

Electron-nuclear double resonance of titanium in silicon: ^{47}Ti and ^{49}Ti ENDOR

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The electron-nuclear double-resonance spectra of interstitial $^{47}\text{Ti}^+$ and $^{49}\text{Ti}^+$ in silicon have been measured at 4.2 K. Spin Hamiltonians for these systems were determined and had to include hyperfine contributions of the type S^3I and S^2I^2 . The isotropic hyperfine interaction parameter A exhibits a small hyperfine anomaly, indicating that it is mainly due to contact interaction. The term involving S^2I^2 is shown to arise from nuclear-electric quadrupole interaction. A crude calculation for the S^3I term, which includes covalency to first order, demonstrates the importance of excited-state contributions and yields some qualitative agreement with experiment.

I. INTRODUCTION

Recently, the observation of titanium in silicon by electron paramagnetic resonance (EPR) was reported.¹ The resonance is related to the impurity occupying an interstitial site of tetrahedral symmetry (crystallographic point group $\bar{4}3m$). The observed paramagnetic state of titanium has electronic configuration $3d^3$ associated with the positively charged impurity Ti^+ , which is the stable state when the Fermi level is between $E_v + 0.25$ eV and $E_c - 0.28$ eV.²⁻⁴

In the previous studies by magnetic resonance substantial effects of covalency on the electronic properties of the ground state were revealed. The g value of the EPR spectrum $g = 1.998\,06 \pm 0.000\,04$ is very close to the free-electron value, which indicates appreciable quenching of the electron orbital moments. This conclusion was supported by an equally large reduction of the contact hyperfine interaction with magnetic ^{47}Ti and ^{49}Ti nuclei as compared to the free-ion case. Such reductions appear to be common for interstitial transition metals in silicon, as shown in Table I, where values of the hyperfine constant A for a number of these impurities are collected. Direct confirmation of the importance of covalency was obtained from electron-nuclear double resonance (ENDOR) on silicon-29 nuclei surrounding the titanium

impurity.⁵ In this experiment a considerable charge transfer of at least 40% was established and mapped by measuring the hyperfine interactions with 214 nuclei in 17 shells of silicon neighbor sites. Similar conclusions were reached by EPR and ENDOR experiments on other $3d$ impurities in silicon, such as iron^{6,7} and chromium.⁸ Also theoretical calculations have indicated considerable spin transfer. Katayama-Yoshida and Zunger⁹ and Beeler, Andersen, and Scheffler,¹⁰ using self-consistent Green's-function calculations, obtained g and A values which are in good agreement with experiment.

The system $\text{Si}:\text{Ti}^+$ is characterized by high values of electronic and nuclear spin. It has been found that higher-order multipole interactions are then sometimes required to analyze the observed spectra. Previously reported cases are mostly on ionic solids,^{11,12} but also include Co^{2+} in covalent crystals.¹³ These interactions, although generally difficult to interpret, may provide additional information to describe the magnetic ground-state properties. For this reason ENDOR measurements on the magnetic ^{47}Ti and ^{49}Ti nuclei were carried out.

II. EXPERIMENTAL PROCEDURE

Floating-zone dislocation-free p -type silicon samples ($20 \times 2 \times 2$ mm³) of various dopings (B, Al, and In) were

TABLE I. Hyperfine interaction parameters A , as given in Refs. 1 and 27, and derived contact spin densities $\delta\rho_{\text{Si}}(0)$ for $3d$ transition-metal ions in silicon. The latter are not corrected for the spin-orbit contribution; the error is however less than 4% for all transition metals quoted, with the exception of Fe^0 , where the spin-orbit contribution amounts to 6.6 MHz. The free-ion values for the $4s$ spin densities are obtained from Ref. 23, the core polarization (CP) values have been taken from Fig. 4 in Ref. 28.

Configuration	Ion	A (MHz)	g_N	$\delta\rho_{\text{Si}}$	$\delta\rho(0) (\text{\AA}^{-3})$	
					$\delta\rho_{4s}$	$\delta\rho_{\text{CP}}$
$3d^3$	Ti^+	± 15.65	-0.3154	± 1.26	$+ 20.08$	-5.2
	V^{2+}	-126.21	$+ 1.471$	-2.19	$+ 22.80$	-5.2
$3d^5$	Cr^+	$+ 31.99$	-0.3163	-4.27	$+ 18.97$	-9.4
	Mn^{2+}	-160.30	$+ 1.387$	-4.86	$+ 29.01$	-9.4
$3d^8$	Mn^-	-213.69	$+ 1.387$	-2.59	$+ 29.01$	-4.0
	Fe^0	± 20.93	$+ 0.81$	± 1.89	$+ 32.61$	-4.0

