Theory of Donor Levels in Silicon

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WE have extended our work on the ground state of a donor electron in Si[1] to estimate the positions of the low-lying excited levels. Our calculations are based on the following model:

(1) The conduction band has 6 minima in the (1,0,0) and equivalent directions.[2] At each minimum the band is nondegenerate.

(2) The effective masses are $m_1=0.19m$ (twice), $m_2=0.98m$.[2]

(3) Except in the immediate vicinity of the donor atom the donor states are described by functions of the form

$$\Psi=\sum_{j=1}^{6}\alpha^{(j)}F^{(j)}(\mathbf{r})\psi(\mathbf{k}^{(j)};\mathbf{r}),$$

where the $F^{(j)}(\mathbf{r})$ are modulating functions satisfying appropriate effective mass equations, the $\psi(\mathbf{k}^{(j)},\mathbf{r})$ are the Bloch functions at the 6 minima $\mathbf{k}^{(j)}$ of the conduction band and the $\alpha^{(j)}$ are constants satisfying the requirements of tetrahedral symmetry.

(4) Shifts of the energy levels relative to their values in the effective mass theory are attributed to failure of the effective mass formalism in the vicinity of the donor atom.[1] From the known shift of the ground state, the shifts of the other levels are estimated.

Table I contains our results. We have included the level positions as calculated from the effective mass Schrödinger equation, and the corrected level positions for P, As, and Sb donors, where allowance for the partial breakdown of the effective mass formalism has been made.

The effects of lattice vibrations have not been included.

Optical transitions from the ground state will take place primarily to the p-states.

A detailed report is being submitted to the Physical Review.

We wish to express our thanks to the staff of the Bell Telephone Laboratories, where this work was begun, for their hospitality and to Dr. R. C. Fletcher, Dr. C. Herring, and Dr. G. Wannier for many stimulating discussions.

[1] J. M. Luttinger and W. Kohn, Phys. Rev. **96**, 802 (1954) and Phys. Rev. **97**, 1721 (1955).
[2] R. N. Dexter *et al.*, Phys. Rev. **96**, 222 (1954).

TABLE I. Level scheme of donor states in silicon.

State	Representations[a] of T_d	Number of degenerate[b] states	(Energy in ev) ×10²[c] Eff. mass theory	P	As	Sb
$1s$, $m=0$	A_1	1	-2.9 ± 0.1	-4.4[d]	-4.9[d]	-3.9[d]
$1s$, $m=0$	$E+T_1$	5	-2.9 ± 0.1	-3.2 ± 0.3	-3.3 ± 0.4	-3.1 ± 0.2
$2p$, $m=0$	A_1+E+T_1	6	-1.13 ± 0.06	-1.13 ± 0.06	-1.13 ± 0.06	-1.13 ± 0.06
$2s$, $m=0$	A_1	1	-0.88 ± 0.06	-1.06 ± 0.10	-1.11 ± 0.10	-0.94 ± 0.08
$2s$, $m=0$	$E+T_1$	5	-0.88 ± 0.06	-0.93 ± 0.11	-0.95 ± 0.13	-0.90 ± 0.08
$2p$, $m=\pm1$	$2T_1+2T_2$	12	-0.59 ± 0.02	-0.59 ± 0.02	-0.59 ± 0.02	-0.59 ± 0.02
$3p$, $m=0$	A_1+E+T_1	6	-0.57 ± 0.06	-0.57 ± 0.06	-0.57 ± 0.06	-0.57 ± 0.06

[a] Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York, 1944), p. 388.
[b] These states are only approximately degenerate, consisting in general of several strictly degenerate sets, as appears from the second column. Spin degeneracy is not included.
[c] The indicated errors represent estimated uncertainties within the framework of the present model.
[d] Experimental.

Thermoelectric Power of Germanium at Low Temperatures

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GUREVICH[1] has pointed out that the lattice vibrations in a metal under a temperature gradient tend to scatter the electrons preferentially toward the colder end of the sample. This effect should create an additional term in the thermoelectric power, Q, which may then be written

$$Q=Q_e+Q_p,$$

where Q_e is due to the usual electron diffusion and Q_p arises from the "phonon drag" mentioned above. Q_p has not so far been detected in thermoelectric power measurements on pure metals (see also MacDonald, Pearson, and White;[2] MacDonald).[3] On the other hand, measurements of Q made on germanium show an anomalous increase below 200°K and to explain these results, Frederikse,[4] Herring,[5] and MacDonald[6] independently derived theoretical expressions for Q_p in semiconductors.

We wish to report here measurements which contribute evidence for the existence of such a term in the thermoelectric power of germanium. The two samples, $S1$ and $S2$, used in these measurements, are of higher purity than those used by Frederikse[5] and by Geballe