PHYSICAL REVIEW VOLUME 117, NUMBER 1 JANUARY 1, 1960

Spin Resonance of Transition Metals in Silicon

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(Received July 23, 1959)

Spin resonance measurements are reported for various charge states of four transition metals in silicon, namely for V^{++}, Cr^{+}, Mn^{-}, Mn^{++}, and Fe^{0}. In each case the g tensor and the hyperfine interaction with the impurity nucleus are isotropic. Thus each element exists in an isolated form in silicon and undergoes no distortion from the site of maximum symmetry. The site may be either the substitutional position or the interstitial position of maximum symmetry in the silicon lattice. For $(V^{51})^{++}$, $S=\frac{3}{2}$, $A=-42.10$; for $(Cr^{53})^{+}$, $S=\frac{5}{2}$, $a=+30.16$, $A=+10.67$; for $(Mn^{55})^{-}$, $S=1$, $A=-71.28$; for $(Mn^{55})^{++}$, $S=\frac{5}{2}$, $a=+19.88$, $A=-53.47$; for $(Fe^{57})^{0}$, $S=1$, $A=6.98$, where a is the cubic field splitting parameter, A is the hyperfine interaction of the isotope noted, and both are expressed in units of 10^{-4} cm^{-1}. Electron-nuclear double resonance was used for accurate measurement of A and for the determination of S. In the case of Fe^{0}, the electron spin was checked by noting that the iron line splits into two fine structure components under uniaxial stress. Association of Cr, Mn, and Fe with acceptors in silicon has been observed, as well as another charge state of isolated Fe.

I. INTRODUCTION

THE earliest reported spin resonance measurements in silicon were on free electrons[1] and on electrons bound at shallow donor impurity sites.[2] The investigation of shallow donor impurities in silicon, namely phosphorus, arsenic, and antimony, has continued, until these are among the best understood of all dilute paramagnetic systems. The hyperfine interaction with the donor nucleus is well resolved and lines are narrow. Relaxation processes have been studied both theoretically[3] and experimentally[4]; one finds concentration-dependent relaxation times which can be as long as hours at helium temperatures. Feher[5] has used the electron-nuclear double resonance technique to study the hyperfine interaction of the donor electron with Si^{29}. By comparing the wave function amplitude with theoretical calculations of Kohn and Luttinger,[6] he has determined the position of the conduction band minimum. The spectra have also been utilized for studying nuclear properties such as magnetic moments,[7] the hyperfine structure anomaly,[8] and for producing nuclear orientation.[9]

The shallow acceptors, boron, aluminum, gallium, and indium, are also quite soluble in silicon. It is not clear why spin resonance due to these has not been observed.

Recently, resonant absorption due to a wide variety of other, less soluble, impurity systems has been detected in silicon. The isolated impurities which have been detected include the transition metals V, Cr, Mn,[10] Fe,[11] Ni, Pd, and Pt. Two species of sulfur[12] also have been detected.

Crystals containing associated impurity pairs have also been prepared. The pairs consist of one atom of chromium, manganese[10] or iron[11] and an atom of a substitutional acceptor such as boron, aluminum, gallium, indium, or gold. Pairs have been studied both by resonance and by electron-nuclear double resonance techniques. Clusters of four manganese atoms have also been observed. In the present paper only the spectra of V^{++}, Cr^{+}, Mn^{-}, Mn^{++}, Fe^{0} and the manganese clusters will be discussed; other systems will be treated in separate publications.

II. EXPERIMENTAL TECHNIQUE

V, Cr, Mn, and Fe can exist as isolated entities in silicon in more than one charge state. Control over the charge state is possible through the introduction of donor impurities, such as phosphorus, which can furnish electrons, or acceptor impurities, such as boron, which can take up electrons. In some cases, however, the use of an acceptor may lead to partial or complete chemical pairing rather than a simple electrical compensation. It is evident that careful sample control is requisite to the study of a particular spectrum.

The procedure we have used is to pull silicon crystals doped with a controlled amount of a shallow donor or acceptor. A bar of convenient size ($\sim 3\times 3\times 10$ mm^3) and crystal orientation is cut, a small amount of the transition metal is alloyed to it and then diffused in at about 1250°C. Generally, the bar is encapsulated in an evacuated quartz tube during the diffusion and the sample is quenched (comparatively slowly) by dropping the tube into water. If a more rapid quench is desired,

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[1] Portis, Kip, Kittel, and Brattain, Phys. Rev. **90**, 988 (1953).

[2] Fletcher, Yager, Pearson, Holden, Read, and Merritt, Phys. Rev. **94**, 1392 (1954); Fletcher, Yager, Pearson, and Merritt, Phys. Rev. **95**, 844 (1954).

[3] Pines, Bardeen, and Slichter, Phys. Rev. **106**, 489 (1957); G. Feher and E. A. Gere, Phys. Rev. **114**, 1245 (1959).

[4] H. Honig and E. Stupp, Phys. Rev. Letters **1**, 275 (1958).

[5] G. Feher, Phys. Rev. **114**, 1219 (1959).

[6] W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1955).

[7] Feher, Fuller, and Gere, Phys. Rev. **107**, 1462 (1957).

[8] J. Eisinger and G. Feher, Phys. Rev. **109**, 1172 (1958).

[9] F. M. Pipkin and J. W. Culvahouse, Phys. Rev. **109**, 1423 (1958).

[10] Ludwig, Woodbury, and Carlson, J. Phys. Chem. Solids **8**, 490 (1959); Woodbury, Carlson, and Ludwig, Bull. Am. Phys. Soc. 4, 22 (1959).

