

FREE TO BOUND RECOMBINATION
AND SCREENING EFFECTS IN Cds

by

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Free-to-Bound Recombination
and Screening Effects in CDS

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Abstract

The main features of the luminescence spectrum of CdS consist of a number of sharp lines from 2.43 ev to the band edge at 2.58 ev and a number of broad bands below 2.43 ev. The highest energy broad band (HEB) is due to a free electron recombining with a hole bound at a shallow acceptor (free-to-bound). The dependence of the peak energy of the HEB on temperature and excitation intensity is investigated in the interval 4.2 - 80°K. Increasing the excitation intensity results in a shift to higher energy. This is interpreted in terms of free carrier screening which reduces the binding energy of the acceptor. An energy shift due to the recombination of hot electrons is also considered. An often neglected donor-acceptor interaction term is discussed and found to be significant. The acceptor binding energy was calculated as 167.5 mev. Experimental observations suggest that screening of excitons due to free carriers is ineffective.

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1. THESIS INTRODUCTION

The dependence on temperature and excitation intensity of excitons and the free-to-bound recombination in cadmium sulphide is investigated. Free carriers screen the coulomb interaction of bound states and reduces their binding energies. Luminescence involving bound states such as the acceptor in the free-to-bound recombination is thus expected to show effects caused by screening as the free carrier concentration is increased. The binding energy of a free exciton is expected to be especially sensitive to screening due to the relatively large ($\sim 29 \text{ \AA}$) electron-hole separation. This thesis reports experimental observations on the exciton and the free-to-bound recombination in the interval 4.2° - 80° K. A simple screening model based on the Debye potential is discussed in some detail. Hot electron recombination and donor-acceptor interaction effects are considered. The temperature dependence of the band gap is obtained and a possible band gap reduction due to a high density of free carriers is discussed in connection with screening of excitons. A brief review of the photoluminescence of single crystal CdS is given to provide a background for the present work.

2. LUMINESCENCE IN CdS

2.1 Introduction

The luminescence of CdS and other II-VI compounds has been extensively studied. Review articles by Reynolds, Litton and Collins (1965) and Shionoya (1970), a book edited by Aven and Prener (1967), and a book by Ray (1969) are excellent sources of information on the optical processes of II-VI compounds.

The main features of the luminescence spectrum of CdS consist of a number of sharp lines from 2.43 eV ($\approx 5100 \text{ \AA}$) to the band edge at 2.58 eV ($\approx 4800 \text{ \AA}$) and a number of broad bands below 2.43 eV. Figure 1 shows a typical photo-luminescence spectrum from an ultra high pure (UHP) crystal of CdS at approximately 5°K.

2.2 The Sharp Emission Lines

The sharp emission lines are attributed to the annihilation of excitons, both free excitons and excitons bound to various impurities. The most extensive studies of excitons in CdS were done by Thomas and Hopfield (1959, 1960, 1961), Hopfield (1960), and Wheeler and Dimmock (1962). A detailed discussion of excitons can be found in Solid State Physics, Supplement 5 (Knox, 1962) and in a book by Dexter and Knox (1965).

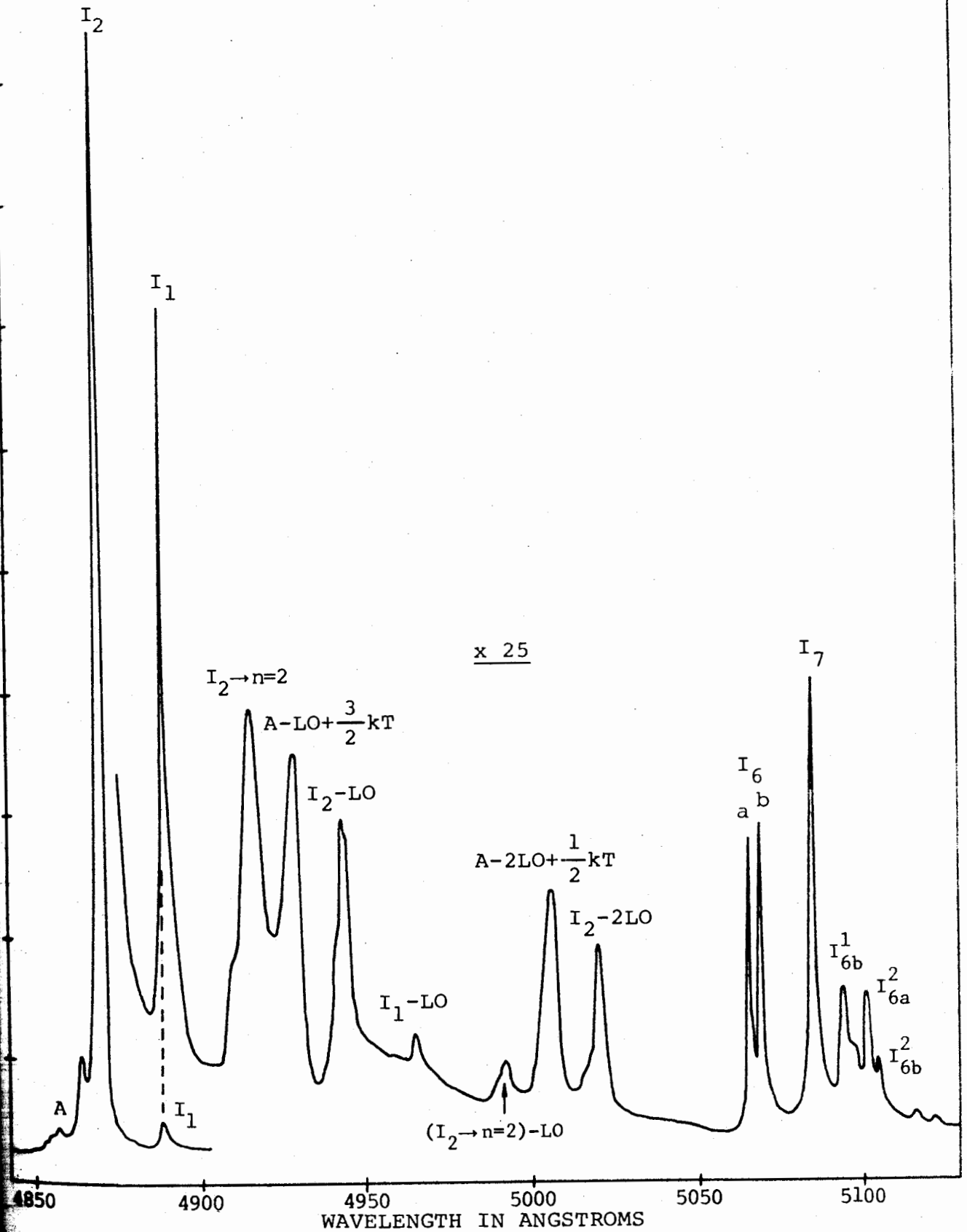


Figure 1 Exciton emission of CdS at 5°K. Line positions and binding energies are listed in Table I.

At liquid helium temperature the main exciton emission lines are the so-called I_1 and I_2 lines. The I_1 line arises from the decay of an exciton bound to a neutral acceptor and I_2 is due to the decay of an exciton bound to a neutral donor. The emission from the annihilation of an exciton bound to an ionized donor can also be observed. Using H_2^+ as a model, Hopfield (1964) calculated that an exciton cannot be bound to an ionized acceptor due to the large effective hole mass to effective electron mass ratio in CdS ($m_h^*/m_e^* \approx 4$). Indeed no such line has been observed.

At liquid helium temperature, the emission lines due to intrinsic excitons (the so-called A and B excitons) are generally much weaker than those due to bound excitons. However, with increasing temperature, bound excitons are dissociated from the impurities, and consequently the emission lines due intrinsic excitons become prominent.

Several sharp lines appear at energies of one or two longitudinal optical (LO) phonon energies below the zero-phonon lines. These are called LO phonon replicas.

Line positions, binding energies and chemical impurities of some of the luminescent excitons are listed in Table 1.

2.3 Broad Band Luminescence

Most of the II-VI compounds show two broad bands (the so-called edge emission) at low temperatures near 5135 Å and

TABLE I

Excitons in CdS

Line	Position λ (Å)	E (ev) *	Impurity	Binding Energy (mev)	Reference	
A	+ -	4854.8	2.55306	intrinsic	29.8	1,2
B	+ -	4826.1	2.56824	intrinsic	29.5	2
I ₁	⊕ + - +	4888.2	2.53562	Na (Li)	17.4	3
I ₂	⊕ - - +	4869.2	2.54548	Cl (F, In, Ga, Br, I)	7.58	1,4,5,7
I ₃	⊕ - +	4866.6	2.54686	Cl (F, In, Ga, Br, I)	6.20	1
I _{6a}	?	5065.5	2.4454	?	?	6,8
I _{6b}	?	5069.2	2.4451	?	?	6,8
I ₇	?	5084.8	2.43758	?	?	6,8

* Evaluated using $E\lambda = 1.23946 \times 10^4 \text{ \AA ev}$

** Exact binding energy of bound excitons depends on chemical impurity to which exciton is bound.

TABLE I (cont'd)

Symbols employed for aggregates of charges:

$\oplus -$	Neutral donor
$\oplus +$	Neutral acceptor
$- +$	Exciton
$\oplus - - +$	Exciton bound to neutral donor
$\oplus + - +$	Exciton bound to neutral acceptor
$\oplus - +$	Exciton bound to ionized donor

References:

- 1 Nassau, Henry and Shiever (1970).
- 2 Hopfield and Thomas (1961).
- 3 Henry, Nassau and Shiever (1970).
- 4 Thomas, Dingle and Cuthbert (1967).
- 5 Thomas and Hopfield (1962).
- 6 Reynolds and Litton (1963).
- 7 Malm and Haering (1971).
- 8 Smeaton and Haering (to be published).

5180 Å, which are repeated at longer wavelengths through the simultaneous emission of one or more longitudinal optical phonons. A typical spectrum of this edge luminescence is shown in Figure 2 for a high purity (HP) crystal of CdS at approximately 27°K. At temperatures less than approximately 20°K, most crystals of CdS show only the low energy band (LEB) near 5180 Å. The LEB arises from the recombination of an electron trapped at a donor with a hole trapped at an acceptor (Thomas, Hopfield and Colbow, 1964; Colbow, 1966). The emission energy from a donor-acceptor pair separated a distance r is given by

$$E(r) = E_G - (E_D + E_A) + \frac{e^2}{\kappa r} - nE_p \quad 2.301$$

where E_G is the band gap energy, E_D and E_A the donor and acceptor ionization energies, respectively, and κ is the static dielectric constant. The term nE_p represents the simultaneous emission of $n = 0, 1, 2, \dots$ phonons of energy $E_p \approx 38$ meV in CdS. The transition probability between the bound electron and the bound hole is proportional to the square of the overlap of the wave functions (Colbow, 1965)

$$W(r) = W_0 e^{-2r/a_0} \quad 2.302$$

where W_0 is a constant and a_0 is the Bohr radius of the shallower state (the donor in CdS). Therefore, the emission

