which represents the infinitesmal variation of $\bar{A}$ with D_{m+1}. Thus we may take

$$\Delta\bar{A} \equiv -(\delta\bar{A}/\delta D_{m+1})D_{m+1} \qquad \text{(C17)}$$

as a first-order estimate of the change that would be introduced into the calculated value of $\bar{A}$ by adding another parameter to the energy distribution and satisfying the expanded set of anisotropy balance equations. It should be noted that $\Delta\bar{A}$ is not unique, but depends upon the particular additional parametrization chosen. A small value of $\Delta\bar{A}$ implies that either the transport quantity $\bar{A}$ is not sensitive to the particular additional parametrization ($\delta\bar{A}/\delta D_{m+1} \to 0$) or the anisotropy balance equation $D_{m+1}=0$ is well satisfied for small α_{m+1}. To establish the quality of the initial m-parameter model, in principle one would have to perform the error test with all possible $m+1$ parametrizations, obtaining small $\Delta\bar{A}$ for each. In practice, *a priori* knowledge of reasonable forms for the energy distribution will allow this test to be carried out with a particular finite set. An example, wherein $\bar{A}$ is the drift velocity, is given in Sec. IV.

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Lifetimes of Bound Excitons in CdS

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Weakly bound excitons in CdS have giant oscillator strengths which lead to exceedingly fast radiative lifetimes. We have been able to measure the lifetime of the I_2 line, an exciton bound to a neutral donor, and the lifetime of the I_1 line, an exciton bound to a neutral acceptor. We find $\tau_{I_2}=0.5\pm0.1$ nsec and $\tau_{I_1}=1.03\pm0.1$ nsec. The measurements were made at 1.6°K. The lifetimes are measured by exciting the luminescence with an argon laser modulated at 100 Mc/sec, and measuring the time delay of the luminescence with a 100-Mc/sec phase-sensitive detector. Previous calculations by Rashba and Guygenishvili predicted radiative lifetimes which were an order of magnitude shorter than our measured values. They used an incorrect value for the exciton mass. When corrected, their theory gives $\tau_{I_2}=0.56$ nsec and $\tau_{I_1}=1.86$ nsec, in reasonably good agreement with our measurements. Thomas and Hopfield measured the absorption oscillator strength of the I_2 line. Their measurements predict a radiative lifetime for the I_2 line of 0.4 ± 0.1 nsec. This is very close to our measured value and shows that the I_2 line decays radiatively. We conclude that the nonradiative Auger effect is negligible for the I_2 line and either negligible or small for the I_1 line. We also calculate the lifetime for donor-acceptor pair recombination to be 2.2 nsec as the pair separation goes to zero. This agrees with Colbow's experimental value of 2.5 ± 1 nsec. Using the same method, we calculate the lifetime of the Te isoelectronic trap to be 27 nsec. This agrees poorly with Cuthbert and Thomas's measured value of 300 nsec.

I. INTRODUCTION

THE edge emission in CdS, at helium temperature, consists primarily of donor-acceptor pair recombination in the green and the decay of excitons bound to neutral donors and acceptors in the blue. The decay of the bound excitons consists of sharp no-phonon lines followed by much weaker phonon sidebands. These transitions are shown in Fig. 1. The I_2 line is the decay of an exciton bound to a neutral donor and the I_1 line is the decay of an exciton bound to a neutral acceptor. In this paper, we report the measurement of the lifetimes of the I_1 and I_2 lines in CdS at 1.6°K.

The I_1 and I_2 lines were analyzed by Thomas and Hopfield[1] in 1962. That same year, Rashba and Gurgenishvili[2] (hereafter referred to as RG) showed that in a direct band gap semiconductor, such as CdS, the oscillator strength for radiative decay of a weakly bound exciton could be simply calculated in terms of the binding energy of the bound exciton, the exciton mass, and the oscillator strength per molecule of the free exciton. They pointed out that excitons, weakly bound to impurities, have giant oscillator strengths that are many orders of magnitude larger than the oscillator strength per molecule of the free exciton. Using values which they thought appropriate for bound excitons (the I_2 lines) in CdS, they concluded that the oscillator strength was roughly a factor of 4×10^4 greater than the oscillator strength of the free exciton per molecule in CdS, i.e., the oscillator strength was about 80. The ideas of RG were qualitatively verified at the time of publication, because they explained why impurity absorption just below the free exciton was so strong in undoped relatively pure semiconductors such as CdS. From the oscillator strength, one can predict both the absorption strength and the radiative lifetime of the bound exciton. Their value of the oscillator strength would give a radiative lifetime of about 0.044 nsec.

[1] D. G. Thomas and J. J. Hopfield, Phys. Rev. **128**, 2135 (1962).
[2] E. I. Rashba and G. E. Gurgenishvili, Fiz. Tverd. Tela **4**, 1029 (1962) [English transl.: Soviet Phys.—Solid State **4**, 759 (1962)] (referred to as RG in this paper).