[11] Ludwig, Carlson, and Woodbury, Bull. Am. Phys. Soc. **4**, 22 (1959); Bull. Am. Phys. Soc. **4**, 144 (1959).

[12] Carlson, Hall, and Pell, J. Phys. Chem. Solids **8**, 81 (1959).

the bar is placed in an open tube under an argon atmosphere during the diffusion, and is blown directly from the furnace into ethylene glycol.

The diffusion temperature is about 1250°C, which is close to the temperature at which the solubilities of these transition metals pass through a maximum. Thus at room temperature the transition metal is in highly supersaturated solution. The association of chromium with (immobile) acceptors has been followed in samples allowed to stand at room temperature for several days. Resonance signals from samples containing iron or manganese have decayed upon aging at room temperature for weeks or months. Such experiments show that chromium, manganese and iron diffuse even at room temperature, and that samples containing them are comparatively unstable over time intervals of days to months.

The spectrometer used for the resonance studies has already been described.[13] A cavity of novel design, however, was used for electron-nuclear double resonance measurements. To do electron-nuclear double resonance one places the sample in a microwave resonant cavity and exposes it to a microwave magnetic field sufficiently large to saturate a given spin resonance line. The sample is then simultaneously exposed to a second, variable-frequency rf magnetic field which induces transitions between the nuclear sub-levels. We have used a cylindrical cavity whose side walls are in the form of a helix to introduce both the microwave and the rf magnetic fields. The cavity is constructed by coating the inside of a ground quartz cylinder with a layer of silver at least several mils thick. A helix of about 10 turns/inch is cut through the coating using a diamond tool. Contact to the resulting coil is made by drilling holes through the quartz cylinder and soldering wires to the coating. The rf field obtained by driving the helix with a suitable generator is comparable to that obtained from a copper coil of similar dimensions. The cylinder is mounted inside a brass shield which excludes refrigerant, thus avoiding microphonics connected with bubbling. The resulting cavity is operated in the TE_{011} mode. Since the side wall currents for this mode are circular, the helical design perturbs these very little, while other modes are effectively suppressed. The microwave Q obtained is higher than that of the brass cavities employed for ordinary resonance measurements. Using such a cavity we have detected double resonance transitions from about 1 to 230 Mc/sec.

III. RESULTS

Silicon crystallizes in the diamond lattice. Each substitutional atom has four nearest neighbors which are in [111] directions from it. Thus each substitutional atom sees a crystalline field of tetrahedral symmetry.

The position of maximum symmetry for an interstitial atom is in a [111] direction from a substitutional site opposite one of the four nearest neighbors. In such a site an interstitial atom also is surrounded by four nearest neighbors in [111] directions. Thus, from the symmetry of the crystalline field interactions, no evidence is deducible as to the substitutional or interstitial nature of the resonant sites.

We believe that chromium and iron are interstitial impurities in silicon; their donor action and rapid diffusion support this view. It is not clear whether the resonant forms of vanadium and manganese are interstitial or not. In either case, if we neglect the hyperfine interaction with the 4.57% abundant Si^{29} isotope and any distortion of the sites from the position of maximum symmetry (no distortion has been observed for the impurities in question), the spectrum of an isolated impurity in silicon must be describable in terms of the following spin Hamiltonian:

$$\mathcal{H}=g\beta\mathbf{H}\cdot\mathbf{S}+A\,\mathbf{S}\cdot\mathbf{I}+\tfrac{1}{6}a[S_x{}^4+S_y{}^4+S_z{}^4 -\tfrac{1}{5}S(S+1)(3S^2+3S-1)]-g_I\beta_N\mathbf{H}\cdot\mathbf{I}. \quad (1)$$

Because of the tetrahedral symmetry of the sites, A (which describes the hyperfine interaction with the transition metal nucleus) and g are constants rather than tensor quantities. The hyperfine interaction terms are necessary, of course, only when dealing with isotopes having nonzero nuclear spin. The term containing the cubic field splitting parameter, a, vanishes if the total electron spin $S\leqslant\frac{3}{2}$. The term $g_I\beta_N\mathbf{H}\cdot\mathbf{I}$, which describes the direct interaction of the transition metal nucleus with the external field, has negligible effect on the ordinary resonance spectrum, but is required for interpretation of the double resonance results.

To second order in the hyperfine interaction, the energy levels $W_{M,m}$ of the unpaired electrons are given by

$$W_{M,m}=Mg\beta H+AMm-g_I\beta_N Hm+\{M[I(I+1)-m^2] -m[S(S+1)-M^2]\}A^2/2g\beta H_0. \quad (2)$$

In Eq. (2), M and m are the quantum numbers specifying the orientation of the electron spin S and the nuclear spin I, respectively. For convenience the cubic field splitting term has been dropped.[14]

In the ordinary resonance experiment the selection rules are $\Delta M=\pm1$, $\Delta m=0$. If we consider the M to $M-1$ transitions, the magnetic field positions of the lines are given by

$$g\beta H=h\nu-Am-[I(I+1)-m^2 +m(2M-1)]A^2/2h\nu, \quad (3)$$

where ν is the kylstron frequency. Even in the absence of a cubic field term the hyperfine lines are split, but only by the small term $m(2M-1)A^2/2h\nu$. If the splitting is resolved the total electron spin S can be

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[13] G. W. Ludwig and H. H. Woodbury, Phys. Rev. **113**, 1014 (1959).

[14] For the effects of the cubic field splitting term see, e.g., W. Low, Phys. Rev. **105**, 793 (1957).