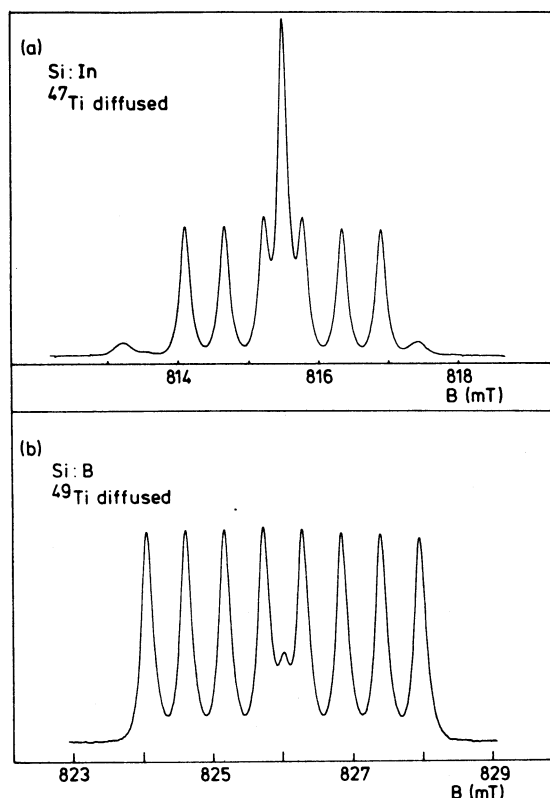


FIG. 1. Recorder traces of the Si: ^{47}Ti (a) and Si: ^{49}Ti (b) EPR spectra at 4.2 K. The center line in both figures is due to the $I=0$ isotopes of Ti. The Si: ^{47}Ti spectrum was recorded at 22.808 GHz microwave frequency in an In-doped sample of initial resistivity 10 Ohm cm; the Si: ^{49}Ti spectrum was obtained from a B-doped sample of initial resistivity 3 Ohm cm at 23.104 GHz microwave frequency.

rubbed with wet TiO_2 powder and subsequently annealed for 10 days at 1380°C under argon atmosphere in a closed ampoule of synthetic quartz. The TiO_2 powder used was either enriched in the ^{47}Ti isotope to $68.5 \pm 0.2\%$, or in the ^{49}Ti isotope to $96.25 \pm 0.01\%$. After annealing the samples were allowed to cool to just below red heat at the entrance of the oven and quenched to room temperature from there. The samples were then stored at 77 K until the measurements were made. In all samples the Ti^+ EPR resonance could be observed; illustrations of the spectra are given in Fig. 1. For best signal-to-noise ratio we selected In-doped samples of initial resistivity 10 Ohm cm (0.12×10^{16} In atoms/cm³) for the ENDOR measurements.

Measurements were performed with a superheterodyne spectrometer operating at 23 GHz and adjusted to detect the dispersion part of the EPR signal at an incident microwave power of 1 μW . The magnetic field could be rotated in the (011) plane of the sample and was modulated at a frequency of 83 Hz. We used a silver-coated Epi-bond cavity; in the thin silver layer on the cylindrical side wall of the cavity a spiral groove was cut, making it suitable as an ENDOR coil.¹⁴ For ENDOR measurements the radio-frequency (rf) field was square-wave modulated at 3.3 Hz to allow double phase-sensitive detection of the signal. The sample was held at 4.2 K.

III. EXPERIMENTAL RESULTS

A spin Hamiltonian which could describe the observed isotropic resonance of titanium in silicon in cubic symmetry is

$$\mathcal{H}_1 = g\mu_B \mathbf{B} \cdot \mathbf{S} - g_N \mu_N \mathbf{B} \cdot \mathbf{I} + A \mathbf{S} \cdot \mathbf{I} \quad (1)$$

and contains the electronic Zeeman, nuclear Zeeman, and hyperfine interaction terms. However, in spite of having a spectrum consisting of a single isotropic resonance, interstitial Ti^+ was demonstrated to have an electronic ground state 4A_2 with electron spin $S=3/2$.¹ Also the ^{47}Ti and ^{49}Ti isotopes have a nuclear spin higher than 1/2. Such systems are not necessarily adequately described by the simple spin Hamiltonian of Eq. (1), as demonstrated by Koster and Statz¹⁵ and Bleaney.¹⁶ In

