LINEAR EFFECT OF APPLIED ELECTRIC FIELD IN ELECTRON SPIN RESONANCE

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In the preceding Letter,[1] Ludwig and Woodbury report observation of linear effects of an applied electric field on the electron spin resonance spectra of two charge states of interstitial iron in silicon, in accord with Bloembergen's prediction[2] that such effects should be in general observable for ions at crystal sites lacking inversion symmetry. The purpose of this Letter is to show explicitly how these effects arise for iron-series transition metal ions that form interstitial defects in silicon. Similar results pertain to other ions with d^n or f^n valence configurations in various crystals.

A phenomenological model that successfully describes interstitial iron series ions in silicon has been given by Ludwig and Woodbury[3]: The ions occupy sites of tetrahedral symmetry; all valence electrons are in the d shell; the threefold degenerate t_2 orbitals are lower in energy than the doubly degenerate e's; Hund's rule is obeyed. However, the t_2 and e wave functions of the interstitial are very different from the $3d$ functions of the free ion,[4] although they have the same behavior under symmetry operations of the tetrahedron. In particular, $3d\,t_2$ functions mix with functions of odd parity on the metal ion, such as $4p$, and form bonds with neighboring silicon atoms. Denoting by x, y, z coordinates with respect to the cube directions, we may represent the t_2 functions schematically by

$$\psi_x = \alpha(yz)_{3d} + \beta(x)_{4p} + \gamma(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4), \quad (1)$$

and ψ_y and ψ_z by cyclic permutation of x, y, z. Here φ_1, φ_2, φ_3, and φ_4 denote σ orbitals on nearest neighbors in the [111], [$\bar{1}\bar{1}$1], [1$\bar{1}\bar{1}$], and [$\bar{1}$1$\bar{1}$] directions, respectively, and for simplicity we ignore other possible bonds.

The interaction $\mathcal{H}_{\mathcal{E}} = e\,\mathcal{E}_z z$ of an electron with an electric field $\mathcal{E}_z$ in the z direction then has only one nonzero matrix element between the t_2 functions:

$$\langle \psi_x | e\,\mathcal{E}_z z | \psi_y \rangle = p\,\mathcal{E}_z. \quad (2)$$

This defines a parameter p. We may for convenience represent the matrix elements between t_2 functions in terms of an operator $\vec{\mathcal{L}}$ which satisfies the commutation rules for angular momentum, with $\mathcal{L} = 1$[5]:

$$\mathcal{H}_{\mathcal{E}} = -\mathcal{E}_z p(\mathcal{L}_x \mathcal{L}_y + \mathcal{L}_y \mathcal{L}_x). \quad (3)$$

$\mathcal{H}_{\mathcal{E}}$ lifts the orbital degeneracy of t_2, energy levels being at 0 and $\pm p\,\mathcal{E}_z$. Thus an electron in a t_2 state in tetrahedral symmetry responds to a field in a cube direction as if the state possessed an electric dipole moment of strength p. From (1) and (2), p is nonzero if the t_2 states are mixtures of functions of opposite parity on the central ion (α and $\beta \neq 0$) or if σ bonding occurs with the nearest neighbors ($\gamma \neq 0$).

For Fe^0 or Mn^- interstitial in Si, the ground state arises from the configuration $t_2^6 e^2$ and has $S = 1$ and no orbital degeneracy.[3] At an energy Δ higher, there is an orbital triplet of the form $t_2^5 e^3$ which is split by an electric field. Between these states and the ground state there are matrix elements of the spin-orbit interaction $\lambda(\vec{\mathrm{L}}\cdot\vec{\mathrm{S}})$, the orbital part of the Zeeman interaction $\beta(\vec{\mathrm{L}}\cdot\vec{\mathrm{H}})$, and the interaction $P(\vec{\mathrm{L}}\cdot\vec{\mathrm{I}})$ between the nuclear moment and the orbital moment of the electrons. Accordingly, from third-order perturbation theory we find for the spin Hamiltonian of the ground state[6]

$$\begin{aligned}\mathcal{H} = {} & g\beta\vec{\mathrm{H}}\cdot\vec{\mathrm{S}} + A\vec{\mathrm{I}}\cdot\vec{\mathrm{S}} - \gamma\beta_N\vec{\mathrm{H}}\cdot\vec{\mathrm{I}} \\ & + \mathcal{E}_z(2\lambda^2 p\alpha^2/\Delta^2)(S_x S_y + S_y S_x) \\ & + \mathcal{E}_z\beta(4\lambda p\alpha\alpha'/\Delta^2)(S_x H_y + S_y H_x) \\ & + \mathcal{E}_z(4\lambda pP\alpha\alpha''/\Delta^2)(S_x I_y + S_y I_x) \\ & + \mathcal{E}_z(2pP^2\alpha''^2/\Delta^2)(I_x I_y + I_y I_x) \\ & + \mathcal{E}_z\beta_N(4pP\alpha'\alpha''/\Delta^2)(\beta/\beta_N)(I_x H_y + I_y H_x). \quad (4)\end{aligned}$$

