

Self-ENDOR of vanadium in silicon

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Abstract. Self-ENDOR measurements for the ^{51}V isotope of double-positive vanadium in silicon are presented. The spin-Hamiltonian parameters have been determined. For an adequate description of the spectrum it was necessary to include a higher-order hyperfine term of the type S^3I in the Hamiltonian. Existing theories do not account in a satisfactory way for the magnitude of the S^3I term.

1. Introduction

Vanadium is one of the least soluble of the 3d metals in silicon [1]. In electron paramagnetic resonance (EPR) it was first detected by Ludwig and Woodbury [2, 3] in p-type material. Apart from EPR they also measured the electron nuclear double resonance (ENDOR) of the ^{51}V isotope, which has nuclear spin $I = \frac{7}{2}$ and a natural abundance of 99.76%. From the observed electron spin $S = \frac{3}{2}$ they concluded that the spectrum was due to interstitial vanadium in the double-positive-charge state: V^{2+} . Their ENDOR spectra could be described by the conventional spin Hamiltonian consisting of the electron and nuclear Zeeman interaction and the hyperfine interaction:

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

ENDOR measurements of V^{2+} in cubic salts such as MgO , KMgF_3 and KZnF_3 showed that a description of the ENDOR spectrum using (1) was inadequate for explaining all the features [4, 5, 6]. Higher-order terms were required. This was first demonstrated in [7] and [8]. These terms have the general form

$$\mathcal{H} = B^a S^b I^c \quad (2)$$

where $a + b + c$ is even and, in the case of $\text{Si}:\text{V}^{2+}$ ($S = \frac{3}{2}$, $I = \frac{7}{2}$), $b \leq 3$ and $c \leq 7$. The procedure to construct the correct expressions for these terms was first given in [9]. The most important term of this kind is S^3I and has been reported for several transition metals in cubic salts. The discrepancy between the measured value of the coupling constant and the theoretical estimate is considerable in the case of these ionic solids. It was argued that even for these ionic salts covalency effects have to be taken into account. Therefore it is interesting to study the presence of higher-order terms in the ENDOR spectrum of V^{2+} when incorporated in a strong covalent crystal such as silicon. In this paper we report that these higher-order terms are also important in silicon.

2. Experimental details

Vanadium was scratched onto the surfaces of the silicon samples with typical dimensions $2 \times 2 \times 15 \text{ mm}^3$. The samples were heated for 10 days at 1380°C in a closed quartz ampoule under an argon atmosphere and subsequently quenched in water. The samples were stored in liquid nitrogen until the measurements were started. ENDOR measurements were performed in a superheterodyne K-band spectrometer tuned to dispersion. The magnetic field could be rotated in a $\{011\}$ plane of the sample and was modulated at 83 Hz. The RF power was on-off modulated at 3 Hz and double phase-sensitive detection was used to observe the ENDOR spectrum. Measurements were done at 4.2 K in a sample containing $10^{16} \text{ B atoms cm}^{-3}$. The vanadium concentration was approximately $10^5 \text{ atoms cm}^{-3}$.

3. Results

In EPR we detected the vanadium-related spectrum in a variety of samples. The g -value of the isotropic spectrum was $g_e = 1.9897 \pm 0.0005$ and the isotropic hyperfine interaction with ^{51}V ($I = \frac{7}{2}$) was $A/h = -126.34 \text{ MHz}$. These values are close to the

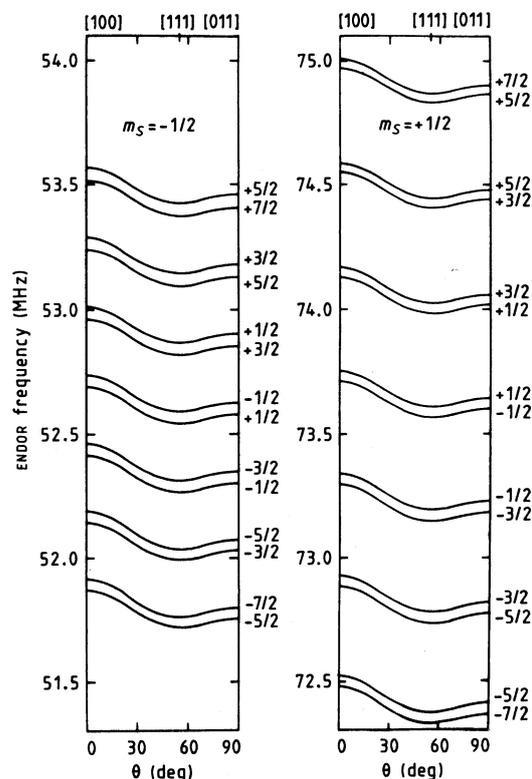


Figure 1. The angular dependence of the ^{51}V ENDOR spectrum for Si:V^{2+} where the magnetic field is in the $(0\bar{1}1)$ plane. A pair of closely spaced lines represents the same ENDOR transition (between the two indicated m_I numbers) but monitored by the EPR of a different hyperfine component (indicated by the values of m_I given on the RHS vertical axes).

