

LETTER TO THE EDITOR

Determination of deep donor binding energies from their g values

O F Schirmer† and M Scheffler‡

† Fraunhofer Institut für Angewandte Festkörperphysik, Eckerstrasse 4, D-7800 Freiburg, Federal Republic of Germany

‡ Physikalisch-Technische Bundesanstalt, Bundesallee 100, D-3300 Braunschweig, Federal Republic of Germany

Received 4 May 1982

Abstract. The g values of simple deep donors in semiconductors tend to decrease with their binding energies. The theoretical background of this rule is discussed. Relevant experimental data for donors in Si and GaP are considered in the light of these results, and the deep level energy of a substitutional sulphur pair in Si is inferred from its g value.

The g values of conduction electrons in semiconductors can be calculated (Roth 1960) using the effective mass approximation. The same approach also holds for shallow donors because their bound states are derived from the Bloch states of the nearest conduction band minima. Deep centres, on the other hand, couple to both conduction and valence band(s). Therefore other approaches are needed to explain measured g values. If such a deep centre has a non-degenerate ground state, the problem can be handled on the basis of the perturbation treatment outlined by Pryce (1950). In this way Watkins and Corbett (1961, 1964) were able to account for the g tensor elements of two defects in irradiated silicon. For paramagnetic centres of tetrahedral symmetry consisting of group IV ions in several II–VI compounds, Watanabe (1966) and Iida (1972) have studied the dependence of the g values on the host lattice composition. They demonstrated that g increases with the strength of spin–orbit interaction at the ions neighbouring the impurity.

Below we shall deal with the g values of several simple deep donors in one host crystal. It is shown that their g values tend to decrease with their binding energies, E_D . In the first part of this communication we discuss the theoretical background of this result. It is based to a great extent on the properties of the deep level wavefunction at the first ligands surrounding the defect ion. A simple rule for the dependence of g on E_D is then derived, which can be used to predict the binding energy of a deep centre from its g value. In particular we discuss the sulphur pair in Si and simple Ga site donors in GaP in the light of these results.

The single-particle Hamiltonian for a defect in an otherwise periodic crystal is given by

$$H = p^2/2m + V(r) + V_{so} \cdot s + \beta B(l + g_0 s). \quad (1)$$

p is the momentum operator, m is the electron mass and $V(r)$ is the self-consistent electrostatic and exchange–correlation potential due to all nuclei and all electrons (see e.g. Jaros 1980, Scheffler 1982). The third term in equation (1) describes the spin–orbit interaction with $V_{so} = \beta/mc(\mathbf{E} \times \mathbf{p})$. Because the electric field \mathbf{E} appears in V_{so} , this interaction is weighted most strongly near the ion cores where the potential gradients are large. Spin–orbit matrix elements thus generally reduce to atomic ones, and contributions from the regions between the ions can be neglected. The fourth term in equation (1) is the interaction of the electron magnetic moment due to orbital angular momentum with respect to the centre of the defect \mathbf{l} and the spin angular momentum \mathbf{s} with an external magnetic field \mathbf{B} . (β is the Bohr magneton and g_0 is the free electron g value.) Second-order perturbation theory then yields (Pryce 1950):

$$g_i = g_i - g_0 = \sum_{|n\rangle \neq \Psi_D} \frac{2\langle \Psi_D | V_{so,i} | n \rangle \langle n | l_i | \Psi_D \rangle}{E_D - E_n} \quad (2a)$$

$$= 2 \sum_{VB} \frac{\langle \Psi_D | V_{so,i} | n \rangle \langle n | l_i | \Psi_D \rangle}{E_D - E_n} - 2 \sum_{CB} \frac{\langle \Psi_D | V_{so,i} | n \rangle \langle n | l_i | \Psi_D \rangle}{E_n - E_D}. \quad (2b)$$

Here the g tensor is already transformed to diagonal form, where the index i stands for the coordinates x, y, z . The sum goes over all eigenfunctions of $\mathbf{p}^2/2m + V(r)$ without the wavefunction of the deep level Ψ_D at energy E_D . In equation (2b) we have split the sum into two pieces: the first one covers the states below E_D (the valence band) and the second one covers those above E_D (the conduction band). It is seen that the net result is a competition between both influences (see also Watkins and Corbett 1961, 1964). The sums in equations (2b) converge rapidly when the energy difference $E_D - E_n$ increases, because the radial parts of the states $|n\rangle$ expanded around the various nuclei become orthogonal to that of Ψ_D with increasing energy difference $E_D - E_n$. Therefore these sums can be terminated to a finite energy range, ΔE , which allows us to use the mean value theorem:

$$2 \sum_{VB} \frac{\langle \Psi_D | V_{so,i} | n \rangle \langle n | l_i | \Psi_D \rangle}{E_n - E_D} = 2\rho(E_v + \varepsilon_v) \frac{\langle \Psi_D | V_{so,i} | n \rangle \langle n | l_i | \Psi_D \rangle}{E_D - E_v - \varepsilon_v} \Delta E = \frac{A}{E_D - E_v - \varepsilon_v} \quad (3a)$$

$$2 \sum_{CB} \frac{\langle \Psi_D | V_{so,i} | n \rangle \langle n | l_i | \Psi_D \rangle}{E_n - E_D} = 2\rho(E_c + \varepsilon_c) \frac{\langle \Psi_D | V_{so,i} | n \rangle \langle n | l_i | \Psi_D \rangle}{E_c - \varepsilon_c - E_D} \Delta E = \frac{B}{E_c + \varepsilon_c - E_D}. \quad (3b)$$

Here, $\rho(E)$ is the density of states.

The general structure of the expression for Δg is thus

$$\Delta g = \frac{A}{E_D - E_v - \varepsilon_v} - \frac{B}{E_c + \varepsilon_c + E_D}. \quad (4)$$

The mean value energies are expressed as $E_v + \varepsilon_v$ and $E_c + \varepsilon_c$ respectively, where E_v and E_c define the band edges. Equation (4) should be useful for deep donors, because for these the four parameters A, B, ε_v and ε_c are expected to be rather independent of the impurity. This is a consequence of the antibonding nature of the deep level wavefunction which implies that it is largely host-like or, more precisely, vacancy-like (Hjalmarson *et al* 1980). An estimate of the parameters entering equation (4) can be obtained

from a cluster model, as outlined by Watanabe (1966) and Iida (1972) for the calculation of g values of tetrahedrally symmetric centres with A_1 ground states in II–VI compounds. Using a cluster of four neighbours surrounding the donor ion, their formulation of equation (2) is:

$$\Delta g = \frac{1}{3}N^2(\zeta/\delta E)(\lambda_o^2 - \lambda_s RM). \quad (5)$$

Here N is the normalisation of the deep level wavefunction and λ_o and λ_s are the fractions of its p and s orbitals at the first ligands surrounding the impurity. ζ is the spin–orbit coupling constant at these ligands. The last term in equation (5) takes into account that the angular momentum matrix elements have to be taken with respect to the symmetry centre of the defect (Watanabe 1966). We shall see below that this term can be neglected, e.g. in the application to deep donors in Si. Because of spin–orbit selection rules in tetrahedral symmetry, this interaction admixes only T_1 states to the A_1 donor ground state. In deriving equation (5) Watanabe and Iida have restricted their attention to admixture of only one such T_1 state, separated from A_1 by δE . It is made up of p states at the first ligands of the impurity, bonding these to their next neighbours, and thus corresponds to valence states in a band picture. Equation (5) therefore has to be compared to the first half of equation (4), yielding $A = \frac{1}{3}N^2\zeta(\lambda_o^2 - \lambda_s RM)$ and $E = E_D - E_v - \varepsilon_v$. No arguments were given by Watanabe and Iida as to why coupling to conduction states was not taken into account. On the basis of the derivation given about it is seen that such contributions can be important. In fact, for a purely covalent semiconductor, such as Si, the valence and conduction bands are built from the same wavefunctions and consequently the parameters A and B should then become identical.

No influence of the central impurity ion of the defect appears in equation (5). This is due to the fact that for the examples discussed in this paper the wavefunctions have s character at the defect sites and thus there is negligible contribution of spin–orbit coupling from these regions.

Orbitals beyond those of the first ligands were not considered in the derivation of equation (5). As will be shown in more detail below, this is also a justified assumption for deep donors in silicon, where most of the spin density is confined to within the first shell surrounding the impurity.

Figure 1 shows the relationship between g values and binding energies of all presently known simple deep donors in Si. Using the experimental data for Se^+ and Te^+ to obtain values for A and B in equation (4), we see that this relation, represented by the straight line in figure 1, roughly reproduces the experimental data of all such centres in Si. As expected from the covalency of Si (see above) the values for A and B , yielding the fit shown in figure 1, are nearly the same: $A = 0.037$ eV and $B = 0.034$ eV. In applying equation (4), $\varepsilon_c = 1.5$ eV and $\varepsilon_v = 1.0$ eV have been used. Watkins and Corbett (1961, 1964) have assumed a stronger coupling to valence than to conduction states. However, we tend to ascribe the smaller influence of conduction states to be due to the larger corresponding energy denominators. Our values of ε_v and ε_c appear to be reasonable because of the following argument: spin–orbit coupling will only admix band components having T_1 symmetry. Band structure calculations for bulk silicon show that the corresponding projected T_1 density of states rises sharply from the valence band edge, whereas it increases more gently to a maximum at about 1.5 eV for conduction states in silicon.