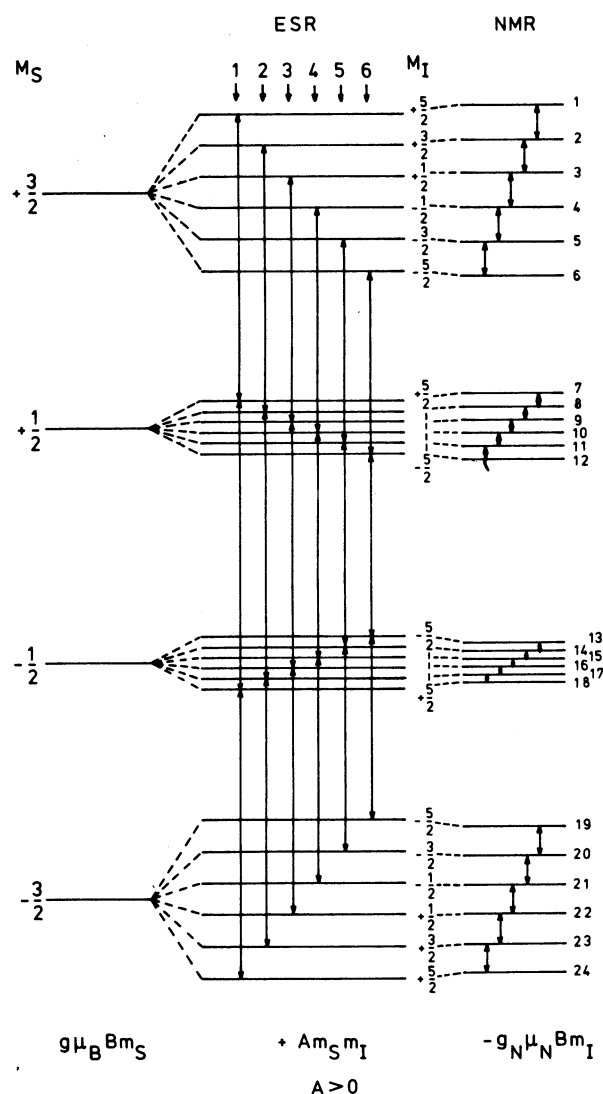


FIG. 2. Level scheme of the Si: ^{47}Ti system ($S=3/2$, $I=5/2$). Level ordering is consistent with $g=+1.99806$ and $A=+15.66$ MHz, but not to scale. The numbering of the EPR transitions relates to the resonances of Fig. 1(a) in the following way: The resonance at lowest (highest) field corresponds to EPR transition 1 (6).

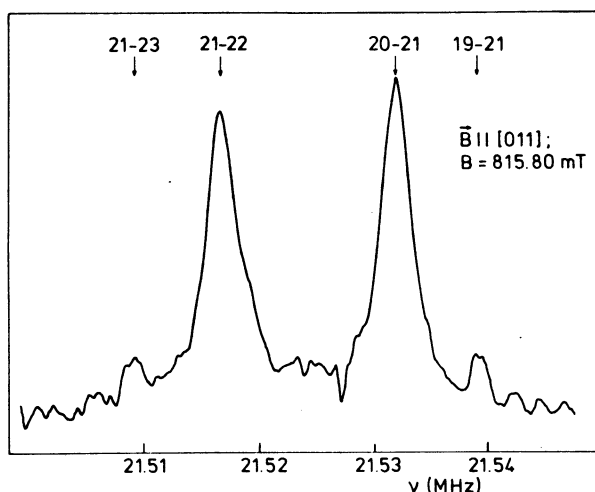


FIG. 3. Recorder trace of the Si:⁴⁷Ti ENDOR spectrum at 4.2 K and microwave frequency 22.808 GHz, $B=815.80$ mT $\parallel [011]$. This ENDOR spectrum was taken on EPR line 4; the numbering of the ENDOR lines corresponds to the transitions given in Fig. 2 if g and A are positive.

these cases of higher electronic or nuclear spin it may be necessary to augment the Hamiltonian of Eq. (1) with terms like S^3I , S^3B , etc., that have nonvanishing matrix elements between the spin basis states of the system. In general, terms of the form $S^aI^bB^c$ with $a \leq 2S$ and $b \leq 2I$ should be included in the Hamiltonian. Since the Hamiltonian satisfies time-reversal symmetry and S , I , and B are time-uneven operators, the sum $a + b + c$ is required to be an even integer. A procedure to construct the spin Hamiltonian of such a system in a given symmetry has been discussed by Ray¹⁷ and Geschwind.¹⁸ Ray explicitly gives the form of the spin Hamiltonian in cubic symmetry for values of a up to 3 and b and c up to 2. Some of these terms must be described by two parameters in cubic symmetry. Many of them have been found experimentally in ENDOR on transition-metal impurities in ionic compounds.^{11-13,16} For interstitial titanium in silicon they may occur as well.

If we apply the Hamiltonian $\mathcal{H}_1$ to the Si:⁴⁷Ti⁺ system, which has $S=3/2$ and $I=5/2$, or to the system Si:⁴⁹Ti⁺, with $S=3/2$ and $I=7/2$, the number of observable ENDOR transitions between the levels equals 20 and 28, respectively, as indicated in Fig. 2 for Si:⁴⁷Ti⁺. The frequencies of these transitions would show no angular variation on rotation of the magnetic field B in the $(0\bar{1}1)$ plane. However, experimentally an angular dependence was observed proportional to

$$p(\theta) = 1 - 5 \sin^2 \theta + \frac{15}{4} \sin^4 \theta, \quad (2)$$

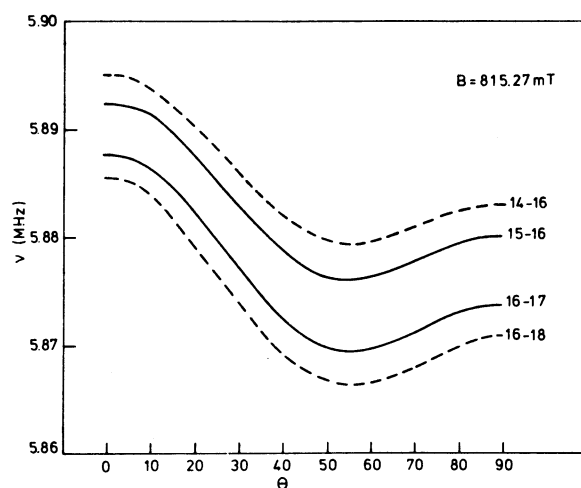


FIG. 4. Angular dependence of ENDOR signals on EPR line 3 at microwave frequency 22.808 GHz and $B=815.27$ mT. The solid lines represent the single-quantum transitions, the dashed lines designate the double-quantum transitions.