TABLE I. Summary of resonance results for transition metal elements in silicon. A and a are expressed in units of 10^{-4} cm^{-1}.

System	S	g	a	Isotope	I	A
V^{++}	$\frac{3}{2}$	1.9892	$\cdots$	V^{51}	$\frac{7}{2}$	-42.10
Cr^{+}	$\frac{5}{2}$	1.9978	$+30.16$	Cr^{53}	$\frac{3}{2}$	$+10.67$
Mn^{-}	1	2.0104	$\cdots$	Mn^{55}	$\frac{5}{2}$	-71.28
Mn^{++}	$\frac{5}{2}$	2.0066	$+19.88$	Mn^{55}	$\frac{5}{2}$	-53.47
$Mn_4{}^0$	2	2.0063	$\cdots$	Mn^{55}	$\frac{5}{2}$	12.8
Fe^0	1	2.0699	$\cdots$	Fe^{57}	$\frac{1}{2}$	6.98

determined by counting the number ($2S$) of fine structure lines.

In the double resonance experiment the selection rules are $\Delta M=0$, $\Delta m=\pm1$. The frequency f of the double resonance transition between the states (M,m) and $(M, m-1)$ is given by

$$f=|AM-g_I\beta_N H-[M(2m-1)+S(S+1)-M^2]A^2/2h\nu|. \quad (4)$$

The absolute value sign is used since the state $(M, m-1)$ may be higher in energy than the state (M,m). Equation (4) has been used both for determination of S and for obtaining accurate values of A.

The parameters in the spin Hamiltonian are summarized in Table I for the transition metals under consideration. The spectrum of each element will be discussed separately.

A. Vanadium

Vanadium is the least soluble of the elements under consideration, the solubility probably being no greater than 10^{15}/cm^3. The spectrum, which is shown in Fig. 1, has been observed only in crystals doped with an acceptor. In addition to the spectrum of Fig. 1, all of the double resonance transitions for $M=\pm\frac{1}{2}$ have been detected. In particular, the $m=\frac{1}{2}$ to $-\frac{1}{2}$ transitions occur at 63.09±7.68 Mc/sec. Using the known nuclear moment of V^{51} (+5.139 nuclear magnetons) one calculates that these transitions should occur at 63.09±5.98, 63.09±7.66, and 63.09±10.49 for $S=\frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$, respectively. Thus the measured transitions are consistent only with an $S=\frac{3}{2}$; this is the basis for the quoted value of S in Table I. The configuration of atomic vanadium is $3d^34s^2$. It seems likely that the resonant species is positively charged since the spectrum has been observed only in low-resistivity p-type crystals. Since $S=\frac{3}{2}$, a likely charge state is V^{++}, resulting from the removal of the two valence-shell electrons.

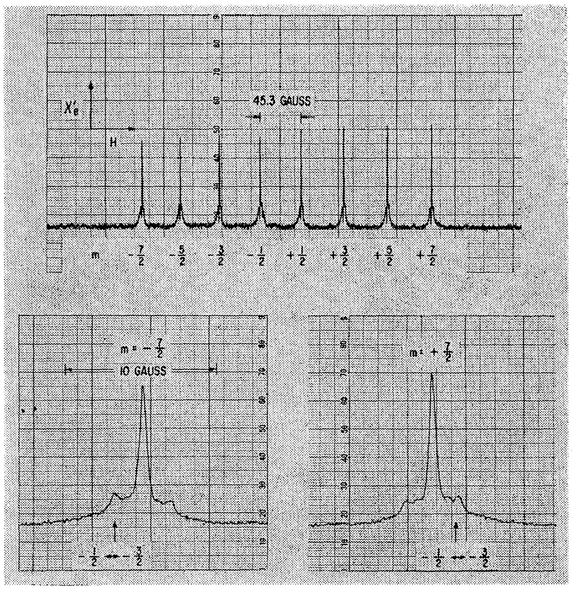

FIG. 1. The spectrum of V^{++} in silicon at 1.3°K. In the lower portion of the figure the $m=-\frac{7}{2}$ and $+\frac{7}{2}$ hyperfine lines are shown on an expanded scale, with the calculated position of the $M=-\frac{1}{2}$ to $-\frac{3}{2}$ transition indicated by an arrow.

The vanadium hyperfine lines shown in Fig. 1 are narrow and well resolved. Since $S=\frac{3}{2}$, one predicts that each hyperfine line is split into three fine structure lines by the term $m(2M-1)A^2/2h\nu$. At the temperature of the recording the predicted relative intensities are 1:2.3:3 for the $M=\frac{3}{2}$ to $\frac{1}{2}$, $\frac{1}{2}$ to $-\frac{1}{2}$, and $-\frac{1}{2}$ to $-\frac{3}{2}$ transitions, respectively. The $\frac{3}{2}$ to $\frac{1}{2}$ and $-\frac{1}{2}$ to $-\frac{3}{2}$ transitions are not resolved. The origin of the shoulders on the lines in Fig. 1 is not understood; if they simply represented the $\frac{3}{2}$ to $\frac{1}{2}$ and $-\frac{1}{2}$ to $-\frac{3}{2}$ transitions, they should move together as one moves to lower $|m|$. However, the shoulders on the lines of large $|m|$ are asymmetric. We believe that the $-\frac{1}{2}$ to $-\frac{3}{2}$ transition is broadened and lies beneath the shoulder which is the more pronounced. This interpretation implies that A is negative.