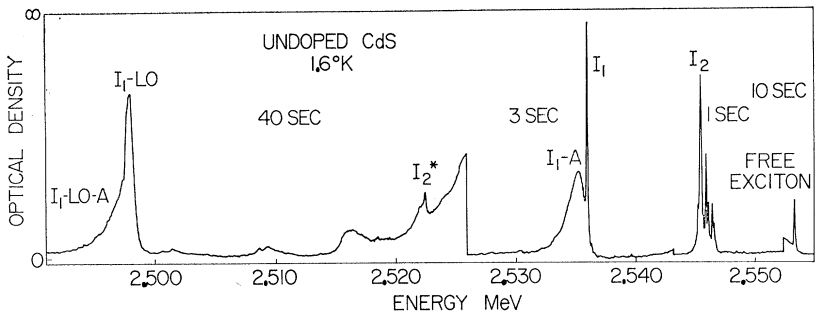

FIG. 1. Densitometer trace showing the I_1 line, its acoustic-phonon replica I_1-A_1 and its longitudinal-phonon replica I_1-LO, the I_2 line, transitions I_2*, in which the donor is left in an excited state, and the free-exciton transition. The exposure times for various regions of the spectrum are given. The spectrum was measured at 1.6°K, exciting an undoped CdS platelet with the 4765-Å line of an argon laser.

Besides radiative decay, excitons bound to neutral donors or acceptors can decay nonradiatively by means of the Auger effect. In the Auger effect, an electron and hole recombine and the energy of the bound exciton is transferred to the other electron (on the donor) or hole (on the acceptor) which is ejected from the impurity with a large kinetic energy. Nelson *et al.*[3] measured the radiative and Auger rates for excitons bound to neutral donors in the indirect semiconductors GaP and Si. The Auger lifetime was 20 nsec in GaP and 80 nsec in Si. It is very difficult to accurately calculate the Auger rate, since it depends upon a knowledge of the wave function and density of states for highly excited electrons (or holes). In roughly estimating the Auger rate in CdS, we are probably better off to appeal to experiment. There is no fundamental reason why the Auger rate should be much faster in a direct semiconductor such as CdS, than in an indirect semiconductor such as GaP. Since the final electron (or hole) acquires enough momentum to take it about half the distance from the zone center to the zone edge, a direct band gap does not appear to have any obvious advantage over an indirect band gap in producing a fast Auger effect. We, thus, expect the Auger lifetime to be of order 10 nsec in CdS.

Since 1962, there have been a number of attempts to measure the lifetimes and oscillator strengths of the weakly bound excitons in CdS. Similar measurements have not yet been carried out on other direct band-gap semiconductors. Using a pulsed electron beam source, Thomas, Dingle, and Cuthbert[4] concluded that the I_1 and I_2 lines decay with lifetimes of 4 nsec or less. They also concluded that the states decayed chiefly nonradiatively by the Auger effect. Bonit a la Guillaume, Debever, and Salvan[5] measured the total emission rise time in samples in which the I_2 line was the emission line using a fast photocell (rise time $\sim$0.5 nsec) and found rise times which ranged from 1 to 9 nsec. Thomas and Hopfield[6] recently measured the oscillator strength of the I_2 line by measuring the area under the I_2 line in absorption and estimating the neutral donor concentration from conductivity measurements. They found an oscillator strength of 9 ± 2 corresponding to a radiative lifetime of about 0.4 ± 0.1 nsec.

In this paper, we report the first reliable measurements of the lifetimes of the I_1 and I_2 lines in CdS. In Sec. II, we discuss our method of lifetime measurement. In Sec. III, we discuss our results and how we distinguish between exciton trapping time and exciton lifetime. In Sec. IV, we give a brief derivation of the RG theory for the lifetime of a bound exciton. Finally, in Sec. V, we compare the theoretical radiative lifetimes for the I_1 line, the I_2 line, donor-acceptor pairs, and the Te isoelectronic trap, with experimentally measured values. The radiative lifetimes are calculated in Appendixes A and B.

II. EXPERIMENTAL METHOD

The apparatus we employed was designed to measure the lifetimes in the range of 0.03–3 nsec.[7] It was meant to complement more conventional apparatus, such as those employed by Cuthbert and Thomas[8] in which a pulsed electron beam source, photomultiplier, and sampling scope are used to measure lifetimes greater than 4 nsec. This method of measurement is very simple in principle. The laser beam exciting the luminescence is modulated at an angular frequency ω. If the luminescence decays exponentially in a time τ, which is small compared to the period of modulation, the luminescence will be delayed by a time τ and there will be a phase delay $\varphi=\omega\tau$ of the luminescence relative to the exciting light. If the signal-to-noise ratio of the luminescence is (S/N), φ can be measured to an accuracy of about $(S/N)^{-1}$. This will produce an error $\Delta\tau\approx(S/N)^{-1}\omega^{-1}$. To accurately measure small luminescent lifetimes, ω and (S/N) must be large. For $S/N=100$ and a modulation frequency of 100 Mc/sec, which were typical experimental conditions, $\Delta\tau=0.016$ nsec.