with θ the angle between B and the $[100]$ direction, for all 20, or 28, transitions. In addition, we observed a number of weaker satellites (Fig. 3) that follow the same angular dependence as the high-intensity resonances (Fig. 4). The weaker lines were found to be proportional to the square of the rf power, whereas the strong ones were directly proportional to the rf power. The weaker satellites may therefore be identified as two-quantum transitions of the same system. The noncoincidence and angular variation of the ENDOR resonances indicate the necessity to include additional terms in the spin Hamiltonian of Eq. (1). Since we have no *a priori* information as to which terms are important, we calculated ENDOR transitions for all permitted terms as given by Ray¹⁷ in first-order perturbation theory. Although many terms yield an angular dependence described by the function $p(\theta)$ of Eq. (2), no single term could reproduce all observed internal and relative multiplet splittings. In analyzing the ENDOR spectra up to 11 terms of fourth power in S , I , and B ($a + b + c = 4$) were considered, added to the spin Hamiltonian of Eq. (1). In their dependence on the quantum numbers m_S and m_I , which label the transitions, all terms give different sets of splittings. The effect of each of the terms can therefore unambiguously be determined. It was found to be necessary to include an S^3I term, with the parameter U , and S^2I^2 terms, with the two parameters a and b . Thus, the Hamiltonian used to fit the data was

$$\begin{aligned} \mathcal{H} = & \mathcal{H}_1 + U \{ S_x^3 I_x + S_y^3 I_y + S_z^3 I_z - \frac{1}{5} [3S(S+1) - 1] (S_x I_x + S_y I_y + S_z I_z) \} \\ & + a [(S_x S_y + S_y S_x)(I_x I_y + I_y I_x) + (S_y S_z + S_z S_y)(I_y I_z + I_z I_y) + (S_z S_x + S_x S_z)(I_z I_x + I_x I_z)] \\ & + b \{ [3S_x^2 - S(S+1)][3I_x^2 - I(I+1)] + [3S_y^2 - S(S+1)][3I_y^2 - I(I+1)] \\ & + [3S_z^2 - S(S+1)][3I_z^2 - I(I+1)] \}. \end{aligned} \quad (3)$$

TABLE II. Spin Hamiltonian parameters of interstitial $^{47}\text{Ti}^+$ and $^{49}\text{Ti}^+$ in silicon.

	^{47}Ti	^{49}Ti
g	$1.998\,06 \pm 0.000\,04$	$1.998\,06 \pm 0.000\,04$
$\mu_N g_N$	$-2.402\,16 \pm 0.000\,04$ MHz/T	$-2.402\,77 \pm 0.000\,05$ MHz/T
A	$15.645\,05 \pm 0.000\,03$ MHz	$15.650\,70 \pm 0.000\,04$ MHz
U	-11.05 ± 0.06 kHz	-11.10 ± 0.09 kHz
a	-0.222 ± 0.005 kHz	-0.085 ± 0.005 kHz
b	0.012 ± 0.001 kHz	0.005 ± 0.001 kHz

A least-squares fit of these parameters to the experimental data was made in a computer diagonalization of the Hamiltonian matrices (dimensions 24×24 for ^{47}Ti and 32×32 for ^{49}Ti). The results of this fit are collected in Table II. The remaining deviations of the data from Eq. (3) did not exhibit any residual $p(\theta)$ dependence or any other systematic deviation. The quality of the fit could, therefore, not be improved by inclusion of additional terms. Typical width of the resonances was, in the case of ^{47}Ti , 3.5 kHz FWHM, allowing line positions to be determined with an accuracy better than 0.5 kHz. Average deviation of calculated hyperfine frequencies from experiment were generally within 0.25 kHz. For unknown reasons these values were approximately twice as large in the case of ^{49}Ti .

IV. DISCUSSION

A. Electronic g value

In the intermediate-field approximation the cubic crystal field splits the free-ion 4F term into a 4A_2 ground state and two excited triplet states 4T_2 and 4T_1 . An analysis of spin Hamiltonian parameters of such a 4A_2 ground state often starts from a perturbation Hamiltonian that contains spin-orbit, electronic and nuclear Zeeman, hyperfine (orbital, dipolar, and core polarization) and, occasionally, spin-spin and quadrupole interaction terms, which can couple the triplet states to the ground state. Low,¹⁹ for instance, gives expressions for the electronic and nuclear g shift and orbital hyperfine-interaction parameter which are correct to second order. The electronic g shift is given by the well-known expression:

