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I_1 line shape as a temperature probe: The thermal relaxation of highly excited CdS

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We demonstrate that analysis of the line shape of the acoustic-phonon wings of the I_1 bound-exciton emission in CdS can provide a means to determine crystal temperature T and use this result to investigate the thermal relaxation of CdS following photoexcitation by an intense N_2-laser pulse. We find $T \sim 15\,^\circ$K for ~1-kW incident power and T varies as the fourth root of the absorbed energy in accord with the Debye theory of specific heat. In addition the crystal-temperature rise is found to persist for long times (~1–100 μsec). From the variation of the crystal temperature with time, we deduce a constant value of heat flow from the sample to the liquid-helium bath (~4 W/cm^2).

I. INTRODUCTION

We demonstrate that a comparison of the Stokes and the anti-Stokes contribution of the CdS I_1 luminescence line[1] allows an accurate determination of crystal temperature, and make use of this result for a detailed study of the temperature of CdS following excitation by an intense optical pulse. The properties of semiconductors excited in this fashion have received considerable attention in recent years.[2] Crystal temperature is one of the important parameters for evaluating the results of these high-intensity experiments and also in attempting a theoretical explanation of the results. However, no systematic measurements of crystal temperature under high-intensity excitation have been reported.[3]

In this paper we report measurements of delayed photoluminescence, which allow us to make use of the I_1 line as a probe of the thermal relaxation of a liquid-helium-cooled CdS crystal following intense photoexcitation. Detailed measurements were made as a function of pump pulse energy [ΔE = (peak power)×(pulse width)] and also as a function of time after the excitation pulse. We find that the crystal temperature varies with E as $T \propto (\Delta E)^{1/4}$, consistent with the variation of lattice specific heat at low temperatures. We also find that it takes several *microseconds* for the crystal to cool to liquid-helium-bath temperature, after excitation by the 10-nsec N_2 laser used, reflecting the poor thermal contact (or high Kapitza resistance) between the sample and liquid He. While the results reported here apply to the specific case of excitation by a 10-nsec laser pulse, we also discuss the extension of these results to other systems. We discuss the unreliability of using the *energy* of the I_1 line as a temperature indicator in an appendix.

II. EXPERIMENTAL TECHNIQUES

Measurements were made on CdS platelets 20–50 μm thick and ~ 2×0.1 mm in area. The platelets were mounted on glass and immersed in superfluid He at 1.8 °K. A N_2 laser (peak power ≈ 100 kW, pulse-width ≈ 10 nsec, $\lambda = 3371$ Å) was weakly focused so as to cover the entire cross section of the sample uniformly. During the laser excitation the details of this luminescence feature are lost in a broad background-emission characteristic of the highly excited crystal. Since the decay time of the near-band-gap electronic states is rapid (~ 1 nsec),[4] we can probe the crystal by reexcitation of these levels with a weaker probe pulse applied after a controlled time delay. To accomplish this we used a cavity-dumped Ar$^+$ laser (peak power ≈ 0.5 W, pulse width ≈ 15 nsec, $\lambda = 4579$ Å) as the probe pulse. This laser was weakly focused on the sample by a cylindrical lens. Although the delay time τ between the two lasers could be varied continuously from 0 to 25 msec (the time between the N_2-laser pulses), meaningful data were difficult to obtain for $\tau < 30$ nsec because it took approximately this long for the N_2-laser output to fall to the level of the Ar$^+$ probe beam.

The emission from the sample was dispersed by a double spectrometer and detected by a gated photomultiplier. The gate on the photomultiplier was turned on only in synchronization with the Ar$^+$-laser pulse to prevent the luminescence excited by the N_2 laser from saturating the photomultiplier. The output from the photomultiplier was fed into a fast boxcar with a 10-nsec gate in synchronization with the Ar$^+$ laser.