[3] D. F. Nelson, J. D. Cuthbert, P. J. Dean, and D. G. Thomas, Phys. Rev. Letters **17**, 45 (1966).
[4] D. G. Thomas, R. Dingle, and J. D. Cuthbert, in *II-VI Semiconducting Compounds*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1967), p. 863.
[5] C. Benoit a la Guillaume, J. M. Debever, and F. Salvan, in *II-VI Semiconducting Compounds*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1967), p. 1448.
[6] D. G. Thomas and J. J. Hopfield, Phys. Rev. **175**, 1021 (1968).
[7] A similar apparatus for lifetime measurement has recently been described by V. P. Sushkov, M. V. Nevskii, E. B. Lzubyanitskaya, and I. I. Kruglov, Conference in Munich, Germany, 1969 (unpublished).
[8] J. D. Cuthbert and D. G. Thomas, Phys. Rev. **154**, 33 (1967).

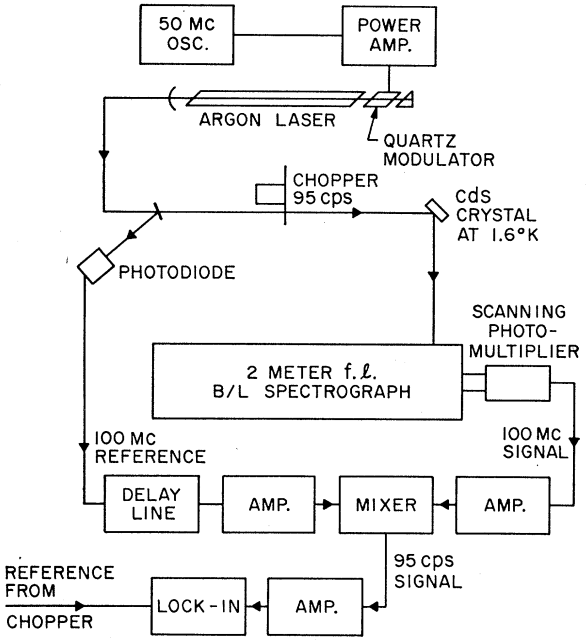

FIG. 2. Block diagram of the apparatus used to measure the lifetime of the luminescence.

A block diagram of the apparatus is shown in Fig. 2. The laser was modulated at 100 Mc/sec by mode locking the laser with a conventional quartz block driven at 50 Mc.[9] A 100 Mc/sec reference signal is generated by sending part of the laser beam to a photodiode. The phase of the reference was varied by sending the reference through a variable-delay line. The component of the 100-Mc photomultiplier signal that was in phase with the reference signal was then detected with a balanced mixer. The laser beam was chopped at 95 cps. When the reference is 90° out of phase to the photomultiplier signal, the audio signal produced by chopping the laser at 95 cps goes to zero. This allows us to determine the phase changes in the photomultiplier signal accurately. To measure the phase delay of the I_2 line, for example, we first detect the laser line (light reflected from the sample) and adjust the variable-delay line until the audio signal goes to zero. Then we detect the I_2 line. The variable delay is increased to again reduce the audio signal to zero. The lifetime of the luminescence is equal to the change in the time delay. Spurious phase shifts in the photomultiplier were eliminated by focusing the light on the center of the photocathode, regulating the dynode voltages with Zener diodes, and adjusting all light signals to give the same photomultiplier current. The measurements on a given sample were usually reproducible to ± 0.04 nsec. The larger errors quoted in Sec. III are due to variations in the measurements of different samples. These variations were at least partly due to background light, detected along with the I_1 and I_2 lines, which had a different delay than the lines being measured. This effect was held to a minimum by using a resolution of 0.2 Å.

[9] L. E. Hargrove, R. L. Fork, and M. A. Pollock, Appl. Phys. Letters **5**, 4 (1964).

III. RESULTS

The major difficulty in carrying out the lifetime measurements of the bound excitons was in separating the time of formation of the bound exciton from the lifetime of the bound exciton. Fortunately, there was no difficulty in doing this for the I_1 line. We could excite the I_1 line luminescence with the above band-gap 4765-Å argon laser line and also with the 4880-Å argon laser line. The 4880-Å line lies lower in energy than the I_2 line, but 4.5 meV above the I_1 line. Light at 4880 Å can excite the I_1 line directly by absorption into an acoustic-phonon wing.[10]

