

## CHARACTERIZATION OF ZnSe:N USING SCREENING EFFECTS

I. KUSKOVSKY, G.F. NEUMARK

Department of Chemical Engineering, Materials Science, & Mining Engineering,  
Columbia University, New York, NY 10027.

### ABSTRACT

Photoluminescence (PL) and Hall measurements allow one to obtain important parameters of semiconductors, such as impurity concentrations, compensation, and activation energies ( $E_A$ ). Usual analyses of such data assume constant  $E_A$ . However, it is well known that  $E_A$  depends on free carrier and impurity concentrations, and thus on temperature, due to screening effects. We here analyze literature data on ZnSe:N using screening effects. An observed decrease of  $E_A$  with temperature (from PL data) had been used to suggest an interstitial site for N. With inclusion of screening, we obtained good agreement with the data, so that the idea of interstitial N is not required. In applying the screening theory to Hall measurements, we obtained lower impurity concentrations than with use of a constant  $E_A$ . It is also to be noted that we fit both optical and electrical data with this approach. We further suggest that screening is the cause of an observed difference between optically observed and thermal activation energies.

### 1. INTRODUCTION

It has long been known that dielectric screening will reduce (in absolute values) the energy levels of impurities in semiconductors [1,2]. Such screening will include both free carrier and impurity ion contributions. The free carrier contribution is treated by the standard theory [3]. Ionic screening may originate from several phenomena: a) from ionic motion until the ions become "frozen" into the lattice[2], b) from preferential ion neutralization due to preferential carrier capture at impurities surrounded by more favorable configurations of other impurities (e.g [4]), c) fluctuation of the ionic potential due to fluctuations in the random distribution of the ions (where this latter effect is important primarily for high degrees of compensation and is neglected here).

These approaches, as far as we know, have so far been applied only to materials in the dark [2,4]. In the present paper, we consider the case of optical excitation as well as the "dark" case, specifically analyzing data for a material of high interest, N doped ZnSe. We show that literature data [5] which was interpreted as showing that the N acceptor was located interstitially can, instead, be explained by screening. Moreover, we show that a well-known discrepancy between optical and thermal activation energies is very likely due, at least in part, to screening.

A further modification of past work is an improved method of evaluating results from the screened Schrodinger equation, which is valid for impurities with sufficiently small Bohr radii.

In the next section we introduce our modified solution of the Schrodinger equation. This is then applied to the case of dark carrier concentrations in ZnSe:N (Section 3a), and to the optical case in Section 3b.

### 2. THEORY

It is well known that the potential ( $U$ ) of a hydrogenic impurity in semiconductors can be described by the screened Coulomb potential [6]:

$$U = \pm \frac{e}{\epsilon r} \exp(-qr) \quad (1)$$

where  $q$  is the inverse screening length,  $\epsilon$  is the dielectric constant,  $e$  is the electron charge, and  $r$  is the spatial coordinate. Let us consider the inverse screening length, for a moment, as a parameter of the problem.

Let us define  $H_0$  as the Hamiltonian for the "infinitely dilute" system (where  $q=0$ ) (see, for example, [7]). Then the Schrödinger equation is:

$$\{H_0 + \frac{e^2}{\epsilon r} (1 - \exp[-qr])\} |\Psi(r)\rangle = E_A |\Psi(r)\rangle \quad (2)$$

where  $E_A$  is the energy in the screened case. N in ZnSe gives a relatively deep acceptor (~110-112 meV) and the Bohr radius ( $a_B$ ) is, therefore, relatively small ( $5 \sim 6 \text{ \AA}$  [8]). Thus, for all  $r$ 's where the probability of finding the hole bound to the acceptor is not vanishingly small, the product  $qr$  is much less than 1. Hence, we can expand the exponent in Eq.2 into series, keeping only the first order terms:

$$\{H_0 + \frac{e^2}{\epsilon} q\} |\Psi(r)\rangle = E_A |\Psi(r)\rangle \quad (3)$$

After bringing the second term on the right side to the left side, Eq.3 will have the form of the "infinitely dilute" Schrödinger equation, so that the ground state energy can be written as:

$$E_A(T) = E_{A0} - \frac{e^2}{\epsilon} q(T) \quad (4)$$

where  $E_{A0}$  is the activation energy without screening. It should be noted that this formulation includes the temperature dependence of the activation energy, since  $q$  is temperature dependent.

