Spectra of shallow donors in multivalley semiconductors

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(Submitted 18 May 1986)
Pis'ma Zh. Eksp. Teor. Fiz. **44**, No. 1, 39–42 (10 July 1986)

The energy spectrum of odd excited states of shallow donors in a multivalley semiconductor is calculated as a function of $\gamma = m_t/m_l$, the ratio of the transverse and longitudinal effective masses of electrons. The spectral pattern found agrees completely with extensive experiments. It predicts new lines in Ge. These lines are seen in the spectra but have not been mentioned previously.

The anisotropy of the effective mass of electrons ($\gamma < 1$) means that variables cannot be separated in the Schrödinger equation describing shallow donors in multivalley semiconductors in the effective-mass approximation, so that an analytic solution is not possible. The spectra of optical transitions in shallow donors in Ge and Si (see the review by Ramdas and Rodriguez[1]), measured since 1969, have been interpreted on the basis of the results of Faulkner's variational calculations. Table I shows the excitation energies which have been measured[3,4] for certain shallow donors in Ge; the measured energy of the transition to the $2P_{\pm}$ states has been subtracted. Also shown in this table are an interpretation of the lines and the corresponding energies from Ref. 2. The discrepancy between the measured energies and those calculated in Ref. 2 goes significantly beyond the experimental error, $\lesssim 5\,\mu$eV, but, even worse, the discrepancy between the theory of Ref. 2 and experiment in some cases [$(5p_{\pm})$,$(6p_{\pm})$] is on the order of or greater than the distance between adjacent levels. Since the calculation accuracy cited in Ref. 2 was high (three significant figures), the poor agreement between Ref. 2 and experiment (which was also noted in Ref. 4) is rather fundamental: It may indicate that even odd excited states are described poorly by the effective-mass approximation and that there are effects of some sort which have not been taken into account. We have accordingly undertaken a calculation of the energies of odd states of shallow donors over the γ interval from 1 (the hydrogen-like atom) to

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TABLE I. Energy levels (in units of meV) of the $nP_{\pm}$ states of donors in Ge, reckoned from the $2P_{\pm}$ states, and interpretation of these energy levels.

Measurements with various impurities				Calculations		Interpretation	
Sb[4]	P[4]	Li – O[3]	"D"[3]	Present study	Faulkner[1]	Present study	On the basis of Ref. 2.
0.682 (4)	0.688 (8)	0.684 (5)	0.684 (5)	0.6828	0.70	$3P_{\pm}$ $(3p_{\pm})$	$(3p_{\pm})$
0.962 (4)	0.971 (8)	0.971 (5)	0.972 (5)	0.9694	1.00	$4P_{\pm}$ $(4p_{\pm})$	$(4p_{\pm})$
1.116 (4)	1.106 (8)	1.112 (5)	1.113 (5)	1.1129	1.12	$5P_{\pm}$ $(4f_{\pm})$	$(4f_{\pm})$
...	...	...	...	1.1465	–	$6P_{\pm}$ $(5p_{\pm})$	–
1.241 (6)	1.252 (8)	1.251 (5)	1.252 (5)	1.2531	1.20	$7P_{\pm}$ $(5f_{\pm})$	$(5p_{\pm})$
1.322 (6)	1.328 (8)	1.320 (5)	1.322 (5)	1.3212	1.32	$8P_{\pm}$ $(6p_{\pm})$	$(5f_{\pm})$
...	...	...	...	1.3361	–	$9P_{\pm}$ $(6f_{\pm})$	–
1.389 (6)	–	1.387 (5)	1.391 (5)	1.3921	1.35	$10P_{\pm}$ $(6h_{\pm})$	$(6p_{\pm})$
1.407 (6)	–	–	–	1.4067	1.41	$11P_{\pm}$ $(7p_{\pm})$	$(6f_{\pm})$

$\gamma_{Ge} = 0.05134$ by the method of boundedness-condition transfer.[5,6] This method yields highly accurate calculations of energy levels, and it is also capable of highly accurate calculations of wave functions, so that the oscillator strengths of the transitions can be found, and spectral lines can be identified more confidently.