The samples used in this experiment were platelets grown by sublimitation using Eagle Pitcher ultrahigh-purity CdS. The samples were either undoped or lightly doped with donors by the addition of excess Cd during growth or the addition of iodine. All measurements were made at 1.6°K. The lightly donor-doped CdS crystals had very high resistivity as did the undoped samples. The spectra of the lightly doped samples could be distinguished from the undoped crystals because the I_1 and I_2 lines were not quite as sharp as in the undoped crystals, the I_2 line was much stronger than the I_1 line, and the transitions to excited donor states,[11] labeled I_2* in Fig. 1, were difficult or impossible to observe. All samples consistently gave a value of 1.03 ± 0.10 nsec for the lifetime of the I_1 line when measured with 4880-Å excitation. When the I_1 line was measured with the above band gap, 4765-Å excitation, there was an additional delay of 0.65–1.3 nsec for the undoped crystals. Similar additional delays were found when lifetimes were measured using the 4825-Å line of the krypton laser. This line is above the free-exciton energy, but not above the band gap. We attribute this additional delay to the time taken to trap the free excitons which are initially produced by the laser light. The exciton trapping became negligible when the samples were lightly doped with donors. In more heavily doped samples, the I_1 line lifetime was reduced to 0.7–0.9 nsec. The acoustic and longitudinal optical-phonon replicas of the I_1 line gave the same delays as the I_1 line. Some of the samples used showed two closely spaced I_1 lines at 4888.53 and 4888.20 Å. Both I_1 lines gave the same lifetime within experimental error.

Unlike the case of the I_1 line, we were unable to measure the lifetime of the I_2 line by direct excitation into a phonon wing. For the measurement of the I_2

[10] J. J. Hopfield, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962*, edited by A. C. Strickland (Bartholomew Press, Dorking, England, 1962), p. 75.

[11] D. C. Reynolds, C. W. Litton, and T. C. Collins, Phys. Rev. **174**, 845 (1968).

lifetime, we could use only the above band-gap 4765-Å line. Our measurement of the I_2 line lifetime was made on the same samples, lightly doped with donors, which gave the same values for the I_1 line lifetime when excited with 4880- and 4765-Å light. Five samples from different growths gave a consistent value of 0.5 ± 0.1 nsec for the lifetime of the I_2 line. Just as with the I_1 line, all undoped samples gave additional delays of about 0.65–1.3 nsec due to the exciton trapping time and more heavily donor-doped samples gave shorter lifetimes of 0.3–0.5 nsec.

IV. THEORY OF RADIATIVE LIFETIME OF BOUND EXCITONS

In this section, we derive the results of RG, for the oscillator strength of a bound exciton, in an elementary manner. In the Appendixes, we carry out more detailed calculations for specific cases.

The oscillator strength of a radiative transition for light of polarization $\hat{\alpha}$ is defined by the contribution of the radiative transition to the dielectric constant ϵ_α

$$\Delta\epsilon_\alpha=(4\pi Ne^2/m_0)f_\alpha/(\omega_0{}^2-\omega^2)\,, \tag{1}$$

where N is the number of centers per unit volume, $\hbar\omega$ is the energy of the light, and m_0 is the free-electron mass.[12] It can be shown that

$$f_\alpha=2|\langle\lambda_f|p_\alpha|\lambda_i\rangle|^2/\hbar m_0\omega_0\,, \tag{2}$$

where λ_i is the initial state, λ_f is the final state, and p_α is the one-electron momentum operator.[12] The radiative lifetime is related to the oscillator strength by[13]

$$\tau=3m_0c^3/2ne^2\omega^2f=4.50\lambda^2/nf\,, \tag{3}$$

where λ is the wavelength of the transition in cm, n is the refractive index of the crystal, and

$$f=\sum_{\alpha=1}^{3}f_\alpha \tag{4}$$

is the total oscillator strength of the transition.

Let $\varphi(\mathbf{r}_e,\mathbf{r}_v)$ be the envelope function for an exciton (free or bound). The oscillator strength of an allowed transition is given by

$$f=C^2\left|\int d\mathbf{x}\;\varphi(\mathbf{x},\mathbf{x})\right|^2\Big/\omega_0\,, \tag{5}$$

where C is a constant of proportionality. The electric dipole matrix element is included in C.

For a free exciton of wave vector $\mathbf{K}$, the envelope function is given by

$$\varphi(\mathbf{r}_e,\mathbf{r}_v)=V^{-1/2}\exp(\mathbf{K}\cdot\mathbf{R})\Phi_{EX}(\mathbf{r}_e-\mathbf{r}_v)\,, \tag{6}$$

where $\mathbf{R}$ is the center-of-mass coordinate

$$\mathbf{R}=(m_e/M)\mathbf{r}_e+(m_v/M)\mathbf{r}_v \tag{7}$$

and Φ_{EX} describes the relative motion of the electron and hole. Transitions are only allowed for $\mathbf{K}=0$. According to Eq. (5), f_{EX}, the oscillator strength of the free exciton per molecule, is

$$f_{EX}=C^2|\Phi_{EX}(0)|^2\Omega_{\rm mol}/\omega_{EX}\,, \tag{8}$$

where $\Omega_{\rm mol}$ is the volume of one CdS molecule.