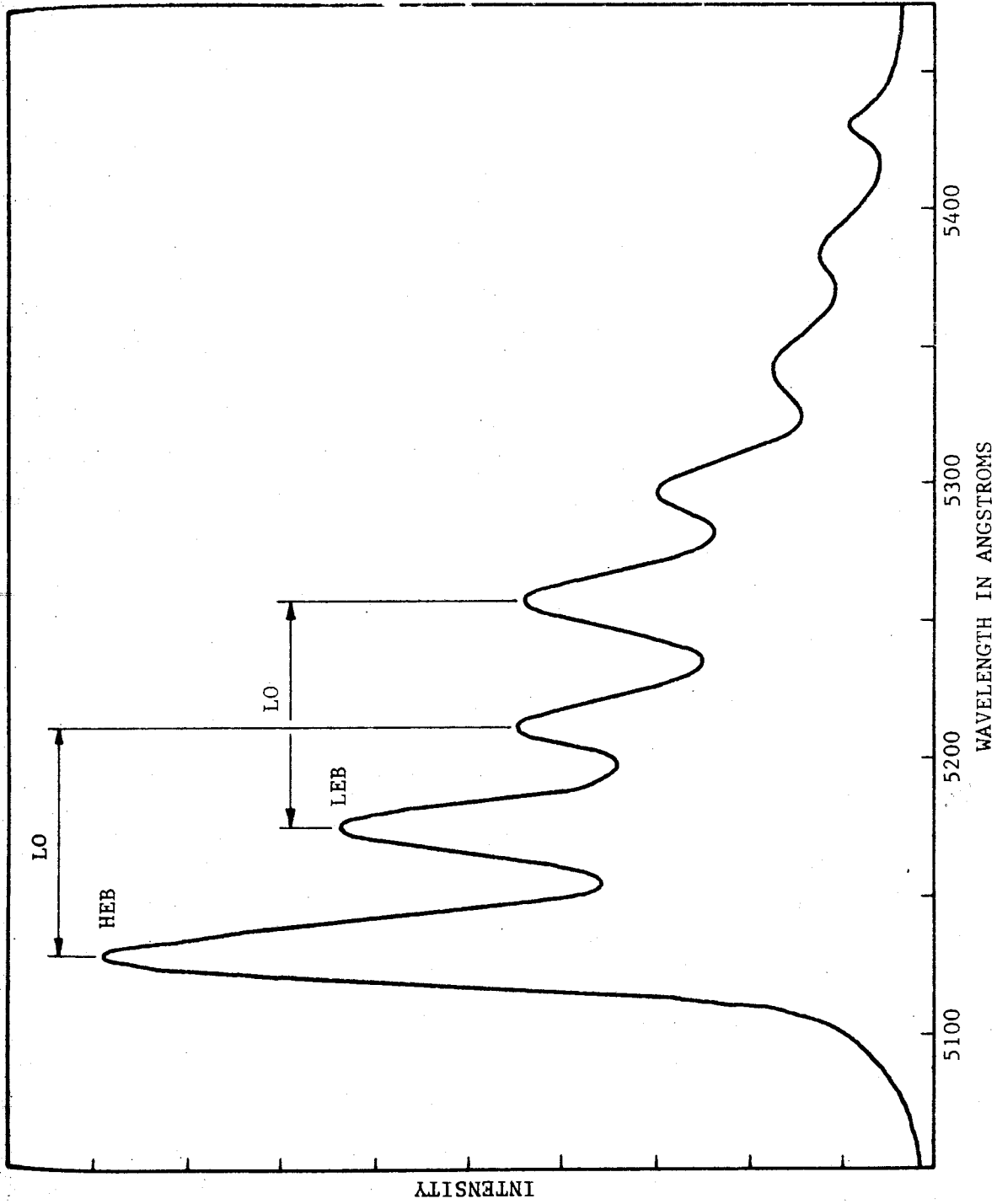


Figure 2 Edge emission of CdS at 27°K. HEB is due to free-to-bound and LEB is due to bound-to-bound transitions.

intensity should increase as the pair separation decreases. However, r has discrete values given by the geometry of the crystal and hence the number of possible pairings decreases as r decreases. For small values of r , the emission spectrum exhibits a fine structure given by Eqn. 2.301. This has been observed in GaP and CdS (Henry et al., 1969; Reynolds et al., 1969). For large r , the energy difference between adjacent lines becomes small, resulting in the observed broad band.

As the temperature is increased ($T > 20^\circ\text{K}$) some of the donor electrons become ionized. The recombination of a free electron with a bound hole results in the high energy band (HEB) near 5135 \AA . The emission energy of the HEB (free-to-bound) is given by (Colbow, 1966; van Doorn, 1966)

$$E = E_G - E_A + E_K + \frac{e^2 \alpha}{\kappa R} - nE_p \quad 2.303$$

E_K is the kinetic energy of the free electron at the instant of recombination. $e^2 \alpha / \kappa R$ represents the lowering of the acceptor binding energy due to donor-acceptor interaction. The significance of this interaction term has often been neglected by many authors. It was first pointed out by van Doorn (1966) that the presence of a nearby impurity will modify the acceptor binding energy, E_A . In particular, a donor impurity will lower the binding energy of a hole trapped at an acceptor resulting in a positive shift of the HEB emission energy. The value of R

is distinct from r used in the expression for the LEB emission energy (Eqn. 2.301). If only nearest neighbor interaction is considered, then R is equal to the most probable distance separating the donors and acceptors and is thus independent of temperature and excitation intensity. α is a numerical factor between zero and one and was introduced to account for screening effects. At very low free carrier concentrations screening effects are negligible and $\alpha = 1$. As the free carrier concentration is increased due to high excitation intensities and/or higher temperatures, the coulomb interaction between donor-acceptor pairs is screened and hence $\alpha < 1$. At very high free carrier concentrations $\alpha \rightarrow 0$ and the donor-acceptor interaction term can be neglected in Eqn. 2.303.

The LEB becomes weaker as the temperature is increased and is difficult to observe at $T > 40^\circ\text{K}$ in most crystals of CdS. At still higher temperatures the hole becomes ionized from the acceptor and the HEB is quenched (Maeda, 1965).

3. EXPERIMENTAL DETAILS

3.1 Apparatus

The experimental arrangement is illustrated schematically in Figure 3. The crystal was mounted on a copper block with a dab of nail polish in a variable temperature cryostat (manufactured by Andonian Associates, Inc.). The crystal was cooled by cold He gas. Temperature was measured using a Au + 0.03% (at) Fe vs. Chromel thermocouple. Temperatures from 4.2°K to 80°K were used for the measurements. The crystal was excited by the light from a 100 watt high pressure mercury arc (PEK Labs., model 911) filtered to obtain relatively high intensity of greater-than-band-edge energy radiation. Excitation light intensity variations were accomplished with neutral density filters. The angle of excitation was 45° to the normal of the crystal face.

The luminescent light was observed normal to the surface of the crystal (same side as incident excitation) and was focused on the entrance slit of a Spex Industries (model 1700) spectrometer which had a linear dispersion of 5 Å/mm in second order. The light was detected at the exit slit with an EMI (type 9558) photomultiplier (S-20 response). The luminescent light was chopped at 80 hz enabling the use of a phase sensitive lock-in amplifier (Princeton Applied Research, model HR-8). The signal vs. wavelength was recorded on a x-y recorder.

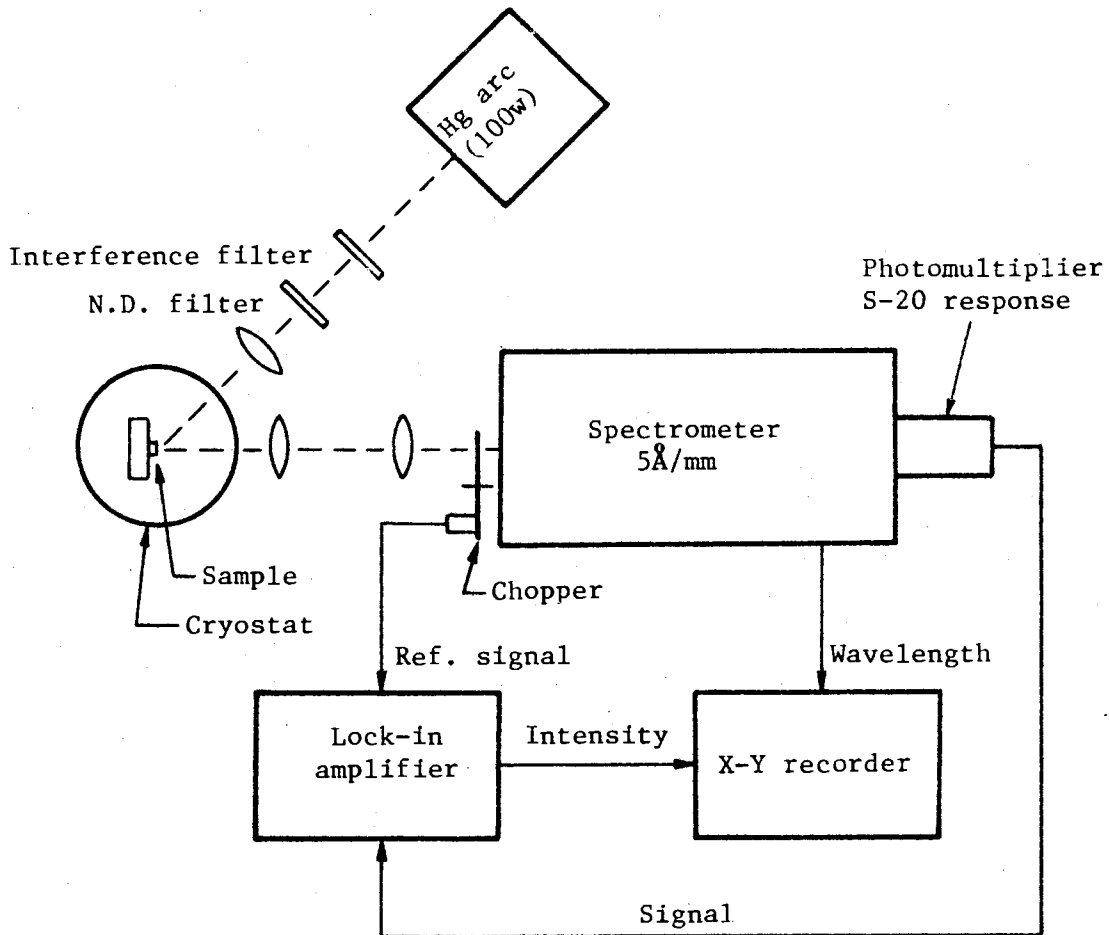


Figure 3 Experimental arrangement for photoluminescence measurements.

The resistance of some crystals was measured with a Keithley (model 600A) electrometer.

3.2 Crystal Preparation

Ultra high purity (UHP) and high purity (HP) crystals grown from the melt were purchased from Eagle-Picher. Some crystals grown by a vapor transport method were also used. Crystals were either cleaved or etched in concentrated HCl followed by a thorough wash in distilled water. For the resistance measurements, ohmic contacts were made by soldering gold wires to opposite sides of the crystal with indium.

It should be noted here that in CdS there must always be at least as many donors as there are acceptors (Goldberg, 1966) due to self-compensation. Hence, CdS crystals are either n-type or compensated but never p-type. In general, UHP crystals are highly conducting (strongly n-type) whereas HP crystals are of lower conductivity.

4. FREE-TO-BOUND RECOMBINATION

4.1 Introduction

In this chapter we shall be concerned with the high energy band (HEB) of the edge emission. In particular we would like to find the dependence of the peak energy of the HEB as a function of temperature and excitation intensity. The HEB results from the recombination of a free electron with a bound hole (see Section 2.3).

We have measured the zero-phonon ($n = 0$) emission peak of the HEB and found that the peak energy is a function of temperature and excitation intensity. A typical energy shift for a 100-fold increase in excitation intensity was found to be approximately 2 meV to higher energies at 25°K. Similar energy shifts were observed by Colbow and Nyberg (1967), Condas and Yee (1966) and Radford et al. (1972). While the exact cause of the energy shifts could not be identified, three mechanisms are suggested in the following sections:

- 1) An effective electron temperature significantly higher than the crystal temperature at high excitation intensities (hot electrons). This increases the value of E_K in Eqn. 2.303.

- 2) Screening of the acceptor by free carriers. This reduces the binding energy of the hole and thus increases the HEB emission energy.

- 3) Screening of the donor-acceptor interaction term ($e^2\alpha/\kappa R$) This reduces the value of α and thus decreases the HEB emission energy.

In order to evaluate Eqn. 2.303 for the peak energy of the HEB we will first discuss the variation of the band gap energy as a function of temperature.

4.2 Temperature Dependence of the Band Gap

The temperature dependence of the band gap was obtained by measuring the position of I_2 (exciton bound to a neutral donor) as a function of temperature. At low temperatures and low excitation intensities the exciton energy is assumed to be a constant distance from the band gap such that the changes in energy of I_2 represent shifts in the valence and conduction band edges. Mahan (1965) used this method to measure the band gap variation in CdTe and found good agreement with predicted band edge shifts. At low temperatures the band shifts show a T^2 dependence due to interaction of holes with acoustical phonons. The temperature dependent shifts in the conduction band are found to be negligible.

The results of our measurements are shown on Figure 4 for a UHP (high conductivity) and a HP (low conductivity) sample at low excitation intensity. In general, the band gap variation agrees with that obtained by Colbow (1966) and Thomas and Hopfield (1960). We found that the exciton emission energies differ slightly (<1 mev) for UHP and HP samples. Increasing the excitation intensity by two orders of magnitude lowered the exciton emission energies by approximately 0.5 to 1.0 mev in most samples. Screening of excitons will be discussed in Chapter 5. For the HEB we will make use of the band gap variation as shown in Figure 4 for the HP sample at low excitation intensity. From conductivity measurements we estimated a free carrier concentration of less than 10^{14} cm^{-3} at $T = 80^\circ\text{K}$ and low excitation intensities. Under these conditions we can neglect screening effects and Figure 4 should represent the band gap variation to a good accuracy.