$$\Delta g = g - 2.0023 = -\frac{8\lambda}{10Dq} \quad (4)$$

with λ the spin-orbit coupling parameter of the ground term and Dq the crystal-field-splitting parameter. Effects of covalency, which are not included in this expression, have been considered for an AB_6 complex by Owen and Thornley.²⁰ Since half of the transferred spin density has been shown to reside on the second-nearest-neighbor shell in the case of Ti^+ ,⁵ we will in a first-order approximation regard the $\text{Si}:\text{Ti}^+$ system as such an AB_6 system and use the expressions for Δg as given by these authors. This means expression (4) will still be valid for Δg , provided that we replace λ by λ' . In the covalent model

$$\lambda' = \pm k_{\sigma\pi} \zeta_{\sigma\pi} / 2S \quad (5a)$$

with

$$k_{\sigma\pi} = N_{\sigma} N_{\pi} \left[1 - 2\alpha_{\pi} S_{\pi} - 2\alpha_{\sigma} S_{\sigma} - 2\alpha_s S_s - \frac{1}{2} \alpha_{\sigma} \alpha_{\pi} - \frac{1}{2} \alpha_{\pi} \alpha_s d \left\langle y \left| \frac{\delta}{\delta y} \right| s \right\rangle \right] \quad (5b)$$

and

$$\zeta_{\sigma\pi} = N_{\sigma} N_{\pi} (\zeta_d - \frac{1}{2} \alpha_{\sigma} \alpha_{\pi} \zeta_p), \quad (5c)$$

where ζ_d is the one-electron spin-orbit constant in a $3d$ orbital, ζ_p is the spin-orbit constant of the silicon neighbors, d is the distance between the ligand and the center of the complex, and S_{σ} , S_{π} , and S_s are overlap integrals of the central transition-metal ion d orbitals with silicon ligand orbitals. The coefficients N_{π} , α_{π} , etc. bear an obvious correspondence to the LCAO coefficients defined in Refs. 5 and 6: $N_{\pi} = \alpha$, $N_{\pi} \alpha_{\pi} = -\epsilon$, etc. We used for N_{π} and $N_{\pi} \alpha_{\pi}$ the coefficients as determined in the Ti^+ ligand ENDOR, assuming the minimum of 40% hybridization of ligand orbitals with t_2 metal orbitals. The coefficients N_{σ} , $N_{\sigma} \alpha_{\sigma}$ are only defined for e orbitals; therefore they cannot be determined from the Ti^+ ligand ENDOR, since the unpaired magnetic electrons are in t_2 orbitals. These coefficients were therefore taken to be equal to the coefficients determined in the Fe^0 ENDOR,⁶ where the paramagnetic electrons are in e states and the ligand hybridization degree was found to be 25%. The overlap integrals were evaluated numerically using Herman-Skillman wave functions.²¹ For $10Dq$ we take 5500 cm^{-1} ; this estimate has been used before¹ and was obtained from an extrapolation of $10Dq$ in II-VI and III-V compounds²² since optical data for transition metals in silicon are not available. The expressions above apply both to d^3 and d^8 so that we can calculate the g shift for interstitial Ti^+ , V^{2+} , Fe^0 and Mn^{2+} . Although for Fe^0 the spin transfer is found to be mainly to the first-neighbor shell, whereas Eqs. (5) are valid for AB_6 , the estimate will not be much worse than for Ti^+ , since the g shift calculated from Eqs. (5) is mainly determined by the product $N_{\sigma}^2 N_{\pi}^2$ ($N_{\pi}^2 = 0.60$ and $N_{\sigma}^2 = 0.75$). The results are collected in Table III, together with the results of self-consistent Green's function calculations by Katayama-Yoshida and Zunger.⁹ It may be noted here, that although the Green's function results appear to be somewhat better than those calculated above, closer agreement with experiment is likely to be obtained if contributions from other shells are also included, since these

TABLE III. Experimental and calculated g shifts. Δg_{CF} is the crystal-field result calculated with Eq. (4), Δg_{OT} is the result from the Owen and Thornley expression [Eqs. (5)], using ligand ENDOR results of Ti^+ and Fe^0 . In calculating these results we assumed $10Dq=5500\text{ cm}^{-1}$. Δg_{GF} are the Green's-function results of Katayama-Yoshida and Zunger (Ref. 9).

Configuration	Ion	Δg_{expt}	Δg_{CF}	Δg_{OT}	Δg_{GF}
$3d^3$	Ti^+	-0.0042	-0.0436	-0.0171	-0.0111
	V^{2+}	-0.0131	-0.0824	-0.0337	-0.0292
$3d^8$	Fe^0	0.0676	0.1854	0.0783	0.0187
	Mn^-	0.0081	0.1854	0.0779	0.0407

will decrease $k_{\sigma\pi}$. In view of the uncertainty in the crystal-field parameter we will not stretch this model any further, however, and just note the qualitative effect of including covalency.