III. I_1 EMISSION LINE AS A PROBE

Accurate determination of crystal temperature is difficult under high-excitation conditions. In the past sharp emission lines, whose energies can be determined very accurately and whose energies are known as a function of the ambient temperature under low-excitation levels, have been used to estimate crystal temperatures. However, these determinations neglect any variation of the band gap or exciton energy resulting from intense optical

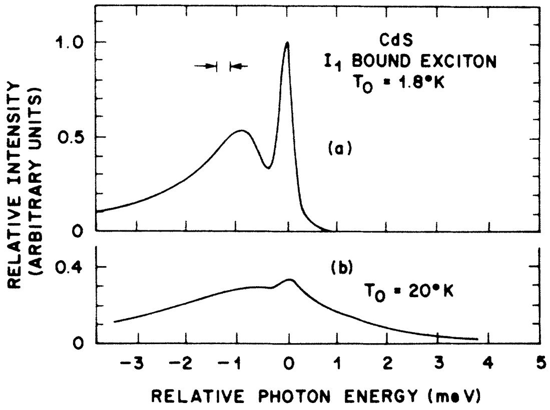

FIG. 1. I_1 emission line shape at low excitation intensity. (a) 1.8 °K, superfluid He, (b) 20.3 °K, liquid H_2.

excitation. We show in the Appendix that shifts in the energy of the emission lines caused by these effects could be sufficiently large to cast doubts about the accuracy of the temperature inferred in this way. Nevertheless, we demonstrate here that the properties of the I_1 emission *line shape* in CdS can be used to determine the crystal temperature quite accurately, independent of any variation in the energy of the peak and with fast response times (~1 nsec). The possible use of the I_1 emission line as a probe for *nonequilibrium* phonons will be discussed elsewhere.

The I_1 emission line corresponds to the radiative recombination of an exciton bound to a neutral acceptor.[1] At helium temperatures, a broad feature associated with this line is present on the low-energy side of the line. This is shown in Fig. 1(a). As the temperature is increased, Fig. 1(b), the line broadens and a broad feature appears on the high-energy side as well. The low- (high) energy component is due to radiative recombination of the bound exciton with emission (absorption) of acoustic phonons. The broad feature is called the acoustic wing and we shall refer to the high- and low-energy wings as the anti-Stokes and the Stokes components, respectively, of the I_1 emission line. Hopfield[5] has developed a theory of this type of electron-phonon coupling in impurity states of semiconductors which includes the possibility of multiphonon interactions and has applied this theory to calculate the I_1 bound-exciton line shape to obtain good agreement with experimentally observed line shapes. Within the framework of Hopfield's theory we can show that even in the presence of multiphonon processes the ratio of the anti-Stokes to Stokes intensity is given by the Boltzmann factor $e^{-E/kT}$. This result, which applies when the phonons are in thermodynamic equilibrium, follows directly from the analysis given by Hopfield. Thus, if equilibrium is achieved among the acoustic phonons the temperature of these low-energy phonons, which by definition is the lattice temperature, can be determined by straightforward analysis of the I_1 line shape.

Since this is a very crucial point in determining the usefulness of the I_1 line shape as a thermal probe, we have measured a low-intensity I_1 emission spectrum with the crystal *immersed* in liquid hydrogen ($T = 20.3\,^\circ K$). The spectrum shown in Fig. 1(b) and the ratio of the anti-Stokes to Stokes intensity at selected energies is plotted in Fig. 3. The solid line is the expected behavior for $T = 20.3\,^\circ K$. The excellent fit provides an experimental confirmation of the theoretical conclusion drawn above.

