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Excitons and the Absorption Edge of Cadmium Sulfide

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Measurements of the absorption coefficient between 10 and 300 cm^{-1} have been made with crystals of CdS in polarized light between 20 and 300°K, at wavelengths near 5000 A. Analysis of the results at various temperatures near 70°K shows that the absorption is in agreement with that calculated for a process involving the simultaneous creation of an exciton and the absorption of a phonon, both particles having a small wave vector. This agreement is strong evidence that the conduction band minimum and the valence band maximum in CdS both occur at the center of the Brillouin zone.

INTRODUCTION

LITTLE is definitely known about the band structure of CdS. In particular it is not clear whether the conduction band has a single minimum at the center of the Brillouin zone (hereafter denoted by $\mathbf{k}=0$) or whether there are several equivalent minima not at $\mathbf{k}=0$. It is generally assumed that the valence band, in common with semiconductors of known band structure, has its maximum at $\mathbf{k}=0$. [A study of excitons in CdS[1] has shown that the optical transitions, which involve the valence band maximum, either occur at $\mathbf{k}=0$ (the point Γ) or along the line Γ-A to the center of the hexagonal face of the Brillouin zone. If the latter is the case symmetry requires that all the valleys have the crystalline c axis as an axis of principal symmetry. For the remainder of this paper it will be assumed that the phenomena occur at $\mathbf{k}=0$ which is the most likely alternative.] Hence if the conduction band minimum falls at $\mathbf{k}=0$ the onset of intrinsic optical absorption across the forbidden gap should correspond to direct (vertical) transitions, whereas if the minimum is not at $\mathbf{k}=0$ the lowest energy absorption should correspond to indirect (nonvertical) transitions. Recent measurements of the absorption edge of single crystals of CdS in polarized light at low temperatures include those of Dutton[2] and those of Böer and Gutjahr.[3] Near 90°K Dutton found that for values of α greater than about 100 cm^{-1}, α, the absorption coefficient, rose exponentially with photon energy according to "Urbach's rule:"

$$\alpha \propto e^{h\nu/kT}.$$

No very definite conclusions could be drawn from this part of the data although Dutton pointed out that the reflection spectrum indicated strong absorption lines close to the rapidly rising absorption edge. Böer and Gutjahr measured the absorption for values of α between about 5 and 700 cm^{-1} at 300°K and at 90°K. They reported breaks in the absorption curves and they interpreted these by supposing that at energies greater than that of the break indirect transitions occurred with phonon emission, and at energies less than the break by phonon absorption. However, the phonon energy deduced from the results is 0.02 ev, and this does not agree with the longitudinal optical phonon energy of 0.038 ev as calculated by Collins[4] from restrahl data, and it is expected, at least at room temperature and above, that the longitudinal optical phonons will be most effective in the scattering process. In addition, it will be shown in the following that the model suggested by Böer and Gutjahr is not in accord with more detailed experimental results. The many valley model (in which the conduction band minima are not along the line Γ-A) has also been suggested to account for an observed longitudinal magnetoresistance effect.[5] It has not been possible, however, to give a detailed explanation of the magnetoresistive results in terms of this model.

Recently Thomas and Hopfield[1] have analyzed the reflection spectrum of CdS and have shown that excitons formed in direct transitions are responsible for very powerful absorption; the lowest energy excitons have ionization energies of about 0.028 ev. The exciton spectrum showed that the valence band consisted of three 2-fold degenerate bands, the highest having the symmetry Γ_9 and the remaining two having the symmetry Γ_7. Allowed exciton transitions occur from the Γ_9 band for light polarized with its E vector polarized perpendicularly to the hexagonal c axis (hereafter denoted $E\perp c$), and from the Γ_7 band for light polarized with $E\perp c$ and $E\|c$. This splitting of the valence band is the essential cause of the dichroism of CdS. Since the exciton transitions are direct and since the valence band maximum probably lies at $\mathbf{k}=0$, it is likely that these excitons involve electrons from a minimum in the conduction band also at $\mathbf{k}=0$. Consequently if the true conduction band minima are multiple and do not fall at $\mathbf{k}=0$ then these should give rise to absorption at energies less than the exciton energies. It is the purpose of this paper to show that the absorption data down to low α values can be explained in terms of direct excitons and phonons, and that no evidence can be found for nonvertical transitions at the threshold of absorption.