The $\frac{3}{2}$ to $\frac{1}{2}$ and $-\frac{1}{2}$ to $-\frac{3}{2}$ transitions may be broadened by crystalline strains. Random crystalline field (D) terms in the Hamiltonian would broaden the above transitions in first order but not the $\frac{1}{2}$ to $-\frac{1}{2}$ transitions. Double resonance for $M=\pm\frac{3}{2}$ has not been detected.

B. Chromium

The spectrum of chromium was first detected in iron-doped silicon crystals, in which it was present unintentionally.[15] The configuration of atomic chromium is $3d^54s$. In crystals which are low resistivity n-type it is believed that the chromium sites are neutral; no resonant absorption due to chromium has been detected in such crystals. If chromium is diffused into silicon crystals doped with an acceptor, a spectrum is seen whose intensity increases with the acceptor concentration to a maximum at about 8×10^{15} acceptors/cm^3, and then decreases again to zero at an acceptor concentration of about 1.6×10^{16}/cm^3. It seems likely that isolated chromium is a double donor in silicon with a solubility $\sim8\times10^{15}$/cm^3 at the diffusion temperature. The upper acceptor level is 0.22 ev from the conduction band, as determined from Hall coefficient and resistivity

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[15] For a time it was believed that the chromium spectrum was due to empty iron donor sites.[11]

measurements.[16] The resonant species would seem to be Cr^+, having a half-filled *d*-shell and no other electrons outside of closed shells. The observed total spin of $\frac{5}{2}$ is in accord with this picture.

The spectrum of Cr^+ is shown in Fig. 2. There are $2S$ well resolved fine structure lines whose positions are described by $S=\frac{5}{2}$ and a cubic field splitting parameter $a=+30.16\times10^{-4}$ cm^{-1} (see Fig. 3). At high temperatures the theoretical relative intensities of the lines are $(S+M)(S-M+1)$ or 8:5:9:5:8; approximately these values are found experimentally. At low temperatures the relative intensities change because of the Boltzmann factor. From the intensity changes, the sign of a was determined. It was then also possible to label each line with the transition which it represents (see Fig. 2).

The four weak lines associated with each fine structure line in Fig. 2 are due to hyperfine interaction with the 9.5% abundant Cr^{53} isotope. Figure 4 shows the spectrum in a crystal doped with chromium enriched in Cr^{53}. As expected, the Cr^{53} hyperfine lines are now dominant. The lines due to the isotopes of spin zero are somewhat larger than would be expected on the basis of the quoted enrichment (96% Cr^{53}). The discrepancy probably is accounted for by contamination of the crystal with chromium of normal isotopic abundances.

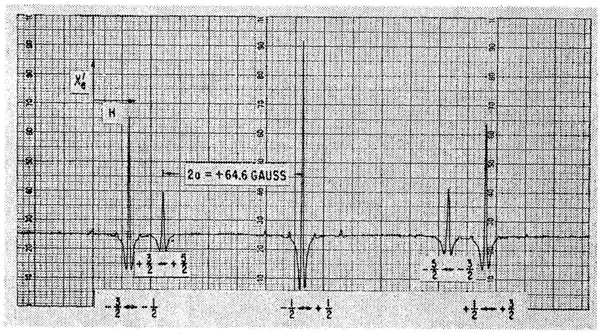

FIG. 2. The spectrum of Cr^+ in silicon at 20.4°K for the magnetic field in the [001] direction. The five fine structure lines are labelled according to the transition which each represents.

At 1.3°K it was possible to observe electron-nuclear double resonance for the $M=\pm\frac{1}{2}$, $\pm\frac{3}{2}$, and $-\frac{5}{2}$ levels. Because of depopulation of the $M=+\frac{5}{2}$ levels at 1.3°K, double resonance was not observed for that case. The double resonance transitions occur in the vicinity of $A/2$ (16 Mc/sec) for $M=\pm\frac{1}{2}$, $3A/2$ for $M=\pm\frac{3}{2}$, and $5A/2$ for $M=-\frac{5}{2}$, as predicted from Eq. (4). Within experimental error, the frequencies are accounted for by the calculated value for A and the known value of the Cr^{53} nuclear moment. Using the known sign of the nuclear moment, the sign of A was determined. For example, the $M=-\frac{5}{2}$, $m=\frac{1}{2}$ to $-\frac{1}{2}$ transition occurs at about 78.86 Mc/sec. For $A<0$, the transition would be expected to fall at $|5A/2|-(5A^2/4h\nu)-g_I\beta_N H$ or 81.23 Mc/sec, and for $A>0$, at $(5A/2)+(5A^2/4h\nu)+g_I\beta_N H$ or 78.84 Mc/sec, showing that $A>0$. The sign and size of the chromium nuclear moment are also obtained from the double resonance experiments. They are in agreement with the published values.

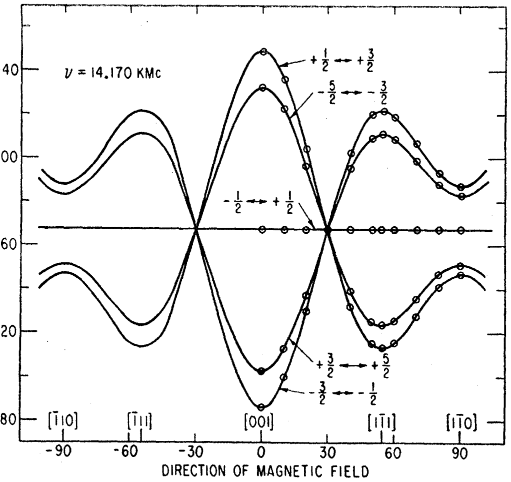

FIG. 3. The cubic field splitting of the Cr^+ spectrum in silicon. The solid lines are theoretical curves calculated from the measured g factor and the measured cubic field splitting in the [001] direction.