The solid lines in Fig. 1 show the γ dependence of the energies of the odd states with $M = \pm 1$ (these states are designated $nP_{\pm}$, where $n = 2,3,...$; the notation according to Ref. 2 is given in parentheses). The energies are expressed in units of $E_d = m_t e^4/\hbar^2\epsilon^2$, where ϵ is the dielectric constant. The smallest value is $\gamma = \gamma_{Ge}$. The dashed lines are the results of Ref. 2; the solid horizontal line segments at the left are the measured donor levels in Ge, while the dotted line segments here are levels which are found in the present study but which have not been mentioned in the experimental papers. Figure 2 shows the oscillator strengths of optical transitions from the ground level to the $nP_{\pm}$ levels (the designations of the levels not mentioned in the experimental papers are underscored). Table I shows the values which we calculated for the differences $E(nP_{\pm}) - E(2P_{\pm})$, along with the measured values of these differences. The accuracy of the present calculations of the dimensionless binding energies E/E_d is about 3×10^{-5}; i.e., at the known value of E_d, the binding energies in Ge are accurate within ~ 0.3 μeV. The accuracy of the calculation of the wave functions is three significant figures.

The level energies calculated in Ref. 2 deviate to a progressively greater extent from those which we calculated as γ decreases (Fig. 1). In the case of Si ($\gamma_{Si} = 0.2079$), the errors of Ref. 2, although greater than the experimental errors, are

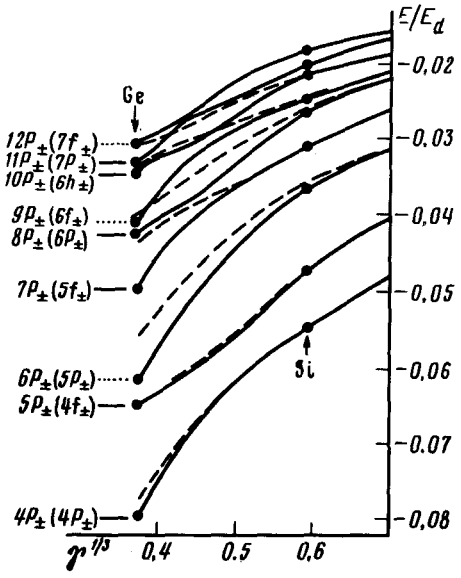

FIG. 1. Level energy versus γ.

nevertheless smaller than the distances between adjacent levels, so that they do not lead to an incorrect identification of lines. At $\gamma = \gamma_{Ge}$, the deviation of the energy calculated in Ref. 2 from the experimental energies and from the values which we find in the case $nP_{\pm}$ with $n = 3, 4$ is far greater than the experimental error. At $n > 5$, the