4.3 Kinetic Energy, E_K

The rate of recombination of the HEB is given by (Colbow, 1966)

$$W(E_K) = N_A^{\circ} n(E_K) v \sigma(E_K) \quad 4.301$$

where N_A° is the concentration of neutral acceptors, v is the velocity of the electrons given by

$$v = (2E_K/m_e^*)^{1/2} \quad 4.302$$

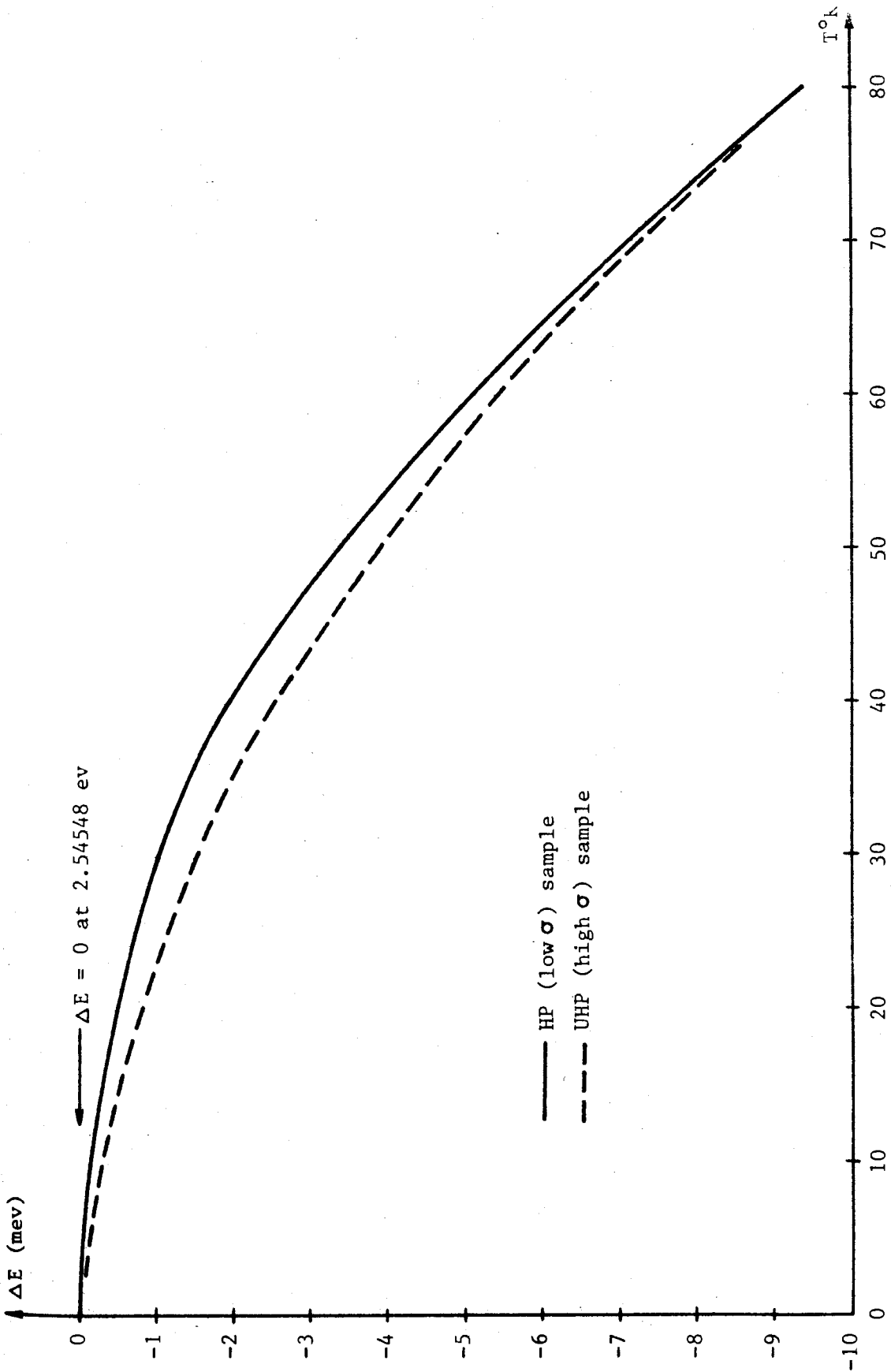


Figure 4 Energy shift of I_2 with temperature at low excitation intensity for a high purity (HP) and an ultra high purity (UHP) sample.

where m_e^* is the electron effective mass, and $\sigma(E_K)$ is the capture cross section for an electron by a neutral acceptor. $n(E_K)$ is the electron concentration as a function of kinetic energy. Assuming a Boltzman distribution for a parabolic conduction band we can write

$$n(E_K) = C\sqrt{E_K} e^{-E_K/kT} \quad 4.303$$

If we assume a capture cross section independent of E_K , the HEB recombination rate is given by (using Eqns. 4.301, 4.302 and 4.303)

$$W(E_K) = W_0 E_K e^{-E_K/kT}$$

where W_0 is a constant. This has a maximum for electrons of kinetic energy $E_K = kT$. The emission energy of the zero-phonon peak of the HEB is then given by

$$E = E_G - E_A + kT + \frac{e^2\alpha}{\kappa R} \quad 4.304$$

At very low free carrier concentrations we can assume E_A and $e^2\alpha/\kappa R$ to be constant such that the energy shift of the HEB emission peak as a function of temperature is given by

$$\Delta E = \Delta E_G(T) + kT$$

This is shown in Figure 5 with $\Delta E = 0$ at $T = 0$.

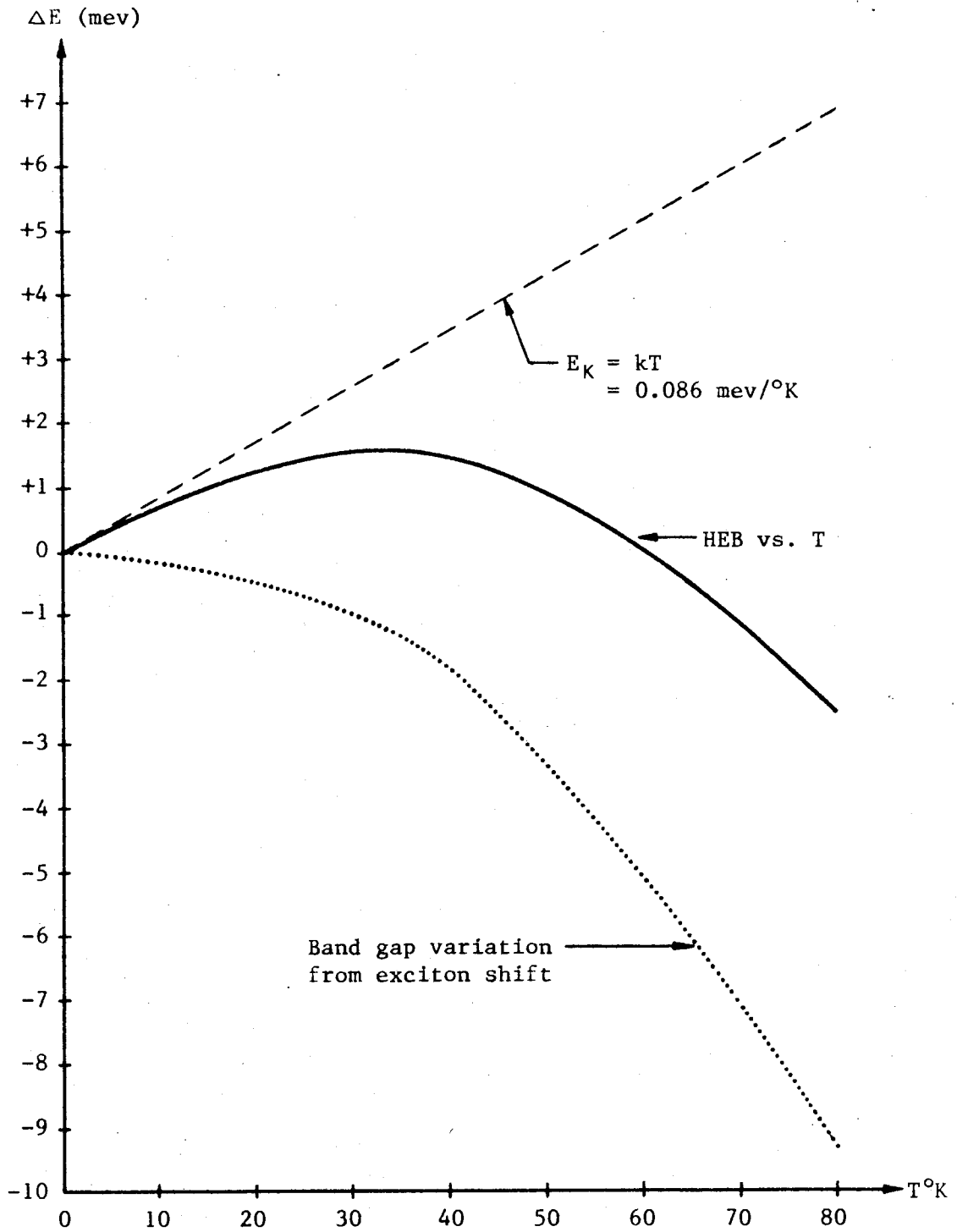


Figure 5 Peak energy variation of HEB as a function of temperature at low free carrier concentration (no screening).

4.4 Hot Carriers

It was suggested by Colbow and Nyberg (1967) that a possible explanation for the observed energy shift of the HEB emission peak could be the recombination of hot electrons with the hole bound to the acceptor. We found earlier that the peak energy of the HEB is given by (Eqn. 4.304)

$$E = E_G - E_A + kT + \frac{e^2 \alpha}{\kappa R} - nE_p$$

where T was assumed to be the lattice temperature. However, if the effective temperature of the electrons in the conduction band is distinct, i.e., higher than the lattice temperature, a higher emission energy would be expected. In particular, with the crystal at some temperature T, an effective electron temperature of $T_e = T + 23^\circ\text{K}$ could account for an energy shift of 2 mev.

It should be noted here that the above idea only applies to semiconductors where the optical transition probability for a transition between a conduction band state and an acceptor level is essentially constant over those conduction band energies which would be occupied by hot electrons. The transition probability was calculated by Dumke (1963) assuming a direct gap between parabolic bands and shallow impurities. The result, derived from time-dependent perturbation theory, is given as

$$A_{ac} = \frac{64\sqrt{2} \pi^3 e^2 \hbar^4 |P_{vc}|_{avg}^2 \delta(\hbar\omega + E_A - E_G - E_{CK}) (N+1) N_A}{n^2 m_o^2 \hbar\omega (m_A E_A)^{3/2} [1 + (m_e^* E_{CK}/m_A E_A)]^4}$$

where

$|P_{vc}|_{avg}$ = averaged interband matrix element of the momentum operator.

E_A = acceptor ionization energy.

E_G = band gap energy.

$E_{CK} = \hbar^2 K^2 / 2m_e^* = \hbar\omega - (E_G - E_A)$ = kinetic energy of an electron of wave number K in the conduction band.

m_0 = free electron mass.

m_e^* = electron effective mass.

$m_A = 2E_A \kappa^2 \hbar^2 / e^4$ = equivalent effective mass for the acceptor.

N_A = density of neutral acceptors.

N = photon density

n = refractive index of crystal

It can be seen that the transition probability becomes smaller as E_{CK} increases. The decrease of A_{ac} occurs at (see Eqn. 4.401)

$$E_{CK} \approx \frac{m_A}{m_e^*} E_A$$

In CdS, m_A/m_e^* is approximately 5 with $E_A = 165$ mev and $\kappa = 8.46$ (Aven and Prener, 1967) and hence

$$\frac{m_A}{m_e^*} E_A \approx 825 \text{ mev}$$

It follows that, for the HEB emission, the transition probability can be essentially constant for the conduction band energies which are of interest in the case of hot electrons.

Radford et al. (1972) compared the emission spectra of CdS produced under photoexcitation and cathodoexcitation. The HEB emission peak at liquid nitrogen temperature was found to occur at 5135 \AA for cathodoexcitation while for photoexcitation the same peak shifted to 5142 \AA , a difference of 7 \AA corresponding to 3.3 mev. At liquid helium temperatures, the HEB emission peak was found to occur at 5129 \AA for cathodoexcitation and at 5138 \AA for photoexcitation, a difference of 9 \AA corresponding to 4.2 mev. Radford et al. interpreted the observed energy shift in terms of a difference between the effective electron temperature of the conduction electrons

for the two modes of excitation. We would like to point out, however, that the two modes of excitation employed by Radford et al. resulted in luminescence spectra of different intensity. In particular, Figure 1 and 2 of Radford's paper show that the cathodoluminescence spectrum is approximately 15 times more intense than the photoluminescence spectrum at 77°K. At liquid helium temperature the difference is approximately 200. That the total green edge emission intensity is much greater for cathodoluminescence than photoluminescence may be explained (Bryant et al., 1970) by the fact that the penetration depth of the cathodoexcitation is much greater than that of the photoexcitation. A greater volume of crystal is thus excited under cathodoexcitation. Also, the free carrier concentrations produced by the two modes of excitation are not the same and an energy shift due to free carrier screening cannot be excluded.