Terms in (4) arising from $\mathcal{E}_x$ and $\mathcal{E}_y$ may be obtained by permutation of indices. Here α, α', and α'' are factors arising because matrix elements of $\lambda(\vec{\mathrm{L}}\cdot\vec{\mathrm{S}})$, $\beta(\vec{\mathrm{L}}\cdot\vec{\mathrm{H}})$, and $P(\vec{\mathrm{L}}\cdot\vec{\mathrm{I}})$ are changed from their free-atom values. The isotropic shift in g provides the relation

$$(8\lambda\alpha\alpha'/\Delta) \cong -(g - 2.0023).$$

For $g\beta H \gg (\lambda^2\alpha^2/\Delta^2)p\,\mathcal{E}$ and arbitrary orientation of $\vec{\mathcal{E}}$ and $\vec{\mathrm{H}}$, the energy levels to first order in $\mathcal{E}$ are given by (with omission of nuclear terms)

$$E(M) = g\beta HM + (6\lambda^2 p\alpha^2/\Delta^2)\,\mathcal{E}M^2\phi + (8\lambda p\alpha\alpha'/\Delta^2)\,\mathcal{E}\beta HM\phi, \tag{5}$$

where

$$\phi = m_z n_x n_y + m_x n_y n_z + m_y n_z n_x, \tag{6}$$

n_x, n_y, n_z and m_x, m_y, m_z being the direction cosines of $\vec{H}$ and $\vec{\mathcal{E}}$, respectively.

For Fe^+ or Mn^0 the ground state is $t_2{}^5e^2$ with $S = \frac{3}{2}$ and a threefold orbital degeneracy describable by an effective orbital angular momentum operator $\vec{\mathcal{L}}$ with $\mathcal{L} = 1$. With $\vec{J} = \vec{\mathcal{L}} + \vec{S}$, the spin-orbit interaction separates the levels with $J = \frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$, placing $J = \frac{1}{2}$ lowest. The effect of $\mathcal{E}_z$ is represented by an operator of the same form as (3), and this, the Zeeman interaction

$$\mathcal{H}_H = g_{\mathcal{L}}\beta\vec{H}\cdot\vec{\mathcal{L}} + g_S\beta\vec{H}\cdot\vec{S},$$

and the hyperfine interaction

$$\mathcal{H}_I = A_{\mathcal{L}}\vec{\mathcal{L}}\cdot\vec{I} + A_S\vec{S}\cdot\vec{I}$$

have matrix elements between the $J = \frac{1}{2}$ and $\frac{3}{2}$ states. Accordingly, from second order perturbation theory the spin Hamiltonian for the $J = \frac{1}{2}$ states has the form

$$\mathcal{H}_{1/2} = (\tfrac{5}{3}g_S - \tfrac{2}{3}g_{\mathcal{L}})\beta\vec{H}\cdot\vec{J} + (\tfrac{5}{3}A_S - \tfrac{2}{3}A_{\mathcal{L}})\vec{J}\cdot\vec{I} - [2p(g_S - g_{\mathcal{L}})/3W]\,\mathcal{E}_z\beta(J_xH_y + J_yH_x) - [2p(A_S - A_{\mathcal{L}})/3W]\,\mathcal{E}_z(J_xI_y + J_yI_x),$$

where $W = [E(\frac{3}{2}) - E(\frac{1}{2})]$.

For interstitial Mn^+ and Cr^0 in silicon the ground state is $t_2{}^4e^2$ ($S = 2$, $\mathcal{L} = 1$). The effect of $\mathcal{E}_z$ is given by (3). This gives a direct Stark splitting of the ground level ($J = 1$) as well as producing shifts in other resonance parameters.

The silicon lattice has two tetrahedral interstitial sites identical in their environments except that one is inverted with respect to the other. The dipole moment p has opposite sign for these sites, and resonance spectra should thus show a symmetrical splitting of lines to first order in $\mathcal{E}$, as is observed.

We have so far ignored the fact that the paramagnetic ion is displaced by the external field from its position of tetrahedral symmetry. This displacement gives rise to a perturbation in the potential seen by the electrons in addition to that produced directly by the applied field. However, we may show from symmetry that to first order in $\mathcal{E}$ this further perturbation can affect only those matrix elements already affected directly by the applied field. Thus the parameter p will be used to represent the net effect of both perturbations.

From the results of Ludwig and Woodbury and Eqs. (4) and (7) we can evaluate the effective one-electron dipole strength p for interstitial Fe^+ and Fe^0 in silicon, using estimates of the other parameters in these formulas obtained from other studies.[4] We obtain $p/e \cong 0.3 \times 10^{-8}$ cm for both Fe^0 and Fe^+. These values are, however, each uncertain to perhaps a factor of 3 because of uncertainties in making correction for local fields and in estimating the other parameters.

If p is of the same magnitude for Mn and Cr in silicon as for Fe, the ground states of Mn^+ and Cr^0 should suffer a linear Stark splitting of ~0.05 cm^{-1} with $\mathcal{E} = 10^4$ v/cm, in zero magnetic field.

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[1] G. W. Ludwig and H. H. Woodbury, preceding Letter [Phys. Rev. Letters 7, 240 (1961)].

[2] N. Bloembergen, Science 133, 1363 (1961); Phys. Rev. Letters 7, 90 (1961).

[3] G. W. Ludwig and H. H. Woodbury, Phys. Rev. Letters 5, 538 (1960).

[4] G. W. Ludwig, H. H. Woodbury, and F. S. Ham (to be published).

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

[6] In writing the coefficients of the terms in (4) we have omitted contributions arising from matrix elements between the ground state and two higher orbital triplets derived from the free atom ^3F and ^3P terms. These additional contributions have the same general form and relative size as those given and must be included in a quantitative treatment. They are proportional to a matrix element of $\mathcal{H}_{\mathcal{E}}$ between the t_2 and e functions instead of to p as defined by (2).