B. Nuclear g value

Low¹⁹ has also given an expression for the nuclear g shift, which may be expressed in terms of the electronic g shift:

$$\mu_N \Delta g_N = - \frac{P \mu_B \Delta g}{\lambda}, \quad (6a)$$

in which

$$P = \frac{\mu_0}{4\pi} g g_N \mu_B \mu_N \langle r^{-3} \rangle_d. \quad (6b)$$

Since the covalency is incorporated in the electronic g shift we use the free-ion values $P = -0.00245\text{ cm}^{-1}$ (Ref. 23), $\lambda = 30\text{ cm}^{-1}$ (Ref. 24), and the experimental electronic g shift $\Delta g = -0.0042$, which yields $\mu_N \Delta g_N = -0.0048\text{ MHz/T}$. Fuller²⁵ has tabulated nuclear magnetic moments with and without corrections for the diamagnetic screening by the closed inner shells.²⁶ Since the screening of the $1s$, $2s$, and $3s$ orbitals is not expected to be dramatically altered if the ion is embedded in a silicon matrix, we will relate our experimental nuclear g shift to the uncorrected NMR experimental values (^{47}Ti : $-2.40015 \pm 0.00018\text{ MHz/T}$, ^{49}Ti : $-2.40081 \pm 0.00020\text{ MHz/T}$) rather than to the corrected values. We find $\mu_N \Delta g_N = -0.0020\text{ MHz/T}$ for both ^{47}Ti and ^{49}Ti , which agrees in sign and order of magnitude with the calculated value. This agreement is as good as could reasonably be expected since the silicon lattice will provide additional diamagnetic screening.

C. Hyperfine interaction SI

The hyperfine-interaction parameter A can be split in three parts: a contribution due to unpaired s electrons, a

contribution due to spin-orbit coupling, and an orbital contribution, the latter being zero in cubic symmetry.¹⁹ The spin-orbit part, according to Low¹⁹ given by $A_{\text{orb}} = P \Delta g$, is calculated to be 0.31 MHz ; if we compare this to the experimental value $|A| = 15.66\text{ MHz}$ it is obvious that the hyperfine constant is mainly determined by contact interaction. This conclusion is further corroborated by a small, but measurable hyperfine anomaly between ^{47}Ti and ^{49}Ti , which can only arise from the difference in distribution of the nuclear magnetic dipole moment over these two nuclei:

$$\frac{A(^{47}Ti)g_N(^{49}Ti)}{A(^{49}Ti)g_N(^{47}Ti)} - 1 = -(1.1 \pm 0.3) \times 10^{-4}. \quad (7)$$

This contact interaction can arise from various sources. First it may arise from a residual spin density in the $4s$ orbital, second it may be due to polarization of the inner s orbitals by the spin density in the outer valence orbitals, and third, spin-polarized valence-band orbitals can have a nonvanishing spin density at the transition-metal nucleus.⁹ The measured hyperfine interaction parameter is opposite in sign to the tabulated values of Morton and Preston for an electron in a $4s$ orbital²³ for all four transition-metal impurities of Table I for which the sign of A has been determined. This excludes the possibility that the first mechanism dominates the value of A , in accordance with the Ludwig and Woodbury model.²⁷ The second contribution, core polarization, has the same sign as the experimental value,²⁸ and probably contributes to a large extent to the hyperfine interaction parameter A , as assumed in Refs. 5 and 6. If we neglect the third mechanism, we can calculate the spin density in the $4s$ orbital. We take into account the (minimum) spin transfer as determined by the ligand ENDOR ($1 - \alpha^2 = 0.40$ for Ti^+ and 0.25 for Fe^0) and subtract the core-polarization contribution $\alpha^2 \delta \rho_{CP}(0)$ from the experimental value $\delta \rho_{Si}(0)$ assumed to be negative. When using the free-ion value of $\delta \rho_{4s}(0)$ (Table I), we arrive at 0.09 and 0.03 electron in the $4s$ orbital for Ti^+ and Fe^0 , respectively. This is of the same magnitude as calculated by Katayama-Yoshida and Zunger⁹ for the $Si:Fe_i^0$ system (0.06). The contribution from the third mechanism is rather hard to estimate; it depends largely on the exact shape and polarization of the silicon orbitals and will therefore not be attempted here.

D. Electron-nuclear interaction S^3I

The higher-order hyperfine interaction term US^3I has been evaluated by several authors. In analogy to the treatment given by Low,¹⁹ one usually considers higher-order perturbation terms in the orbital hyperfine energy. Ham *et al.*¹³ considered

$$\frac{\langle {}^4A_2 | \lambda \mathbf{L} \cdot \mathbf{S} | {}^4T_2 \rangle \langle {}^4T_2 | \lambda \mathbf{L} \cdot \mathbf{S} | {}^4T_1 \rangle \langle {}^4T_1 | \mathbf{P} \cdot \mathbf{I} | {}^4T_2 \rangle \langle {}^4T_2 | \lambda \mathbf{L} \cdot \mathbf{S} | {}^4A_2 \rangle}{E_{20}^2 E_{10}}, \quad (8)$$

which yielded an S^3I interaction term. Here E_{20} is the energy difference between the 4T_2 and 4A_2 states, and E_{10} is the energy difference between the 4T_1 - 4A_2 states. Their result was

