in CdS[4] and hot phonons in various materials[5] have also been observed recently.

We report the simultaneous observation of hot electrons and hot excitons in CdSe in this paper. There are several features of interest in the data. First of all, the electron and the exciton temperatures are vastly different. Furthermore, the results in CdSe and GaAs[1] are consistent with each other, i.e., we can calculate the electron temperature T_e in CdSe if we know T_e in GaAs at the same excitation intensity. This shows that the formulation developed for GaAs[1] applies equally well to other semiconductors in which polar-optical-mode scattering dominates. Also, at very-high-excitation intensities, we find that the temperature T_e increases slower than logarithmically with excitation intensity I. Even this departure from the usual dependence on I can be explained within the framework of the theory. Thus the dynamics of the carrier heating is reasonably well understood. The dynamics of exciton heating, on the other hand, is not well understood at present.

II. EXPERIMENTAL TECHNIQUES

These experiments were performed on thin (~ 20 μm) CdSe platelets kindly supplied to us by D. C. Reynolds of Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio. A platelet was mounted on a copper block and was immersed in superfluid helium. The photoexcitation source was a Spectra Physics argon laser operating in a cavity-dumped mode at 5145 Å. The output of the laser was in the form of ~ 20-nsec-wide pulses occurring at a rate as high as 10^6 per second. The peak power was ~ 50 W. The laser was sharply focused on the sample so as to give intensity as high as 5×10^6 W/cm^2. Experimental conditions were selected in such a manner that there was no average heating of the sample,[6] i.e., the lattice temperature was approximately the same as the helium-bath temperature. Photoluminescence spectra were analyzed by a double spectrometer and detected by an extended S-20 photomultiplier tube. A box-car detector was used to sample only the central 10-nsec part of the luminescence pulse.

III. EXPERIMENTAL RESULTS

Figure 1 shows a portion of the emission spectrum of CdSe at 2 °K for three different excitation energies. The band gap at 2 °K is indicated on the figure. We see that the emission extends considerably above the band-gap energy. Other features of luminescence (not shown in the figure) are characteristic of low temperatures and the results of a systematic study of heating effects (to be reported elsewhere[6]) show that heating of the lattice under present experimental conditions is negligible. Thus the observation of extended high-energy tail implies that the electron and hole temperatures are significantly higher than the lattice temperature. At the highest intensities, the electron temperature is ≈ 140 °K while the lattice is < 10 °K. The electron temperature T_e quoted above is obtained by measuring the slope of the high-energy emission tail, which is expected to have $e^{-\hbar\omega/kT_e}$ dependence. The temperatures deduced by this method are also shown in Fig. 1.

The reciprocal of the electron temperature T_e is plotted as a function of the photoexcitation in-

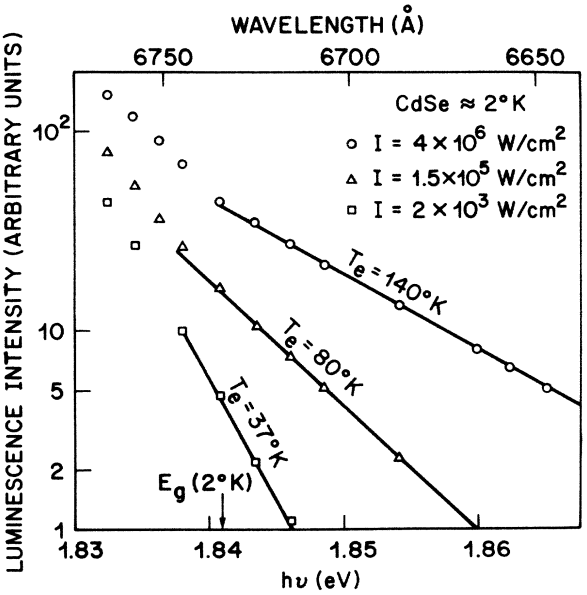

FIG. 1. Radiative recombination from photoexcited free carriers in CdSe immersed in liquid helium (T_L <2 °K) for three different excitation intensities. The intensities and effective-carrier temperatures are indicated.

tensity I in Fig. 2 on a semilog scale. We can see that the plot is linear for most of the range, but begins to deviate from linearity at very high intensities. In the linear range, $I \propto e^{-T_0/T_e}$ where $kT_0 = 26$ meV, as determined from Fig. 2.