4.5 Screening of Bound States

For semiconductors, the effective mass approximation consists in treating the electron [holes] as free particles whose motion is determined by the properties of the conduction [valence] band near the minimum with an effective mass m^* . In particular, if a physical quantity is given by

$$F = f(m_0)$$

for free electrons, then for electrons in the semiconductor the same quantity is determined by

$$F^* = f(m^*)$$

where m_0 is the mass of the free electron and m^* the effective mass of the electron in the semiconductor. m^* can be deduced from the measured properties of F^* if the function f is known. The effective mass approximation is useful if the same value for m^* describes many physical quantities such as F^* . Kohn (1957) discusses in detail the effective mass approximation of shallow donor and acceptor states in elemental semiconductors. The effective mass equation for an electron bound to a donor is given as

$$\frac{-\hbar^2}{2m_e^*} \nabla^2 \psi - \frac{e^2}{\kappa r} \psi = E_D \psi \quad 4.501$$

By analogy to the Schrödinger equation for the hydrogen atom, the binding energy of the ground state of a neutral donor defect in a semiconductor is thus given by

$$E_D = \frac{e^4 m_e^*}{2\kappa^2 \hbar^2} = (13.6 \text{ ev}) \frac{m_e^*}{m_0 \kappa^2} \quad 4.502$$

m_e^*/m_0 is the electron effective mass ratio and κ is the static dielectric constant which takes account of the reduction of

the coulomb force between charges due to the electronic polarization of the crystal. For an acceptor impurity, E_A is obtained by replacing m_e^* by m_h^* , the hole effective mass.

The Bohr radius of the ground state of hydrogen is given by $\hbar^2/m_0 e^2$. In a semiconductor

$$a_0 = \frac{\kappa \hbar^2}{m_e^* e^2} \quad 4.503$$

where a_0 is the "Bohr radius" of the donor state. Combining Eqns. 4.502 and 4.503 we can write

$$E_D = \frac{e^2}{2\kappa a_0} \quad 4.504$$

Expressing E_D in meV and r_0 in \AA , Eqn. 4.504 reduces to

$$E_D (\text{meV}) = 851/a_0 (\text{\AA})$$

where we used $\kappa = 8.46$ for CdS.

So far, we have assumed that there is no interaction between neighboring impurities and between impurities and free carriers. If the impurity concentration is large, there is an overlap of the electron wave functions of neighboring impurity centers which causes a broadening of the electron [hole] levels to form an impurity band (Fistul, 1969). A level broadens symmetrically above and below its original position and thus E_D and E_A

become smaller. We can neglect this type of interaction since all our samples were undoped (for impurity conduction in doped crystals of CdS see eg. Toyotomi et al., 1968).

We cannot neglect the interaction between impurities and free carriers. At high excitation intensities the concentration of free carriers is large even at low temperatures. The presence of free carriers screens the Coulomb interaction between the bound electron [hole] and the impurity ion which results in a reduced binding energy. Bonch-Bruевич (1963), Colbow and Nyberg (1967), Krieger (1969) and Colbow and Dunn (1970) investigated the screening effect of free carriers by using the Debye-Huckel form for the potential

$$V(r) = \frac{-e^2}{\kappa r} e^{-r/\lambda} \quad 4.505$$

where λ is the Debye screening length given by

$$\lambda = \left(\frac{\kappa kT}{4\pi n e^2} \right)^{1/2} = 6.9 \left(\frac{\kappa T}{n} \right)^{1/2} \text{ (cm)}$$

and n is the free carrier density. For a derivation of Eqn. 5 see Appendix A.

To calculate the impurity ionization energy in the presence of screening we substitute the Debye-Huckel potential, Eqn. 4.505, into the effective mass Eqn. 4.501; i.e., we seek the ground state energy of the Schrödinger equation

$$-\frac{\hbar^2}{2m_e^*} \nabla^2 \psi - \frac{e^2}{\kappa r} e^{-r/\lambda} \psi = E_D \psi \quad 4.506$$

To find E_A , the acceptor ionization energy, m_e^* is replaced by m_h^* . The solution to Eqn. 4.506 can be approximated by first order perturbation techniques (Colbow and Dunn, 1970) or by a variational approach (Colbow and Nyberg, 1967; Krieger, 1969). Both solutions are outlined below -

a) perturbation method:

The energy shift is given by

$$\Delta E_D = E - E_0 = \langle \psi_0 | V'(r) | \psi_0 \rangle \quad 4.507$$

where E_0 is the impurity ionization energy in the absence of free carrier screening and $V'(r)$ is the difference in potential energy with and without screening and is found to be

$$V'(r) = \left(\frac{-e^2}{\kappa r} e^{-r/\lambda} \right) - \left(\frac{-e^2}{\kappa r} \right) = \frac{e^2}{\kappa r} (1 - e^{-r/\lambda})$$

The only case considered is that in which ψ_0 is a hydrogenic wave function:

$$\psi_0 = (\pi a_0^3)^{-1/2} e^{-r/a_0}$$

Eqn. 4.507 then becomes:

$$\Delta E_D = (\pi a_0^3)^{-1} \langle e^{-r/a_0} | \frac{e^2}{\kappa r} | e^{-r/a_0} \rangle$$

$$- (\pi a_0^3)^{-1} \langle e^{-r/a_0} | \frac{e^2}{\kappa r} e^{-r/\lambda} | e^{-r/a_0} \rangle$$

Evaluating the integral over all space and simplifying yields

$$\Delta E_D = 2E_0 \left[1 - \left(1 + \frac{e^2}{4\kappa E_0 \lambda} \right)^{-2} \right] \quad 4.508$$

The energy shift of the acceptor involved in the HEB emission was obtained from Eqn. 4.508 and is shown in Fig. 6 for various temperatures and a range of free carrier concentrations. We assumed $E_0 = 165$ mev and κ was taken to be 8.46 (Aven and Prener, 1967). Expanding the term

$$\left(1 + \frac{e^2}{4\kappa E_0 \lambda} \right)^{-2} = 1 - 2 \left(\frac{e^2}{4\kappa E_0 \lambda} \right) + 3 \left(\frac{e^2}{4\kappa E_0 \lambda} \right)^2 - \dots$$

in Eqn. 4.508 and keeping only the first two terms, we get

$$\Delta E \approx 8.5 \times 10^{-7} \sqrt{n/T} \quad 4.509$$

where ΔE is given in mev. ΔE is thus proportional to \sqrt{n} , as expected, but inversely proportional to \sqrt{T} . The temperature dependence can be understood if one considers the kinetic

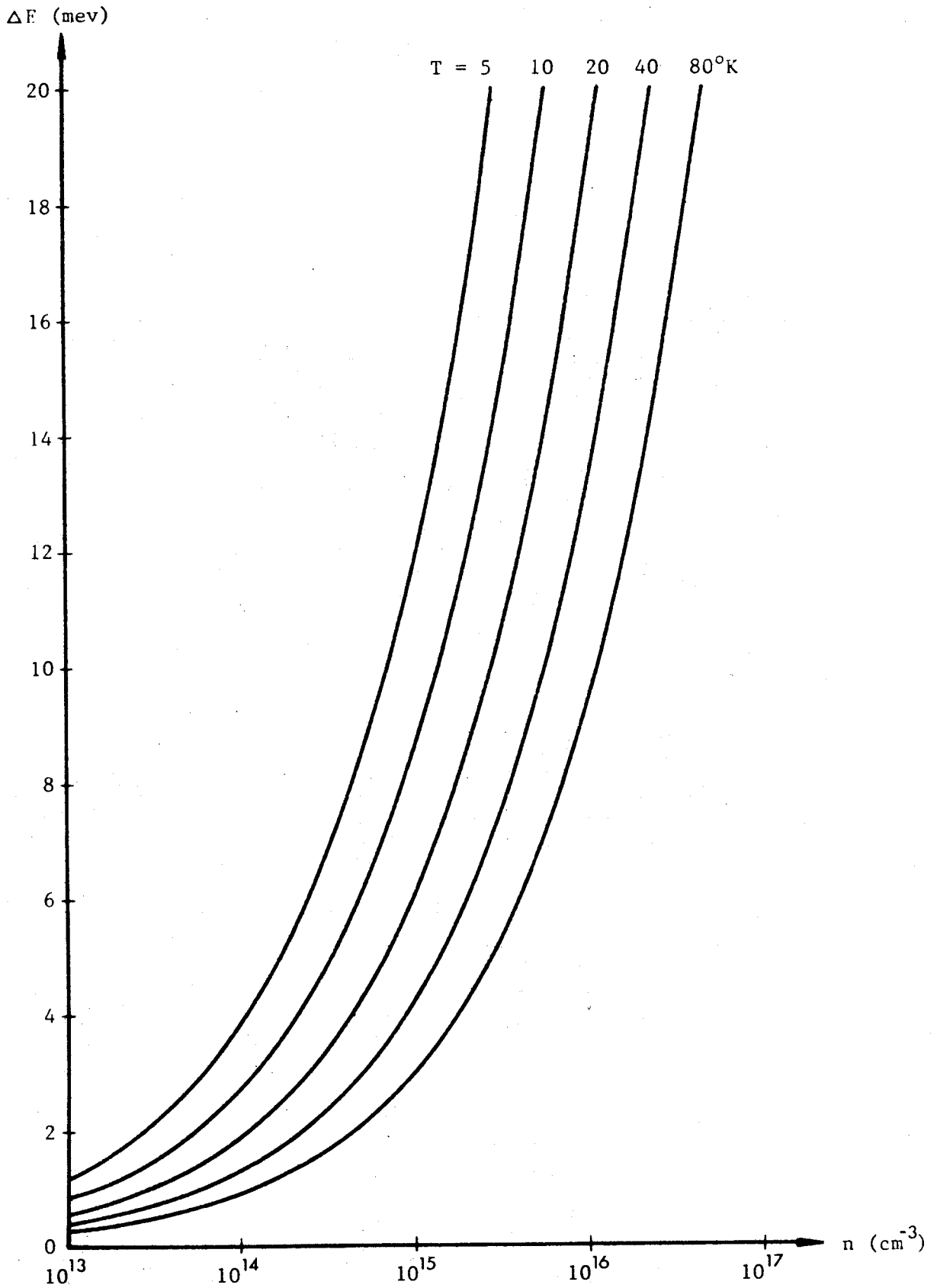


Figure 6 Decrease of the acceptor binding energy due to screening at various temperatures ($E_0 = 165\text{mev}$).

energy of the free carriers. At high temperatures the kinetic energy is large such that it is more difficult for a space charge to build up around the impurity and hence the screening is not as effective as it would be at a lower temperature.

b) variational method:

The Hamiltonian for the bound electron [hole] is given by

$$H = \frac{-\hbar^2}{2m_e^*} \left(\frac{d^2}{dr^2} + \frac{2}{r} \cdot \frac{d}{dr} \right) - \frac{e^2}{\kappa r} e^{-r/\lambda}$$

We assume a trial wave function of the form

$$\chi = \frac{\beta^{3/2}}{\sqrt{\pi a_0^3}} e^{-\beta r/a_0}$$

where β is the variational parameter and a_0 is the "Bohr radius" given by Eq. 4.504. The ionization energy of the impurity is readily found by choosing β so as to minimize the ground state energy given by

$$\langle \chi | H | \chi \rangle = \frac{\beta^3}{\pi a_0^3} \langle e^{-\beta r/a_0} | H | e^{-\beta r/a_0} \rangle$$

The energy shift due to screening is then given as

$$\Delta E_D = E_0 \left[1 + \beta^2 - 2\beta^3 \left(\beta + \frac{a_0}{2\lambda} \right)^{-2} \right] \quad 4.510$$

which has a minimum with respect to β for

$$\beta^3 + \beta^2 \left(\frac{3a_0}{2\lambda} - 1 \right) + \beta \left(\frac{3a_0^2}{4\lambda^2} - \frac{3a_0}{2\lambda} \right) + \left(\frac{a_0}{2\lambda} \right)^3 = 0 \quad 4.511$$

E_0 is the impurity ionization energy in the absence of free carrier screening and is related to a_0 by

$$E_0 = \frac{e^2}{2\kappa a_0} \quad 4.512$$

Eqn. 4.511 has been solved for β as a function of a_0/λ where

$$\frac{a_0}{\lambda} = \frac{1.23 \times 10^{-6}}{E_0 \text{ (mev)}} \left(\frac{n}{\kappa T} \right)^{\frac{1}{2}}$$

The solution is shown in Fig. 7. It can be seen that $\beta = 0.5$ if $a_0 = \lambda$. Substituting $\beta = 0.5$ into Eq. 4.510 gives $\Delta E = E_0$. Hence, no bound states can exist if the Debye length is less than or equal to the "Bohr radius".