EXPERIMENTAL

Transmission measurements were made on single crystals of CdS in polarized light using the sample in-

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[1] D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959).
[2] D. Dutton, Phys. Rev. **112**, 785 (1958).
[3] K. W. Böer and H. Gutjahr, Z. Physik **155**, 328 (1959).
[4] R. J. Collins, J. Appl. Phys. **30**, 1135 (1959).
[5] T. Masumi, J. Phys. Soc. Japan **14**, 47 (1959).

sample out technique. For this purpose two identical slots were cut in a molybdenum plate, one of which was covered by the crystal. The plate was fixed in a Dewar vessel which could be shifted between two stops so that one or the other of the slots was at a focus of the exit slit of a monochromator. The monochromator was a Perkin-Elmer double pass instrument equipped with an NaCl prism; a slit width of 0.015 mm was used giving a spectral slit width of about 0.0015 ev in the wavelength region of interest. This value and the instrumental wavelength calibration were obtained using a helium spectral lamp. The photon energies quoted are accurate to about ±0.0015 ev. The analyzer was a Glan-Thomson prism used in front of the photomultiplier detector. Care was taken that mirrors between the crystal and the analyzer did not alter the polarization properties of the light. The Dewar vessel used for low-temperature measurements was made of metal. The plate holding the crystal was screwed onto a copper block which was in contact with the refrigerant. The refrigerants used were liquid oxygen, liquid nitrogen, pumped liquid and solid nitrogen, and liquid hydrogen. Surrounding this structure was a separate liquid nitrogen shield which included two plane quartz windows which were in thermal contact with the cold shield. Finally, there were two quartz windows at room temperature. Thus, although the crystal was mounted in the vacuum space, all its surroundings were cold and heat leaks from these surroundings were minimized. The crystal was held to its plate by gallium and the temperature of the copper block to which the plate was fastened was measured with a thermocouple. The temperature of the crystal was therefore taken to be that of the copper block, and at least for temperatures near 77°K it is felt that little error was introduced by this procedure.

It is known that polishing crystals can strongly affect the absorption properties in the exciton region because of surface damage spreading out the very strong exciton absorption.[6] Consequently, the crystals were used as grown. Because of surface imperfections the measured transmission of the crystals at wavelengths longer than about 5100 A (2.44 ev) (at low temperatures) fell somewhat short of the values calculated from the detailed refractive index data available.[7] However in this region the transmission is observed to be constant, and all the transmission results were normalized to the theoretical value in this region. The α values were determined from the transmission in the usual way taking into account the variation of refractive index for each mode of polarization with both temperature and wavelength. These data are known[7] at 300° and 90°K, and for other temperatures the curves were shifted by amounts corresponding to the shift of the exciton positions (see the following). Although these corrections were made they did not materially affect the absorption curves in the region of interest.

RESULTS

Most of the results were obtained with one crystal 150 μ in thickness. However at room temperature there was consistent overlap with data from another thicker crystal as shown in Fig. 1 in which, for convenience, the square root of the absorption coefficient is plotted against photon energy. In addition Fig. 1 shows that there is good agreement between our results and those of Böer and Gutjahr. Our data did not extend to sufficiently high α values for there to be positive identification of the break described by Böer and Gutjahr. At low temperatures there was similar agreement between the two sets of data. Consequently, it is thought, at least for α values in excess of about 10 cm^{-1}, that the results represent intrinsic properties of CdS and not impurity effects. Böer and Gutjahr arrived at a similar conclusion. Below $\alpha = 10$ cm^{-1} our data are not very reliable and further work with thicker crystals is planned to investigate this region.

In Figs. 2 and 3 the absorption data at low temperatures are presented for the two modes of polarization of the light. Also indicated in these figures are the positions of the lowest energy excitons active in the polarization direction being considered. (Thomas and Hopfield[1] have