In analyzing the results of our experiment, we take the position that if we measure an equilibrium line shape following optical excitation, then this implies that the acoustic phonons have achieved an equivalent temperature as determined by that line shape. Our experimental results show that the I_1 line shape corresponds to an equilibrium line shape (at elevated temperature) at the earliest time after excitation that meaningful measurements can be made (~ 30 nsec). This implies that the inelastic scattering times for phonons is shorter than 30 nsec. In an unexcited crystal boundary scattering is the dominant scattering mechanism at 1.8 °K and would lead to relaxation times of the order of 10 nsec for our samples. In addition, the significant photoexcited phonon population is expected to result in frequent inelastic scattering among the phonons. We know of no detailed calculation of the phonon-relaxation processes in such a system, but we have made some order-of-magnitude estimates of these times using very simple models and find that times shorter than 10 nsec are not unreasonable. Thus, our assumption that equilibrium is achieved within the time resolution of our experiment (30 nsec) is reasonable.

Since the I_1 emission line becomes less intense with increasing temperature and disappears at ~ 30 °K, this is the upper limit of its useful range. The lower limit is determined by the presence of unrelated emission on the anti-Stokes side, primarily due to the presence of an I_2 line at $E = +11$ meV. Our experience indicates that we can measure ~ 3.5 °K with about 10% accuracy using a 6-sec time constant in the apparatus described in Sec. II.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A typical set of data obtained in the course of present experiments is shown in Fig. 2. For all these curves the Ar^+-laser probe occurred 100 nsec after the N_2-laser pulse. The spectra shown here correspond to the condition of the sample at the time of the Ar^+ probe pulse. In Fig. 2(a), the N_2 laser is blocked so that the spectrum is that of the unperturbed crystal. Since the bath temperature is 1.8 °K, no anti-Stokes wing is visible. In Fig. 2(b), the N_2-laser power was 0.03 kW (peak). One can see a broadening of the line, a change in the spectral shape, and the appearance of the anti-Stokes wing. The ratio of anti-Stokes to Stokes intensities, plotted in Fig. 3, gives a crystal temperature of 8.3 °K. Similarly Fig. 2(c) corresponds to 1-kW peak power and gives a crystal temperature of 14 °K.

Similar data were taken and analyzed for various incident N_2-laser powers. In Fig. 4 we have plotted $[(T/T_0)^4 - 1]$ vs the relative pump intensity on a log-log scale. We can see that it is linear over approximately three orders of magnitude of incident power. Since $[(T/T_0)^4 - 1] \approx (T/T_0)^4$ for $T \geq 2T_0$, this implies that the temperature of the crystal increases as $(\Delta E)^{1/4}$, where ΔE is the energy of the N_2-laser pulse. This result is a consequence of the lattice contribution to the specific heat which is proportional to T^3 at low temperature[6]; the electronic contribution to specific heat is negligible in our crystal (because of low electron density). Taking $C_v = \alpha T^3$, the temperature of the crystal for a given absorbed energy ΔE is given by

$$\Delta E = \tfrac{1}{4}\alpha[(T/T_0)^4 - 1]T_0^4 ,$$

where T_0 is the ambient temperature. α is related to the Debye temperature Θ_D and the crystal volume V by

$$\alpha = 234\,\rho N k_B V (1/\Theta_D)^3 ,$$

where ρ is the density of the crystal, N is Avogadro's number, and k_B is the Boltzmann constant. Using the data of Fig. 4 one can deduce Θ_D, the Debye temperature of the material. We find a value of 200 °K, which compares well with that determined from comparisons with other semiconductor materials.[7] We thus have a determination of Θ_D for CdS. The agreement between this analysis and the data of Fig. 4 shows that the temperature of the crystal for given energy input can be predicted with confidence.