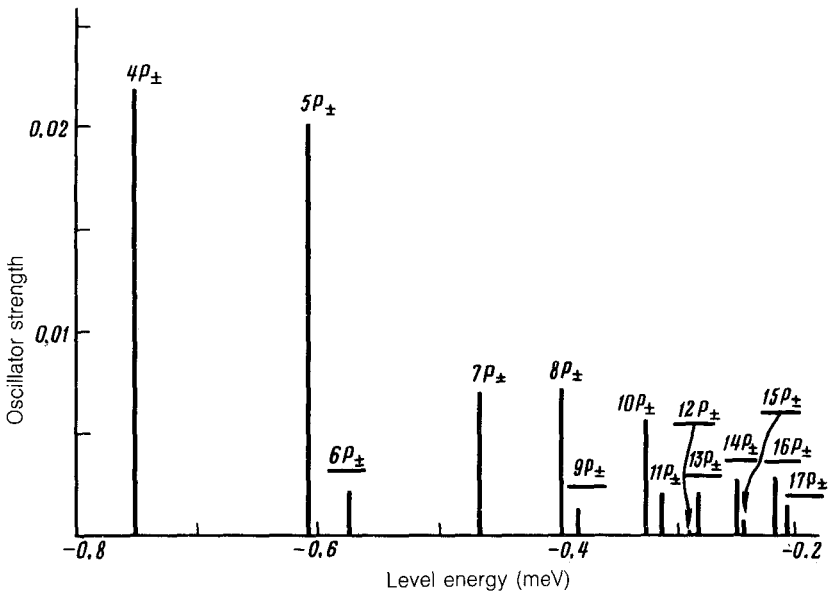

FIG. 2. Oscillator strengths of transitions from the ground state in Ge.

deviation becomes comparable to or greater than the distance between adjacent levels, with the consequence that all of the transitions beginning with $6P_{\pm}$ are identified incorrectly. The error of the interpretation of the donor spectra in Ge on the basis of Ref. 2 has not been noted previously, because, in particular, transitions to the $nP_{\pm}$ states with $n = 6$ and 9 were missed in the experimental studies, and some of the levels calculated in Ref. 2 for Ge [$(5f_{\pm})$ and $(6f_{\pm})$] have by chance fallen beside experimental points (Fig. 1), which actually correspond to other states [$(6p_{\pm})$ and $(7p_{\pm})$ in the notation of Ref. 2]. It can be seen from Fig. 2 that the oscillator strength of the lines which were missed are several times smaller than the strengths of adjacent lines. However, these transitions can be seen in the experimental spectra of the photothermic ionization of various donors in Ge: The transition to $6P_{\pm}$ is seen as a small peak, while that to $9P_{\pm}$ is seen at a knee on the slope of the $8P_{\pm}$ line. Also shown in Fig. 2 are binding energies and oscillator strengths of donor levels in Ge up to $17P_{\pm}$.

At small values of $1-\gamma$ the states which arise from the $n = 4$ and 5 levels of hydrogen actually contain only functions with $L = 1$ and $L = 3$. Interestingly, the lower level $(np_{\pm})$ of each such doublet is an almost pure f level, while the upper level $(nf_{\pm})$ is a nearly pure p level, providing it more evidence that the level designations adopted in Ref. 2 for $\gamma \neq 1$ are purely arbitrary. In Si, the oscillator strengths of the transitions to the lower levels of the doublets are higher than those of the transitions of the upper levels, and the oscillator strengths generally fall off monotonically with increasing n [we note, however, that in Si the oscillator strength of $(6f_{\pm})$ is negligible in comparison with that of $(6h_{\pm})$]. In the case of Ge, the wave function of each state receives an important contribution from a large number of terms with different (odd) values of L (in the case of $17P_{\pm}$, we can still see a significant contribution at $L = 21$). The oscillator strengths vary nonmonotonically with increasing energy (Fig. 2), and the oscillator strengths of the lines nP_0 with $n > 3$ are negligible. We conclude from all this evidence that a shallow donor in Ge, thought of as a quantum-mechanical system, is greatly different from the hydrogen-like atom.

Following Ref. 2, we find a value of ϵ for Ge by fitting the calculated levels to the experimental results: $\epsilon = 15.40$ [in Ref. 2, the value $\epsilon = 15.36$ was found from the energy difference $(2p_{\pm}) - (2p_0)$]. We see from Table I that with this value of ϵ the energies found in the present calculations for the $nP_{\pm}$ levels of donors in Ge agree with all the measurements of Ref. 3 within the experimental error ($\lesssim 5$ μeV). This agreement means that the effective-mass approximation is surprisingly accurate in describing the odd states of shallow donors in Ge. Effects which go beyond the scope of the effective-mass approximation (e.g., polaron effects), if they exist, are beyond the accuracy of the spectrascopic measurements.

To the extent that we can draw conclusions from the experimental spectra, there is also a complete agreement between the calculated and observed line intensities.

We are very indebted to A. F. Polupanov and É. I. Rashba for a discussion.

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Translated by Dave Parsons