Pair spectra and evaluation of the dielectric constant:
Application to ZnSe

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(Received 19 September 1983)

Discrete pair luminescence lines have frequently been used to estimate the low-frequency dielectric constant and/or the sum of donor and acceptor energies. However, *accurate* values of these parameters have not usually been obtained by this method. I show that a linear regression analysis together with quantum-mechanical corrections is able to give such accurate values. The technique is illustrated for ZnSe (In,Li) with use of literature data; the results give $\epsilon_0 = 8.84$.

The low-frequency dielectric constant ( ) is a parameter useful in characterizing various semiconductor properties. It is thus unfortunate that it still is not accurately known for some relatively well-studied materials. An example here is ZnSe, with some recent values[1-3] (since 1976) ranging from 8.8 to 9.4 (at 4.2 K). One method for obtaining this dielectric constant, and indeed the one used by Kartheuser, Evrard, and Williams[2] (henceforth referred to as KEW), to obtain the 9.4 value is via analysis of the luminescence of individual pair lines. Use of this method can be easily understood by considering the well-known relation, valid at large separation between a donor and its nearest acceptor (the pair), that[4]

$$h\nu(R) = h\nu^\infty + e^2/\epsilon_0 R \quad , \tag{1a}$$

$$h\nu^\infty = E_g - (E_D + E_A) \quad . \tag{1b}$$

Here, R is the separation between the pair, $h\nu$ is the frequency emitted by a pair at a separation R, $h\nu^\infty$ is that at $R = \infty$, E_g is the band gap, E_D and E_A are the donor and acceptor energies, respectively, and e is the electron charge. A curve fit can thus give ϵ_0 and, in addition, also $h\nu^\infty$. The problem with the application of Eqs. (1) to actual systems is that sharp discrete pair lines, giving accurate values of $h\nu(R)$, are not generally observed at large R, where Eq. (1a) is valid. In the large R range pair lines are close together and thus observed spectra tend to be broad.

One possible method of using Eqs. (1) was suggested by Vink, van der Heyden, and van der Does de Bye,[5] who carried out a computer analysis for broadened lines to extend the fit to larger R. Here, from the results of Vink *et al.*,[5] it appears that for good results Eq. (1a) can be used only provided $R \gtrsim 1.5a_B$, where a_B is the Bohr radius of the shallower impurity.

An alternate approach to use of Eq. (1a) and, in principle, a very elegant one, has recently been proposed by KEW; it consists of a linear regression analysis of $h\nu(R)$ vs $1/R$ at lower R, using sharp line spectra. KEW carry out this linear regression analysis in the range where the plot gives a straight line of $h\nu$ vs $1/R$, and assume that since the functional dependence is here that of Eq. (1a) this equation is therefore valid in this range. However, checking their[2] detailed analysis of Merz's line data for ZnSe (In,Li), one can see that the criterion of Vink *et al.*[5] is now not fulfilled: The highest available[6] value for the pair separation (R_{max}) was $\cong 45$ Å, and the fit was done from there down to 30 Å; however, quantum calculations[2] give $a_B \cong 28$ Å, i.e., over

most of the fitting range $R \lesssim 1.5a_B$. Moreover, KEW's values for $(E_D + E_A)$ and for ϵ_0 were not in good agreement with other literature values, as shown in Table I.

Since this linear regression analysis seems to be a very nice technique, but since there nevertheless appear to be discrepancies, I decided to reinvestigate this problem. In principle, Eq. (1a) can be applied at any value of R by using the form

$$h\nu(R) = h\nu^\infty + e^2/\epsilon_0 R - \Delta E(R) \quad , \tag{2}$$

where ΔE is a correction term due to the donor-acceptor interaction at close R. Here, ΔE is often unknown or poorly known. I will revert to estimation of ΔE shortly, but first I wish to make an important point: if at relatively large R, but not yet large enough for Eq. (1a) to be satisfactory, ΔE varies approximately as

$$\Delta E \cong a + b(1/R) \quad , \tag{3}$$

then a plot of $h\nu$ vs $1/R$ will give a straight line, but a fit to this line will give values for $E_D + E_A + a$ and $(e^2/\epsilon_0) + b$, *not* values for $E_D + E_A$ and e^2/ϵ_0. Moreover, over a limited range any function can be approximated linearly (e.g., via a Taylor series).

As regards evaluation of ΔE, energies for donor-acceptor pairs ($\equiv E_p$) can be estimated quantum mechanically. These energies will determine[2,4] the emitted frequencies $h\nu$. Here, similarly to Eq. (2), one can express the E_p's as the energies of the isolated pair, i.e., at $R = \infty$ ($\equiv E_p^\infty$) and a

TABLE I. Values of $h\nu^\infty$ for (In,Li) and of ϵ_0.