Fig. 7 also shows that

$$\beta \approx 1 \text{ for } \frac{a_0}{\lambda} < 0.1.$$

Substituting $\beta = 1$ into Eqn. 4.510 and making use of Eqn. 4.512 gives

$$\Delta E = 2E_0 \left[1 - \left(1 + \frac{e^2}{4\kappa E_0 \lambda} \right)^{-2} \right]$$

This is identical to Eqn. 4.508 which was derived from first order perturbation principles. The condition $(a_0/\lambda) < 0.1$ corresponds to carrier concentrations

$$n < 1.5 \times 10^{16}, T = 10^\circ \text{K}$$

$$n < 1.5 \times 10^{17}, T = 100^\circ \text{K}$$

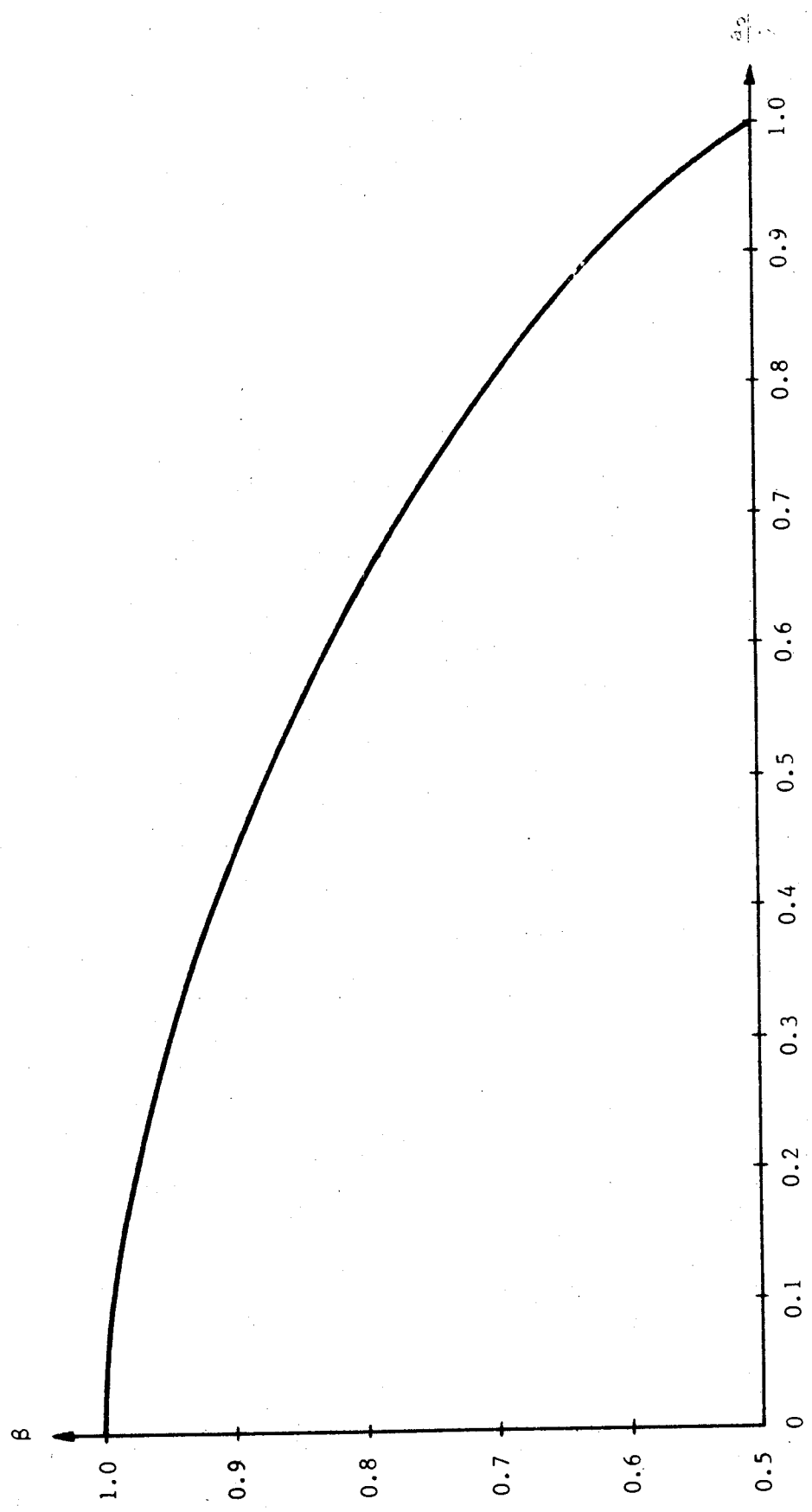


Figure 7 Solution to Equation 4.511: β as a function of $\frac{a_0}{\lambda}$

with $E_0 = 165$ mev and $\kappa = 8.46$. At higher carrier concentrations the energy shifts predicted by Eqns. 4.508 and 4.510 differ slightly. The ionization energy goes to zero less sharply at the critical density ($\lambda \approx a_0$) as predicted by the variational solution.

It is known that for the Debye-Huckel potential (Eqn. 4.505) the number of discrete energy eigenvalues is always finite, in contrast to the purely coulombic potential. Further, any departure of the potential from a strict $1/r$ dependence will remove the ℓ -degeneracy which is characteristic for the hydrogen problem. Bonch-Bruevich and Glasko (1963) have investigated the energy spectrum of a particle in a Debye field by numerical methods. In particular, the equation

$$\frac{-\hbar^2}{2m^*} \left\{ \frac{d^2u}{dr^2} - \frac{\ell(\ell+1)}{r^2} \right\} u - \frac{e^2}{r^2} e^{-r/\lambda} u = Eu$$

was reduced to the eigenvalue problem

$$u'' = \{\alpha + f(x)\} u, \quad u(0) = u(+\infty) = 0$$

by a proper choice of dimensionless variables. Approximate eigensolutions of the above equation with $\ell = 0$ were also calculated by Hulthén and Laurikainen (1951) with emphasis on the mathematical aspect of the problem. The results of Bonch-Bruevich et al. show that the energy levels are pulled closer to the conduction band as a result of increasing free carrier concentration and, finally, disappear. From their

data, we have calculated the energy shift for a donor impurity with an electron effective mass ratio $m_e^*/m_c = 0.17$ (Ray, 1963) and a static dielectric constant $\kappa = 8.46$. The results are shown in Figure 8 together with the energy shift as predicted by Eqn. 4.508 (perturbation method). As can be seen, the agreement is quite good.

It has been shown in this section that screening of the acceptor could account for the observed energy shifts in the HEB luminescence. As the excitation intensity is increased, more free carriers are generated. The increased free carrier concentration reduces the binding energy of the hole on the acceptor due to screening of the coulomb interaction. A reduction in E_A increases the energy of the HEB emission peak (Eqn. 4.304).

4.6 Donor-Acceptor Interaction, $e^2\alpha/\kappa R$

The significance of the donor-acceptor interaction term has often been neglected by many authors. It was first pointed out by Van Doorn (1966) but without the parameter α which we introduced to account for screening effects.

Consider first a hole bound to an ionized donor-acceptor pair. The most important effect of the ionized donor is to raise the average potential energy of the hole by an amount

$$\Delta E_A = \frac{e^2}{\kappa r}$$

4.601

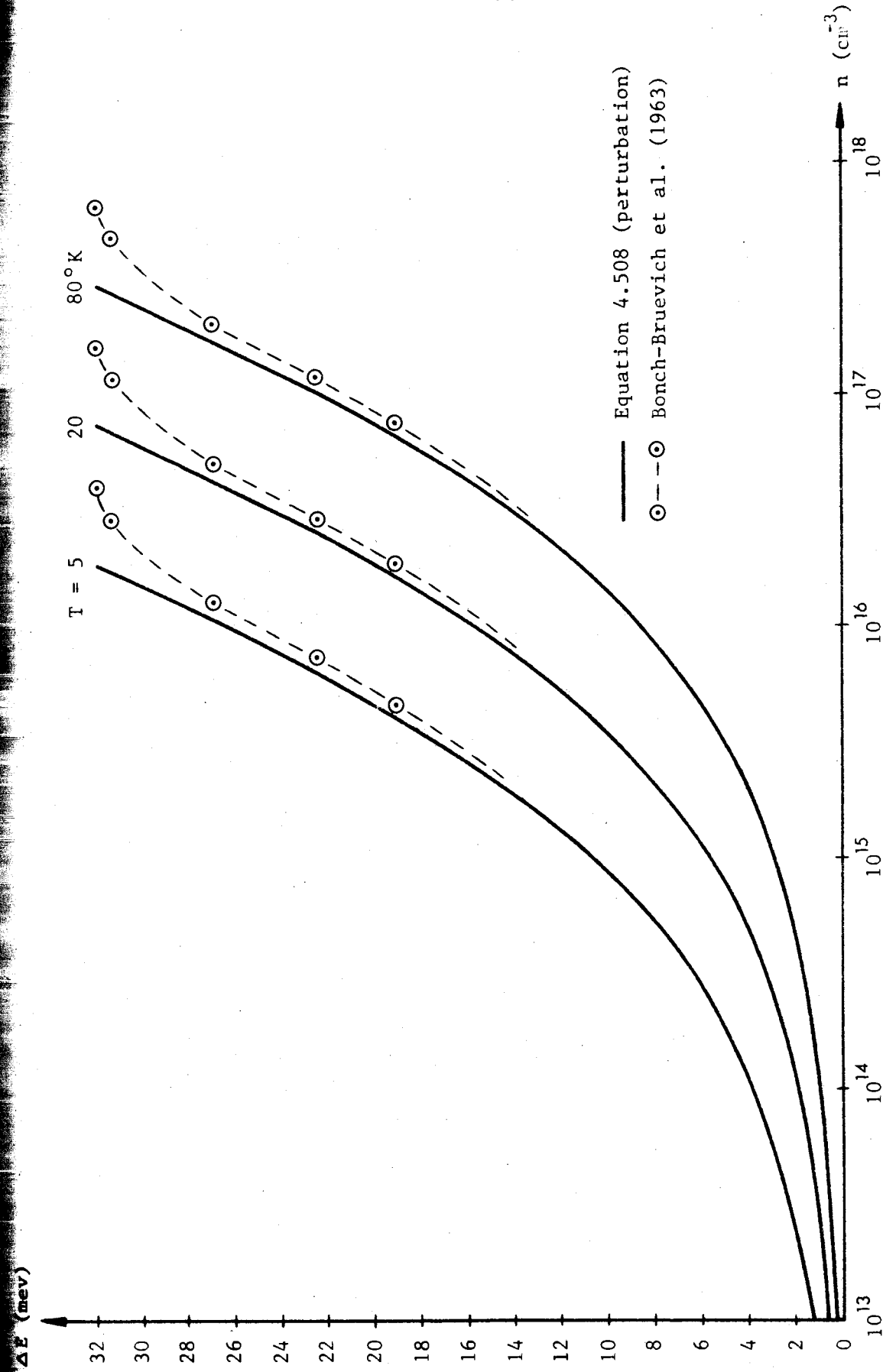


Figure 8 Decrease of the donor binding energy due to screening at various temperatures ($E_0 = 32\text{mev}$).

where r is the donor-acceptor separation. Fig. 9 shows the fractional energy shift ($\Delta E_A/E_A$) of the hole as a function of r/a_0 , where E_A is the acceptor ionization energy and a_0 the acceptor "Bohr radius" (Eqn. 4.504). It can be seen that for a critical separation $r_c = 2a_0$ the hole becomes unbound. Hopfield (1964) calculated r_c in various approximations, taking into account the finite spatial extent of the hole wavefunction and the acceptor polarizability, and found that

$$r_c \approx 1.75 a_0$$

The total binding energy of an electron-hole pair to a donor-acceptor pair is given by (Thomas et al., 1964; Williams, 1968)

$$E_b = E_D + E_A + J - \frac{e^2}{kr} + \frac{ea^6}{kr^6} \quad 4.602$$

where J includes four coulomb interactions and is equal to the cohesive energy of the neutral donor-acceptor pair ($J \geq 0$ in Eq. 4.602), e^2/kr is due to the core interaction which remains after ionization, and ea^6/kr^6 is the Van der Waals attraction between the neutral donor and acceptor (a = effective Van der Waals coefficient). If the donor-acceptor separation, r , is large compared to the radii of the donor and acceptor states, J and the Van der Waals

