

electron value support this view. Assuming that one is dealing with an orbital singlet one can use second order perturbation theory, in the manner of Abragam and Pryce,⁵ to calculate the effect of excited electronic states on the electronic g factor. As they show, $g_{ij} = 2.0023\delta_{ij} - 2\lambda\Lambda_{ij}$, where λ is the spin-orbit coupling constant and $\Lambda_{ij} = \sum_{n \neq 0} \langle 0 | L_i | n \rangle \langle n | L_j | 0 \rangle / (E_n - E_0)$. For the case of present interest $\Lambda_{ij} = 0$ for $i \neq j$, $\Lambda_{ii} = \Lambda_{jj} = \Lambda$, and $g = 2.0023 - 2\lambda\Lambda$. Abragam and Pryce omitted (as generally small) the corresponding perturbation of the nuclear g factor. One finds $g_I' = g_I + 2p\Lambda(\beta/\beta_N)$, where $p = 2g_I\beta\beta_N\langle r^{-3} \rangle$. Combining the equations for g and g_I' , the nuclear g factor can be calculated from the effective nuclear g factor and the departure of the electronic g factor from the free electron value:

$$g_I = g_I' - (2.0023 - g)p\beta/\lambda\beta_N. \quad (3)$$

The spectra of several (interstitial) transition metals in silicon are consistent with the hypothesis that in the crystal the $4s$ electrons are transferred to the $3d$ shell, e.g., that the electron configuration of neutral iron is $3d^8$. Using the Lande interval rule, $\lambda \simeq -127 \text{ cm}^{-1}$ for this configuration of the free atom.⁶ To evaluate p , $\langle r^{-3} \rangle$ was calculated from wave functions of Watson⁷ for the $3d^8$ configuration of neutral iron. The value obtained for $\langle r^{-3} \rangle$, 3.9 atomic units, may be compared with the experimental value, 4.3 atomic units, obtained by interpolation from Table 2 of Abragam, Horowitz, and Pryce.⁸ Taking $\langle r^{-3} \rangle$ as 4 atomic units, one finds from Eq. (3) that g_I is 1.2% lower than g_I' , or

⁵ A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

⁶ 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.

⁷ R. E. Watson, Technical Report No. 12, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, June 15, 1959 (unpublished).

⁸ A. Abragam, J. Horowitz, and M. H. L. Pryce, Proc. Roy. Soc. (London) **A230**, 169 (1955).

$g_I = +0.1806 \pm 0.0013$, $\mu = +0.0903 \pm 0.0007 \text{ nm}$ for Fe⁵⁷, where an uncertainty of 50% has been assigned to the calculation of the correction term.⁹

Supporting evidence that the above analysis gives an accurate value of g_I for Fe⁵⁷ is furnished by measurements on (Mn⁵⁵)⁻ in silicon,⁴ which is isoelectronic with (Fe⁵⁷)⁰. Analysis of the electron-nuclear double resonance data gives $g_I' = 1.386 \pm 0.002 \text{ nm}$ for (Mn⁵⁵)⁻. Taking $g = 2.0104$, $\lambda = -127 \text{ cm}^{-1}$, $\langle r^{-3} \rangle = 4.0$ atomic units, and using Eq. (3), one finds $g_I = 1.385 \pm 0.002 \text{ nm}$ for Mn⁵⁵, in agreement with the published value.

Electron-nuclear double resonance measurements have also been made on isolated (Fe⁵⁷)⁺ and on neutral (Fe⁵⁷Ga⁷¹) pairs in silicon (see Table I). For (Fe⁵⁷)⁺ two double resonance transitions were observed corresponding to $M = \pm \frac{1}{2}$. These were analyzed using Eq. (2) and lead to $|g_I'| = 0.1976 \pm 0.0018$ for (Fe⁵⁷)⁺. For (Fe⁵⁷Ga⁷¹)⁰ pairs the $M = \pm \frac{1}{2}$ double resonance transitions are readily interpretable only for the magnetic field along the [111] axis of the pair.¹⁰ In this direction $|g_I'| = 0.2071 \pm 0.0008$. In these spectra the electronic g factor is displaced considerably from the free electron value and the ground state may not be an orbital singlet. We have not yet been able to calculate g_I from the measured g_I' for these spectra.