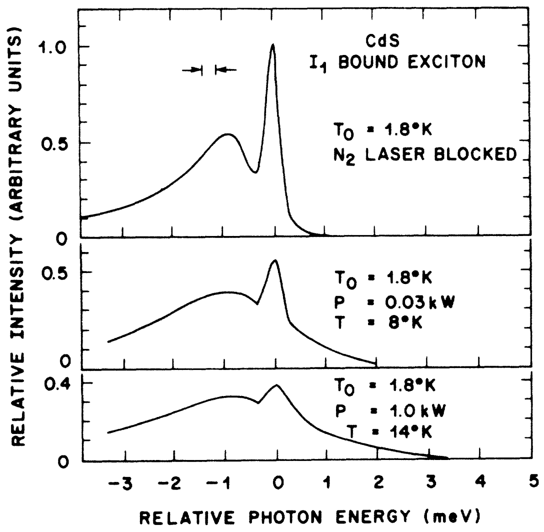

FIG. 2. I_1 emission excited by an Ar^+-laser probe pulse occurring 100 nsec after the N_2-laser pulse. Crystal immersed in superfluid He at 1.8 °K. Top trace, N_2-N_2 laser, blocked [same as Fig. 1(a)]; middle trace, N_2-laser, 0.03-kW peak power; bottom trace, N_2-laser, 1 kW peak power. The temperatures indicated are as determined in Fig. 3.

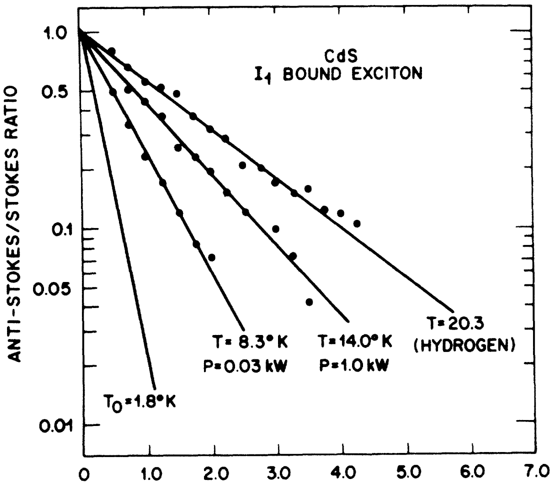

FIG. 3. Ratio of anti-Stokes to Stokes intensities of I_1 line as a function of phonon energy E for various experimental curves in Fig. 1 and Fig. 2. The temperature is determined from the slope of the straight lines.

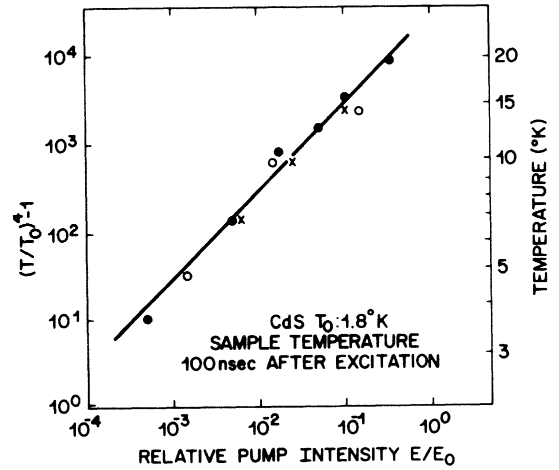

FIG. 4. $[(T/T_0)^4-1]$ vs relative pump power. The maximum pump power is kW (peak).

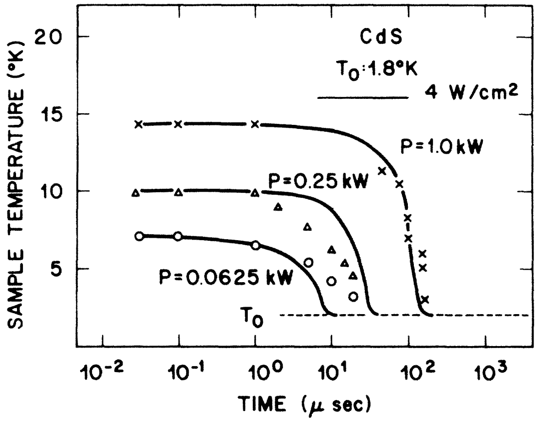

FIG. 5. Crystal temperature T vs t, the delay after N_2 pulse excitation. Note the time scale is logarithmic.