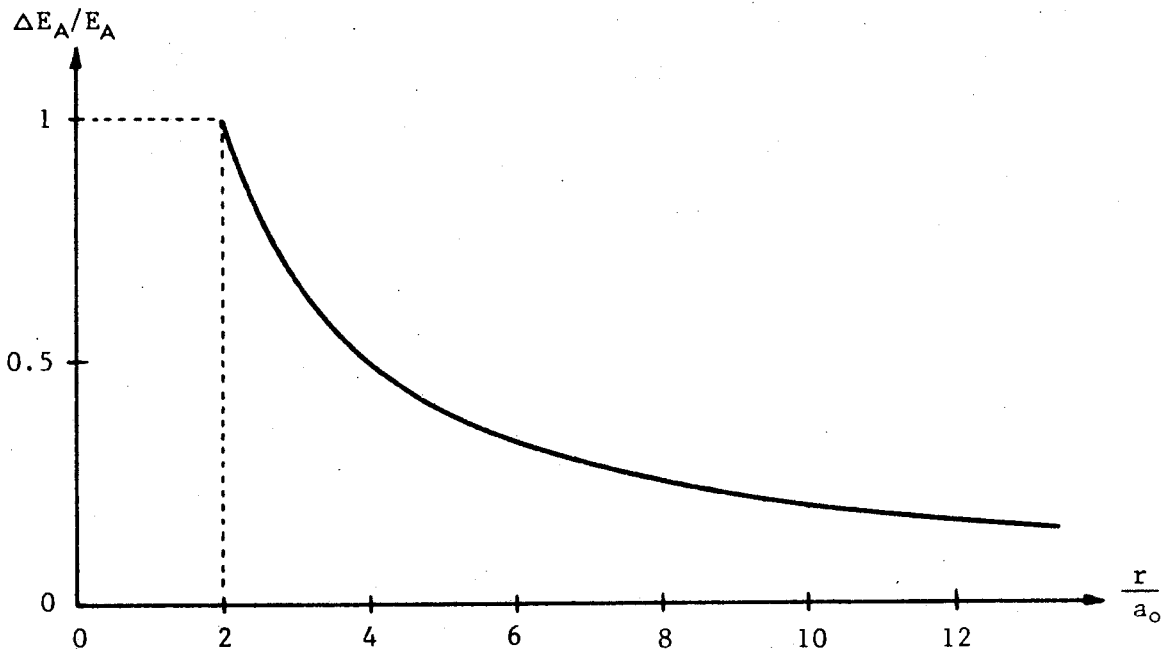
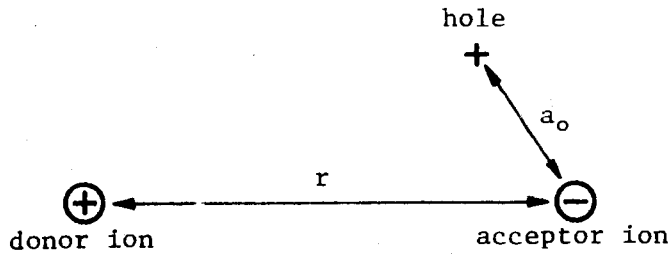


Figure 9 top: Hole bound to ionized donor-acceptor pair.
bottom: Fractional energy shift of the hole binding energy as a function of donor-acceptor separation.

term vanish such that the binding energy of the electron-hole pair becomes

$$E_b \approx E_D + E_A - \frac{e^2}{\kappa r}$$

What fraction of $e^2/\kappa r$ modifies the ground state of either of the two impurities depends on the values of E_D and E_A . For the special case in which $E_D = E_A$, both impurities have their binding energies decreased by $e^2/2\kappa r$. If, on the other hand, the binding energies are such that $E_D \ll E_A$, the weakly bound particle (the electron) is unaffected by the presence of the neutral acceptor such that the strongly bound particle (the hole) experiences a modification of its binding energy by $e^2/\kappa r$. In CdS, $E_D \approx 32$ mev and $E_A \approx 165$ mev. We will thus assume that the binding energy of the electron-hole pair is given by the one particle binding curve (Fig. 8) plus the donor binding energy. The consequence is that the donor-acceptor interaction term which is of interest for the HEB recombination does not depend on whether the donor is neutral or ionized and is thus given by Eqn. 4.601.

We now have to find an expression for the most probable separation of the donor-acceptor pairs. For definiteness, and in agreement with the present experimental situation, we will assume that the donor concentration is larger than the acceptor concentration such that the most probable separation

of the donor-acceptor pairs will be a function of donor concentration only.

Let $g(r)dr$ be the probability of finding a donor at a distance r from a given acceptor with no other impurity inside the sphere $4\pi r^3/3$ centered at the acceptor. The simplest solution is obtained by neglecting all interactions between ions. The probability that there is a donor at a distance r from the acceptor is then given by

$$(4\pi r^2 dr)N_D \quad 4.603$$

The probability that there is no other impurity inside the sphere $4\pi r^3/3$ is

$$1 - G(r) \quad 4.604$$

where $G(r)$ is the probability that there is another impurity inside the sphere and is simply given by

$$G(r) = \int_0^r g(x)dx \quad 4.605$$

From Eqns. 4.603, 4.604 and 4.605 we then obtain the integral equation

$$g(r) = 4\pi r^2 N_D [1 - \int_0^r g(x)dx]$$

whose solution is

$$g(r) = 4\pi r^2 N_D \exp[-4\pi r^3 N_D / 3] \quad 4.606$$

(This can be verified by back-substitution). The function $g(r)$ is shown in Fig.10 as a function of r for three different donor concentrations. Differentiation of Eqn. 4.606 gives for the most probable donor-acceptor separation

$$R = (2\pi N_D)^{-1/3} \quad 4.607$$

This is approximately equal to $(4\pi N_D / 3)^{-1/3}$, the radius of the average volume per particle.

It is now clear that R is different from the value of r used in Eqns. 2.201 and 2.202 for the LEB emission (bound to bound). r is clearly a function of excitation intensity: 1) more neutral donor-acceptor pairs are created at high excitation intensities such that, on the average, r is reduced, 2) high excitation results in saturation of the long distance pairs (longer recombination time) such that more recombinations take place between short distance pairs, again reducing the average value of r . Both effects (1 & 2) cause a shift of the LEB emission peak to higher energy. In contrast to this, the value of R is independent of excitation intensity and constant for a given acceptor-donor concentration. The exact value of R to be used in Eqn. 4.304 is, of course, only approximately given by Eqn. 4.607. If

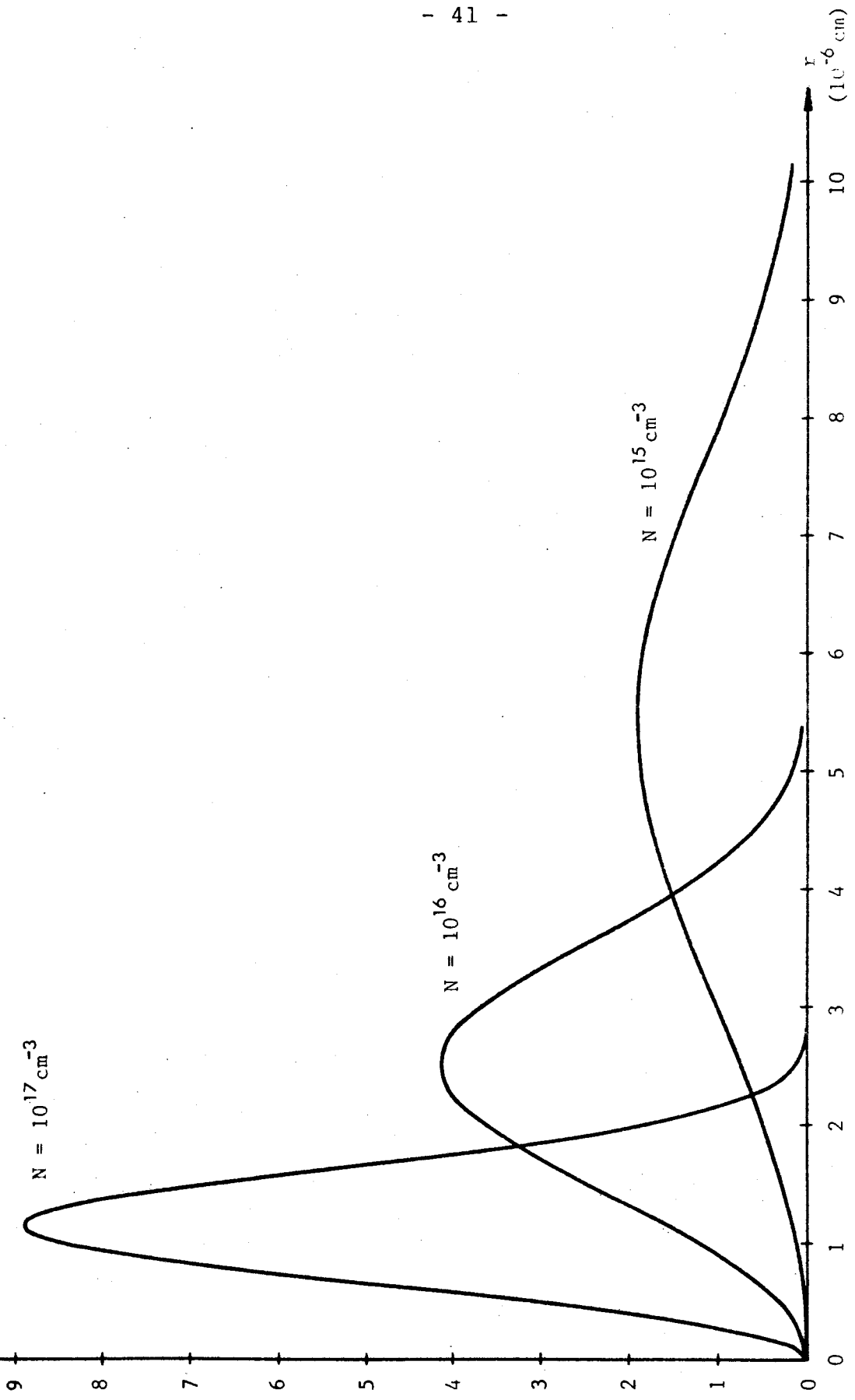


Figure 10 Probability function $g(r)$ of finding a donor at a distance r from the acceptor. N is the donor concentration.

interaction between impurities is taken into account one would expect a smaller value for R due to coulomb interaction between the impurities during crystal preparation. Moreover, the probability for an acceptor to capture a hole is influenced by the presence of a nearby donor which would increase the effective value of R .

Using Eqn. 4.607, we find that

$$R \approx 252 \text{ \AA}$$

for a donor concentration of 10^{16} cm^{-3} . Assuming $\alpha = 1$ and $\kappa = 8.46$, this gives a donor-acceptor interaction energy (Eqn. 4.304)

$$\frac{e^2}{\kappa R} = 6.75 \text{ meV}$$

The coulomb interaction between donor-acceptor pairs will be subject to screening at large free carrier concentrations. The potential due to the donor ion will then be given by the Debye potential (Eqn. 4.505)

$$V(R) = \frac{e^2}{\kappa R} e^{-R/\lambda}$$

The parameter α in Eqn. 4.304 is thus given by

$$\alpha = e^{-R/\lambda}$$

4.608

We have shown that the donor-acceptor interaction term can be significant at high donor concentrations and low excitation intensity. In particular, the interaction term must be taken into account if Eqn. 4.304 is to be used to calculate the value of the acceptor ionization energy from experimental data. The contribution of the interaction term to the total emission energy becomes less important at high free carrier concentrations due to screening.

4.7 RESULTS AND DISCUSSION

It was shown in this chapter that the peak energy of the HEB emission is a function of temperature and excitation intensity. The peak energy is given by

$$E = E_G - E_A + kT + \frac{e^2}{\kappa R} e^{-R/\lambda} - nE_p \quad 4.701$$

where

E_G = band gap energy (Fig. 4)

E_A = acceptor binding energy (Eqn. 4.508)

kT = kinetic energy of electrons at the instant
of recombination

$\frac{e^2}{\kappa R} e^{-R/\lambda}$ = donor-acceptor interaction term
(Eqns. 4.607 and 4.608)

nE_p = phonon emission energy ($n = 0, 1, 2, \dots$)

Equation 4.701 can be used to estimate E_A from the measured position of the zero-phonon peak and the known band gap energy at very low temperatures and low excitation intensity. Under these conditions the free carrier concentration is small such that screening effects can be neglected. The energy of the HEB emission peak at 4.2°K was measured as 2.4186 ev for a high purity sample of CdS. Using Eqn. 4.701 with $E_G = 2.5826$ ev and $kT = 0.0004$ ev we find

$$E_A = 164.4 \text{ meV} + \frac{e^2}{\kappa R} e^{-R/\lambda} \quad 4.702$$

To evaluate the donor-acceptor interaction term we used an approximate value of the donor concentration. The Hall mobility as a function of temperature was taken from Ray (1969). The numerical factor c relating the Hall mobility R to the drift mobility μ_n

$$\mu_n = c R$$

was assumed unity. The electron concentration as a function of temperature was calculated from conductivity measurements using

$$n = \sigma / \mu_n e \quad (N_D \gg N_A)$$

An approximate value of the donor concentration could then be obtained from n vs. $1/T$ in the temperature region of impurity

saturation. Hence

$$N_D \approx 10^{15} \text{ cm}^{-3}$$

Using Eqn. 4.697 we find the most probable donor-acceptor separation

$$R \approx 542 \text{ \AA}$$

which leads to an interaction energy

$$\frac{e^2}{\kappa R} \alpha \approx 3.1 \text{ meV}$$

with $\kappa = 8.46$ and $\alpha = 1$. Substitution into Eqn. 4.702 gives

$$E_A \approx 167.5 \text{ meV}$$

with an uncertainty of about 2.5 meV due to the estimate of N_D . This compares well with the value of 170 meV from Colbow (1966) and 165 meV from the results of Henry et al. (1970). We note that the interaction term was not included by Colbow and Henry et al.

Figure 11 shows some experimental points which were obtained from two high purity samples at very low and at maximum excitation intensity using above band gap radiation from a mercury arc (see Chapter 3 for experimental details).