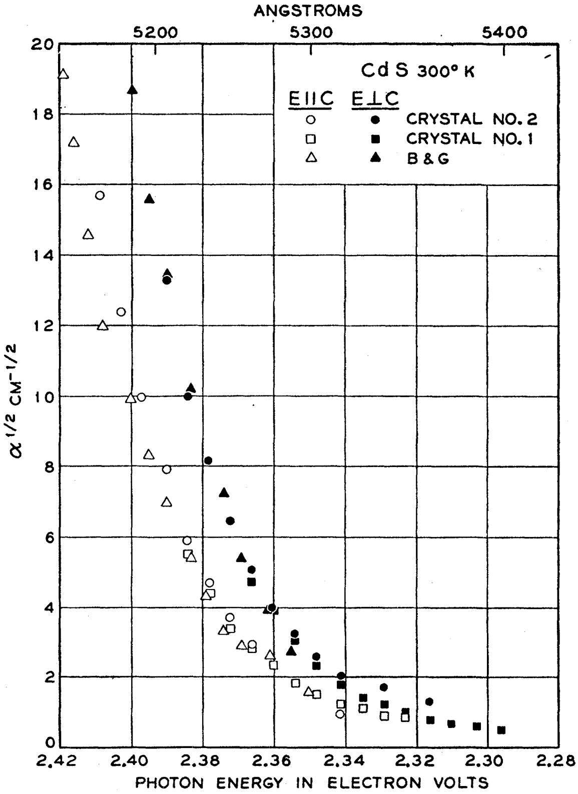

FIG. 1. The absorption edge of CdS at 300°K. There is quite good agreement between different results. The data of Böer and Gutjahr were obtained from their drawings.

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[6] D. G. Thomas, J. Phys. Chem. Solids (to be published).

[7] H. Gobrecht and A. Bartschat, Z. Physik 156, 131 (1959).

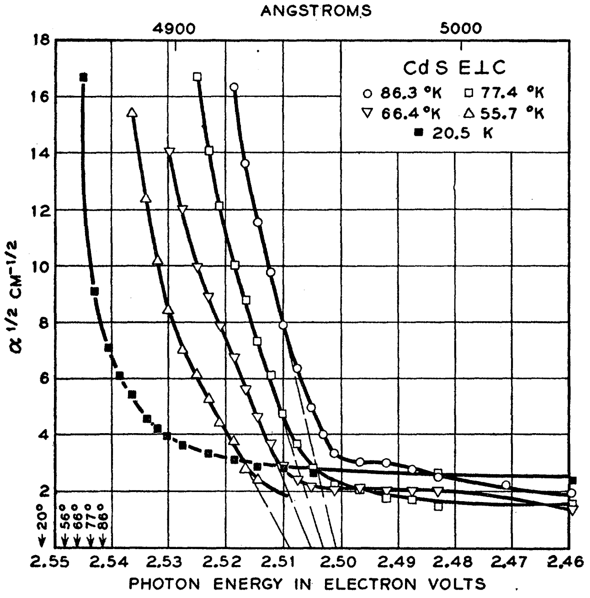

FIG. 2. The absorption edge of CdS for light polarized with $E \perp c$ at various low temperatures. The corresponding exciton positions are marked by arrows.

termed the lowest energy exciton for $E \perp c$ exciton A, and for $E \| c$ exciton B.) The positions were determined from the reflection spectrum of CdS determined at 4.2°, 20.5°, 77.4°, and 90°K and drawing a smooth curve through these points. To the energy of the appropriate reflection peak is added 0.001 ev to give the resonant energy of the exciton.[1] The positions quoted have an absolute accuracy of about ±0.0015 ev.

For light polarized with $E \perp c$ between 56° and 86°K, it can be seen that the curves have an approximately linear section. As the temperature falls, this linear region becomes less marked and at 20.5°K it has vanished. If the linear sections are extended back their points of intersection with the $\alpha = 0$ axis is in all cases 0.040 ± 0.001 ev less than the corresponding exciton position. Within experimental error this value equals the longitudinal optical phonon energy of 0.038 ev. This result suggests that apart from a weak residual absorption, optical transitions initially occur by a process which involves the formation of an exciton and the simultaneous absorption of a phonon. As is expected as the temperature is lowered, the process becomes less important since the phonon concentration decreases. This observation invalidates the suggestion of Böer and Gutjahr[3] that the steep section of the curve occurs with phonon emission since this process would vary as $(1 - e^{-\theta/T})^{-1}$, where θ is the equivalent phonon temperature, and so at these temperatures should be practically independent of temperature. As the photon energy approaches that of the exciton it may be expected that lower energy phonons can participate in the absorption, and in addition within about 0.01 ev of the exciton various "impurity exciton" transitions may occur.[1] Consequently, no simple behavior is expected in this region.

For light polarized with $E \| c$ (Fig. 3) the curves are not so revealing; there is no definite linear portion of the curves and strong absorption commences at photon energies only slightly higher than for $E \perp c$ although the lowest energy exciton for $E \| c$ lies 0.016 ev above that for $E \perp c$.