In Fig. 3 we have plotted the emission line shape of the free-exciton–2LO recombination process in CdSe at two different excitation intensities. The background due to other processes has been subtracted out. We can see that the high-energy tail of this emission process also becomes more pronounced as the excitation intensity is increased. Assuming[3] that the line shape is given by an equation of the form

$$I(E) \propto (E - E_0)^{1/2} e^{-(E-E_0)/kT_x} \qquad (1)$$

we can obtain the value of the exciton temperature at a given pump intensity. Here $E_0 = E_x - 2\hbar\omega_0$, where E_x is the free-exciton energy, $\hbar\omega_0$ is the LO-phonon energy, and T_x is the exciton temperature. The solid curves in Fig. 3 are plots of Eq. (1) for two different values of T_x, selected to obtain the best fit with the experimental points. The best fit values of T_x are indicated on the curves. We see that the exciton temperatures are much smaller than T_e and that the change in exciton temperature when the intensity is changed by a factor of 50 is only ~10 °K. This implies that (i) the excitons are not getting much excess energy or (ii) there is an efficient mechanism by which they lose energy to the lattice.

IV. DISCUSSION

The fact that the high-energy tail of electron-hole recombination is very close to an exponential (Fig. 1) and that the line shape of the exciton-2LO system can be fitted well to an expression given by Eq. (1) implies that the electrons and holes have thermalized among themselves and the excitons have also thermalized among themselves. However, the fact that electron and exciton temperatures at a given pump intensity are vastly different (e.g., $T_e = 140$ °K and $T_x \approx 25$ °K at $I = 4\times10^6$ W/cm^2) implies that (i) the free carriers and the excitons are *not* in equilibrium with each other and/or (ii) the free-carrier and exciton emission originate from different parts of the sample. It will require some sophisticated experiments to determine the importance of (ii). The true significance of our result that $T_e \gg T_x$ cannot be evaluated until such experiments are performed. The picture is further complicated by the fact that the dynamics of exciton heating is not well understood. However, our experimental results and the available theories[7] have given us a good insight into processes which lead to heating of the electrons. We will begin our discussion by considering these processes.

A. Hot electrons and holes

In order to understand the dynamics of electrons and holes, we must know the answers to several questions: How does a photoexcited electron lose its excess energy? How does the electron system acquire excess energy? When is it meaningful to ascribe a temperature to a system of electrons?

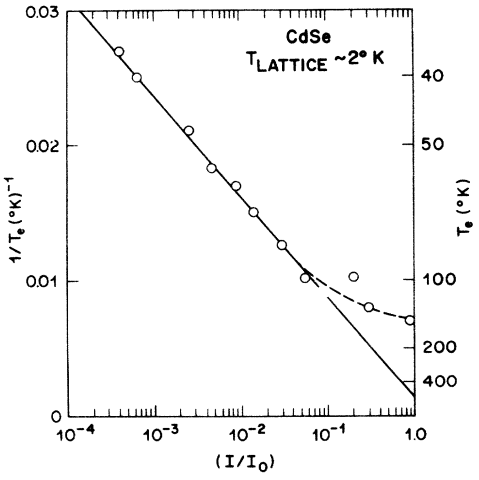

FIG. 2. Inverse-effective-carrier temperature vs excitation intensity on a semilog scale. $I_0 = 4\times10^6$ W/cm^2. The points are experimental. The solid curve has a slope of 26.5 meV $= \hbar\omega_0$ [Eq. (12)]. The dashed curve is calculated by assuming that $n/n_c^* = 2$ at $I = 2\times10^5$ W/cm^2 and $n \propto I$.

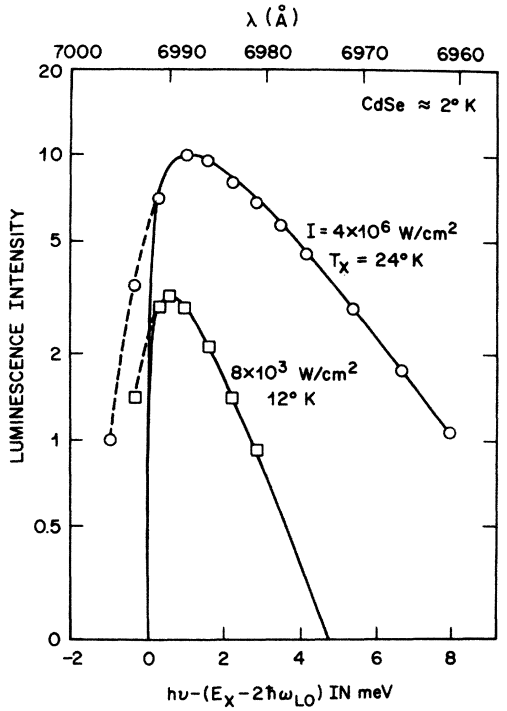

FIG. 3. Free-exciton–2LO recombination in CdSe. The effective temperatures and excitation intensities are as indicated.