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⁹ Even if the configuration of neutral iron is not $3d^8$, the correction term as calculated in the text probably is in error by less than 50%. For example, for the $3d^6 4s^2$ configuration $\lambda \simeq -100 \text{ cm}^{-1}$ as compared to $\lambda \simeq -127 \text{ cm}^{-1}$ for the $3d^8$ configuration. The assumed value for $\langle r^{-3} \rangle$ is probably correct to within 20%.

¹⁰ See H. H. Woodbury and G. W. Ludwig, following paper.

Magnetic Moment of Au¹⁹⁷

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Chromium-gold and manganese-gold impurity pairs in silicon have been observed by electron spin resonance techniques. Electron-nuclear double resonance studies of the gold hyperfine structure lead to a value of $0.1439 \pm 0.0004 \text{ nm}$ for the magnetic moment of Au¹⁹⁷.

IN the course of a study of chemical impurities in Si by spin resonance techniques, several interesting systems involving Au¹⁹⁷ have been detected. The use of electron-nuclear double resonance has permitted a rather precise determination of the magnetic moment of this nucleus, namely $0.1439 \pm 0.0004 \text{ nm}$.

Spin resonance associated with isolated Au in silicon has not been reported. However, resonant absorption for some of the transition metals has been observed.¹ It has been found that under appropriate conditions

¹ H. H. Woodbury and G. W. Ludwig, Phys. Rev. **117**, 100 (1960).

certain transition metal impurities may form pairs with acceptors such as B, Ga, or Au. These impurity pairs also show resonant absorption.² A pair that has been particularly suitable for the study of the Au hyperfine interaction is that formed between Cr and Au.

The Cr and Au are both introduced into Si by diffusion at about 1300°C. A model consistent with the observation of this and similar impurity pairs in Si is as follows: The Au finds substitutional sites in the lattice while the Cr remains interstitial at the diffusion temperature. As the sample is cooled, the Cr atoms move to interstitial positions adjacent to and in [111] directions from the substitutional Au atoms and form the pairs that are seen.

The experimental observations are consistent with the (CrAu) pair being neutral and having a total electron spin of $\frac{3}{2}$. However, the interaction of the atoms in the pair results in a splitting of the energy levels. The splitting can be described by a DS_z^2 term in the Hamiltonian, where the z direction is the axis of the pair. In the case of (CrAu)⁰, D is of the order of $+6.7 \text{ cm}^{-1}$ and is much greater than the magnetic interaction (0.5 cm^{-1}) of the electron spin with the applied magnetic field. The DS_z^2 term raises the $M=\pm\frac{3}{2}$ levels relative to the $M=\pm\frac{1}{2}$ levels such that only the $M=+\frac{1}{2}$ to $M=-\frac{1}{2}$ transition can be observed. The resonant absorption due to this transition can be described by an effective electron spin $S'=\frac{1}{2}$ and an effective spin Hamiltonian given by

$$\begin{aligned} \mathcal{H} = & \beta[g_{\parallel}'S_z'H_z + g_{\perp}'(S_x'H_x + S_y'H_y)] + A'S_z'I_z \\ & + B'(S_x'I_x + S_y'I_y) + P'[I_z^2 - \frac{1}{3}I(I+1)] \\ & - \beta N[(g_I)_{\parallel}H_zI_z + (g_I)_{\perp}(H_xI_x + H_yI_y)], \quad (1) \end{aligned}$$

where the electronic g factors are $g_{\parallel}'=2.0145$ and $g_{\perp}'=3.9817$. A' and B' are the hyperfine interaction parameters parallel and perpendicular to the pair axis, respectively, and P' is the effective nuclear quadrupole interaction parameter. For Au¹⁹⁷ in the (CrAu)⁰ pair, $A'=+4.54 \times 10^{-4} \text{ cm}^{-1}$, $B'=+5.26 \times 10^{-4} \text{ cm}^{-1}$, while $|P'| \gg A'$. The last term in Eq. (1) represents the interaction of the external field with the nucleus. Although it is the smallest term in the above Hamiltonian, it is the one which makes possible the determination of the nuclear moments. If both nuclei of the pair have nonzero spins, the interaction terms of both must be included.

