ELECTRONIC STRUCTURE OF TRANSITION METAL IONS IN A TETRAHEDRAL LATTICE

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Although transition metal ions have been studied for many years as impurities in lattices of tetrahedral symmetry (e.g., silicon and germanium), little information has emerged as to their electronic structure in such an environment.[1] In this Letter the authors present a model for the electronic structure of ions of the $3d$ transition metals in silicon, deduced from electron spin resonance measurements. This model is the following[2]:

1. The tetrahedral crystalline field partially lifts the fivefold orbital degeneracy of the $3d$ shell. In substitutional transition metal ions the resulting threefold degenerate t_2 states lie higher in energy than the doubly degenerate e states. The reverse is true for the interstitial ions.
2. The substitutional transition metal ions transfer enough $3d$-shell electrons to the valence shell to form tetrahedral bonds with the silicon nearest neighbors. The interstitial ions transfer all valence-shell electrons to the $3d$ shell.

The effect on transition metal ions of a crystalline field of octahedral symmetry is well known.[3,4] Consider a single $3d$ electron ($l=2$). A cubic crystalline field splits the fivefold orbital degeneracy into a doublet (e_g) and a triplet (t_{2g}). The lobes of the doublet wave functions point in the cubic crystalline directions (the angular dependences are as $3z^2-r^2$ and as x^2-y^2) while the lobes of the triplet wave functions point along the face diagonals (the angular dependences are as xy, yz, and zx). For a positive ion surrounded by an octahedron of negative ions, the energy of the e_g states is higher than that of the t_{2g} states, since the lobes of the wave functions of the e_g states extend toward the negative ions. Calculations have also been made for a tetrahedral arrangement of negative ions about a central positive ion. In this case the order of the levels is reversed.[4]

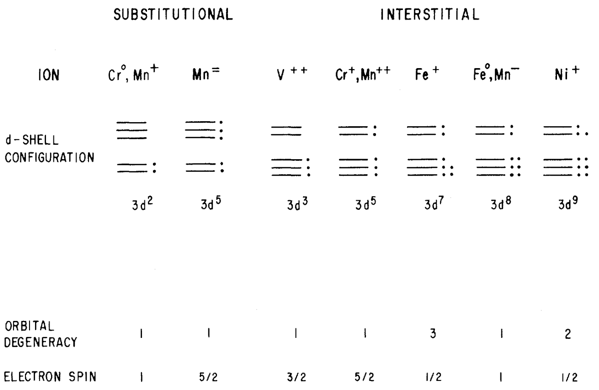

FIG. 1. Proposed electronic structure of $3d$ transition metal ions in silicon. The orbital degeneracy and electron spin values (derived from the proposed structure) agree with the spin resonance results. The spin of 1/2 for Fe^{+} results from spin-orbit interaction (see text).

Transition metal ions in silicon represent a somewhat different case, since the silicon atoms are bound covalently. Still, it is expected that for substitutional ions the e states lie lower in energy than the t_2 states, since the regions of lower electron density are in the cubic directions. Electron spin resonance measurements on substitutional Mn and Cr ions support this view.[5,6] Substitutional $Mn^{=}$ has an electron spin of 5/2; the proposed model is that four electrons are used to form tetrahedral bonds to the silicon nearest neighbors, leaving the configuration $3d^5$ for the manganese (see Fig. 1). The charge state of manganese can be varied by varying the concentration and type of the doping agent, thereby varying the position of the Fermi level in the crystal. If the t_2 levels are higher in energy, as assumed, and if the $Mn^{=}$ ion loses electrons from the d shell rather than from the bonding orbitals when its charge state is changed, then substitutional Mn^{-} and Mn^{0} are orbital triplets. The orbital and spin degeneracy of such triplets is partially lifted by spin-orbit interaction. However, the resulting states are frequently spaced so closely that relaxation times are short even at low temperature and spin resonance is difficult to detect.[7] The authors have not been able to detect Mn^{0} or Mn^{-} in suitably prepared crystals at temperatures as low as 10°K.

Removing a third electron would result in an orbital singlet (Mn^{+}). Electron spin resonance due to substitutional Mn in this charge state, and due to the isoelectronic Cr^{0}, has been detected at 20.4°K. The observed electron spin values and the long relaxation times substantiate the view that the electron configuration is $3d^2$ and that the t_2 levels lie higher in energy.

The spectra of interstitial transition metal ions in silicon[5] cannot be explained by the assumptions used in the substitutional case. The results can be accounted for if the triply degenerate t_2 states lie lower in energy than the e states. A qualitative explanation for this is as follows: While the symmetry of the four nearest neighbors to an interstitial site is tetrahedral, the six second nearest neighbors, which are almost as close (the ratio of distances being $2/\sqrt{3}$), are arranged in a regular octahedron. Apparently the tendency of the second nearest neighbors to raise the energy of the e states overrides the relative lowering of these states via interaction with the nearest neighbor silicon atoms.