DISCUSSION

The Theoretical Form of the Absorption Edge

The energy as a function of wave vector for low-lying exciton states is shown in Fig. 4. The ground state of the crystal is represented by a point; the exciton states by bands. Observed direct excitons have energies given by the exciton band energies at $\mathbf{k} = 0$. Below the lowest lying exciton state, optical absorption can occur due to processes of the type

$$\text{photon} + \text{phonon} \rightarrow \underset{\text{(intermediate state)}}{\text{exciton} + \text{phonon}} \rightarrow \text{exciton}'.$$

The absorption of the phonon provides the additional energy necessary to conserve energy.

The calculation of the absorption edge due to such a "direct" process with phonon cooperation is very similar to the calculation by Dumke[8] of the phonon-cooperative absorption in InSb, except for the fact that exciton states now play an essential role. The calculation can be made tractable by noting at the start the limitations and approximations which are involved. In CdS, there are *four* different nonzero energies of $\mathbf{k} = 0$ phonons. The highest of these, the longitudinal optical phonon, has an energy of 0.038 ev, two of the other three characteristic energies are not known. It is therefore profitless to try to compute the form of the absorption more than perhaps 0.020 ev above the one-phonon threshold.

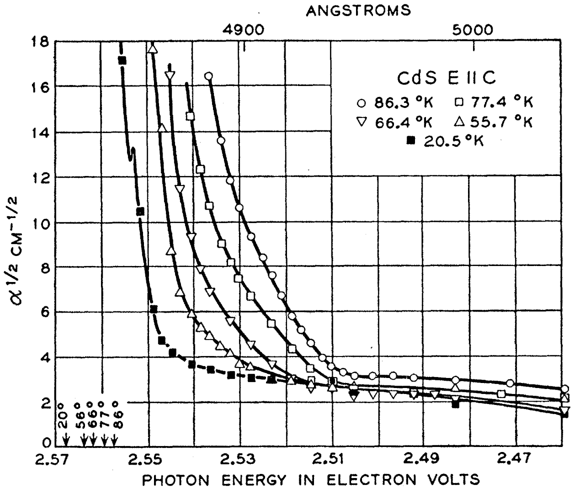

FIG. 3. The same as Fig. 2 except for $E \| c$.

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[8] W. P. Dumke, Phys. Rev. **108**, 1419 (1957).

The only important intermediate states in the transition have the form

$$|\text{ exciton (no photon)}+\text{phonon}\rangle.$$

The exciton binding energy in CdS is 0.028 ev. Exciton line oscillator strengths are proportional to $1/n^3$ for allowed excitons in the hydrogenic approximation (where n is the principle quantum number). Higher exciton states than $n=1$ can be neglected as intermediate states because of the fall off in oscillator strength. The continuum states can be effectively ignored as intermediate states because of the relatively large intermediate state energy denominator (which enters squared) and the relative difficulty of scattering by phonons into the bound state. Thus only the lowest lying exciton state active in a given polarization is an important intermediate state.

Case I. $E\perp c$

For this geometry, the only important intermediate state is the $n=1$ state of excitons formed from the upper valence band. The matrix element for longitudinal optical mode scattering of the exciton (without change of internal state) is proportional to $|\mathbf{k}|$ for small $\mathbf{k}$. The optical matrix element is a constant. The intermediate state energy denominator is $E-E_0$ (E_0 is the energy of the lowest exciton band at $\mathbf{k}=0$, and E is the photon energy). For parabolic electron and hole bands, one finds (from second-order perturbation theory)

$$\alpha=\alpha_0\left(\frac{E+\hbar\omega-E_0}{E_0}\right)^{\frac{3}{2}}\left(\frac{E_0}{E-E_0}\right)^2\frac{1}{1+e^{\hbar\omega/KT}}. \quad (1)$$

In (1), $\hbar\omega$ is the energy of the $\mathbf{k}=0$ longitudinal optical phonon, (it is also assumed that $\hbar\omega$ is independent of $\mathbf{k}$, which will be true for the small $\mathbf{k}$ values considered) and α_0 is a constant independent of E and T. The theoretical expression for α_0 is given in the Appendix.

Case II. $E\|c$

For this geometry, the only important intermediate state is the $n=1$ state of excitons formed from the second valence band, where an exciton is strongly active in this mode of polarization. Two kinds of final states are possible. The simplest final states are states corresponding to scattering this $n=1$ intermediate state exciton within its own band. This process leads to an absorption coefficient of the same form as case I, with the parameters appropriate to the second valence band substituted into 1. The threshold for this process is 0.016 ev higher than that for $E\perp c$ due to the 0.016-ev valence band splitting.