### 3a. DISCUSSION OF ELECTRICAL DATA

As an example of electrical measurements, we have analyzed literature data [9,10] of free hole concentrations ( $p$ ), obtained by Hall measurements. We have fitted the experimental data to the standard formula (e.g. Ref.2)

$$p = -0.5(N_D + p_1) + 0.5\sqrt{(N_D + p_1)^2 + 4(N_A - N_D)p_1} \quad (5)$$

where  $N_D$  - donor concentration,  $N_A$  - acceptor concentration, and

$$p_1 = \frac{N_v}{g} \exp[-E_A(T)/k_B T] \quad (6)$$

Here,  $N_v$  - effective density of states,  $g$  - degeneracy factor, and  $E_A(T)$  is calculated self-consistently by using Eq.4. Donor and acceptor concentrations were used as fitting parameters. To use Eq.4 we have to determine the inverse screening length ( $q$ ). To account for the ion contribution to the screening we have employed here Brooks-Herring approach [11] (see Eq.7 in Ref.12), which incorporates preferential ion neutralization. In general there are several ways to include the effect of ions, but we have utilized the Brooks-Herring approach since it is conventionally used for mobility calculations. Figs.1 and 2 show the results of the fitting, where  $g=4$ , and the effective mass  $m^* = (m_l^{3/2} + m_h^{3/2})^{2/3}$ , with  $m_l = 0.15m_0$  and  $m_h = 0.78m_0$  [13]. Table I compares our values of  $N_A$  and  $N_D$  with those obtained by the “conventional” approach of using a constant  $E_A$  as a parameter in the fitting procedure. As expected, results for a lightly doped sample [10] do not differ very much, while for a relatively higher doped sample [9] there is a clear difference; larger differences would be expected for still heavier doping (we found no appropriate data for heavier doping).

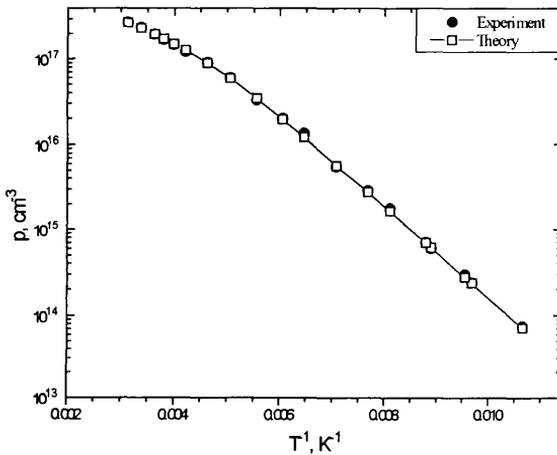


Fig. 1. Fit of data of hole concentration [9] calculated using screening.

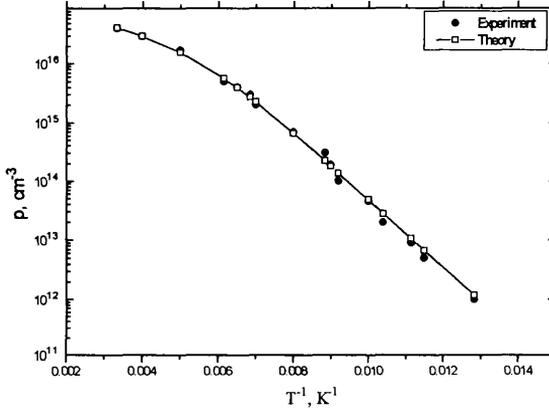


Fig.2. Fit of data of hole concentration [10] calculated using screening.

Table I.  
Electrical properties of ZnSe:N

	$N_A$ ( $10^{17} \text{ cm}^{-3}$ )	$N_D$ ( $10^{16} \text{ cm}^{-3}$ )	$N_A - N_D$ ( $10^{17} \text{ cm}^{-3}$ )	$E_{A0}$ (meV)	$E_A(\text{RT})$ (meV)
Ref.[9]	9.54	10.10	8.53	92*	92*
This work	6.80	7.10	6.09	112	81.5
Ref.[10]	0.776	0.692	0.707	106*	106*
This work	0.670	0.650	0.650	112	99.8

\*) Constant as a function of temperature.

### 3b. DISCUSSION OF OPTICAL EXPERIMENTS

The case of optical excitation is somewhat different from that of the “dark” electrical case. Of course the free carriers will again contribute to the screening. However, the ionic contribution due to preferential neutralization is a consequence of thermal equilibrium, and would not be expected from optical excitation, where carrier capture is likely to be determined by kinetic factors. In this instance, any ion distribution is now equally probable. Thus in the optical calculations we will use the inverse screening length due to only free carriers [6]. For the free carrier concentration, we use the values measured in the dark, i.e. we assume that the photo-generated concentration is relatively small.

As an example, we again consider ZnSe:N. One method to determine  $E_A$  optically is via “free-to-bound” transitions, with the free electron-to-acceptor transition (FA) used in p-type semiconductors. A substantial decrease of  $E_A$  (up to 30 meV) was reported for ZnSe:N in [5], and we have observed similar results in one of our samples. It can be noted that in much of the literature this type of analysis for  $E_A(T)$  has not been done, but shifts, although smaller than the above examples, can often be seen. However in the case of small shifts in activation energy, the FA transition is observed only over a relatively small temperature range; large shifts are observed only at relatively high temperatures, where the (dark) carrier concentration is high enough to produce an appreciable decrease in the energy.