values reported by Woodbury and Ludwig [2] (1.9892 and -126.21 MHz respectively). The interpretation of Woodbury and Ludwig concerning the asymmetric shoulders of the EPR lines of large m_I implies that A is negative [2]. Unlike Ludwig and Woodbury we observed this spectrum in intrinsic and n-type material as well. We will discuss this point later.

The frequencies of the ENDOR transitions $\Delta m_S = 0$ and $\Delta m_I = \pm 1$, determined by (1), are given in second order by

$$hf = |Am_S - g_N\mu_N B - [m_S(2m_I - 1) + S(S + 1) - m_S^2]A^2/2h\nu|. \quad (3)$$

Just like Ludwig and Woodbury we could only detect ENDOR frequencies for $m_S = \pm \frac{1}{2}$, in total 14 transitions. The total electron spin can be determined because the ENDOR measurements are in fair agreement with (3) only when taking $S = \frac{3}{2}$. The angular variation of the spectrum, measured in the $\{011\}$ plane, is depicted in figure 1 and showed the $p(\theta)$ angular dependence that is characteristic for fourth-order spin-Hamiltonian terms. The function $p(\theta)$ is given by

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

where θ is the angle between B in the $(0\bar{1}1)$ plane and the $[100]$ direction.

A fit to the measurements was made by adding to (1) the fourth-order terms from (2) and making a least-squares fit by diagonalising of the Hamiltonian. In these parameter fitting procedures the electronic g -value was kept constant. It appeared that the main contribution to the angular dependence was arising from the S^3I term, written as [10]

$$S^3I = U\{(S_x^3I_x + S_y^3I_y + S_z^3I_z) - \frac{1}{3}[3S(S + 1) - 1]S \cdot I\}. \quad (5)$$

A slight improvement to the fit could be obtained by adding to the Hamiltonian [10] the term

$$\begin{aligned} S^2I^2 = & V[(S_xS_y + S_yS_x)(I_xI_y + I_yI_x) + (S_yS_z + S_zS_y)(I_yI_z + I_zI_y) \\ & + (S_zS_x + S_xS_z)(I_zI_x + I_xI_z)] \\ & + W\{[3S_x^2 - S(S + 1)] \\ & \times [3I_x^2 - I(I + 1)] + [3S_y^2 - S(S + 1)][3I_y^2 - I(I + 1)] \\ & + [3S_z^2 - S(S + 1)][3I_z^2 - I(I + 1)]\}. \end{aligned} \quad (6)$$

The resulting parameters are listed in table 1. For these parameters the calculated ENDOR frequencies were well within the linewidth (2 kHz) of the observed ENDOR lines. The residuals did not show any $p(\theta)$ dependence so the fit cannot be improved by adding any other fourth-order Hamiltonian term.

Table 1. Spin-Hamiltonian parameters of $^{51}\text{V}^{2+}$ in silicon (with g_e kept constant: $g_e = 1.9897$).

| | |
|--------------|------------------------|
| A/h | -126.34 ± 0.01 MHz |
| $g_N\mu_N/h$ | 11.241 ± 0.005 MHz |
| U/h | 98.8 ± 0.1 kHz |
| V/h | 0.08 ± 0.01 kHz |
| W/h | 0.00 ± 0.01 kHz |

4. Discussion

Vanadium in the double-positive-charge state has a $3d^3$ configuration. According to the Ludwig and Woodbury model for transition-metal impurities in a cubic lattice position [2, 3] the d level is split into an e doublet and a t_2 triplet level and the three electrons will occupy the low-lying t_2 level. Because the spins are aligned to give maximum multiplicity, $S = \frac{3}{2}$, the ground state is an orbital singlet. Many calculations are performed according to the intermediate-field scheme, rather than this strong-field model. In the intermediate-field the free-ion ($3d^3$) 4F ground state of V^{2+} is split by the crystal field into a singlet 4A_2 ground state and excited triplet states 4T_2 and 4T_1 . The g -shift between the real value and the free-electron value is then explained by an admixture of orbital momentum of the excited states into the ground state. The result using crystal-field theory is given by