What are the mechanisms by which the electron system loses energy to the lattice? What is the rate of this energy loss? We shall address ourselves to these questions and apply them to CdSe and GaAs in this section.

1. General considerations

A photoexcited electron is created with an excess energy ΔE_e given by

$$\Delta E_e = (h\nu_l - E_g)\left(\frac{1}{1+m_e/m_h}\right), \tag{2}$$

where $h\nu_l$ is the laser photon energy, E_g is the energy band gap of the semiconductor, and m_e (m_h) is the effective mass of electrons (holes). The hole excess energy ΔE_h is given by

$$\Delta E_h = \Delta E_e(m_e/m_h). \tag{3}$$

If $m_e \ll m_h$, most of the excess energy is given to the electron. In what follows, we will concentrate on the electron and drop the subscript e from ΔE_e. In materials like GaAs or CdSe in which polar optical scattering dominates,[7] this photoexcited electron will lose its excess energy ΔE by successively emitting LO phonons and by colliding with other electrons (n-type crystal) already present in the photoexcited region. The relative importance of these two processes will depend on the density of carriers n in the photoexcited region. Let n_c^* be defined as the critical density at which a photoexcited electron of excess energy ΔE loses as much energy to the electrons as to LO phonons. It can be shown[7] that for electrons of excess energy $\Delta E \gg \hbar\omega_0$, the LO phonon energy n_c^* is given by

$$n_c^* = (8\pi/e^{*4})|e|E_0\hbar\omega_0 \ln[2(\Delta E/\hbar\omega_0)^{1/2}], \tag{4}$$

where $e^{*2} = e^2/\bar{\epsilon}$, e is the electronic charge, $\bar{\epsilon}$ is a suitable dielectric constant,

$$|e|E_0 = m_e\frac{e^2\omega_0}{\hbar}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s}\right), \tag{5}$$

and ϵ_∞ and ϵ_s are the optical and static dielectric constants, respectively. Thus a photoexcited carrier will lose a fraction f of its excess energy ΔE to the electron systems, where f is given by

$$f = n/(n+n_c^*). \tag{6}$$

Assuming that each absorbed photon generates one electron-hole pair, the power *per electron* transferred from the exciting laser to the electron gas is given by

$$P = \frac{I}{d(h\nu_l)} f\Delta E\frac{1}{n}, \tag{7}$$

where d is the ambipolar diffusion length, $h\nu_l$ the laser photon energy, I is the excitation intensity (power absorbed per unit area) at the sample, and n is the electron density.

This excess energy may change the electron distribution function from the usual Fermi-Dirac or Maxwell-Boltzmann distribution. However, if the electron-electron collisions are more frequent than the electron-phonon collisions by which the electrons lose energy to the lattice, the electrons will thermalize among themselves and one can assign a temperature T_e to the electrons. It can be shown[8] that, when polar-optical scattering is the dominant energy-loss mechanism for this electron gas, the electron-electron collisions are more frequent than the electron-phonon collisions if $n > n_c$, where

$$n_c = |e|E_0\hbar\omega_0(kT_e/\hbar\omega_0)^{1/2}(1/2\pi e^{*4})e^{-\hbar\omega_0/kT_e}, \tag{8}$$

where T_e is the electron temperature. Note that n_c^* is the density of the electron gas at which an electron of excess energy ΔE loses equal amounts of energy to the electron-gas and to the optical phonons. n_c, on the other hand, is the density of electron gas at which intercarrier collisions in this electron gas are as frequent as the collisions of these carriers with the polar-optical phonons. If the condition $n > n_c$ is satisfied, it is meaningful to ascribe a temperature to the electron system. Under these conditions, it can be shown that the rate

of energy loss of the electron system for polar-optical-mode scattering is given by[8]

$$P(T_e) = (2\hbar\omega_0/\pi m_e)^{1/2} |e| E_0 [(e^{x_0 - x_e} - 1)/(e^{x_0} - 1)] \times [x_e^{1/2} K_0(\tfrac{1}{2}x_e) e^{x_e/2}], \quad (9)$$

where $P(T_e)$ is the power *per electron* transferred from the electron system to the lattice through polar-optical scattering. Here $x_0 = (\hbar\omega_0/kT_p)$, $x_e = (\hbar\omega_0/kT_e)$, T_p is the optical-phonon temperature, and K_0 is the modified Bessel function of the order zero. In the temperature ranges of our experiment, the second square bracket is $\approx\sqrt{\pi}$ so that

$$P(T_e) = (2\hbar\omega_0/m_e)^{1/2} |e| E_0 e^{-\hbar\omega_0/kT_e} \quad (10)$$

if $(x_0 - x_e) > 3$ as in our experiments. Thus the steady-state electron temperature, given by Eqs. (7) and (10), is

$$e^{-\hbar\omega_0/kT_e} = \left[\frac{I}{d(h\nu_l)} \frac{1}{n + n_c^*} \frac{(h\nu_l - E_g)}{1 + m_e/m_h}\right] \left(\frac{m_e}{2\hbar\omega_0}\right)^{1/2} \times \frac{1}{|e| E_0}. \quad (11)$$

