

The quantitative success of this admittedly simplified theory in fitting the experimental splittings exceeded the expectations of the authors. Possibly the agreement will degenerate somewhat as the theory is developed in more general and sophisticated form. Nonetheless, the presumption seems strong that many of the complicated exchange processes in the rare earth compounds can be successfully and meaningfully treated, using the exchange potential formalism and viewpoint.

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<sup>1</sup>Though not the same as in the aluminum garnet (see Table I).

<sup>2</sup>K. A. Wickersheim and R. L. White, Phys. Rev. Letters 4, 123 (1960); K. A. Wickersheim, Phys. Rev. 122, 1376 (1961).

<sup>3</sup>Proposed by W. P. Wolf, Proc. Phys. Soc. (London) 74, 665 (1959).

<sup>4</sup>In both instances the exchange field is oppositely directed from the applied field. However, for the  $J = \frac{7}{2}$  state the total magnetic moment  $\mu_J$ , upon which the applied field acts, and the spin component of the magnetic moment  $\mu_S$ , upon which the exchange field acts, are parallel, while for the  $J = \frac{5}{2}$  state they are antiparallel.

<sup>5</sup>H. M. Crosswhite, Johns Hopkins University (private communication).

<sup>6</sup>J. C. Slater, Phys. Rev. 81, 385 (1951).

## INFRARED ABSORPTION SPECTRUM OF SULFUR-DOPED SILICON

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Sulfur, a group VI element, when diffused into silicon, gives rise to two donor-type impurity levels.<sup>1</sup> The positions of these donor levels have been found from photoconductivity and Hall measurements to be located 0.18 eV and 0.37 eV below the conduction band edge for the neutral and singly ionized sulfur atoms, respectively. We have observed the optical absorptions corresponding to excitation from the ground to the excited states of both the neutral and singly ionized impurities.

Since sulfur is a group VI element, substitutional sulfur has two extra electrons to contribute as donor electrons after the four tetrahedral bonds have formed. Neutral S in Si is, therefore, the analog of a helium atom, and  $S^+$  is the analog of  $He^+$ . One portion of the neutral S spectrum is due to transitions from the ground state to a set of excited He-like  $p$  states; and one portion of the  $S^+$  spectrum is due to transitions from the ground state to a set of  $He^+$ -like  $p$  states. Additional lines have been observed, which are probably due to transitions from the ground level to many-valley orbital triplet levels for both neutral S and  $S^+$ .

The measurements were made at  $\approx 10^\circ K$  on polished samples about 1 cm thick containing  $10^{15}$ - $10^{16}$  sulfur atoms/cm<sup>3</sup>. A Perkin Elmer Model 12-C monochromator, modified for use

with a 150 line/mm grating, and an NaCl fore-prism give us a resolution of  $\approx 0.0005$  eV. Atmospheric water vapor absorption lines were used for calibration. Table I lists all of the absorption lines seen in any of our samples with

Table I. Measured optical absorptions and their identification.

Energy (in eV)	Identification
Neutral sulfur transitions	
0.1555 } 0.1602 } 0.1624 }	(1)(1) $\rightarrow$ (1)(3)
0.1750	(1)(1) $\rightarrow$ (1)(2 $p_0$ )
0.1802	(1)(1) $\rightarrow$ (1)(2 $p_{\pm}$ )
0.1809	(1)(1) $\rightarrow$ (1)(3 $p_0$ )
0.1833	(1)(1) $\rightarrow$ (1)(3 $p_{\pm}$ )
Singly ionized sulfur transitions	
0.2197 } 0.2338 }	(1) $\rightarrow$ (3)
0.3219	(1) $\rightarrow$ (2 $p_0$ )
0.3425	(1) $\rightarrow$ (2 $p_{\pm}$ )
0.3468	(1) $\rightarrow$ (3 $p_0$ )
0.3563	(1) $\rightarrow$ (3 $p_{\pm}$ )
0.3599	(1) $\rightarrow$ (4 $p_0$ )

their identifications. We have, of course, seen the set of lines we attribute to neutral sulfur in certain samples without the set we attribute to the singly ionized sulfur, and vice versa.