$$\Delta g_e = g_e - 2.0023 = -8\lambda/10Dq \quad (7)$$

with $10Dq = E({}^4T_2) - E({}^4A_2)$ and where λ is the spin-orbit coupling constant. For V^{2+} in silicon no experimental data for the energy difference between the levels is available but $10Dq = 0.75$ eV (6000 cm^{-1}) is a realistic estimate. Taking for λ the free-ion value $\lambda = 7.1$ meV (57 cm^{-1} [11]) we calculate $\Delta g_e = -0.076$. The difference from the experimental value $\Delta g_e = -0.0126$ is explained by a reduction of the spin-orbit coupling with respect to the free ion. This reduction, mainly ascribed to covalency, amounts to 85%. The effects of covalency for ions with an orbital singlet ground state have been calculated for an AB_6 complex in [12]. The spin-orbit coupling constant is then expressed in admixture coefficients of ligand wavefunctions (B) into the central-ion orbitals (A) and overlap integrals between metal and ligand orbitals. Since no accurate figures for these quantities are available in the case of V^{2+} we will restrict ourselves to some estimates. In the case of the AB_6 complex a spin transfer to the neighbouring atoms of about 15% already accounts for a reduction of λ of 85%. From various ${}^{29}\text{Si}$ ENDOR measurements of transition metals in silicon, Ti^+ , Cr^+ , Fe^0 , Fe^+ [13, 14, 15, 16, 17] it is known that the spin transfer to all the ligands can be expected to be of the order of 25 to 50%. It is quite conceivable, therefore, that covalency is the main cause for the reduction of λ .

The value of the hyperfine constant $A/h = -126.34$ MHz is also indicative of a substantial covalency. The hyperfine interaction, arising from contact interaction, is mainly caused by polarisation of the inner s orbitals by the valence orbitals. Residual $4s$ orbitals cannot provide the main contribution because this leads to a hyperfine interaction of the wrong sign. The unpaired spin density at the nucleus $|\psi(0)|^2$ is related to A by

$$A = (1/2S)\frac{2}{3}\mu_0 g_e \mu_B g_N \mu_N |\psi(0)|^2. \quad (8)$$

Using the data in table 1, we compute for V^{2+} $|\psi(0)|^2 = 0.33$ au^{-3} . The free-ion value, as calculated by the spin-polarised Hartree-Fock method [18], is $|\psi(0)|^2 = 0.77$ au^{-3} . The reduction in spin density is about 50%.

As for the nuclear g -shift, Low [19] calculated in second order of perturbation the g -shift caused by admixture of 4T_1 and 4T_2 orbitals due to orbital momentum. It follows that the nuclear and electronic g -shifts are related by

$$\mu_N \Delta g_N = -P \mu_B \Delta g_e / \lambda \quad (9)$$

with $P = (\mu_0/4\pi) g_e g_N \mu_B \mu_N \langle r^{-3} \rangle_d$. The free-ion value for V^{2+} is $P = 1.6$ μ eV (0.013 cm^{-1} [20]). With covalency effects already accounted for in Δg_e , equation (9) gives $\mu_N \Delta g_N = 40$ kHz T^{-1} . Using the free-ion value as tabulated in [21], $\mu_N g_N / h = 11.193$ MHz T^{-1} we

find $\mu_N \Delta g_N = 48 \text{ kHz T}^{-1}$. Thus the experimental data are in fair agreement with (9). The small discrepancy might be removed if diamagnetic screening effects of the silicon lattice are taken into account.

The parameter U is given by [5]:

$$U = [E(m_S = \frac{3}{2}) - 3E(m_S = \frac{1}{2})]/3\langle I_z \rangle. \quad (10)$$

The first calculation of U is reported in [22]. The contribution to U of $L \cdot S$ and $L \cdot I$ interactions with the excited triplet states 4T_1 and 4T_2 is given by [10]:

$$U = \langle {}^4A_2 | \lambda L \cdot S | {}^4T_2 \rangle \langle {}^4T_2 | \lambda L \cdot S | {}^4T_1 \rangle \langle {}^4T_1 | PL \cdot I | {}^4T_2 \rangle \\ \times \langle {}^4T_2 | \lambda L \cdot S | {}^4A_2 \rangle / \{ [E({}^4A_2) - E({}^4T_2)]^2 [E({}^4A_2) - E({}^4T_1)] \} \quad (11)$$

giving

$$U = 120P\lambda^3 / \{ [E({}^4T_2) - E({}^4A_2)]^2 [E({}^4T_1) - E({}^4A_2)] \}. \quad (12)$$