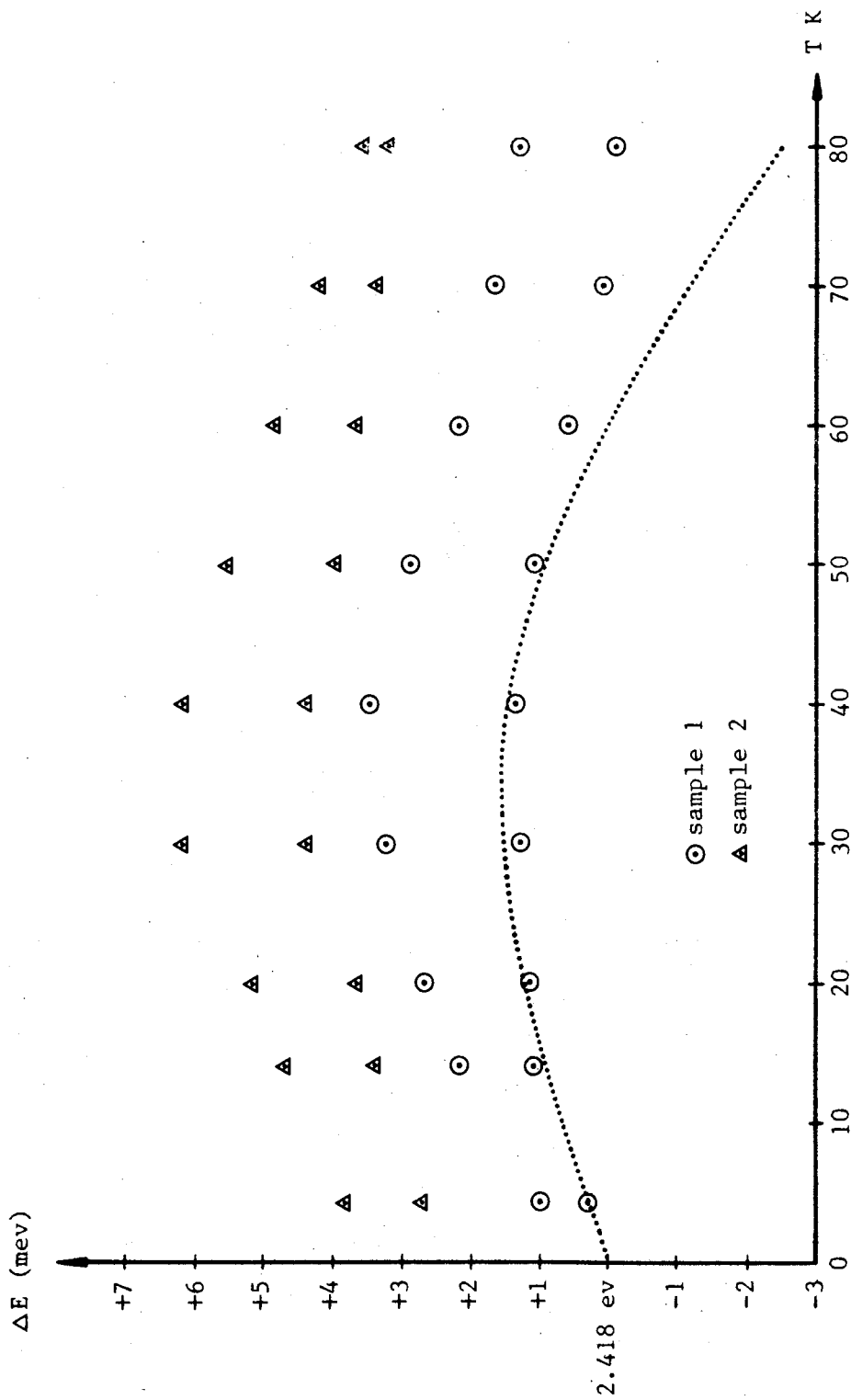


Figure 11 Peak energy of HEB as a function of temperature at very low and maximum excitation intensity for two HP samples of Cds. For both samples, the lower energy data points correspond to low excitation. The dotted line represents the temperature dependence in the absence of any screening effects (Fig. 5)

The acceptor binding energy calculated above was obtained from sample 1.

a) Low excitation intensity:

From Figure 11 it can be seen that the peak energy for the two samples differs by about 2.4 meV at 4.2°K. This can be accounted for by a difference in the donor-acceptor interaction term for sample 2. A donor concentration of $5.4 \times 10^{15} \text{ cm}^{-3}$ gives an interaction energy equal to 5.5 meV (assuming $\alpha = 1$) which differs from the interaction energy of sample 1 by 2.4 meV (Eqn. 4.703). This illustrates the uncertainty in obtaining the acceptor binding energy from the measured HEB peak energy if the exact value of the interaction term (or the donor concentration) is unknown.

Aside from this energy shift due to different donor concentrations we see that the measured peak energies agree well with the predicted temperature dependence (dotted line in Fig. 11) for $T < 60^\circ\text{K}$. Since the free carrier density increases as the temperature is raised, both E_A and the donor-acceptor interaction term, $e^2\alpha/\kappa R$, are subject to screening. For a free carrier concentration of 10^{14} cm^{-3} at 50°K, for example, we find from Figure 6: $\Delta E_A \approx 1 \text{ meV}$. From Eqn. 4.608 and 4.703 we obtain a change in the interaction term of $\sim 1 \text{ meV}$ for the same carrier concentration and temperature. Since ΔE_A increases the peak emission energy and $\Delta(e^2\alpha/\kappa R)$ results in an energy decrease, no net

effect is observed. At higher temperatures, and thus higher carrier concentrations, screening of the acceptor becomes more dominant resulting in the observed deviation from the dotted line in Figure 11. For example, at a free carrier concentration of $3 \times 10^{15} \text{ cm}^{-3}$ and a temperature of 80°K we find for sample 1 ($N_D \approx 10^{15}$)

$$\begin{aligned}\Delta E_A &\approx 5 \text{ meV} \\ \Delta(e^2\alpha/\kappa R) &\approx 2.5 \text{ meV}\end{aligned}$$

with a net shift of 2.5 meV to higher energy.

b) High excitation intensity:

The observed shift of the measured emission peak is according to expectation and can again be explained by the screening model. Increasing the excitation intensity creates more free carriers which screen the interaction between the hole and the acceptor and also between donor-acceptor pairs. At high free carrier densities the screening of the hole-acceptor interaction is dominant resulting in the observed shift to higher energy. We note (Fig. 11) that the energy shift with respect to the dotted line increases with temperature for both samples as expected. However, the energy difference between the low excitation and the high excitation peaks is a maximum at around 40°K for both samples and decreases

at higher temperatures, becoming negligible at 80°K for sample 2. This is probably because the percentage change in free carrier concentration in going from low excitation to high excitation becomes less as the temperature is increased.

The energy shift in the high excitation case could also be explained in terms of hot carriers (an increase in the value of kT in Eqn. 4.701). However, hot electron recombination could not explain the positive energy shift at $T > 60^\circ\text{K}$ which was observed in the low excitation case. It should be noted that screening due to hot electrons is less effective since screening is inversely proportional to \sqrt{T} (cf. Eqn. 4.509). Thus hot electron effects would be partially compensated by a decrease in screening.

It is not certain whether a decrease in band gap energy due to large free carrier densities is important. Gay (1971) postulated a band gap reduction due to self screening of the free carrier plasma (see Section 5.2).

The actual energy shift is expected to be somewhat larger than was observed since a slight increase in sample temperature can probably not be avoided at high excitation intensities. An increase in temperature reduces E_G and thus the HEB emission energy. The sample temperature was measured with a thermocouple which was mounted on the sample using silver paste for good thermal contact. Sample

heating at increasing excitation levels was also checked by observing the relative strengths of the I_2 and I_1 excitons. I_2 is less tightly bound than I_1 (see Table I) and is therefore thermally ionized more readily. The ratio of peak values thus serves as a reliable internal temperature standard.

We have measured the temperature and excitation intensity dependence of various HP samples of CdS from different sources. All samples produced results which were in general agreement with the behaviour of sample 1 and 2 discussed above.

5. SCREENING OF EXCITONS

5.1 Introduction

If a crystal satisfies the effective mass approximation, and the extrema of the energy bands lie in the center of the Brillouin zone, then the total energy of an exciton is given by

$$E = E_G - \frac{e^2}{2\kappa a_0 n^2} + \frac{\hbar^2 K^2}{2(m_e^* + m_h^*)}, \quad n = 1, 2, 3, \dots \quad 5.101$$

E_G is the band gap energy, κ the dielectric constant of the medium, and a_0 the exciton Bohr radius given by

$$a_0 = \frac{\hbar^2 \kappa}{\mu e^2} \quad 5.102$$

where μ is the reduced mass of the exciton defined by

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

with m_e^* and m_h^* being the electron and hole effective masses.

K is the wave vector of the exciton

$$\bar{K} = \bar{K}_e + \bar{K}_H$$

The positive hole and the negative electron thus form a bound system similar to the hydrogen atom. The exciton

spectrum consists of a series of discrete parabolic bands below E_G which merge into a continuum at higher energies. The last term in Eqn. 5.101 represents the kinetic energy of the exciton which results in a slight broadening of the exciton levels. Using Eqn. 5.102 with $\mu = 0.155 m_0$ and $K = 8.46$ appropriate for CdS we obtain an exciton Bohr radius of $\sim 29 \text{ \AA}$. The exciton is thus large compared to the lattice constant and embraces many atoms.

Intrinsic (free) excitons have a tendency to form ion-like or molecule-like complexes at low temperatures. For example, two intrinsic excitons may form an excitonic molecule (similar to H_2) or an intrinsic exciton may be captured by an impurity atom (acceptor or donor) to form a bound exciton complex.

5.2 Screening of Excitons

From the discussion of screening of bound states (4.5) it is expected that the binding energy of excitons would decrease at high densities of free carriers which would be created at high excitation intensities. A decrease in binding energy would result in a corresponding increase in the energy of recombination. However, we found that the exciton energy decreased slightly ($<1 \text{ mev}$) as the excitation intensity was increased. This was the case for

both intrinsic and bound excitons. From conductivity measurements we estimated a free carrier concentration greater than 10^{15} cm^{-3} at 30°K and maximum excitation intensity for the UHP (high conductivity) samples. Thus, if Eqn. 4.508 is applicable, a shift of approximately 4.5 meV to higher energy should have been observed for the intrinsic exciton. This discrepancy is believed to be due to the internal motion of the exciton which makes it more difficult for a space charge to be formed than in the case of the stationary acceptor (or donor) ion. The angular frequency of motion of an exciton (characteristic frequency) is given by (Dexter and Knox, 1965)

$$\omega_{\text{ex}} = \frac{\text{angular momentum}}{\text{mass} \times (\text{radius})^2} \sim \frac{\hbar}{\mu a_0^2} = \frac{2E_b}{\hbar}$$

where E_b is the binding energy of the exciton given by (see Eqn. 5.101)

$$E_b = \frac{e^2}{2\kappa a_0}$$

With $a_0 = 29 \text{ \AA}$ we obtain $\omega_{\text{ex}} = 8.9 \times 10^{13} \text{ rads sec}^{-1}$.

In comparison, the plasma frequency of the electrons in a solid is given by

$$\omega_p = \left(\frac{4\pi n e^2}{\kappa m_e^*} \right)^{1/2}$$

With $n = 10^{15} \text{ cm}^{-3}$, $\kappa = 8.46$, and $m_e^* = 0.17 m_0$
we obtain $\omega_p = 1.5 \times 10^{12} \text{ rads sec}^{-1}$, that is to say

$$\omega_p \ll \omega_{ex}$$

For $\omega_p = \omega_{ex}$, a carrier concentration of $3.6 \times 10^{18} \text{ cm}^{-3}$ is required. This simple argument would suggest that the free carrier plasma is too sluggish to follow the internal motion of the exciton and thus screening due to free carriers would not be very effective. Therefore, the simple screening model based on the Debye potential can not be applied to excitons.