The second hypothesis used to account for the spin resonance observations on interstitial ions is that all valence-shell electrons are transferred to the $3d$ shell.[8] In free space, such a transfer requires about 1 to 4 ev per neutral atom, and about 0 to 1 ev per singly charged positive ion.[9]

The electronic structures assigned to the various interstitial ions in silicon are shown in Fig. 1. In the case of V^{++}, all of the valence-shell electrons are ionized and the d-shell configuration is that of the free atom. Since the t_2 states lie lower in energy, the ground state is an orbital singlet and resonance absorption near $g=2$ is observed ($S=3/2$). Resonance due to Mn^{++} and Mn^- is observed, since these ions are orbital singlets; again the g factors are near two, and the electron spin values are as predicted. Resonance due to Mn^+ and Mn^0 has not been observed at temperatures as low as 10°K; the ground state is an orbital triplet. The spectrum of Fe^0 is similar to that of Mn^-, indicating that the electron configurations are identical. If the configuration of Fe^0 were that of the atom in free space, the observed electron spin would be two rather than one.

The model predicts that the ground state of Fe^+ in silicon is an orbital triplet (neglecting spin-orbit interaction) and that the spectrum is similar to that of Co^{++} in a crystalline field of octahedral symmetry. One indeed only detects resonance for Fe^+ at very low temperatures ($T \lesssim 10$°K); the g factor (3.5) is similar to those found for Co^{++}. Following Abragam and Pryce,[10] it appears that this g factor (and the spin of 1/2) can be accounted for in terms of a tetrahedral crystalline field, spin-orbit interaction, and the mixing of states derived from the atomic ^4P term with those of the ^4F ground state.

The model predicts a Jahn-Teller distortion and a spin of 1/2 for Ni^+, and such is observed.[5]

We thus feel that the occupation of the $3d$ shell of transition metal ions in silicon varies widely depending upon whether the ion is substitutional or interstitial, and depending on its charge state. In particular, the configuration[11] of manganese ranges from $3d^2$ to $3d^8$. Contrary to what might have been anticipated, in interstitial ions the t_2 states lie lower in energy than the e states.

The authors are indebted to F. Ham for valuable discussions

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[1] See, for example, N. B. Hannay, Semiconductors (Reinhold Publishing Corporation, New York, 1959), p. 340 ff; Richard A. Bube, Photoconductivity of Solids (John Wiley and Sons, Inc., New York, 1960), p. 135 ff, 158 ff; W. Low and M. Weger, Phys. Rev. 118, 20 (1960).

[2] The notation used to describe the $3d$ states follows that of J. D. Dunitz and L. E. Orgel [J. Phys. Chem. Solids 3, 20 (1957)]. See also R. S. Mulliken, Phys. Rev. 43, 279 (1933).

[3] H. A. Bethe, Ann. Physik 3, 133 (1929); K. D. Bowers and J. Owen, Reports on Progress in Physics (The Physical Society, London, 1955), Vol. 18, p. 305; J. D. Dunitz and L. E. Orgel, J. Chem. Phys. Solids 3, 20 (1957).

[4] See, for example, W. Low, in Solid-State Physics, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1960), Suppl. 2, Chap. II.

[5] H. H. Woodbury and G. W. Ludwig, Phys. Rev. 117, 102 (1960); G. W. Ludwig and H. H. Woodbury, Phys. Rev. 117, 1286 (1960); H. H. Woodbury and G. W. Ludwig, Bull. Am. Phys. Soc. 5, 158 (1960).

[6] All of the transition metal ions reported on in reference 5 are interstitial. Since that time we have been able to produce and detect manganese and chromium in a substitutional form as well. These experiments, and evidence for the substitutional or interstitial character of ions, are discussed in the preceding Letter [H. H. Woodbury and G. W. Ludwig, Phys. Rev. Letters 5, 96 (1960)].

[7] See, for example, W. Gordy, W. V. Smith, and R. F. Trambarulo, Microwave Spectroscopy (John Wiley & Sons, New York, 1953), p. 224.

[8] This hypothesis was first suggested to us by G. D. Watkins. He reasoned that the radial extent of the $4s$ orbital is greater than that of the $3d$ orbitals, and that in the interstitial site overlap with orbitals of the neighboring silicon atoms raises its energy above that of the $3d$ shell.

[9] C. E. Moore, Atomic Energy Levels, National Bureau of Standards Circular No. 467, August 15, 1952 (U. S. Government Printing Office, Washington, D. C., 1952), Vol. 2.

[10] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc.

(London) A206, 173 (1951).

[11] It is noted that the 3*d* orbitals in the solid may be hybridized with other orbitals having similar transformation properties, and, as W. Marshall has pointed out to us, their radial extent may be considerably greater than that in the free atom.