Thus

$$e^{-\hbar\omega_0/kT_e} \propto I/(n + n_c^*).$$

2. *Application to* CdSe

We will assume the following values of the constants in CdSe[9]: $E_g = 1.8415$ eV (2 °K), $\hbar\omega_0 = 26.5$ meV, $m_e = 0.13 m_0$, $m_h = 0.59 m_0$, $\epsilon_\infty = 6$, $\epsilon_s = 9.75$, and $\bar{\epsilon} = 7.9$. With these constants and $h\nu_l = 2.4097$ eV (for 5145-Å line of the laser) we calculate that $\Delta E = 0.47$ eV ($\gg \hbar\omega_0$). We also calculate $n_c^* \cong 1\times10^{18}$ cm^{-3}, $n_c \approx 2\times10^{14}$ cm^{-3}, and estimate that the electron density $n > n_c$, in the entire range of excitation intensity used by us.

It is, therefore, meaningful to ascribe a temperature to the electron gas. This theoretical prediction is in accord with the experimental fact that the luminescence tail is essentially exponential. For $I < 2\times10^5$ W/cm^2, $n \leq 0.1\, n_c^*$, so that

$$e^{-\hbar\omega_0/kT_e} \cong \left[\frac{\Delta E}{d h\nu_l n_c^*} \left(\frac{m_e}{2\hbar\omega_0}\right)^{1/2} \frac{1}{eE_0}\right] I. \quad (12)$$

Thus we expect that $1/kT_e$ will decrease logarithmically with increase in I, a result which is experimentally obtained in Fig. 2 except at very high intensities. The slope of this variation should be the phonon energy $\hbar\omega_0 = 26.5$ meV. Experimentally we obtain the value of 26 meV for the slope (Fig. 2), in good agreement with the theoretical expectations.

We can also compare the experimental value of P at one excitation intensity with the theoretical prediction. From Eq. (10), we find $P(T_e) = 1.7\times10^{-7} e^{-\hbar\omega_0/kT_e}$ W, whereas $P \cong (6\times10^{-15} I)$ W from Eq. (7) if we assume $d = 0.3$ μm and I is in units of W/cm^2. For $I = 2\times10^5$ W/cm^2, the upper limit on the linear segment of the experimental curve, $P \approx 1.2\times10^{-9}$ W, whereas $P(T_e) = 5\times10^{-9}$ W at the temperature (85 °K) observed at $I = 2\times10^5$ W/cm^2.

We thus find a good agreement between theory and experiments except at very high intensities. For $I > 2\times10^5$ W/cm^2, we see from Fig. 2 that the electron temperature increases less rapidly than predicted by the theory. There are two possible explanations of this behavior. First, a new more-efficient loss mechanism begins to dominate at higher excitation intensities. The second possibility is that one or more of the assumptions made in deriving Eq. (12) begin to break down. We recall here that Eq. (12) involves the assumption that $n \ll n_c^*$. If at very high intensities n becomes comparable to n_c^*, the energy that the photoexcited electron loses to the electron system becomes comparable to the energy loss to the phonons. As a result, the power per electron transferred to the electron system by the laser increases sublinearly with excitation intensity I. This may result in slower increase in T_e with I [see Eq. (11)].

We have calculated that $n/n_c^* \approx 2$ is sufficient to explain the departure from linearity observed at $I = 2\times10^6$ W/cm^2. Since $n_c^* = 1\times10^{18}$ cm^{-3}, this implies that $n = 2\times10^{18}$ cm^{-3} at this I. A lifetime of $\tau \approx 0.3\times10^{-10}$ sec needed to explain this electron density is not unreasonable. We have also calculated n/n_c^* at other intensities and find that n/n_c^* is roughly proportional to I. However, the errors are large and more extensive measurements are required to establish the dependence of n/n_c^* on I accurately.

3. *Comparison between* GaAs *and* CdSe

We have shown above that the theory based on polar mode scattering explains the experimental results in CdSe. Similar conclusion was reached in the case of GaAs in Ref. 1. It is therefore clear that the results in the two materials are consistent with each other. It is, however, instructive to show this explicitly.