	$h\nu^\infty = E_g - (E_D + E_A)$	ϵ_0
Present analysis	2.680 eV	8.8
KEW analysis	2.682 eV	9.4
Other recent literature data	2.680[a] eV	8.8[b] 9.1[c]

[a]Using $E_g = 2.822$ (Ref. 3), $E_D = 0.028$ eV (Ref. 3), and $E_A = 0.114$ eV (Ref. 10).
[b]Reference 1.
[c]Reference 3.

correction term ΔE_p. Thus

$$E_p = E_p^\infty - \Delta E_p \quad . \tag{4}$$

Note that for an exact calculation E_p^∞ is the sum of the donor and acceptor energies, i.e., $(E_p^\infty)_{\text{exact}} = E_D + E_A$. I now assume that as long as this condition is approximately valid, i.e.,

$$E_p^\infty \cong E_D + E_A \quad , \tag{5}$$

then one has the corresponding relation

$$\Delta E \cong \Delta E_p \quad . \tag{6}$$

Values of E_p for ZnSe have, for instance, been obtained by KEW up to $R = 35$ Å with use of both s and p functions as impurity envelope functions in a variational treatment. Values at higher R can be estimated with use of s functions only (Appendix), and this gives $E_p^\infty = 0.1427$ eV.

Specifically, one desires[7] values for $\Delta E(R)$ in the range where $h\nu$ is linear in $1/R$, i.e., from 30 Å, the beginning of this range,[2] up to 45 Å, at which point Merz[6] was no longer able to identify sharp lines. To obtain the values in this range, I used an exponential curve fit (a good approximation) to the three highest R theoretical points of KEW: $\Delta E_p(35 \text{ Å}) = 0.0007$ eV, $\Delta E_p(30 \text{ Å}) = 0.0013$ eV, and $\Delta E_p(25 \text{ Å}) = 0.0026$ eV. The result was

$$\Delta E_p = 6.823 \times 10^{-2} \exp(-0.1312R) \quad . \tag{7}$$

As the concluding step I used a linear regression analysis, by use[8] of Eqs. (2), (6), and (7), on the resultant equation

$$(h\nu + \Delta E_p) = h\nu^\infty + e^2/\epsilon_0 R \quad , \tag{8}$$

with $R = (m/2)^{1/2} a_0$, where m is the shell number and a_0 is the lattice constant (e.g., Ref. 4). The quantities $h\nu$ and m are given by Merz,[6] and $a_0 = 5.6676$ Å (Ref. 9). The results were $h\nu^\infty = 2.6801$ eV and $\epsilon_0 = 8.836$. As shown in Table I, these values are in excellent agreement with independent literature determinations, far better than the results obtained by KEW. The coefficient of determination (r^2) given by the present analysis is 0.99985, i.e., a line gives a very good fit (r^2 for the KEW approach was 1.00015).

In summary, the present work shows that, provided sharp line pair spectra are available over a sufficient range, one can obtain good values of the low-frequency dielectric constant and of $h\nu^\infty$. This can be done by a linear regression analysis of corrected values of $h\nu$ vs $1/R$, where the correction to $h\nu$ is calculated via quantum mechanics; with reasonably good quantum calculations, even if the total energies are not fully satisfactory, corrections[7] to E_p^∞ are apparently of sufficient accuracy.

ACKNOWLEDGMENTS

APPENDIX

For the present analysis of the data of Merz,[6] one requires the energy corrections up to $R = 45$ Å, whereas KEW give the pair energy only up to $R = 35$ Å. However, at large pair separations the donor and acceptor will each act as an *isolated* hydrogenic impurity, so there is no need to include p functions. This simplifies the required calculations. I have determined, using only s functions, that for $R > 70$ Å the resultant sum $(E_D + E_A)$ is 0.1427 eV, and remains constant to 0.0001 eV at larger R. This is the basis for the value of E_p^∞ which I have used.

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[1]I. Strzalkowski, S. Joshi, and C. R. Crowell, Appl. Phys. Lett. **28**, 350 (1976).

[2]E. Kartheuser, R. Evrard, and F. Williams, Phys. Rev. B **21**, 648 (1980).

[3]P. J. Dean, D. C. Herbert, C. J. Werkhoven, B. J. Fitzpatrick, and R. N. Bhargava, Phys. Rev. B **23**, 4888 (1981).

[4]For a review see, for example, P. J. Dean, in *Progress in Solid State Chemistry*, edited by J. O. McCaldin and G. Somorjai (Pergamon, New York, 1973), Vol. 8, p. 1, or F. Williams, Phys. Status Solidi **25**, 493 (1968).

[5]A. T. Vink, R. L. A. van der Heyden, and J. A. W. van der Does de Bye, J. Lumin. **8**, 105 (1973).

[6]J. L. Merz, Phys. Rev. B **9**, 4593 (1974).

[7]In principle, if sufficiently accurate values of E_p were available, one should be able to correct $h\nu$ also in the lower R range, where the uncorrected plot of $h\nu$ vs $1/R$ is not linear. However, the magnitude of the correction (ΔE_p) increases with decreasing R, and I feel such corrections are more reliable where they are smaller, i.e., at larger R.

[8]It should be noted that the quantum results (the E_p's) were obtained with $\epsilon_0 = 9.4$, which has now been shown to be incorrect. Nevertheless, I assume that Eq. (6) holds sufficiently well, since Eq. (5) applies with $E_p^\infty = 0.143$ eV and $E_D + E_A = 0.142$ eV (Table I). For $\epsilon_0 = 8.8$, the present value, Eq. (5), holds less well, since $E_p^\infty = 0.155$ eV for this case.

[9]R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Interscience, New York, 1963), Vol. 1.

[10]H. Tews, H. Venghaus, and P. J. Dean, Phys. Rev. B **19**, 5178 (1979).