Solving the above Hamiltonian for the double resonance transitions (i.e., the difference in energy between the (M, m) and $(M, m-1)$ hyperfine levels) with the magnetic field along the axis of the pair, one obtains to second order in A' and B'

$$f = |A'M - [(2m-1)M(B')^2/2\nu] - (g_I)_{\parallel}\beta_N H + (2m-1)P' - (B')^2/4\nu|, \quad (2)$$

² G. W. Ludwig and H. H. Woodbury (to be published). Reference 1 contains a brief discussion of some of the pairs that have been observed.

where ν is the klystron frequency and the other parameters are expressed in frequency units. Analysis of the model in which the only excited states of importance are the $M=\pm\frac{3}{2}$ states indicates that $(g_I)_{\parallel}=g_I$, the nuclear g factor. Off axis this formula must be modified. It is noted that $(g_I)_{\perp}$ may be quite different from g_I and that from such differences, D can be calculated.^{2,3}

An average of measurements at 1.3°K of the $(\pm\frac{1}{2}, +\frac{1}{2})$ to $(\pm\frac{1}{2}, -\frac{1}{2})$ transitions gave the following numerical values: $f=6.7920 \pm 0.3621 \text{ Mc/sec}$, $H=4889.5 \text{ gauss}$, and $\nu=13.785 \text{ kMc/sec}$. Assuming the published sign of the moment, one calculates from Eq. (1) that $g_I(\text{Au}^{197})=+0.0959 \pm 0.0003$ and $\mu(\text{Au}^{197})=+0.1439 \pm 0.0004 \text{ nm}$. The uncertainty in g_I arises from the uncertainty in crystal alignment and in the measurement of f . The $m=+\frac{3}{2}$ to $m=+\frac{1}{2}$ and $m=-\frac{1}{2}$ to $m=-\frac{3}{2}$ transitions ($I=\frac{3}{2}$ for Au¹⁹⁷) were not observed. This was because of the large value of P' which put these transitions outside our radio frequency range ($f > 200 \text{ Mc/sec}$).

Even with the magnetic field along the axis of the pair one might measure a nuclear g factor differing from that of the isolated nucleus because of nearby excited electronic states other than the $M=\pm\frac{3}{2}$ states.^{3,4} In the present case it is not clear how the correction to g_I should be calculated. However, it is believed to be small since g' is close to the free electron value. To check that g_I' is not perturbed appreciably from g_I for the other member of the pair, samples were prepared using enriched Cr⁵³ in place of the normal Cr (90.45% spin-zero isotopes) and the magnetic moment of Cr⁵³ was measured. Within the accuracy of this experiment (0.2%), the published moment was observed.

Double resonance measurements have been made on two other impurity pairs in Si involving Au, namely (MnAu)⁺ and (MnAu)⁻. For both of these species, Eq. (2) did not fully account for the observed variations of f with m . The deviations from Eq. (1) were at most 2%. Within this accuracy, values were obtained for the magnetic moments of Mn⁵⁵ and Au¹⁹⁷ that agreed with those published for Mn and the above-determined value for Au.

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³ For some considerations as to how an "effective" nuclear g value may arise because of excited electronic levels, see J. M. Baker and B. Bleaney, Proc. Roy. Soc. (London) A245, 156 (1958).

⁴ G. W. Ludwig and H. H. Woodbury, Phys. Rev. (preceding paper).