INTERACTION OF PHONONS AND SPIN WAVES IN YTTRIUM IRON GARNET

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Schlömann[1] has shown that certain spin wave pairs can be made to grow in amplitude when coupled by a uniform rf magnetic field applied parallel to the dc biasing field. The strength of the rf field required to initiate unstable growth is a measure of the width, ΔH_k, of the spin wave resonance. If a given biasing field is applied to a small sample of ferrimagnetic material in a microwave cavity, measurement of the power level at which the return loss from the cavity changes discontinuously allows one to plot a curve such as Fig. 1. The branch labelled $\theta = \pi/2$ is of particular interest since it corresponds to spin waves of known wavelength propagating in a particular direction. The linewidth of these spin waves is given by[1] $4\pi\gamma M h_{\mathrm{rf}}/\omega_p = \Delta H_k$, where ω_p is the pumping frequency and the wave number, k, of the $\omega_p/2$ spin waves is specified by[2]

$$Dk^2/\gamma\hbar = H_m - H. \qquad (1)$$

Here H is the applied dc field and H_m is the limiting value of H for $\frac{1}{2}\pi$-directed spin waves as k approaches zero. Since the ΔH_k of specific spin waves is determined by this experiment, one can check the adequacy of the Kasuya, Sparks, and Kittel[3,4] linewidth theory and measure D at a higher temperature than is possible with other techniques.[5-7] This experiment is still in progress and will be reported on jointly with E. G. Spencer and R. C. LeCraw later.

The magnitude of ΔH_k is shown in Fig. 2 as a function of $(H_m - H)^{1/2}$ for a 0.019-inch yttrium

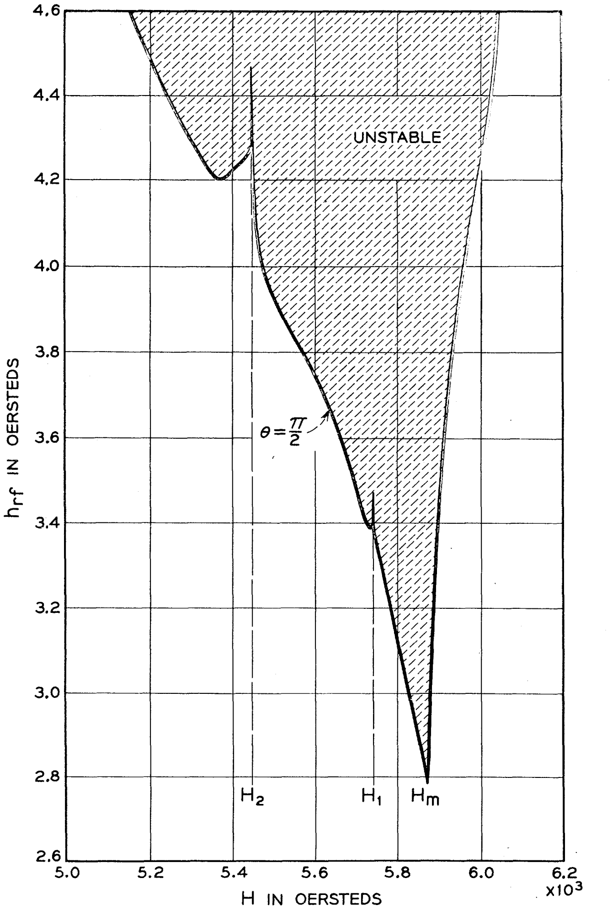

FIG. 1. Rf field strength required to excite spin wave pairs as a function of applied field. Pumping frequency is 34.627 kMc/sec, and fields are along [111] crystal axis.

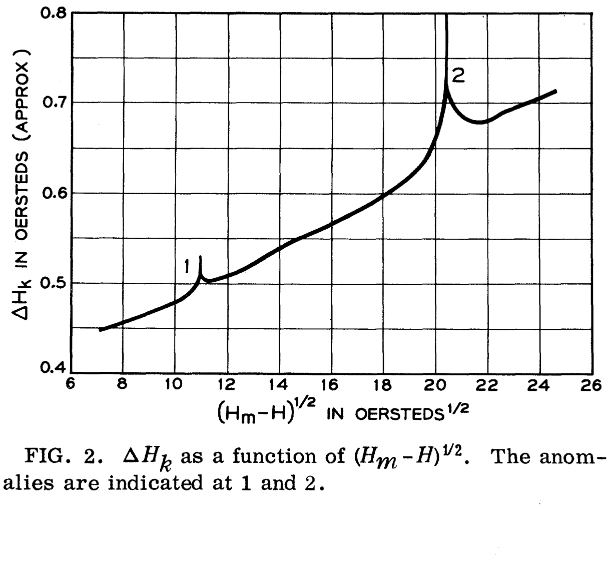

FIG. 2. ΔH_k as a function of $(H_m - H)^{1/2}$. The anomalies are indicated at 1 and 2.