Substituting for C in Eq. (5), we find

$$f=f_{EX}\left(\left|\int d\mathbf{x}\Phi(\mathbf{x},\mathbf{x})\right|^2\Big/|\Phi_{EX}(0)|^2\Omega_{\rm mol}\right)\omega_{EX}/\omega_0\,. \tag{9}$$

For a weakly bound exciton with envelope function $F(\mathbf{R})\Phi_{EX}(\mathbf{r}_e-\mathbf{r}_v)$, Eq. (9) becomes

$$f=f_{EX}\left|\int d\mathbf{x}F(\mathbf{x})\right|^2\omega_{EX}\Big/\Omega_{\rm mol}\omega_0\,. \tag{10}$$

For a bound electron and hole, described by a product envelope function $\Phi_A(\mathbf{r}_v)\Phi_D(\mathbf{r}_e)$, where the spread of the electron envelope function is much greater than the hole, Eq. (5) reduces to

$$f=f_{EX}(|\Phi_D(0)/\Phi_{EX}(0)|)^2\times\left(\left|\int\Phi_A(\mathbf{x})d\mathbf{x}\right|^2\Big/\Omega_{\rm mol}\right)\omega_{EX}/\omega_0\,. \tag{11}$$

Crudely speaking, these results show that the oscillator strength of a bound exciton is given by the oscillator strength per molecule of the free exciton, multiplied by the number of CdS molecules covered by the overlap of the electron and hole. For CdS, $f_{EX}=0.00256$.[14] The overlap can cover $\approx10^3$ CdS molecules, resulting in oscillator strengths of order unity and radiative lifetimes of order 1 nsec.

V. DISCUSSION

In this section, we will compare the experimental and theoretical lifetimes for the four radiative transitions in CdS that have been studied up to now. These transitions are the I_2 line, measured here and also measured in absorption by Thomas and Hopfield[6]; the I_1 line, measured here; donor-acceptor pair recombination giving rise to the green-edge emission, measured by Colbow[15]; and the Te isoelectronic trap, measured by

[12] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Co., New York, 1940), Sec. 148.

[13] D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 361. In Eqs. (1) and (3), we have neglected the local effective field correction. This correction should be small. In any case, our results will not change if this correction is the same for both the free and bound excitons.

[14] D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959).

[15] K. Colbow, Phys. Rev. **141**, 742 (1966).

TABLE I. Comparison of theoretical and experimental lifetimes for radiative transitions in CdS.

Transition	τ (expt) (nsec)	τ (theor) (nsec)
I_2	0.5 ±0.1 0.4 ±0.1[a]	0.56
I_1	1.03±0.1	1.85
Donor-Acceptor pairs ($R\to 0$)	2.5 ±1.0[b]	2.3
Te isoelectronic trap	300.0[c]	27.0

[a] Reference 6. [b] Reference 15. [c] Reference 16.

Cuthbert and Thomas.[16] The results are summarized in Table I.

A. Lifetime of I_1 and I_2 Lines

The I_1 and I_2 lines can decay nonradiatively via the Auger effect. As we mentioned earlier, an accurate estimate of the Auger rate requires an elaborate calculation which can only be carried out if an accurate knowledge of the band structure ≈ 2.5 eV above the conduction band and below the valence band exist. This is clearly beyond the scope of this paper. However, it would be surprising if the Auger lifetime were much faster than about 10 nsec in view of its measure value of 20 nsec in GaP and 80 nsec in Si.[3]

In contrast to the Auger lifetime, the radiative lifetime may be calculated quite directly for a direct band-gap semiconductor, if the bound states can be described by the effective-mass approximation. We have calculated the radiative lifetimes of the I_1 and I_2 lines in Sec. IV and Appendix A. This calculation is essentially the same as that carried out by RG, but more detailed than their calculation and takes into account the fact that there are two identical electrons (or holes) in a singlet state. We make the same assumption as RG, that the exciton can be thought of as an entity that is weakly bound to the donor or acceptor. Our simple formula for the radiative lifetime, given by Eqs. (3) and (A15), is exactly the same as obtained by RG. Using values of the band masses of the conduction band and upper most valence band measured by Hopfield and Thomas,[17] we found that the equivalent mass of the bound exciton was 1.62. This resulted in a theoretical lifetime of 0.56 nsec for the I_2 line and 1.85 nsec for the lifetime of the I_1 line. RG used the inaccurate estimate of 0.36 for the equivalent exciton mass and as a result would have predicted a much shorter radiative lifetime of about 0.044 nsec. A better numerical estimate was recently made by Hopfield.[18] It is difficult to know how accurate our calculation is. The calculation should be best when the binding energy of the exciton is small compared to the internal binding energy of the free exciton, which is 29.8 meV.[17] This condition is better satisfied for the I_2 line $E_B=8.3$ meV than for the I_1 line $E_B=18.3$ meV.