A second set of final states in which the intermediate state exciton is scattered into an $n=1$ exciton of the top valence band is also possible as indicated in Fig. 4(b). This process cannot be computed from ordinary polar mode scattering formulas for it represents interband scattering. The dominant part of the polar scattering interaction (the electrostatic scattering) is much weakened for this interband scattering. It is therefore to be expected that the absorption edge for $E\|c$ should look rather similar to that for $E\perp c$ displaced 0.016 ev to higher energies, except for the existence of a tail extending down to the threshold for $E\perp c$ absorption due to interband scattering.

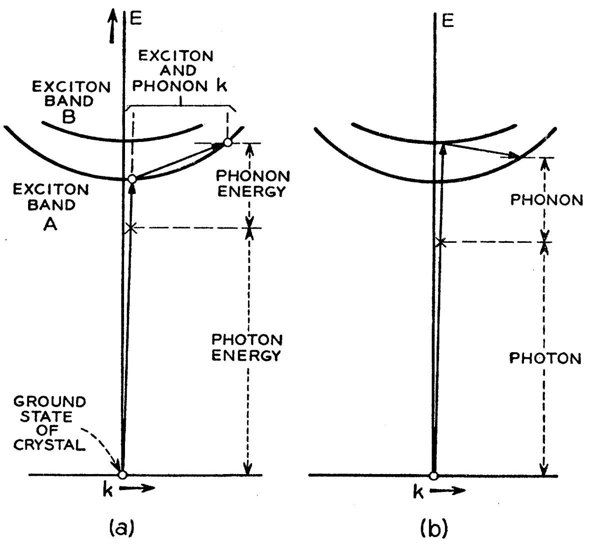

FIG. 4. (a) $E(k)$ curves for low-lying exciton states. The electronic part of the process, photon+phonon → exciton+phonon → exciton for light polarized with $E\perp c$ is indicated by the arrows. (The first stage is not represented as a vertical transition since a photon has a small but finite momentum. This point is not essential to the discussion presented here.) (b) The same as Fig. 4(a) except that an interband scattering process from exciton band B to exciton band A is illustrated.

Comparison with Experiment

The comparison of theory and experiment will be made only for $E\perp c$, where no interband phonon processes occur. The results are shown in Fig. 5. In this figure the points represent the experimental points from which have been subtracted a residual absorption taken to be equal to the absorption at 20.5°K at the corresponding photon energy. The lines represent the behavior predicted by (1) putting $\alpha_0=1.52\times10^3$ cm^{-1}, using the E_0 values obtained from the reflection spectra and a value of $\hbar\omega=0.038_5$ ev. Although the agreement between theory and experiment is not perfect, it is thought that possible errors in the assumed background absorption and the temperature of the crystal could account for the discrepancies. Certainly the variation with temperature is in general agreement with theory, and in the appendix a theoretical estimate of $\alpha_0=3.2\times10^3$ cm^{-1} is obtained which is in satisfactory agreement with the experimental value.

At room temperature analogous processes are expected. However the reflection spectra show no exciton

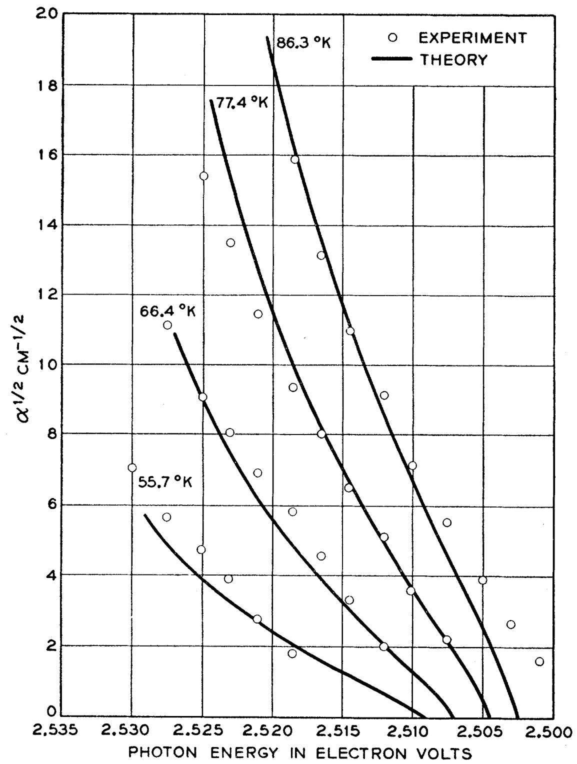

FIG. 5. Comparison of theory and experiment at various temperatures. The solid lines represent Eq. (1) using $\hbar\omega = 0.038_5$ ev, E_0 as obtained from reflection experiments and $\alpha_0 = 1.52\times 10^3$ cm^{-1}. The points represent the data of Fig. 2 after a background subtraction has been made.