In the ordinary resonance experiment, the hyperfine interaction with Si^{29} is not well resolved. However, a large number of Si^{29} double resonance transitions have been resolved, indicating a maximum hyperfine interaction with Si^{29} which is less than 1×10^{-4} cm^{-1}. Analysis of the Si^{29} hyperfine interaction should prove interesting since virtually no information presently is available as to the extent of the wave functions about deep level impurity atoms. Feher[5] has already performed the analogous experiment on shallow donors in silicon.

Cr^+ samples are not stable at room temperature; in a week's time most of the Cr^+ associates with the acceptor which is present. The spectra of pairs formed between chromium and boron, gallium, aluminum, and gold have been studied, and will be reported on in a later publication.

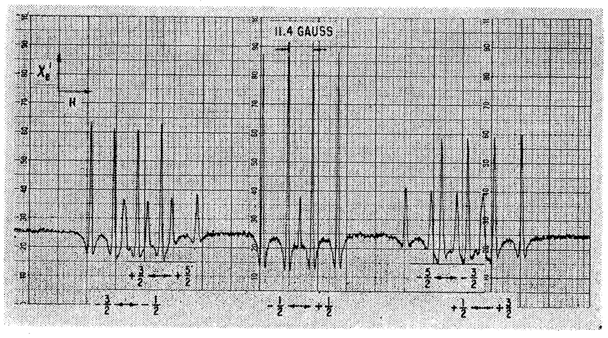

FIG. 4. The spectrum of Cr^+ in silicon at 20.4°K obtained using Cr enriched to 96% in Cr^{53}. Since $I=\frac{3}{2}$ for Cr^{53} each fine structure line is split into four by the hyperfine interaction.

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[16] The electrical measurements were made by R. O. Carlson.

C. Manganese

Crystals can readily be prepared which contain isolated manganese atoms, clusters of four manganese atoms, or manganese-acceptor pairs. To obtain isolated Mn^-, manganese is diffused into crystals doped with a donor impurity, such as phosphorus, and the sample is quenched rapidly as described in Sec. II. Such a procedure results in a reduction in the concentration of neutral phosphorus atoms which is roughly equal to the concentration introduced of the resonant form of isolated manganese. The maximum solubility is about $2\times 10^{15}/\text{cm}^3$. The spectrum of Mn^- is shown in Fig. 5. There are six manganese hyperfine lines each of which is split into two by the term $m(2M-1)A^2/2h\nu$ of Eq. (3); thus $S=1$. Inspection of the relative amplitudes of the fine structure lines at low temperatures shows that $A<0$.

To confirm that $S=1$, electron-nuclear double resonance measurements were made on the $M=0$ and $M=\pm 1$ levels. Since A is large, Eq. (4) was not sufficiently accurate for their interpretation and more refined expressions, based on calculations by F. Ham, were used. These expressions are given in the Appendix. As seen there, the $M=0$ transitions (which occur in the neighborhood of 8.5 Mc/sec) depend upon m because of $(A/h\nu)^3$ and higher order terms. Terms involving $(A/h\nu)^3$ also are necessary for interpretation of the $M=\pm 1$ transitions which are in the range 200–228 Mc/sec. The sign of the $(A/h\nu)^3$ terms gives independent evidence that $A<0$. Quantitative agreement with the theoretical expressions is obtained if and only if $S=1$.

Clusters of four manganese atoms are produced if manganese is diffused into low resistivity n-type or high resistivity silicon crystals, and the samples are cooled relatively slowly. The spectrum of such clusters has been described elsewhere.[10] Twenty-one manganese hyperfine lines showing a characteristic envelope of intensities are observed, corresponding to the twenty-one possible values of $m=\sum_{k=1}^{4} m_k$. From the crystalline field splittings of the spectrum it appears that $S=2$; attempts to detect manganese double resonance and confirm this value for S were unsuccessful.

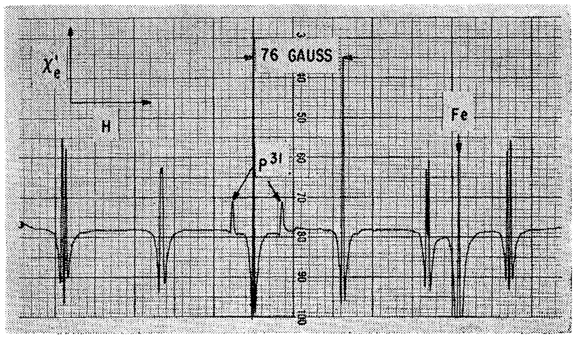

FIG. 5. The spectrum of Mn^- in silicon at 20.4°K for the magnetic field in the [111] direction. Six manganese hyperfine lines are visible, each of which is split into two by a second order hyperfine term involving m and M.

If manganese is diffused into p-type samples which are cooled relatively slowly, manganese-acceptor pairs are formed. The pairs formed between manganese and acceptors such as boron, aluminum, gold,[10] and platinum have been studied but will not be discussed here.

Samples containing manganese and an acceptor such as boron or gallium have also been rapidly quenched from the diffusion temperature. When this is done, a new spectrum is observed which is tentatively attributed to isolated Mn^{++} (see Table I). The spectrum shows five well resolved fine structure lines ($S=\frac{5}{2}$ in a cubic field) each of which is split into six by hyperfine interaction with the Mn^{55} nucleus. The sign of the cubic field splitting parameter was determined from measurements of relative intensities at low temperature. The relative sign of a and A was determined in the manner described by Low.[14] This new spectrum shows roughly the same intensity as the spectrum of Mn^-. Thus, the two spectra may represent the same manganese site in different charge states.