Our value for the total lifetime of the I_2 line of 0.5±0.1 nsec and Thomas and Hopfield's value for the radiative lifetime of 0.4±0.1 nsec, from absorption measurements, are in excellent agreement. This agreement leaves little room for a significant Auger effect. Our calculated value of 0.56 nsec for the radiative lifetime is also in excellent agreement with the experimental values.

Our experimental value for the I_1 lifetime of 1.03±0.1 nsec is in only fair agreement with our value of 1.85 nsec for the calculated radiative lifetime. This discrepancy could be due equally well to either inaccuracies in the calculated radiative lifetime or to an Auger lifetime of about 2.3 nsec for the I_1 line. The Auger rate may be greater for the I_1 line than the I_2 line, due to the greater localization of the holes for the complex giving rise to the I_1 line. This, together with the slower radiative rate for I_1, may explain why there is a small but significant Auger speedup for I_1, but not I_2.

B. Lifetimes of Donor-Acceptor Pairs

In CdS, the donor Bohr radius ($a_D\approx 25$ Å) is large compared to the acceptor Bohr radius (≈ 6 Å). In this case, the lifetime of a pair of separation R will be

$$\tau(R)=\tau_0 e^{+2R/a_D}. \tag{12}$$

Colbow used this expression to fit the time behavior of donor-acceptor pairs in CdS and concluded that τ_0, the extrapolated lifetime for close pairs, was 2.5±1 nsec. Our calculated value of τ_0, calculated in Appendix B, is 2.2 nsec, in remarkably good agreement with Colbow's number.[15]

C. Lifetime of Te Isoelectronic Trap

Cuthbert and Thomas[16] have measured the lifetime of the Te isoelectronic trap to be 300 nsec. This lifetime is two orders of magnitude larger than the measured value of τ_0 for donor-acceptor pairs. This is remarkable when one considers how similar the two transitions are. Both consist of a weakly bound electron, bound by Coulomb attraction and a moderately deep hole. The hole on the acceptor is bound by ≈ 160 meV, while the hole on Te is bound by ≈ 200 meV. In Appendix B, we calculate the lifetime of the Te isoelectronic trap and find it to be 27 nsec. This value is about one order of magnitude larger than our calculated value for τ_0, due primarily to the hole on Te being bound by a short-range potential and, thus, having a more compact wave function than the hole on the acceptor. We are at a loss to explain why the experimental lifetime of the exciton bound to Te is two orders of magnitude larger than τ_0, instead of one order of magnitude.

[16] J. D. Cuthbert and D. G. Thomas, J. Appl. Phys. **39**, 1573 (1968).
[17] J. J. Hopfield and D. G. Thomas, Phys. Rev. **122**, 35 (1961).
[18] J. J. Hopfield, Phys. Rev. **182**, 945 (1969). Hopfield estimated an oscillator strength corresponding to a radiative lifetime of 0.29 nsec by using an equivalent exciton mass of unity.

ACKNOWLEDGMENTS

We are indebted to A. M. Sergent, J. W. Shiever, and J. W. Hansen for their expert assistance in these experiments. We thank H. C. Montgomery for making electrical measurements on some of our samples and Professor G. C. Whitfield for helpful discussions.

APPENDIX A: CALCULATION OF LIFETIMES OF I_1 AND I_2 LINES

We will now calculate the I_1 and I_2 lifetimes, taking into account that these complexes have three particles, two of them identical and in a singlet spin state. The oscillator strengths of the I_1 and I_2 line transitions can be calculated from Eq. (2). We will make the effective-mass approximation and take the wave functions to be envelope functions multiplied by zone-center Bloch functions. To be specific, we will discuss the I_2 line transition. The final state will be that of a neutral donor in its ground state with envelope function $\Phi_D(\mathbf{r})$. For the initial state, we make essentially the same approximation as RG and regard the exciton as an entity bound to the donor. We take the envelope function of the bound exciton to be

$$\Phi_D(\mathbf{r}_1)\Phi_{EX}(\boldsymbol{\varrho}_{2v})F(\mathbf{R}_{2v}),$$

where Φ_{EX} describes the internal motion of the bound exciton, $\boldsymbol{\varrho}_{2v}=\mathbf{r}_2-\mathbf{r}_v$ is the separation of the electron and hole, and F is a wave function describing the binding of the exciton by a short-range force, $\mathbf{R}_{2v}=(m_e\mathbf{r}_2+m_v\mathbf{r}_v)/M$ is the center-of-mass coordinate of the electron and the hole (in the uppermost valence band) and $M=m_e+m_v$. We take the electron wave function to be symmetric in the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ and in a singlet (antisymmetric) spin state. The symmetric k-space envelope function of the bound state is then given by