peak, indicating considerable thermal broadening, and multiphonon processes may also make appreciable contributions to the absorption. In view of these complications no attempt has been made to interpret the results at this temperature.

It might be possible to interpret the observed absorption on the basis of conduction band valleys not at $\mathbf{k}=0$ (nor on the line Γ-A), but this would require that the "indirect" excitons involving these valleys should be at or above the energy level of the "direct" excitons. It is most unlikely that the two types of excitons should be at the same energy, and as the ionization energy of the direct excitons is only about 0.028 ev it is clear that the indirect exciton cannot be much above the direct exciton and still have the indirect minimum in the conduction band an absolute minimum.

Although detailed experiments with crystals of suitable thickness have not been carried out it does appear that there is a residual absorption at energies lower than that of the exciton-phonon process just described, and that this absorption does not vary rapidly with temperature in the range reported here. Because of the weak temperature dependence two phonon processes are probably not involved. The wavelength dependence of the effect indicates that it is not caused by indirect band to band transitions with phonon emission. It may be that local strains in the crystal decrease the energy gap sufficiently to cause absorption in this region There is also the possibility of direct transitions from ionized or compensated acceptors to the conduction band or from the valence band to ionized donors. Such transitions have not been described for silicon or germanium presumably because they are masked by indirect transitions.

CONCLUSIONS

It has been shown that all but the very weakest absorption displayed by CdS can be explained in terms of exciton transitions at $\mathbf{k}=0$ with the cooperation of phonons. This is strong evidence that the conduction band has one minimum located at $\mathbf{k}=0$. However, if there are other valleys in the conduction band which play a role in electronic conduction, then their energies must be within a few hundredths of an ev of the $\mathbf{k}=0$ minimum.

ACKNOWLEDGMENTS

We wish to thank Dr. Y. T. Sihvonen of the G. M. Research Laboratories, Detroit, Michigan, for the CdS crystals used in this work.

APPENDIX

The constant α_0 can be calculated for spherical bands and ordinary polar mode scattering. One obtains

$$\alpha_0 = \left(\frac{4\pi\beta}{\epsilon^{\frac{1}{2}}}\right)\left(\frac{\omega}{16c}\right)\left(\frac{1}{{n_0}^2}-\frac{1}{\epsilon'}\right) \times\left(\frac{2M}{\hbar^2}\right)^{\frac{5}{2}}\left(\frac{m_e-m_n}{m_e+m_n}\right)^2 {a_0}^4 {E_0}^{\frac{3}{2}} e^2.$$

The definitions of the symbols and values appropriate to CdS (as determined from the exciton studies of Thomas and Hopfield and the work of Collins on the restrahl of CdS) are given in the following: ω = angular frequency of the $\mathbf{k}=0$ longitudinal optical phonon = 305 cm^{-1}, c = velocity of light, ${n_0}^2$ = "high-frequency dielectric constant" = 5.8, ϵ' = low-frequency dielectric constant = 9.3, m_e = electron mass $\approx$ 0.6 m, m_n = hole mass $\approx 0.25\ m$, M = density of states mass for excitons $= m_e + m_n$, a_0 = Bohr radius for $n=1$ excitons = 28 A, E_0 = energy of the intermediate state exciton $\approx$ 2.55 ev, e = electronic charge, ϵ = contribution of all sources except the exciton under study to the energy dependent dielectric constant at $E = E_0 (\epsilon \approx 7)$, and $4\pi\beta$ = contribution of the exciton under study to the high frequency dielectric constant ${n_0}^2$. $4\pi\beta = 6.8\times 10^{-3}$ for the lowest energy exciton in CdS observed with light polarized perpendicular to the hexagonal axis. Combining these parameters, we find a theoretical value of 3.2×10^3 cm^{-1} for α_0. It is interesting that this quantity is large enough to result in appreciable absorption even at temperatures at which the fractional occupancy of phonon states is very small.