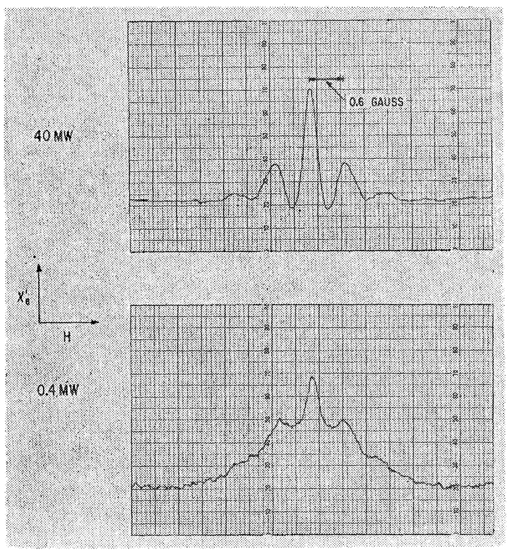

FIG. 6. Spectrum of neutral iron at 20.4°K for the magnetic field in the [111] direction and two different levels of microwave power, 0.4 and 40 mw.

D. Iron

The maximum solubility of iron in silicon is about $1.5\times 10^{16}/\text{cm}^3$. When the Fermi level is above the donor level of iron (which is 0.40 ev from the valence band), it is believed that the iron sites are neutral. The observation that diffusing iron into n-type crystals leaves the resistivity unchanged supports this view. The spectrum of neutral iron sites[17] is shown in Fig. 6 for iron of normal isotopic abundance. One line showing pro-

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[17] Prior to our measurements, this spectrum was observed by G. Feher (see reference 5).

nounced structure at high microwave power levels is observed. The structure is not understood; it may represent hyperfine interaction with Si^{29} nuclei. In crystals doped with iron enriched in Fe^{57}, the Fe^{57} hyperfine structure is well resolved and has been used for verification of the Fe^{57} nuclear spin.[18] The relaxation time of the iron resonance is just sufficiently long at pumped helium temperatures (1.3°K) to allow observation of electron-nuclear double resonance. Thus it has been possible to determine S using double resonance and to determine the Fe^{57} nuclear moment from this spectrum. These measurements will be reported in a separate communication.

No resolved fine structure is observed as long as the tetrahedral symmetry of the iron sites is undisturbed. However, it is possible to destroy the tetrahedral symmetry of the sites by subjecting the crystal to a uniaxial stress. The appearance of two well-resolved fine structure lines under such stress (see Fig. 7) confirms that $S=1$. That $S=1$ can also be deduced from the assigned charge state (Fe^0), which implies that the site contains an even number of unpaired electrons and thus has integral spin. The absence of any cubic field splitting shows that $S\leq\frac{3}{2}$.

The width of the iron spectrum varies with the direction of the applied magnetic field. This variation may be due to small strains present in the sample.

If iron is diffused into silicon crystals doped with an acceptor such as B, Ga, Al, or In and the crystals are cooled slowly, iron-acceptor pairs[11] are formed.

An isotropic line at $g=3.5$ has been observed in p-type samples containing iron that were rapidly quenched. This spectrum may be due to a positively charged form of isolated iron (e.g., Fe^+). Further study of this spectrum is in progress.

IV. DISCUSSION

From the foregoing it is clear that V, Cr, Mn, and Fe can be introduced into silicon crystals as isolated entities. Both the g factors and the hyperfine interactions with the impurity nuclei are isotropic. Since the symmetry about the sites is tetrahedral, only cubic crystalline field splittings are present. The spectra are consistent with the spin Hamiltonian of Eq. (1).

The electron configurations of isolated V, Cr, Mn, and Fe atoms are $3d^34s^2$, $3d^54s$, $3d^54s^2$, and $3d^64s^2$, respectively. The simplest method of accounting for the electron spins of V^{++}, Cr^+, and Mn^{++} in silicon is to assume that the $4s$ electrons have been lost, while the d-shell configurations are unchanged. Mn^- and Fe^0 show $S=1$. It is thought that their electron configuration is $3d^8$; i.e., that transferral of outer-shell electrons to the $3d$-shell is energetically favored in the silicon lattice for these (presumably interstitial) impurities.

The Cr^+ and Fe^0 spectra have been observed from 78°K to 1.3°K. The resistivity of samples containing V^{++}, Mn^-, or Mn^{++} was not sufficiently high at 78°K for resonance studies, but sharp lines have been observed at 20.4°K. Thus relaxation times associated with the resonances are relatively long at liquid hydrogen temperatures and often above. Except in the case of iron, the relaxation times at 1.3°K are of the order of seconds or longer.

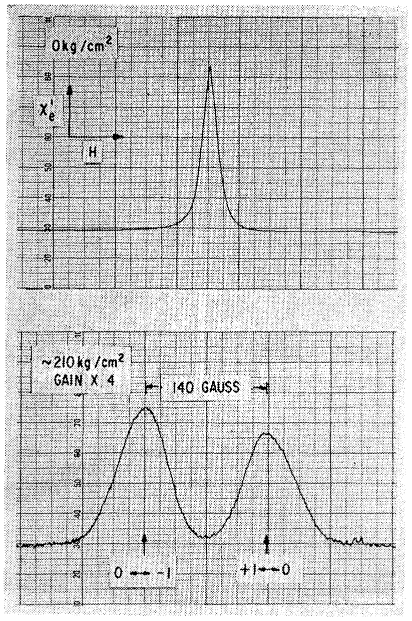

FIG. 7. The spectrum of neutral iron in silicon at ~10°K for the magnetic field in the [011] direction and a stress applied in the [100] direction. The splitting between the fine structure lines remains constant as the magnetic field is rotated in the (100) plane.