$$U = 120 \frac{P\lambda^3}{E_{20}^2 E_{10}}, \quad (9)$$

which Ham *et al.* reexpressed as

$$U = -\frac{25}{192} P(\Delta g)^3 \quad (10)$$

using the crystal-field result $E_{20}/E_{10} = \frac{5}{9}$ and Eq. (4) where $E_{20} = 10Dq$. Substituting the experimental g shift and the free-ion value for P , we obtain $U = -7 \times 10^{-4}$ kHz, which is clearly of the wrong magnitude when compared with the experimental value. As we noted already, the covalent reductions are to a large extent determined by the product $N_\pi^2 N_\sigma^2$ in the g -shift case. This would mean that the U value as given by Eq. (10) is reduced by at least $N_\sigma^6 N_\pi^6$ compared to the ionic case. This certainly overestimates the effect of covalency and is due to the reexpression of Eq. (9) in Δg . If we recall that the states 4A_2 , 2E , 2T_2 , and 2T_1 all arise from the t_2^3 configuration and 4T_2 and 4T_1 from $t_2^2 e$ in the strong-field limit, we rather expect Eq. (8) to be reduced by approximately $N_\pi^2 N_\sigma^6$ in comparison to the ionic case. Under this assumption and using $10Dq = 5500 \text{ cm}^{-1}$ and the same values for N_σ^2 and N_π^2 as before, we calculate $U \approx -0.26$ kHz for Ti^+ . Although still far from correct, this value is already a lot closer to the experimental value.

A more detailed calculation by Woodward and Chatterjee,²⁹ who also included contributions due to spin-spin interactions, yielded U parameters of the wrong sign and magnitude when compared to (ionic) experimental values. In order to obtain agreement between experiment and theory they extended their treatment to include contributions from the 4P and 2G states. They found the 4P -state contributions to be rather small, but the 2G contributions could explain the experimental data. This agreement was shown to be fortuitous by Takeuchi, Horai, and Arakawa³⁰ who eliminated some errors from the calculation and found a somewhat different expression for the 2G -state contributions. As a result, the theoretical estimate falls short by a factor of 5, which they attributed to covalency in their ionic case.

In our more covalent system we will give a (rough) estimate of the magnitude of this U parameter for the two $3d^3$ transition-metal ions in silicon: Ti^+ and V^{2+} . To this end we corrected for covalency as indicated above; contributions to U from the 4F state were calculated to be $+0.90$ kHz for Ti^+ and -10.3 kHz for V^{2+} . Experimentally the signs of the hyperfine interaction parameters A , U , a , and b have not been determined, but the signs of U , a , and b are fixed with respect to that of A . For Ti^+ the sign of A is calculated to be positive,⁹ which would make $U = -11.1$ kHz. It appears that the situation is similar to the ionic case, i.e., the calculated contribution of the 4F state is an order of magnitude too small and of the wrong sign. In order to calculate the contribution from the 2T_1 , 2T_2 , and 2E states to the U parameter we estimated their positions with respect to the 4A_2 state

from an extrapolation of the Racah parameter B in II-VI and III-V compounds in a similar way as the crystal-field parameter^{1,22} and find $B \approx 200 \text{ cm}^{-1}$. From the ratio $Dq/B \approx 2.75$ and a figure from Sugano, Tanabe, and Kamimura,³¹ we determined the energy-level positions as given in Table IV, in which we also list the parameters used. The value of the spin-spin parameter ρ and the integrals M^0 and M^2 (defined in Ref. 32) for Ti^+ were found by extrapolation from the series Cr^{3+} ($\rho = 0.17 \text{ cm}^{-1}$) and V^{2+} (0.11 cm^{-1}). We feel justified to do so, because of the regularity in the $3d^4$ series Fe^{4+} , Mn^{3+} , and Cr^{2+} , where ρ decreases monotonously from 0.25 to 0.18, and 0.12 cm^{-1} , respectively.³² We used the expression of Takeuchi *et al.*, rather than that of Woodward and Chatterjee,³³ and give the results of the computation in Table IV. No undue reliance should be placed on the exact numbers in view of the approximations made and the fact that the resulting U value is the sum of several equally large contributions, some of which are of opposite sign. It is, however, in our view a reasonable estimate for the order of magnitude of the U parameter for both $\text{Si}:\text{Ti}^+$ and $\text{Si}:\text{V}^{2+}$. At this stage we note the following similarities to the ionic case: (1) The U parameter is of opposite sign as compared to A , (2) the most important contributions to U come from the 2G state and are probably of the same sign as experiment, (3) the 4F contributions are of opposite sign and somewhat smaller, (4) the theoretical value falls short of the experimental value.

In this estimate the U parameter for $\text{Si}:\text{V}^{2+}$ is expected to be considerably larger than for $\text{Si}:\text{Ti}^+$, which has actually been found experimentally.³⁴ Although some qualitative agreement is therefore obtained in both the ionic

TABLE IV. Energy levels, spin-orbit parameters ζ , spin-spin parameters ρ , M^k integrals, dipole parameters P , and covalency parameters N_σ^2 and N_π^2 used to compute the 4F and 2G contributions to the hyperfine parameter U . U_R denotes the range in which the separate contributions of Takeuchi's expressions fall for this choice of parameters. The experimental value of U for V^{2+} is taken from van Kooten, van Kootwijk, and Ammerlaan (Ref. 34).