$$\begin{aligned}&\psi'(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_v)\\&\quad=N[\varphi_D'(\mathbf{k}_1)\varphi_{EX}'((\mathbf{k}_v m_e+\mathbf{k}_2 m_v)/M)F'^*(\mathbf{k}_2-\mathbf{k}_v)\\&\quad+\varphi_D'(\mathbf{k}_2)\varphi_{EX}'((\mathbf{k}_v m_e+\mathbf{k}_1 m_v)/M)F'^*(\mathbf{k}_1-\mathbf{k}_v)],\end{aligned}\tag{A1}$$

where φ_D', φ_{EX}', and F' denote the Fourier transforms of φ_D, φ_{EX}, and F. The normalization constant $N\approx 1/\sqrt{2}$, if the overlap between envelope function and the envelope function with the electron coordinates exchanged is small. We will assume this is the case. The initial state wave function is given by

$$\begin{aligned}|\lambda_i\rangle=&\sum_{\substack{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_v\\ \sigma_1\sigma_2}}\psi'(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_v)\\&\times\chi_{\text{singlet}}(\sigma_1,\sigma_2)C_{ck_1\sigma_1}^{\dagger}C_{ck_2\sigma_2}^{\dagger}C_{vk_v\uparrow}|G\rangle.\end{aligned}\tag{A2}$$

The final state is given by

$$|\lambda_f\rangle=\sum_{\mathbf{k}_f}\varphi'(\mathbf{k}_f)C_{ck_f\downarrow}^{\dagger}|G\rangle,\tag{A3}$$

where $|G\rangle$ is the ground state of the crystal and $C_{n\mathbf{k}\sigma}^{\dagger}$ is the electron-creation operator. In the effective-mass approximation, the operator p_α of Eq. (2) is given by

$$p_\alpha=\sum_{nn'\mathbf{k}\sigma}\langle n'|p_\alpha|n\rangle C_{n'\mathbf{k}\sigma}^{\dagger}C_{n\mathbf{k}\sigma},\tag{A4}$$

where n and n' denote zone-center Block functions. Substituting Eqs. (A2)–(A4) into Eq. (2), we find

$$f=f_g(\omega_g/\omega_0)I,\tag{A5}$$

where f_g is the oscillator strength of the valence-band–to–conduction-band transition at the center of the zone and $\hbar\omega_g$ is the band-gap energy.

$$f_g=2|\langle v_x|p_x|c\rangle|^2/\hbar\omega_g m_0\tag{A6}$$

and

$$\begin{aligned}I=&\sqrt{2}N\sum_{\mathbf{k}_v}\varphi_{EX}'(\mathbf{k}_v)F'(0)^*\\&+\sqrt{2}N\sum_{\mathbf{k}_v\mathbf{k}_{fc}}\varphi_D'(\mathbf{k}_{fc})^*\varphi_D(k_v)\\&\times\varphi_{EX}\left(\frac{m_e}{M}\mathbf{k}_v+\frac{m_v}{M}\mathbf{k}_{fc}\right)F'(\mathbf{k}_{fc}-\mathbf{k}_v)^*.\end{aligned}\tag{A7}$$

If we neglect the second term compared to the first and take $N=1/\sqrt{2}$,

$$I=\sum_{\mathbf{k}_v}\varphi_{EX}'(\mathbf{k}_v)F'(0)^*=\varphi_{EX}(0)\int d^3xF(x)^*.\tag{A8}$$

The oscillator strength of the transition is then given by

$$f=(\omega_g/\omega_0)f_g|\varphi_{EX}(0)|^2\left|\int F(\mathbf{x})d\mathbf{x}\right|^2.\tag{A9}$$

$f_g|\varphi_{EX}(0)|^2$ may be evaluated from the measured value of f_{EX}, the free-exciton oscillator strength per CdS molecule, which may be shown easily by a calculation similar to the one we have carried out here and in Sec. IV to be

$$f_g|\Phi_{EX}(0)|^2=f_{EX}\omega_{EX}/\omega_g\Omega_{\text{mol}},\tag{A10}$$

where Ω_{mol} is the volume of one CdS molecule. Substituting (A10) into (A9) gives

$$\begin{aligned}f=&f_{EX}\omega_{EX}\left|\int F(\mathbf{x})d^3x\right|^2\Big/\omega_g\Omega_{\text{mol}}\\&\approx f_{EX}\left|\int F(\mathbf{x})d\mathbf{x}\right|^2\Big/\Omega_{\text{mol}}.\end{aligned}\tag{A11}$$