A theoretical study of screening of excitons based on a dielectric function approach was done by Gay (1971). The study avoids the region of carrier concentration for which the plasma frequency (ω_p) is comparable to the characteristic frequency of the exciton (ω_{ex}). In the region $\omega_p \ll \omega_{ex}$ (low carrier concentration) it was found that the free carrier plasma responds only to the time-average charge density of the exciton which results in a slight lowering of the exciton energy measured from the top of the valence band. This is in agreement with our observations. As the density of free carriers increases the plasma becomes less sluggish and begins to respond to the relative motion of the

electron and hole. For $\omega_p \gg \omega_{ex}$ the plasma can follow the internal motion of the exciton essentially instantly resulting in the effective screening of the electron-hole coulomb interaction. Gay's calculations show, however, that the exciton energy (relative to the valence band) does not change significantly due to the large free carrier concentration. The energy of assembly of an exciton is shown to be given by

$$W(r) = V(r) + W_\infty$$

where

$$V(r) = \frac{-e^2}{\kappa r} e^{-r/\lambda}$$

$$W_\infty = \frac{-2e^2}{\kappa\pi\lambda} \tan^{-1} \frac{2\lambda(2kT\mu)^{1/2}}{\hbar} \quad 5.201$$

r is the electron-hole separation, λ the Debye screening length, and μ the reduced mass of the electron-hole pair. $V(r)$ is the Debye potential of a screened electron-hole pair (cf. Eqn. 4.505) and W_∞ is composed of clothing energies of the electron and hole. The value of $\tan^{-1} (2\lambda(2kT\mu)^{1/2}/\hbar)$ is close to $\pi/2$ such that

$$W_\infty \approx \frac{-e^2}{\kappa\lambda}$$

The change in potential energy due to a change in $V(r)$ is

given by (cf. Eqns. 4.508, 4.509)

$$\Delta E = \langle \psi | \frac{e^2}{\kappa r} (1 - e^{-r/\lambda}) | \psi \rangle \approx \frac{e^2}{\kappa \lambda}$$

It follows that any change in potential energy due to a change in $V(r)$ is cancelled by an equal but opposite change in the value of W_∞ . Hence, no change in exciton energy is observed. Gay interprets W_∞ as a decrease in the conduction band edge. It is not clear to us how this conclusion was arrived at. A band gap reduction given by Eqn. 5.201 would be remarkable and should show its effects in other optical processes. For example, Levy et al. (1972) investigated the exciton-exciton emission line (called M-line by them) in CdS as a function of excitation intensity. The M-line appears at high excitation levels and is the result of an exciton-exciton interaction in which one of the excitons scatters into the dissociation state, while the other exciton scatters into a photon-like state. The emitted photon has an energy

$$\hbar\omega \approx E - E_b = E_G - 2E_b \quad 5.202$$

where

E_G = band gap energy

E_b = exciton binding energy

$E = E_G - E_b$ = exciton energy

If E_b decreases by an amount Δ due to a high free carrier concentration then, according to Gay's paper, E_G decreases by approximately Δ as well such that E remains unchanged. From Eqn. 5.202 it is thus expected that the photon energy increases by an amount Δ . However, the peak energy of the M-line shifts towards the low energy side (~ 8 mev) of the spectrum when the excitation intensity is increased. It was noted by Levy et al. that I_2 (exciton bound to a neutral donor) and the intrinsic exciton emission energies show no appreciable shift, in agreement with Gay's analysis. The negative energy shift of the M-line was explained by Levy et al. to be due to a filling of states at the extrema of the bands by a high density of free carriers. The unbound electron-hole pairs created by exciton-exciton interaction thus require a higher energy which reduces the energy of the emitted photon. Eqn. 5.202 should then be written as

$$\hbar\omega = E_G - 2E_b - E_K^h - E_K^e$$

where E_K^h and E_K^e are the kinetic energies of the created hole and electron. A shift of ~ 8 mev requires a free carrier density of approximately 10^{18} cm^{-3} as shown by Levy et al. This example speaks against a band gap reduction due to a high free carrier density.

5.3 Conclusions

It was found experimentally that the exciton energies (both intrinsic and bound) do not change significantly as a function of excitation intensity. This agrees with observations by other workers (eg. Levy et al., 1972). A theoretical study of screening of excitons was done by Gay (1971) who was able to give a qualitative description in agreement with experimental observations. Aside from a nearly constant exciton energy (measured from the valence band), Gay also postulates a remarkable band gap reduction due to self-screening of the free carrier plasma. No direct experimental evidence is available for such a band gap reduction.

6. SUMMARY

The edge emission in CdS consists of two series of narrow bands. The higher energy series (HEB) is due to the recombination of a free electron with a hole bound at a shallow acceptor. The dependence of the peak energy of the HEB on temperature and excitation intensity was investigated in the interval 4.2 - 80°K. Agreement with predicted temperature dependence for low excitation intensities was good. The band gap variation as a function of temperature was obtained from the measured peak energy shifts of a bound exciton. An average kinetic energy of the electrons equal to kT at the instant of recombination was found to give good agreement with the measured peak energies of the HEB. An often neglected donor-acceptor interaction term was included in the discussion and found to be important especially for accurate measurements of the acceptor binding energy. The interaction term is dependent on the impurity concentrations and can explain the observed difference in the HEB peak energies for different samples. A shift to higher energies at high excitation intensities was measured for two samples from 4.2 - 80°K. No positive identification could be made of the effect causing the energy shift. A reduction in the acceptor binding energy due to screening by free carriers was discussed in some detail and found to be the most likely

cause of the observed energy shift. An energy shift due to the recombination of hot electrons was considered and could not be ruled out. In agreement with other workers it was found that exciton energies (intrinsic and bound) remain essentially constant even for large changes in excitation intensities. Screening of excitons was discussed and reference was made to a theoretical model proposed by Gay (1971).

APPENDIX A

The electronic current density at any point in a solid is given by

$$\vec{j} = \mu en\vec{\epsilon} - D\nabla n$$

where μ is the mobility of the electrons, n their concentration, D their diffusion constant and $\vec{\epsilon}$ the local electric field. A similar expression can be written for the holes. If no external field is present, $\vec{\epsilon}$ results from the presence of the ionized impurities and of the space charge. The electrostatic potential $\phi(\vec{r})$ felt by an electron far from the ionized impurities will not be simply that due to ionized impurities alone. An ionized impurity acts to polarize the electrons in its immediate vicinity; a distant electron therefore responds both to the ionized impurity and the induced space charge.

Let us consider the following model: an electron gas is moving in a neutralizing background with uniform charge density $n_0 e$. The average electron concentration is n_0 . Now introduce an additional point charge q at the origin ($r = 0$) of the electron gas. We want to show that this additional charge gives rise to a small spherically symmetric charge $\phi(r)$ in the electrostatic potential given by

$$\phi(r) = \frac{q}{\kappa r} e^{-r/\lambda}$$

where

$$\lambda = \left(\frac{\kappa kT}{4\pi e^2 n_0} \right)^{1/2}$$

The electrostatic potential $\phi(r)$ will obey Poisson's equation

$$\frac{-\kappa}{4\pi} \nabla \cdot \bar{\epsilon} = \frac{\kappa}{4\pi} \nabla^2 \phi(r) = en(r) - en_0 - q\delta(r) \quad A1$$

At equilibrium, $n(r)$ is related to $\phi(r)$ through Boltzmann's formula

$$n(r) = Ae^{e\phi(r)/kT} \quad A2$$

where the constant A is determined by

$$\int_V n(\bar{r}) d^3\bar{r} = N$$

N being the total number of electrons in the volume V . In the thermodynamic limit as the volume $V \rightarrow \infty$, $N \rightarrow \infty$ such that $N/V = n_0 = \text{constant}$. It is clear that $\phi(r) \rightarrow 0$ as $r \rightarrow \infty$. It then follows that $A = n_0$.

Substituting Boltzmann's formula (Eqn. A2) into Poisson's equation (A1) yields a nonlinear differential equation for ϕ :

$$\frac{\kappa}{4\pi} \nabla^2 \phi(r) = en_0 \left[e^{e\phi/kT} - 1 \right] - q\delta(r)$$

We can expand the exponential to first order if we assume

$$\frac{e\phi}{kT} \ll 1$$

Hence

$$\frac{\kappa}{4\pi} \nabla^2 \phi(r) - \frac{n_o e^2}{kT} \phi(r) = - q \delta(r)$$

$$\nabla^2 \phi(r) - \frac{1}{\lambda^2} \phi(r) = \frac{-4\pi q}{\kappa} \delta(r) \quad \text{A3}$$

where

$$\lambda^2 = \frac{\kappa kT}{4\pi n_o e^2}$$

It is easy to verify that the solution to equation A3 is given by

$$\phi(r) = \frac{q}{\kappa r} e^{-r/\lambda} \quad \text{A4}$$

where

$$\lambda = 6.9 \left(\frac{\kappa T}{n_o} \right)^{1/2} \text{ cm} \quad \text{A5}$$

Thus the potential around a charged impurity is a screened Coulomb potential. The constant λ , which measures the order of magnitude of the spherical region in which the electron density is increased (if q is positive), is called the Debye attenuation length (P. Debye and E. Hückel, 1923). λ is determined by the competition between the influence of the potential energy and kinetic energy on the motion of the electrons. Screening is the result of the interaction between the electrons and is opposed by their kinetic energy which represents the degree of random motion. Fig.12 shows the

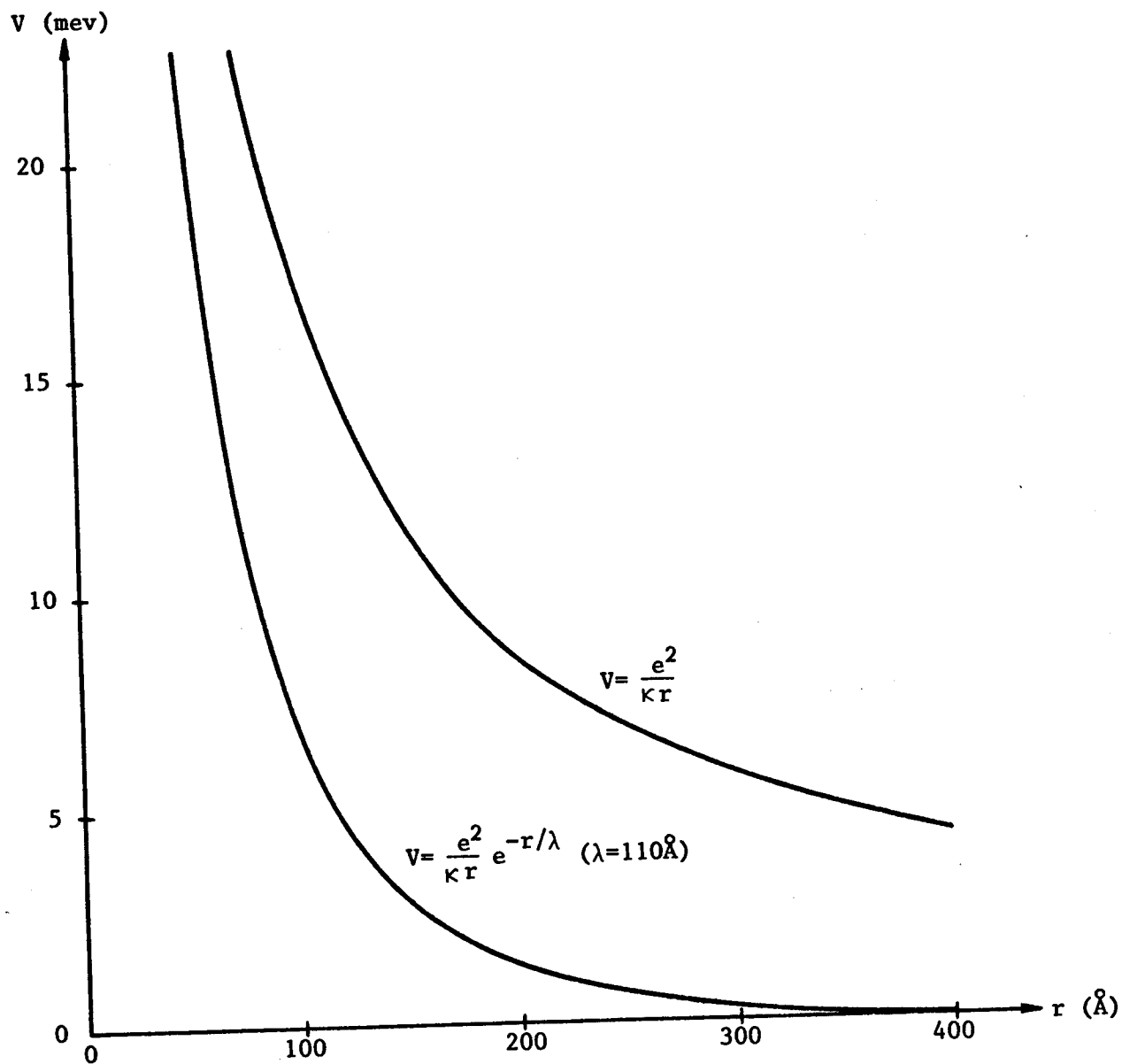


Figure 12 Debye potential as a function of r for $n=10^{16} \text{ cm}^{-3}$, $T=30^\circ\text{K}$, and $\kappa=8.46$. Also shown is the pure coulomb potential.

Coulomb potential due to a point charge with and without screening as a function of r .

It should be noted that in the above derivation it was assumed that the charge density is continuous such that $\varphi(r)$ varies slowly over an interparticle distance. This would require at least one charge in the Debye sphere, or

$$n_0 (4\pi/3)\lambda^3 > 1$$

Substituting Eqn. A5 then gives

$$n_0 < 10^6 (\kappa T)^3$$

A6

Using a random-phase approximation, Colbow and Dunn (1970) found that the Debye potential, Eqn. A4, is valid even for carrier concentrations which fall outside the classical region of validity as given by A6.

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