The above analysis implicitly assumes that a significant fraction of the energy dissipated in the crystal by the N_2 laser does not flow out of the crystal (into liquid He) within 100 nsec. This assumption is well supported by the data of Fig. 5. Keeping the incident N_2-laser power constant, we varied the time delay between the Ar^+ probe pulse and the N_2 excitation pulse. The temperature we measured at each delay is plotted as a function of the delay in Fig. 5. There are three sets of points for three different N_2-laser pump power levels as indicated in the figure. The highest level corresponds to an energy input of 10 μJ. At this energy level we note that it takes approximately 150 μsec for the heat to flow out of the crystal. There is hardly any temperature change in the first microseconds, indicating that the assumption of negligible outflow of energy in the first 100 nsec is valid.

It is important to note that the time scale in Fig. 5 is logarithmic. The data are presented in this way to accommodate the wide variation of the relaxation time with pump power. Note that the time it takes for the temperature to decay to $(1/e)$ of its initial value varies from ≈ 100 μsec at 1 kW to ≈ 10 μsec at 0.0625 kW, indicating that the relaxation time decreases with decreasing pump power. Furthermore, attempts to fit the data to an exponential decay with time were not successful. From this we conclude that the rate of energy flow from the sample to liquid He is not simply proportional to the energy in the crystal. The fact that the relaxation time is nearly proportional to the pump power suggests that this rate of flow is nearly a constant independent of temperature. The solid lines in Fig. 4 were drawn with the assumption that this rate of flow is 4 W/cm^2.

The flow of heat from a solid into a cryogenic fluid is a complicated problem when the temperature of the solid is greater than the boiling point of the fluid. This problem has been studied extensively for the case of metals where it is found that the rate of heat flow from the metal into liquid He is approximately constant ($\sim 1-10$ W/cm^2) over the range of temperatures encountered in the present experiments.[8] This is a result of "film boiling" and we expect that similar phenomenon will be important for semiconductors. While the assumption of a constant energy flow is probably an oversimplification, we see from Fig. 4 that it is a good first-order approximation. These results indicate that the Kapitza, or the boundary resistance, between CdS and liquid He is quite high and limits the heat flow to ~ 4 W/cm^2.

It is of some interest to extrapolate these results to the case of a cw excitation source which uniformly pumps the face of a sample. From the previous discussion we can estimate that the crystal temperature will be less than 20°K if the power absorbed is less than 4 W/cm^2 of the sample area. The case of a focused cw excitation source is more complicated; the temperature of the crystal will be nonuniform. The heat flow out of the crystal will not exceed 4 W/cm^2 of the sample area for $T \leq 20$°K.

SUMMARY AND CONCLUSIONS

We have demonstrated that analysis of the I_1 emission line shape in CdS provides an accurate method of determining the lattice temperature and have used this technique to determine the heating effects of intense optical pumping. We find that the increase in lattice temperature is roughly proportional to the fourth root of the energy in the excitation pulse, consistent with the Debye theory of lattice contribution to the specific heat. This observation leads to a value of 200°K for the Debye temperature of CdS. Our measurements demonstrate that the heating caused by an intense optical excitation pulse can persist for a considerable time (as long as 100 μsec) after the termination of the excitation pulse. From these results, we deduce that in the temperature range studied here the outflow of heat from CdS to the helium bath is nearly constant and ≈ 4 W/cm^2. This implies that the Kapitza resistance between CdS and He is quite high.

We have discussed the implications of these results for the case of cw excitation to illustrate how the heat flow into the bath limits the allowable incident power for a given temperature rise.

ACKNOWLEDGMENTS

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APPENDIX: OSCILLATORY BEHAVIOR OF I_1 EMISSION LINE

We present here some data which show that the use of the *energy* of a sharp emission line as a temperature probe is unreliable after intense photoexcitation of the crystal.