It is instructive to consider the spacings of levels in H and He atoms, to get a preliminary idea of what to expect for the spectra of S and  $S^+$  in Si. The spacings of  $(2p)-(3p)$ ,  $(3p)-(4p)$ ,  $(4p)-(5p)$  in H and He are equal to within  $\approx 1\%$ , indicating that the electron in excited  $p$  states in He sees a potential due to the nucleus plus one ground-state electron, much like that of a single positive charge. We may then anticipate that, in the solid, the spacings of one-electron excited  $p$  states of neutral S will be very nearly the same as the  $p$ -state spacings of any one-electron donor in Si.

In the case of impurities in Si, one other type of transition can occur, which has no analog in H or He. Because of the presence of many valleys, the ground state of the one-electron donor in the effective mass approximation is sixfold degenerate. The presence of central-cell corrections to the effective mass theory leads to a splitting into a lowest energy singlet (1), a doublet (2), and a triplet (3). A weak electric dipole transition from the singlet to the triplet can occur because of third order terms in the  $\vec{k}\cdot\vec{p}$  approximation.<sup>2</sup> From symmetry, the direct transition from singlet to doublet is not allowed. Since the doublet and triplet wave functions have small amplitude in the central cell, their energies should lie much closer to the theoretical ef-

fective mass ground state than the singlet energy. Furthermore, in neutral S, where exchange and overlap effects may be quite small for the system with one singlet and one triplet electron, we might expect this excited state,  $(1)(3)$ , to have an energy close to the theoretical effective mass ground state, relative to the states in which one electron is in a singlet state, and one in a  $p$  state,  $(1)(np)$ .

The relative intensities observed for the neutral S  $(1)(1) \rightarrow (1)(np)$  and  $S^+ (1) \rightarrow (np)$  transitions agree fairly well with those expected from theory,<sup>3</sup> as well as with those observed in shallow donors in Si. We have presented the energies of the observed transitions in Table II in a form suitable for comparison with theory. The energy differences of transitions for neutral S are given in the sixth column. However, since the spectrum of  $S^+$  is expected to be like that of  $He^+$ , the energies are scaled up from those of a hydrogenic impurity by a factor 4, and the ninth column, therefore, presents energy differences divided by 4. Except for the case  $(2p_{\pm} \rightarrow 3p_0)$ , the theoretical and experimental  $p$ -level differences are seen to be in good agreement with theory as well as with the results for As in Si.

Since effective mass theory seems to fit the data so well, we can use the identified transitions to compute the positions of the ground state relative to the conduction band edge. If we assume that the  $2p_0$  state in neutral S is  $-0.0109$  eV relative to the band edge, and  $-4(0.0109)$  eV relative to the band edge for  $S^+$ , we obtain ground-

Table II. Energy states and differences for impurities in silicon.

Eff. mass state	Theor. energy below band edge (eV)	Diffs. (eV)	S transitions	Energy (eV)	Diffs. (eV)	$S^+$ transitions	Energy (eV)	$\frac{1}{4}$ Diffs. (eV)	As diffs. (eV)
Ground state	0.029		$(1)(1) \rightarrow (1)(3)$	$\sim 0.1594$		$(1) \rightarrow (3)$	$\sim 0.2268$		
$2p_0$	0.0109	0.0181	$(1)(1) \rightarrow (1)(2p_0)$	0.1750	0.0156	$(1) \rightarrow (2p_0)$	0.3219	0.0238	
$2p_{\pm}$	0.0059	0.0050	$(1)(1) \rightarrow (1)(2p_{\pm})$	0.1802	0.0052	$(1) \rightarrow (2p_{\pm})$	0.3425	0.0052	0.0053
$3p_0$	0.0057	0.0002	$(1)(1) \rightarrow (1)(3p_0)$	0.1809	0.0007	$(1) \rightarrow (3p_0)$	0.3468	0.0011	0.0032
$3p_{\pm}$	0.0029	0.0028	$(1)(1) \rightarrow (1)(3p_{\pm})$	0.1833	0.0026	$(1) \rightarrow (3p_{\pm})$	0.3563	0.0024	0.0023
$4p_0$							0.3599	0.0009	0.0002

state energies of  $-0.1859$  eV for neutral S and  $-0.3655$  eV for  $S^+$ . These agree quite well with binding energies obtained from photoconductivity and Hall data.