It can be added that small shifts in energy would probably not be noticeable for relatively shallow impurities, where the Mott transition occurs at low carrier concentrations; due to the deep acceptor in ZnSe:N, shifts can be observed up to high carrier concentrations prior to the onset of this transition.

Using Eq.4 and the electrical (dark) carrier concentration of Ref.14, we plotted the calculated activation energy vs. the experimental data, which is shown in Fig.3; we used the same  $E_{AO}$  (112 meV) in this calculation as in the electrical case.

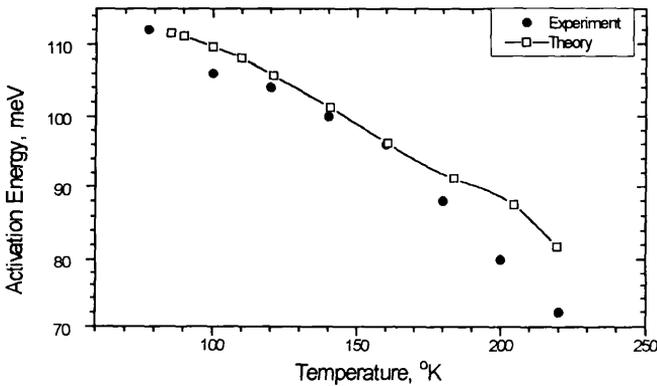


Fig.3. Calculated acceptor activation energy (Eq.4) plotted vs. the experimental data [5]

As one can see, at higher temperatures the experiment shows a larger shift in the activation energy as compared to the screening theory. We attribute this to the contributions from excited states and/or an increased phonon coupling, which are neglected in our treatment.

#### 4. CONCLUSIONS

Consideration of screening in ZnSe has led us to a better understanding of two important phenomena:

1) An observed decrease, with increasing temperature, of the activation energy of the N acceptor in ZnSe, which had earlier been attributed to an interstitial location of N [5]. The authors of Ref.5 argued that substitutional impurities would not show a temperature dependent activation energy. However, as we have shown, this is not correct if one includes screening. Moreover, Ref.15 gives strong evidence “that the incorporated N atoms are located at the substitutional sites”. In addition we know of no theoretical evidence that an interstitial location, by itself, would lead to a temperature dependent activation energy. On the other hand, screening effects allow us to explain such a temperature dependence straightforwardly, with nitrogen on the “standard” substitutional site.

2) The activation energies obtained by electrical measurements (via a fit to the data) and by optical means usually differ. This has not had an adequate explanation. We suggest that correct account of screening effects can give an understanding of this phenomenon. As we saw, it is possible to use the same “unscreened” activation energy for both types of experiments.

Thus, screening effects cannot be ignored in characterization of semiconductors.

## ACKNOWLEDGMENTS

We gratefully acknowledge support from NSF, Grant DMR 91-21302, and from ARPA/ONR, Grant N-00014-92-J-1895.

## REFERENCES.

1. J.B. Krieger, Phys. Rev., **178**, 1337 (1969)
2. G.F. Neumark, Phys. Rev. B, **5**, 408 (1972)
3. J.M. Ziman, Principals of the Theory of Solids, 2nd ed. (Cambridge University Press, 1972).
4. G.F. Neumark, J. Appl. Phys., **48**, 3618 (1977).
5. K.A. Bowers, Z. Yu, K.J. Gossett, J.W. Cook, Jr., and J.F. Schetzina, J. Elect. Mat., **23**, 251 (1994).
6. R.B. Dingel. Phil. Mag., **46**, 831 (1955).
7. A. Baldareschi, N.O. Lipari, Phys. Rev. B, **8**, 2697 (1973).
8. G.-J. Yi and G.F. Neumark, Phys. Rev. B, **48**, 17043 (1993).
9. J. Han, Y. Fan, M.D. Ringle, L. He, D.C. Grillo, R.L. Gunshor, G.C.Hua, and N. Otsuka, J. Crystal Growth, **138**, 464 (1994).
10. Y. Fan, J. Han, L. He, R.L. Gunshor, M. Hagerott, and A.V. Nurmikko, J. Elect. Mat., **23**, 245 (1994)
11. H. Brooks, in Advances in Electronic and Electron Physics, **7**, (Academic Press, New York, 1955), p. 156.
12. G.F. Neumark and D.K. Schroder, J. Appl. Phys., **52**, 855 (1981).
13. D. Kranzer, Phys. Status Solidi A, **26**, 11 (1974).
14. J.F. Schetzina, private communication.
15. T. Yao, T. Matsumoto, S. Sasaki, C.K. Chung, Z. Zhu. F. Nishiyama, J. Crystal Growth, **138**, 290, (1994).