	$\text{Si}:\text{Ti}^+$	$\text{Si}:\text{V}^{2+}$
$E({}^4T_2) (\text{cm}^{-1})$	5460	5460
$E({}^4T_1) (\text{cm}^{-1})$	7560	7560
$E({}^2E) (\text{cm}^{-1})$	4140	4140
$E({}^2T_1) (\text{cm}^{-1})$	4280	4280
$E({}^2T_2) (\text{cm}^{-1})$	6220	6220
$\zeta (\text{cm}^{-1})$	90	168
$P (\text{cm}^{-1})$	-0.002 45	+0.013
$\rho (\text{cm}^{-1})$	0.05	0.11
M^0	0.40	0.915
M^2	0.20	0.499
N_σ^2	0.75	0.75
N_π^2	0.6	0.6
$U_R({}^4F) (\text{kHz})$	-0.27 - +0.62	-11.4 - +9.2
$U({}^4F) (\text{kHz})$	+0.90	-10.3
$U_R({}^2G) (\text{kHz})$	-1.89 - +1.06	-19.9 - +35.2
$U({}^2G) (\text{kHz})$	-2.01	+36.5
$U({}^4F + {}^2G) (\text{kHz})$	-1.11	+26.2
$U(\text{expt}) (\text{kHz})$	± 11.1	98.8

and covalent case, the quantitative agreement is poor. In view of the similarities mentioned it is not very likely that covalency effects should be held responsible for this, as proposed by Takeuchi *et al.*, but this cannot be excluded without accurate optical data for transition-metal ions in silicon which are thus far unavailable. The similarity to the ionic case suggests, however, that the magnitude of the U parameter is basically determined by core shells rather than by the electron spins in the $3d$ shell, since the former are less affected by a change in ligands. The fact that the far larger hyperfine parameter A is to a large extent determined by contact interaction is certainly not in contrast to this supposition. In that case the failure of the above calculation to reproduce the experimental results is not very surprising since it is limited to $3d^3$ and does not take such configuration interactions into account. A real understanding of the origin of the U parameter may possibly be obtained from a more comprehensive treatment of the problem using, for example, self-consistent Green's-function methods. They fall, however, outside the scope of this paper.

E. Electron-nuclear interaction S^2I^2

The origin of the S^2I^2 terms may be the same as for S^3I . If one takes for instance $PL \cdot I$ twice in the perturbation expression illustrated in Eq. (8) and $\lambda L \cdot S$ twice, one generates terms of the type S^2I^2 . These terms are magnetic in origin, but are sometimes called pseudoquadrupole interaction terms, since they transform in the same way as the real electric quadrupole interaction. It is generally stated that the electric quadrupole interaction vanishes in cubic symmetry, but such a statement refers only to ions devoid of angular momentum. Due to admixture of orbital angular momentum from higher states into the ground state, the $3d$ electrons of the Ti^+ ion may certainly cause an electric-field gradient. As evidenced by the g shift, some angular momentum has been mixed into the ground state, therefore allowing (small) quadrupole coupling with the nucleus. For this type of interaction Bleaney³⁵ has demonstrated that

$$a = -\frac{e^2Q}{I(2I-1)} \langle r_q^{-3} \rangle \frac{3n}{4} \quad (11a)$$

and

$$b = -\frac{e^2Q}{I(2I-1)} \langle r_q^{-3} \rangle \frac{m}{6} \quad (11b)$$

with Q the nuclear electric quadrupole moment, n and m constants not necessarily equal in cubic symmetry, and $\langle r_q^{-3} \rangle$ is the expectation value of r^{-3} over the unbalanced charge density. If the electric quadrupole interaction determines a and b , we expect

$$\frac{a(^{49}Ti)}{a(^{47}Ti)} = \frac{b(^{49}Ti)}{b(^{47}Ti)} = \frac{10Q(^{49}Ti)}{21Q(^{47}Ti)} \quad (12)$$

Using Fullers values²⁵ for $Q(^{47}Ti) = 0.29 \times 10^{-28} \text{ m}^2$ and $Q(^{49}Ti) = 0.24 \times 10^{-28} \text{ m}^2$, we find the ratio in Eq. (12) to be 0.39 ± 0.02 . Experimentally we find 0.38 ± 0.02 and 0.42 ± 0.11 for a and b , respectively. We therefore conclude that the S^2I^2 term is caused by nuclear-electric quadrupole interaction. The ratio n/m is found to be ≈ -4 .

V. CONCLUSIONS

The observed electronic and nuclear g shifts are attributed to mixing of the 4T_2 state into the 4A_2 ground state by spin-orbit coupling. The magnitudes of these shifts are governed by covalency, and in the case of the nuclear g shift, also by diamagnetic screening of the nucleus. The hyperfine constant A is determined by contact interaction as evidenced by the observed hyperfine anomaly between the ^{47}Ti and ^{49}Ti nuclei. A preliminary estimate of the magnitude of the U parameter yielded some qualitative agreement with experiment, but the quantitative agreement remained poor, similar to the ionic case. Therefore, no definite conclusion on its origin can be made. The S^2I^2 term has been shown to arise from nuclear-electric quadrupole interaction.

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