During the course of our experiments we measured the *energy* of the I_1 central peak very accurately. From the known band-gap variation with temperature we can calculate the expected energy of the I_1 central peak at the temperature determined from the line shape analysis. We find that this calculated energy does not agree with the measured energy of the peak. For example, at 100-nsec delay and 0.3-kW incident power, we expect a shift of −0.3 meV, whereas we observe only −0.18 meV. (If conversely we used the shift as a measure of the temperature change, we would estimate $T = 10\,^\circ\mathrm{K}$, an error of $-5\,^\circ\mathrm{K}$.) At longer delays, the temperature decreases and so does the measured shift in I_1 emission energy. However, the calculated and measured I position never agree. In fact, for times greater than 10 μsec, when the sample temperature as determined by the phonon wings has returned to the helium-bath temperature, the shift in the energy of the peak has become positive and oscillates between 0 and +0.3 meV with a period of about 40 μsec. The shift in the energy vs time delay is plotted in Fig. 6(a). We also indicate the variation of the width of the peak over the same period of time in Fig. 6(b). While the linewidth does not show the same fluctuation behavior, it is significantly wider (~50%) than the unperturbed linewidth shown by the dotted line.

The important point to emphasize here is that each point on curves 6(a) is taken from a trace similar to the ones shown in Fig. 2. Furthermore, the experimental setup is such that we were continuously monitoring the I_1 line of the unperturbed crystal—so the measured shift was a difference in energy between two traces taken simultaneously. Thus, our accuracy in measuring the shift is ~±0.05 meV and the possibility of spurious effects giving rise to the observed oscillations is ruled out.

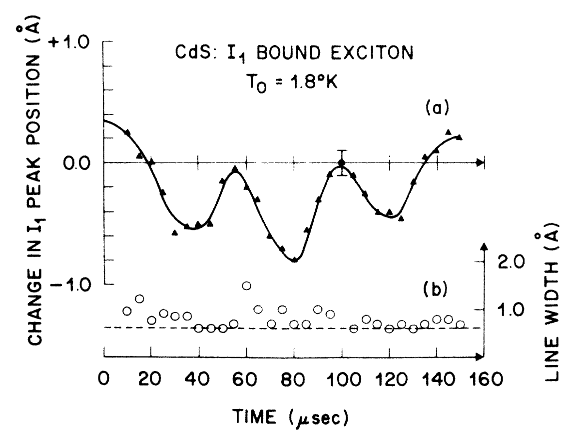

FIG. 6. Long-time behavior of I_1 emission for $P = 0.25$ kW. (a) Variation of I_1 peak position with respect to peak position of 10 msec reference. (b) Variation of I_1 linewidth.

The results presented above indicate the difficulty connected with using the energy of a sharp emission line as an indicator of sample temperature. These results further indicate that some mechanism is operating which can shift the band gap, and therefore the energies of the near-band-gap states, to higher energy as a result of the intense excitation of the crystal by the N_2 laser. This effect can persist for periods $\gtrsim 150$ μsec. While we have no understanding of this effect, we believe it results from a stress applied to the crystal as a result of the pumping pulse. Rowe *et al.*[9] have measured the shift of the *A* exciton in CdS as a result of uniaxial stress applied to the crystal along the *c* axis and found that at $77\,^\circ\mathrm{K}$ the *A* exciton shifted at $\simeq 50\ \mathrm{meV}/(10^9\ \mathrm{dyn/cm^2})$. If a similar mechanism is responsible for our observed shift then the equivalent stress, to shift the bound exciton by 0.25 meV, is $\approx 5\times10^6\ \mathrm{dyn/cm^2}$. This magnitude of stress agrees with estimates based on models of high-density electron-hole plasma injection by optical pumping,[10] however, we do not have any clear explanation for the observed long period of the oscillation. The observed period of 40 μsec is about two orders of magnitude larger than the ballistic-phonon transit time along the longest dimension of the crystal and, in addition, does not appear to correspond to any simple mechanical oscillation of the crystal.

In conclusion, we have presented data which show that the use of the energy of a sharp emission like the I_1 as a temperature indicator following an intense optical pulse is unreliable.

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