The cluster model described above can be used to obtain rough estimates for A and B . From ENDOR investigations on Si:S^+ (Ludwig 1965) it is known (Grimmeiss *et al* 1981) that the donor ground state has nearly exclusively Si-3p character at the first ligands of S^+ . This justifies neglecting the term proportional to λ_s in equation (5). From

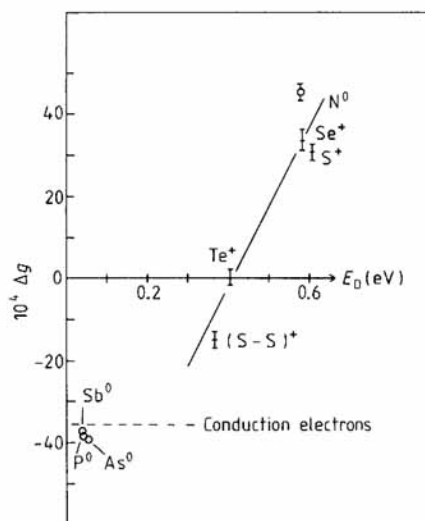


Figure 1. Zeeman splitting factors g of simple deep donors in silicon against their ground state binding energies E_D . The shown fit to the data is based on arguments described in the text. $\Delta g = g - 2.0023$. Resonance (r) and energy (e) data were taken from the following references: N^0 Brower (1980) (r (the average of the g tensor diagonal is shown), b); S^+ Ludwig (1965) (r); Krag *et al* (1968) (e); Se^+ Grimmeiss *et al* (1981) (r); Swartz *et al* (1980) (e); Te^+ Grimmeiss *et al* (1981) (r, e). For $(S-S)^+$, see text.

these measurements (Ludwig 1965) it is further derived (Grimmeiss *et al* 1981) that the probability of finding the donor electron near the first ligand ions, corresponding to $N^2\lambda_D^2$, is about 50%. The preponderance of the Si-3p character over Si-3s in the S^+ donor ground state and the degree of localisation of this wavefunction at the first ligands is also correctly predicted by a self-consistent Green's function calculation of the properties of this donor (Bernholm *et al* 1981 and to be published). Using $\zeta = 0.03$ eV (Watkins and Corbett 1961, 1964), equation (5) then leads to $A = 0.02$ eV. This compares favourably with the values of A and B as determined from the experiment. The remaining discrepancy might be attributed to contributions from the donor ground-state wavefunctions from beyond the first shell.

Using an empirical tight-binding calculation, Shang Yuan Ren *et al* (1982) demonstrated that the deep-level wavefunctions for all the chalcogen donors in silicon are rather independent of the particular centre. Because deep defects generally have the tendency to be vacancy-like (Hjalmarson *et al* 1980), this 'universality' is expected to hold also for the other deep centres contained in figure 1. This is reflected by the fact that the g values of all these donors can be described by the same parameters in equation (4).

Therefore the empirical rule implied by figure 1 can be used to infer the ground-state energy of a deep donor, if its g value is known. We like to apply this rule tentatively to the singly positive state of the sulphur pair in silicon (Ludwig 1965). It should be noted, however, that the application to this situation is only approximately valid, since the deep level wavefunction entering the matrix elements in equation (3) is now somewhat modified, if compared to the other centres in figure 1, having tetrahedral symmetry. The ESR of the singly positive state of the sulphur pair, $(S-S)^+$, is found at $g = 2.0008$ (Ludwig 1965). From figure 1 a ground-state energy of ~ 0.34 eV is thus predicted. This

value is close to the 0.37 eV deduced by Krag *et al* (1968) from optical absorption of a sulphur related centre in silicon, having lower than tetrahedral symmetry. We therefore tend to ascribe this absorption and the corresponding energy level to $(S-S)^+$. This is in line with conclusions deduced by Camphausen *et al* (1970) and by Brotherton *et al* (1981) from Hall effect and DLTS investigations†. Apparently the electronic structure of such a pair of equivalent donor ions is such that the above reasoning can also be applied here.

As a further example where the above reasoning can be used, we mention the deep Ga site donors in GaP. From the trend described above we predict that the three donors Ge_{Ga}^0 , P_{Ga}^+ and C_{Ga}^0 should have increasing g values. This is in fact known for the first two. The g values of these centres are 2.000 (Mehran *et al* 1972) and 2.007 (Kaufmann *et al* 1981), and their binding energies are found to be 0.2 eV (Mehran *et al* 1972) and 1.1 eV (Kaufmann *et al* 1981) respectively. The single donor C_{Ga} , however, has not yet been identified experimentally. But if we follow the suggestion (Scheffler *et al* 1981) that the ESR in electron-irradiated GaP at $g = 2.016$ (Kennedy and Wilsey 1978) may be due to C_{Ga}^0 we predict a deep level binding energy in the lower half of the gap. This is in fact consistent with the theoretical prediction of this centre.