The transitions listed in the table for  $(1)(1) \rightarrow (1)(3)$  in S and  $(1) \rightarrow (3)$  in  $S^+$  are the mean values for the lines observed in these regions, and their identification is not completely certain. From the energy differences shown, these groups of lines do seem to fall close to the effective mass ground state relative to the  $2p_0$  levels. If they are  $(1) \rightarrow (3)$  transitions, it is not, as yet, clear what has caused the splitting into two or possibly three lines for  $S^+$  and three lines for neutral S. Spin-orbit interaction could cause a splitting of the lines, but the free S-atom spin-orbit splitting is so small that it does not seem likely that residual spin-orbit effect in the solid could be this large. It is also possible that there are a number of different inequivalent sites for sulfur impurities in the Si samples which produce a number of  $(1) \rightarrow (3)$  lines. A similar pair of lines, split by  $\sim 0.001$  eV, has been seen in the spectrum of Bi in Si. Bi has a large atomic spin-orbit inter-

action, and the observed splitting in Si is consistent with a rough estimate of residual spin-orbit effect.<sup>2</sup>

We have observed a preliminary effect of pressure on the  $(1) \rightarrow (3)$  absorption lines, and hope that further experiments will clarify the nature of these transitions. Experiments are also under way on the absorption spectra of other group VI elements in Si.

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<sup>1</sup>R. O. Carlson, R. N. Hall, and E. M. Pell, J. Phys. Chem. Solids **8**, 81 (1959).

<sup>2</sup>L. M. Roth (private communication).

<sup>3</sup>W. Kohn, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. V, p. 257.

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## DEPENDENCE OF THE ATOMIC MAGNETIC MOMENT IN $\alpha$ IRON ON LATTICE SPACING

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It has been suggested by Galperin<sup>1</sup> that an increase in the lattice parameter of iron would cause an increase in the atomic magnetic moment. On the other hand, in the application of the Weiss theory of intrinsic magnetization, it is generally assumed that the atomic magnetic moment remains constant over the entire ferromagnetic range of temperature with a sudden (apparent) increase occurring upon passing into the paramagnetic region. It will be shown that by regarding the electronic configuration of the iron atom at the Curie temperature as being equivalent to that of the isolated iron atom ( $3d^64s^2$  with 4 net spins per atom), various discrepancies in the Weiss theory can be resolved. In particular, by regarding the atomic magnetic moment as increasing with lattice expansion (and therefore with the temperature), it is possible to compute from the Weiss theory, using intrinsic magnetization data, the variation of atomic magnetic moment with

temperature.

The internal field hypothesis of Weiss leads to a theoretical expression for the intrinsic magnetization curve of ferromagnetic materials which Wannier<sup>2</sup> presents in the following way:

$$M/N = \tanh \frac{M/N\mu}{(kT/\alpha)N\mu^2}. \quad (1)$$

Here  $M$  is the intrinsic magnetization at temperature  $T$ ,  $N$  is the number of spins per unit volume,  $\mu$  is the Bohr magneton,  $\alpha$  is the Weiss constant, and  $k$  is Boltzmann's constant. If the viewpoint is adopted that  $N$  is a function of  $T$ , then (1) may be rearranged to solve for  $N$  (or  $n$ , the number of spins per atom) in terms of  $M/N(0)\mu$  (to be called  $x$ ) and  $T/T_c$  (to be called  $y$ ) where  $T_c$  is the observed Curie temperature. If this is done, it is found that

$$n(T) = \frac{n(0)x}{\tanh[x/(yn(T_c)/n(0))]} \quad (2)$$