This is just the result of RG. Following RG, we take

$$F(\mathbf{R})=\exp(-R/\lambda)/(2\pi\lambda)^{1/2}R,\tag{A12}$$

which is the appropriate wave function for a particle of mass M bound by a short-range potential. The range of the wave function λ is given by

$$\lambda=(\hbar^2/2ME_B)^{1/2},\tag{A13}$$

where E_B is the binding energy of the exciton. RG pointed out that, for cases of an anisotropic valence band mass as in CdS, the appropriate value of M is

$$M=[(m_e+m_{v\perp})^2(m_e+m_{v\parallel})]^{1/3}. \quad \text{(A14)}$$

Evaluating the integral in (A11) gives

$$f=f_{EX}8\pi\lambda^3/\Omega_{\mathrm{mol}}. \quad \text{(A15)}$$

For CdS, $m_e=0.2m_0$, $m_{v\perp}=0.7m_0$, $m_{v\parallel}\approx 5m_0$,[13] $f_{ex}=2.56\times 10^{-3}$,[15] $\Omega_{\mathrm{mol}}=49.4$ Å^3, $E_{I_1}=18.3$ meV, and $E_{I_2}=8.3$ meV. We find $M\approx 1.62$, $\lambda_{I_1}=11.3$ Å, and $\lambda_{I_2}=16.8$ Å. Using (A15),

$$f_{I_2}=2410f_{EX}=6.2,$$
$$f_{I_1}=734f_{EX}=1.9.$$

RG used an incorrect exciton mass of 0.33, which caused them to overestimate f_{EX} by an order of magnitude. Evaluating Eq. (3) and using $n=3.05$, we find $\tau_{I_2}=0.56$ nsec and $\tau_{I_1}=1.85$ nsec.

APPENDIX B: CALCULATION OF RADIATIVE LIFETIMES OF Te ISOELECTRONIC TRAP AND DONOR-ACCEPTOR PAIRS

Using the methods of Sec. IV, we can attempt to calculate to the lifetimes of donor-acceptor pairs and the lifetime of the Te isoelectronic trap, which have previously been measured in CdS.[15,16] In both of these cases, we are dealing with a single electron and hole. The hole is tightly bound compared to the electron, which may be thought of as having a donor wave function. The oscillator strengths for these transitions may be calculated from Eq. (11).

For donor-acceptor pairs separated by R,

$$\Phi_A(\mathbf{x})=(\pi a_A{}^3)^{-1/2}e^{-x/a_A}, \quad \text{(B1)}$$

$$\Phi_D(\mathbf{x})=(\pi a_D{}^3)^{-1/2}e^{-|\mathbf{x}-\mathbf{R}|/a_D}, \quad \text{(B2)}$$

where $a_D\gg a_A$. The oscillator strength is

$$f_{DA}=(\omega_{EX}/\omega_0)e^{-2R/a_D}(32\pi a_A{}^3/\Omega_{\mathrm{mol}})\times|\Phi_D(0)/\Phi_{EX}(0)|^2f_{EX}. \quad \text{(B3)}$$

An extra factor of $\frac{1}{2}$ has been included in (B3) because $\frac{1}{2}$ of the transitions are forbidden. It can be shown,[19,20] using the strong-coupling polaron theory, that for states bound by Coulomb forces with binding energies large compared to an LO phonon, the effective dielectric constant is

$$\epsilon_{\mathrm{eff}}=[(5/16)(1/\epsilon_\infty)+(11/16)(1/\epsilon_0)]^{-1}\approx 7.3 \quad \text{(B4)}$$

in CdS. Using the hydrogenic acceptor formulas

$$E_A=E_Hm_A/\epsilon_{\mathrm{eff}}{}^2, \quad a_A=a_H\epsilon_{\mathrm{eff}}/m_A, \quad \text{(B5)}$$

and assuming the acceptor binding energy to be 160 meV, we find $m_A=0.63m_0$ and $a_A=6.15$ Å. The factor $|\Phi_D(0)/\Phi_{EX}(0)|^2$ is given by

$$|\Phi_D(0)/\Phi_{EX}(0)|^2=(a_{EX}/a_D)^3=(m_e/\mu)^3=(0.209/0.172)^3=1.79.$$

Evaluating (B4), we find

$$f_{DA}=e^{-2R/a_D}(2.3). \quad \text{(B6)}$$

Substituting this value of the oscillator strength into Eq. (3), the extrapolated lifetime for close pairs ($R\rightarrow 0$) is 2.2 nsec.

For the Te isoelectronic trap, we assume the hole to be bound by $E=200$ meV,[16] and again use the value $m_H=0.63m_0$ for the hole mass. The hole is bound by a short-range potential and we take its envelope function to be

$$\Phi_A=(2\pi\lambda)^{-1/2}e^{-x/\lambda}, \quad \text{(B7)}$$

where

$$\lambda=(\hbar^2/2m_HE)^{1/2}=5.5 \text{ Å}. \quad \text{(B8)}$$

This gives

$$f_{\mathrm{Te}}=(\omega_{ex}/\omega)(4\pi\lambda^3/\Omega_{\mathrm{mol}})\times|\Phi_D(0)/\Phi_{EX}(0)|^2f_{EX}=0.24, \quad \text{(B9)}$$

$$\tau_{\mathrm{Te}}=27 \text{ nsec}. \quad \text{(B10)}$$

[19] R. J. Kubo, Phys. Soc. Japan **3**, 254 (1948).
[20] J. H. Simpson, Proc. Roy. Soc. (London) **A197**, 269 (1949).