At low temperatures the lines are narrow (the widths at 10°K are of order one gauss). Nevertheless, in no case is the hyperfine interaction with Si^{29} well resolved. Electron-nuclear double resonance would seem the most promising method for investigating this interaction. Such an investigation should allow one to decide conclusively whether a given impurity is substitutional or interstitial since the second nearest neighbor positions are different for the two cases. A substitutional atom has twelve second nearest neighbors which are in [110] directions from it; an interstitial atom located in the symmetric site has six second nearest neighbors which are in [100] directions.

In all the cases studied, the electron-nuclear double resonance spectra are well accounted for in terms of the assigned S, the hyperfine interaction (A) measured by ordinary resonance, and the known nuclear g factor. In accordance with the tetrahedral symmetry of the sites, no quadrupolar terms are necessary. Since the true nuclear g factor accounts for the double resonance results, there are no nearby electronic states.[19] Since in

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[18] Ludwig, Woodbury, and Carlson, Phys. Rev. Letters **1**, 295 (1958).

[19] One effect of nearby states is to introduce energy terms which can be considered as giving rise to an effective nuclear g factor different from the true one. See, for example, J. M. Baker and B. Bleaney, Proc. Roy. Soc. (London) **A245**, 156 (1958).

addition the states giving rise to the spectra are not depopulated at low temperatures, they must be the ground states of the impurities in question.

V. ACKNOWLEDGMENTS

The authors are indebted to R. O. Carlson and G. D. Brower for preparing the many samples required for these studies. C. R. Trzaskos assisted in all phases of the measurements and was largely responsible for the production of successful double resonance cavities. G. Watkins, and in particular F. Ham, have contributed to the interpretation. The idea for the double resonance cavity was conceived jointly with R. L. Watters.

APPENDIX

Starting with Eq. (1) of the text, F. Ham has derived the following exact expressions for the energy levels $W_{M,m}$ for $S=1$.

$$W_{1,m}=g\beta H+Am-g_I\beta_N Hm+\tfrac{1}{2}A^2(I+m+1)(I-m)[W_{1,m}+g_I\beta_N H(m+1)]^{-1}$$

$$\cdot\left\{1-\frac{\tfrac{1}{2}A^2(I-m-1)(I+m+2)}{[W_{1,m}+g_I\beta_N H(m+1)][W_{1,m}+g\beta H+g_I\beta_N H(m+2)+A(m+2)]}\right\}^{-1},$$

$$W_{0,m}=-g_I\beta_N Hm+\tfrac{1}{2}A^2(I+m)(I-m+1)[W_{0,m}-g\beta H+g_I\beta_N H(m-1)-A(m-1)]^{-1}$$

$$+\tfrac{1}{2}A^2(I-m)(I+m+1)[W_{0,m}+g\beta H+g_I\beta_N H(m+1)+A(m+1)]^{-1},$$

$$W_{-1,m}=-g\beta H-Am-g_I\beta_N Hm+\tfrac{1}{2}A^2(I-m+1)(I+m)[W_{-1,m}+g_I\beta_N H(m-1)]^{-1}$$

$$\cdot\left\{1-\frac{\tfrac{1}{2}A^2(I+m-1)(I-m+2)}{[W_{-1,m}+g_I\beta_N H(m-1)][W_{-1,m}-g\beta H+g_I\beta_N H(m-2)-A(m-2)]}\right\}^{-1},$$

where the notation follows that of the text. By expanding the expression for $W_{0,m}$, one finds that the frequency of the $(0,m)$ to $(0,m-1)$ double resonance transition is given approximately by

$$f_{0,m}=\nu|\gamma+(1-\gamma)(A/h\nu)^2-2(2m-1)(A/h\nu)^3$$
$$-(12m^2-12m+5)(A/h\nu)^4|$$

where $\gamma=g_I\beta_N H/h\nu$. Similarly, including third order terms in $A/h\nu$, the $(\pm1,m)$ to $(\pm1,m-1)$ double resonance transitions are given by

$$f_{\pm1,m}=\nu|(A/h\nu)+\tfrac{1}{2}(2m-1)(1-\gamma)(A/h\nu)^2$$
$$+\tfrac{1}{2}(3m^2-3m+1-I^2-I)(A/h\nu)^3$$
$$\pm[\tfrac{1}{2}(1-\gamma)(A/h\nu)^2+\gamma+\tfrac{1}{2}(1-2m)(A/h\nu)^3]|.$$

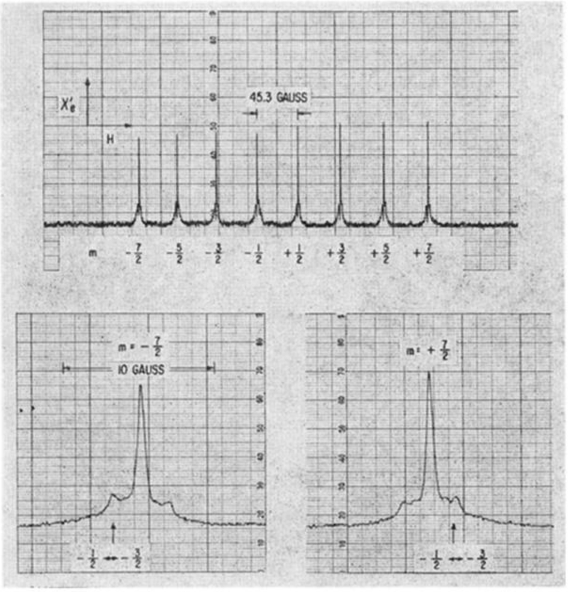

FIG. 1. The spectrum of V^{++} in silicon at 1.3°K. In the lower portion of the figure the $m=-\frac{7}{2}$ and $+\frac{7}{2}$ hyperfine lines are shown on an expanded scale, with the calculated position of the $M=-\frac{1}{2}$ to $-\frac{3}{2}$ transition indicated by an arrow.