This can be expressed in terms of Δg_e using formula (7) and the crystal-field result

$$[E({}^4T_2) - E({}^4A_2)] / [E({}^4T_1) - E({}^4A_2)] = \frac{5}{3}. \quad (13)$$

We get

$$U = -\frac{25}{192} P \Delta g_e^3. \quad (14)$$

Substituting the observed g -shift of -0.0126 and the P -value listed above, we obtain $U/h = 0.1 \text{ kHz}$. This result clearly is of the wrong order of magnitude as compared with the experimental value $U/h = 98.8 \text{ kHz}$. As indicated in [23] the substitution of the experimental g -shift might overestimate the effects of covalency on U . However if one completely neglects covalency effects and calculates U (13) using the free-ion value $\Delta g_e = -0.076$ one obtains $U/h = 22 \text{ kHz}$, a result that is still substantially different from the experimental result. Considering these results we conclude that a calculation as in [22] is unable to account for the experimental data.

The higher-order S^3I term for V^{2+} was first found in the MgO host crystal by De Wijn and Schrama [4]. They tried to account for the S^3I term by calculating up to fourth order the effects of a perturbation Hamiltonian that, apart from spin-orbit and hyperfine interaction, also contained spin-spin interactions. The calculation was restricted within the 4F ground state of the d^3 configuration. It was argued by other workers [5, 6] that the contribution of excited states has to be taken into account and the S^3I term was calculated including the 2G and 4P terms. It was demonstrated that the contribution of the 2G state was especially important. However even for ionic crystals the discrepancy between theory and experiments is considerable (a factor of five). Comparing the result for V^{2+} in silicon and in ionic crystals [4, 6] we note that U has the same magnitude (about 100 kHz) in all cases. Also the sign of U (relative to the hyperfine constant A) is the same. Because of this similarity in ionic and covalent crystals we think it is unlikely that covalency effects are important as suggested by [6]. Inspection of the contributions to U in successive orders of perturbation [6] shows that there is no rapid convergence. It does not seem likely that higher-order perturbation theory will account for the discrepancy of a factor of five. At present no satisfactory theory for these higher-order terms is available. As for the origin of the S^2I^2 term, we refer to the results of the ENDOR measurements for ${}^{47}\text{Ti}$ and ${}^{49}\text{Ti}$ [23].

There remain some unclarified features of the Si:V defect. Firstly, unlike Ludwig and Woodbury, we also detected the vanadium spectrum in intrinsic and n-type material.

Secondly, both in this work and in [2], no ENDOR transitions arising from $m_s = \pm \frac{3}{2}$ were detected. We could not think of experimental limitations causing the disappearance of these lines. With the same spectrometer ENDOR in the frequency range around 180 MHz has been detected [24]. For these reasons one might question the assignment $S = \frac{3}{2}$ and the double-positive-charge state. A possible explanation for the missing $|m_s| = \frac{3}{2}$ transitions is to assume $S = \frac{1}{2}$. However, the measured frequencies only fit to (3) when taking $S = \frac{3}{2}$. Other spin values are excluded. Furthermore, in a description with $S = \frac{1}{2}$, a S^3I term is not allowed. Concerning the appearance of the vanadium EPR spectrum in various types of material, one might suggest that vanadium is in the neutral charge state: V^0 , with the configuration $3d^5$. This configuration is difficult to match with the deduced spin $S = \frac{3}{2}$. According to the Ludwig and Woodbury model, d^5 is in the maximum-spin state, i.e. $S = \frac{5}{2}$. Recent theoretical studies [25, 26] indicate that the ground state of V^0 is the low-spin state. In that case one will have a partially filled t_2 shell with $S = \frac{1}{2}$ and $L' = 1$. The g -factors corresponding to these configurations are 0.67 for both $J = \frac{1}{2}$ and $\frac{3}{2}$, at variance with the observed value $g \approx 2$. The assumption that vanadium is situated on a substitutional site leads to $S = \frac{1}{2}$ and can be rejected as well. A single positive or negative charge state will always lead to integer values of S and is excluded. On the basis of the experiments we conclude that V^{2+} still gives the best explanation for the observed data.

5. Conclusions

The ^{51}V ENDOR measurements for $\text{Si}:V^{2+}$ showed that higher-order hyperfine terms were necessary for describing this centre. The S^3I term accounts almost completely for the observed anisotropy in the ENDOR spectrum. The magnitude of the corresponding parameter U is approximately equal to the observed value for vanadium in ionic crystals. On the basis of available perturbation treatments, a satisfactory theoretical explanation cannot be given.

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