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Even-Parity Levels of Donors in Si†

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Fifteen excited "even-parity" levels of donor impurities in Si are identified. Observed photoexcitation to these levels in violation of electric-dipole selection rules is attributed to effects of polarization of the donor by other defects and to breakdown of the effective-mass approximation.

In this Letter we identify fifteen peaks in the absorption spectra of seven donor centers in Si with (transitions to) levels having even parity in the effective-mass approximation (EMA).[1] The binding energies of these levels,[2-11] as well as two excited and seven ground even-parity levels previously identified,[3-10] are given in Table I,[12-15] together with corresponding binding energies[16] calculated[12] in the EMA. Figure 1 shows these levels graphically in relation to nearby p levels.[2-12] We have typically identified an observed level with the nearest effective-mass (EM) level, a procedure which can be carried out with little ambiguity and which can be justified by the fol-

Table I. Observed and EM binding energies (in MeV) of some even-parity donor levels in Si. Newly identified levels are indicated by an asterisk. When more than one reference is cited for an entry, the tabulated value is determined from the first reference, which usually gives the sharpest absorption peak, although values from other references usually agree within experimental error.

	Ground	$2s$	$3s$	$3d_0$
EM[a]	31.27	8.83	4.75	3.75
P	45.54[b-d]			4.1±0.03*[d,c]
As	53.76[b-e]	9.11[e]		3.8±0.03*[d,e]
Bi	70.97[f-g]	8.78[g,i,f]	4.72±0.03*[h]	3.79±0.07*[h,g]
S_A[j]	109.53			3.83*
S_B[j]	187.66	8.21 (A_1)*	4.56 (A_1)*	3.90*
		8.84 (E)*	4.8 (E)*	
S_C[j]	370.49	7.61*[k]		3.75*
S_D[j]	613.55	10.14*	5.13*	3.73*

[a]Ref. 12.
[b]Ref. 2.
[c]Ref. 3.
[d]Ref. 4.
[e]Ref. 5.
[f]Ref. 6.
[g]Ref. 7.
[h]Ref. 8.
[i]Ref. 9.
[j]Ref. 11, but see Ref. 10.
[k]Note that the direction of the shift due to central cell corrections is opposite to that expected.

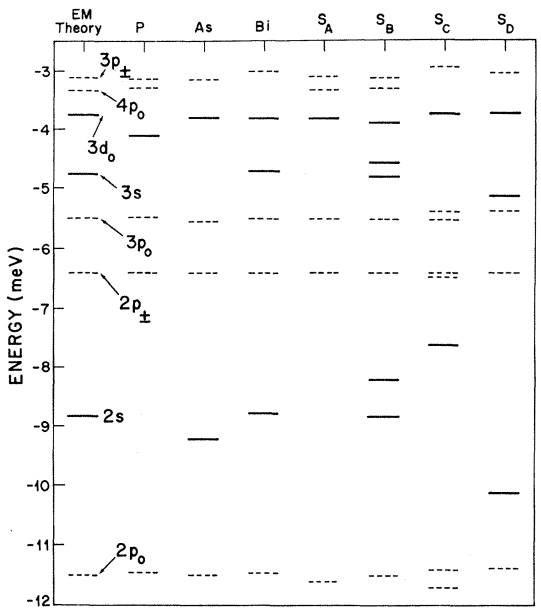

FIG. 1. Some donor energy levels in Si. For clarity, only levels from the $2p_0$ to the $3p_\pm$ are shown. Odd-parity levels are indicated by dashed lines and even-parity (s and d_0) levels by solid lines. EM theory: all levels from Ref. 12. P: p levels from Refs. 2 and 3; $3d_0$ level from Ref. 4. As: p levels from Refs. 2 and 3; $2s$ from Ref. 5; $3d_0$ from Ref. 4. Bi: $2p_0$, $2p_\pm$, $3p_0$ from Ref. 6; $2s$ from Ref. 9; $3s$, $3d_0$, $3p_\pm$ from Ref. 8. S_A, S_B, S_C, S_D: all levels from Refs. 10 and 11.

lowing considerations.