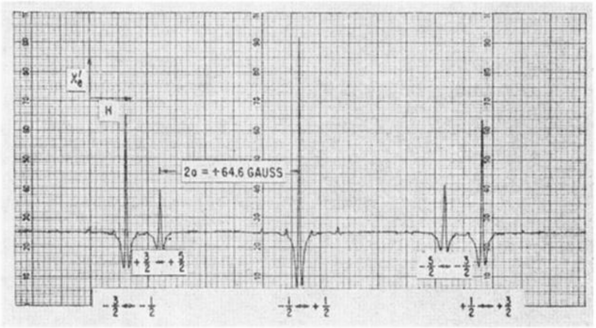

FIG. 2. The spectrum of Cr^+ in silicon at 20.4°K for the magnetic field in the [001] direction. The five fine structure lines are labelled according to the transition which each represents.

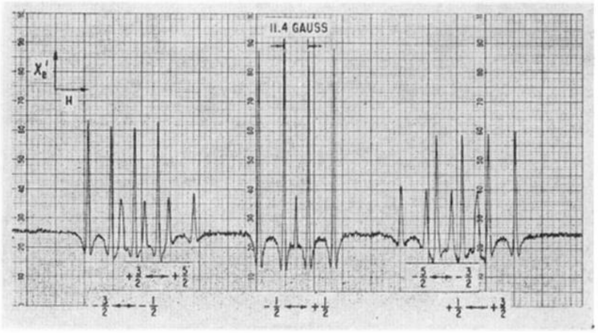

FIG. 4. The spectrum of Cr^+ in silicon at 20.4°K obtained using Cr enriched to 96% in Cr^{53}. Since $I=\frac{3}{2}$ for Cr^{53} each fine structure line is split into four by the hyperfine interaction.

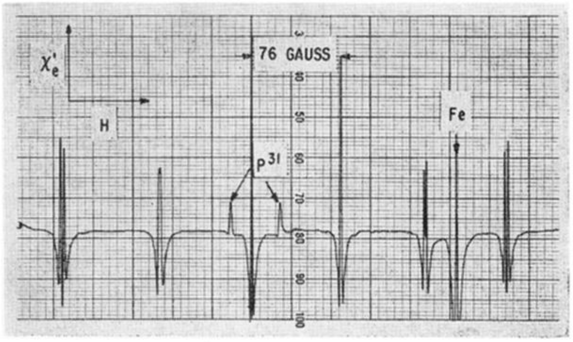

FIG. 5. The spectrum of Mn^- in silicon at 20.4°K for the magnetic field in the [111] direction. Six manganese hyperfine lines are visible, each of which is split into two by a second order hyperfine term involving m and M.

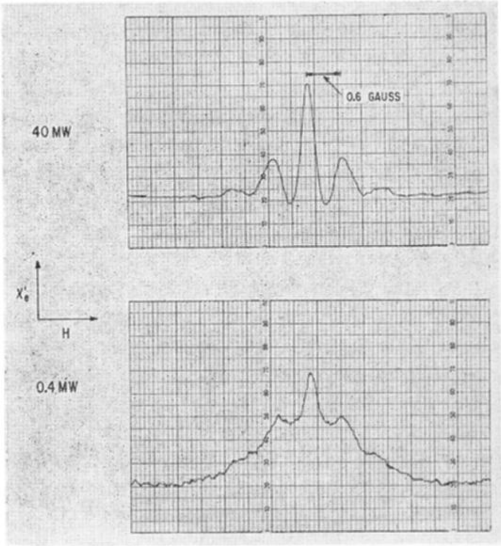

FIG. 6. Spectrum of neutral iron at 20.4°K for the magnetic field in the [111] direction and two different levels of microwave power, 0.4 and 40 mw.

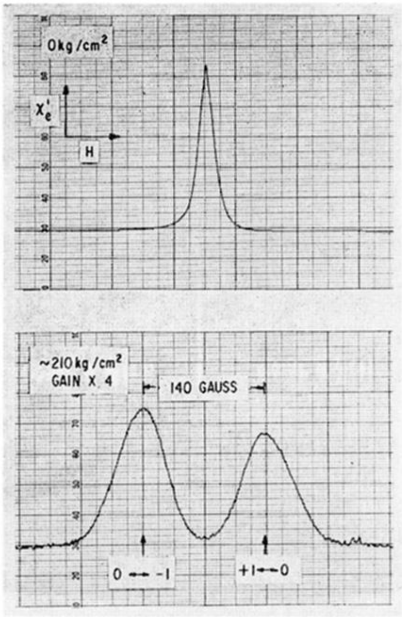

FIG. 7. The spectrum of neutral iron in silicon at ∼10°K for the magnetic field in the [011] direction and a stress applied in the [100] direction. The splitting between the fine structure lines remains constant as the magnetic field is rotated in the (100) plane.