Let subscripts 1 and 2 denote GaAs and CdSe, respectively. Since Eq. (12) holds for each semiconductor, we have

$$\exp\left(\frac{\hbar\omega_2}{kT_2} - \frac{\hbar\omega_1}{kT_1}\right) = \frac{\Delta E_1}{\Delta E_2} \frac{d_2}{d_1} \frac{n_2^*}{n_1^*} \frac{E_2}{E_1} \left(\frac{m_1}{m_2} \frac{\hbar\omega_2}{\hbar\omega_1}\right)^{1/2} \quad (13)$$

for a given excitation intensity I in both cases. At the highest excitation intensity used in GaAs, $I \cong 5\times10^3$ W/cm^2, $T_1 = 76$ °K. Therefore, with the values of the constants used in Ref. 1 and this

paper, we calculate from Eq. (13) that $T_2 = 35\,^\circ$K in CdSe at $I = 5\times10^3$ W/cm^2. This is in agreement with the experimental value in Fig. 2, as expected. This example illustrates the important point that one can predict with some confidence the electron temperature in any photoexcited semiconductor in which polar-optical scattering dominates.

B. Hot excitons

Our understanding of the processes leading to exciton heating is incomplete. Expressions are available in the literature[10] for the exciton-phonon collision rates for the optical and acoustical phonons. But, to the author's knowledge, there is no theory either for the rate of energy loss from the exciton system to the lattice or for the mechanisms by which and the rate at which the exciton system acquires its excess energy. It is hoped that the present work will stimulate theoretical interest in this direction.

Since theory sheds so little light on the dynamics of exciton heating at the present time, it may not be inappropriate to consider various possibilities from a qualitative point of view. There appear to be three mechanisms by which the exciton system might acquire excess energy. (i) The photoexcited electron gives a part of its large excess energy to the excitons, just as it does to the electron system and the LO phonons. (ii) The heated electron system loses part of its excess energy by giving it to the exciton system. (iii) The third possibility, that the photoexcited hot phonons[2] give some energy to the excitons, must also be considered. The exciton system loses its excess energy by interaction with either optical or acoustic phonons. It is known[10] that exciton-acoustic phonon interactions are much more frequent than exciton-LO phonon interactions. But the latter involve much larger energy exchanges and cannot be neglected without detailed considerations. Theoretical expressions for the rate of energy transfer from the excitons to the lattice will be very useful in resolving this question.

V. SUMMARY AND CONCLUSIONS

Simultaneous observation of photoexcited hot carriers and hot excitons reveals the interesting fact that the carriers and excitons are not at the same temperatures. The electron-hole system reaches a temperature as high as $\approx 140\,^\circ$K, whereas the exciton temperature is $\approx 25\,^\circ$K at the same excitation intensity of $\sim 4\times10^6$ W/cm^2. The heating of the electrons and holes can be quantitatively explained in terms of polar-optical-mode scattering of carriers. The observed departure from the usual logarithmic dependence on excitation intensity can also be explained if we assume that the carrier density exceeds a certain critical density. It is interesting to note in this connection that, as the optical-phonon temperature approaches the electron temperature, the efficiency of polar-mode scattering as a loss mechanism diminishes, and we would expect a faster increase of the carrier temperature with excitation intensity. We see no evidence of this experimentally. The results on CdSe, taken together with those on GaAs,[1] give us confidence that we can predict the electron temperature of a photoexcited semiconductor. This should prove to be useful when calculating certain properties of highly excited semiconductors, where the carrier temperature, rather than the lattice temperature, may be the relevant parameter. On the other hand, understanding of the processes leading to exciton heating must await further theoretical developments.

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[6] One has to worry about two kinds of heating: average heating and heating during the excitation pulse. The average heating would be determined by the average power incident on the sample. For a given peak power and pulse width, the average power depends on the pulse-repetition frequency. We have varied the pulse-repetition frequency by several orders of magnitude and detected no change in the observed spectra, indicating that average heating is not present under our experimental conditions. The heating during the pulse can be estimated by measuring the difference in the energy of a sharp emission line at low and high intensities, and comparing it with the known temperature dependence of the band gap. From this measurement, we estimate that $T_L < 10\,^\circ$K in our experiments. This estimate agrees with the temperature rise calculated on the basis of volumetric-specific-heat considerations. Validity of this approach is amply supported by a two-pulse experiment on CdS which the author has performed with R. F. Leheny. For a preliminary report, see R. F. Leheny and Jagdeep Shah, Bull. Am. Phys. Soc. 18, 414 (1973).

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