Si donor levels with $m=0$ $(s, p_0, d_0, \cdots)$[1] are six-fold degenerate[17,18] in the EMA (neglecting spin), there being one eigenstate for each of the six valleys of the Si conduction-band edge. When central-cell corrections[17] to the EMA are taken into account, an $m=0$ level splits in the case of a donor with tetrahedral T_d site symmetry (such as Li,[19] P, As, Sb, Bi, or S_D[11]) into a nondegenerate A_1, a doubly degenerate E, and a triply degenerate T_2. Except for Li,[14,19] the ground level is the $1s(A_1)$. Electric dipole transitions from an A_1 level are allowed only to T_2 levels.

In the EMA the $m=0$ E and $m=0$ T_2 (and also the $m=\pm1$ T_2) wave functions can be chosen to have nodes at the impurity center, so that central-cell corrections are expected to be small and the associated energies are expected to be reasonably well predicted by the EM equation. This expectation is fulfilled for the $1s(E)$ and $1s(T_2)$ levels of Li,[14] P,[2] As,[2] and Sb,[2] and for the $1s(T_2)$ of Bi.[13] One would expect even better agreement for higher s levels.

For $m\neq0$, for odd-parity $m=0$, and approximately[20] for non-s even-parity $m=0$, the envelope factors[17] of donor wave functions in the EMA can themselves be chosen to have nodes at the impurity center. Consequently, for such levels one would expect especially good agreement with EM energies. The agreement for p levels is known to be excellent.[12]

Figure 1 and Table I show that these expectations are fulfilled for a number of additional even-parity levels. For $3d_0$ the agreement with EM is remarkably good,[21] even for the deep donors (Bi and the four S centers) where breakdown of the EMA is expected to be greatest.[22] The identification of the $3d_0$ is corroborated by the $m=0$ character indicated by Bi Zeeman spectra.[8,23,24] As expected, the agreement for $3d_0$ levels is generally better than for $1s$, $2s$, and $3s$ levels; this is particularly noticeable for the deepest donor S_D.

We now turn our attention from level positions to absorption-line intensities and shapes. In the EMA no even-parity levels of an isolated Si donor should be observable in photoexcitation spectra, since electric-dipole transitions from a $1s$ ground level to an even-parity level are parity forbidden. The observation of even-parity levels can be accounted for as a result of (1) effects of other crystal defects and/or (2) breakdown of the EMA. No even-parity peaks of a relatively isolated shallow donor have so far been reported, indicating that breakdown of the EMA is not significant for shallow donors. However, the $3d_0$ is evident for P[4,3,25] and As[4,25] in more heavily doped samples, where the peaks are broader, and where the $4p_0$, which is seen as a weak peak in the sharp spectra[14] so far available, is unfortunately obscured[26] by the $3p_\pm$. We attribute the presence of these broadened $3d_0$ peaks and broadening of the p peaks to perturbing effects of other defects, possibly ionized impurities. For example, an ionized acceptor polarizes the donor states, mixing in components of opposite parity and destroying the parity selection rule.

The absence of s peaks in the shallow donor spectra is likely due to differences in the induced oscillator strengths: Estimates based on impurity Stark perturbations and neglecting EM anisotropy in calculating matrix elements give ≈4 for the $3d_0$-to-$2s$ intensity ratio. In this approximation we find also that the (second order) Stark shift of the $3d_0$ (due mainly to $4f$ level effects) is downward, in agreement with observation, particularly for P (see Fig. 1). These ideas can be tested by using samples with controlled doping and/or applied electric fields, together with

spectral line-shape theory developed in the EMA, which should apply for shallow donors; some use of such an approach has already been made for excitation spectra of B acceptors in Si.[27]

As the donor binding energy increases, breakdown of the EMA apparently becomes more important, as expected, at least for seeing s levels, for which the oscillator strengths are typically seen to increase markedly relative to p levels. For the neutral donors S_A and S_B, ionized-impurity effects should be a minor factor, indicating the importance of breakdown of the EMA in the observation of even-parity levels. This is consistent with the observation that the S_A and S_B peaks are generally narrower than those of the ionized donors S_C and S_D.[11]

The identifications made above (1) provide confidence for a more general search for even-parity levels of impurities (acceptors as well as donors) for which odd-parity levels are adequately described in the EMA, and (2) indicate the usefulness of controlled doping and of the Stark effect for inducing otherwise forbidden transitions.

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[24]The possibility that the $3d_{\pm}$ contributes to the observed peaks cannot be entirely ruled out, since the EM $3d_{\pm}$ position is not known, the Bi Zeeman (Ref. 8) evidence seems not conclusive, and S_B and S_C spectra under uniaxial stress suggest $m = \pm 1$ character (Ref. 23).

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