The validity of equation (4) breaks down for shallow impurities (see figure 1; P^0 , As^0 , Sb^0) and thus the poles of equation (4) lying in the neighbouring bands are not harmful. This restriction of equation (4) to deep centres is due to the fact that the wavefunctions of shallow levels become more and more delocalised with decreasing binding energy. Then the coefficients A and B become energy dependent, and equation (4) is not applicable any more. Because of the large extension of their wavefunctions, the g values of shallow donors are nearly equal to those of conduction electrons. It should be remarked that for the case of shallow donors or free electrons in silicon or other semiconductors the valence band contributions generally lead to a negative Δg . The relevant theory of Roth (1960) shows that in this case the admixture of valence band states occurs to one order higher than in the present approach, leading essentially to squared energy denominators in the perturbation treatment. Therefore the sign of these denominators, so important in the present case, loses its significance.

Physically, the transition from a shallow to a deep donor means a contraction of the wavefunction, leading to rather steep gradients of its amplitude at, e.g., the first ligands of the impurity and consequently to a non-tetrahedral charge distribution around these sites (see, e.g., Scheffler 1982). Because of this asymmetry, corresponding to large local p -character, spin-orbit coupling can admix excited p -states in first order, leading to a perturbed state having a finite expectation value of the angular momentum components l_i , and consequently of Δg_i . Shallow donor states, on the other hand, are derived from conduction states, which by symmetry (Roth 1960) can lead to contributions to Δg only by double admixture of valence states via $k \cdot p$ perturbation.

We thank M Krystek for helpful discussions and J Schneider for comments on the manuscript.

References

Bernholc J, Lipari N O, Pantelides S T and Scheffler M 1981 *Inst. Phys. Conf. Ser.* **59** 1

† Since the first and second ionisation energies of deep double donors in silicon are generally found to have approximately the ratio 1:2 (Grimmeiss *et al* 1981), it is likely that the level reported at 0.187 eV by Krag *et al* (1968) should be attributed to $(S-S)^0$ (see also Camphausen *et al* 1970 and Brotherton *et al* 1981).

- Brotherton S D, King M J and Parker G J 1981 *J. Appl. Phys.* **52** 4649
- Brower K L 1980 *Phys. Rev. Lett.* **44** 1627
- Camphausen D L, James H M and Sladek R J 1970 *Phys. Rev.* **B2** 1899
- Grimmeiss H G, Janzén E, Ennen H, Schirmer O F, Schneider J, Wörner R, Holm C, Sirtl E and Wagner P 1981 *Phys. Rev.* **B24** 4571
- Hjalmarson H P, Vogl P, Wolford D J and Dow J D 1980 *Phys. Rev. Lett.* **44** 810
- Ho L T and Ramdas A K 1972 *Phys. Rev.* **B5** 462
- Iida T 1972 *J. Phys. Chem. Solids* **33** 1423
- Jaros M 1980 *Adv. Phys.* **29** 409
- Kaufmann U, Schneider J, Wörner R, Kennedy T A and Wilsey N D 1981 *J. Phys. C: Solid State Phys.* **14** L951
- Kennedy T A and Wilsey N D 1978 *Phys. Rev. Lett.* **41** 1977
- Krag W E, Kleiner W H, Zeiger H J and Fischler S 1968 *J. Phys. Soc. Japan* **21** suppl 230
- Ludwig G W 1965 *Phys. Rev.* **137** A1520
- Mehran F, Morgan T N, Title R S and Blum S E 1972 *Solid State Commun.* **11** 661
- Pryce M H L 1950 *Proc. Phys. Soc.* **A63** 25
- Roth L M 1960 *Phys. Rev.* **118** 1534
- Scheffler M 1982 *Festkörperprobleme XXII* to be published
- Scheffler M, Pantelides S T, Lipari N O and Bernholc J 1981 *Phys. Rev. Lett.* **47** 413
- Shang Yuan Ren, Wei Min Hu, Sankey O F and Dow J D 1982 to be published
- Swartz J C, Lemmon D H and Thomas R N 1980 *Solid State Commun.* **36** 331
- Watanabe H 1966 *Phys. Rev.* **149** 402
- Watkins G D and Corbett J W 1961 *Phys. Rev.* **121** 1001
- 1964 *Phys. Rev.* **134** A1359