Localization and Magnetism of an Interstitial Iron Impurity in Silicon

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The apparent dichotomy between the covalently delocalized nature of Si:Fe (as suggested by its reduced hyperfine field, its extended spin density, and the occurrence of two closely spaced stable charge states within 0.4 eV) and the atomically localized picture (suggested, among other reasons, by the stability of a high-spin ground-state configuration) is resolved through a self-consistent Green's-function calculation with the self-interaction–corrected local-spin-density formalism.

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Iron is the commonest transition-metal impurity in silicon,[1-9] occupying under normal diffusion conditions[7] an undistorted tetrahedral interstitial site.[1,3,6] Experimental data[1-7] on Si:Fe suggest paradoxically both a model of a covalently delocalized impurity and its opposite: that of an atomically localized impurity. Arguing for the first picture, we note the following. First, the impurity hyperfine field H_{hf} and the contact spin density[3,4] $\delta\rho(0)$ at the nucleus of Si:Fe^0 are reduced by 43% relative to the free atom (using the calculated Hartree-Fock value[10]), whereas these quantities for Fe in ionic solids[11] are close to the free-ion values. A similar conclusion is apparent from the recent electron nuclear double resonance (ENDOR) experiment,[6] which shows the spin density to be expanded at least up to the fifth Si shell surrounding the impurity. Second, as noted by Ludwig and Woodbury,[3] the electron paramagnetic resonance (EPR) parameters, including the spin values for the neutral impurity Si:Fe^0 ($S=1$) and the charged-ion impurity Si:Fe$^+$ ($S=\frac{3}{2}$), indicate that the s electrons of the free atom (d^6s^2) are converted in the solid into d orbitals (d^8 for Fe^0, d^7 for Fe$^+$). However, this $s \rightarrow d$ population inversion must suggest a strong covalency: If the impurity orbitals were atomically localized, the substantial s-d Coulomb repulsion U^{sd} would have resisted such a transfer.[12] Third, the stability of the "overcrowded" d^8 configuration also suggests substantial covalency. The Fe^0/Fe$^+$ donor ionization energy[1,2,5] $E_D=E_v+0.385\pm0.01$ eV, when referred to vacuum (i.e., subtracting it from the position of the valence-band maximum E_v relative to vacuum, approximately 5.2 ± 0.2 eV) is $\sim4.8\pm0.2$ eV. If the d electrons were atomically localized on the Fe impurity, the Fe^0/Fe$^+$ ionization energy would have been reduced relative to the Fe^{2+}/Fe^{3+} ionization energy (30.6 eV in the ion[12]) by twice the atomic d-d Coulomb repulsion energy U^{dd} (about 15–25 eV for $3d$ ions[12]); hence Fe^0,d^8 would have been unbound. This picture of a covalently delocalized impurity is also consistent with the anticipated[13,14] large crystal-field splitting Δ_{CF} (which increases with covalency, and is already 0.45 eV in the less covalent GaP:Fe system[15]).

In contrast with this picture, there is substantial evidence that suggests the impurity to be localized, and the crystalline environment to be only a weak perturbation on its atomic states. First, Si:Fe$^+$ appears, like the free ion, in a (Hund's rule) high-spin ($S=\frac{3}{2}$) configuration,[3] indicating that as large as the crystal-field splitting Δ_{CF} may be, the impurity orbitals must be sufficiently localized to have an exchange splitting Δ_x that exceeds Δ_{CF}. Second, despite the propagation of the spin density up to at least five shells of Si atoms, the impurity central cell includes as much as 80% of the spin density.[6] Third, the coupling to the host crystal must be weak enough (Δ_x large) to explain the absence[3,4] of any measurable static Jahn-Teller distortion in Si:Fe$^+$ despite the degeneracy of its $^4T_1$ ground state. Fourth, the total angular momentum J is consistent with the interpretation of atomically localized $3d$ electrons.[3] Finally, the very low solubility and superfast diffusivity[1] suggest a weak interference with the solid, i.e., that no strong bonds are formed or broken upon insertion and migration, respectively, of Fe in silicon. In this Letter we analyze the duality in the nature of the localization in Si:Fe and its peculiarities, with a nonempirical, self-consistent Green's-function calculation for interstitial Fe^0 and Fe$^+$ impurities in silicon, within the self-interaction–corrected,[16] local-spin-density (LSD) formalism.

We use the impurity Green's-function formalism proposed by Williams, Feibelman, and Lang[17] and applied by Katayama-Yoshida and Shindo previously,[18] with the following modifications needed for the present application: (i) An all-electron potential, rather than a pseudopotential, is used to describe the impurity core: (ii) the 1*s*-through-4*f* impurity basis orbitals are optimized iteratively and nonlinearly, allowing them to adjust to the changes in the self-consistent potential obtained from the Green's-function problem; (iii) we apply self-consistently the self-interaction correction[16] to the LSD in a fully spin-polarized manner. Recent calculations of the multiplet energies for 3*d* impurities in semiconductors[15] indicate that most of the multiplet energy is exchange derived and hence well represented by a spin-polarized calculation. We use the Ceperley-Alder exchange-correlation as given by Perdew and Zunger,[16] adjust the host band structure to fit the experimentally observed interband transitions, and assume an unrelaxed crystal geometry.

Figure 1 displays for Si:Fe^0 the changes $\Delta n^{\sigma}_{\Gamma,\alpha}(\epsilon)$ in the local density of states for spin $\sigma = \pm$ and representation $\Gamma = a_1$, e, and t_2, projected on the local orbitals $\alpha = 3d$, $4s$, and $4p$. We find a spin-down antibonding t_2 level in the gap at $E_v + 0.26$ eV, and a spin-up e level above it at $E_v + 0.44$ eV. The latter contributes a local (as defined by the impurity basis orbitals) magnetic moment of $\mu_e^{\text{gap}} = 0.384\mu_B$, whereas the former contributes $\mu_{t_2}^{\text{gap}} = -0.576\mu_B$. In ionic crystals, the 3*d* impurity orbitals are isolated exclusively as gap states.[19] In contrast, we find that most ($\sim 80\%$) of the 3*d* amplitude in the impurity orbital subspace in silicon exists as localized resonances inside the valence band [shaded areas in Fig. 1, showing bonding (b) and antibonding (a) resonances (R)], dominating the magnetism ($\mu^{\text{VB}} = 1.61\mu_B$ vs $\mu^{\text{gap}} = -0.19\mu_B$) and the impurity charge (6.76 out of 8.0 valence electrons are in the valence band, and 18 are in the core). We will see that this coexistence, in a similar energy range, of localized impurity states with itinerant-electron host states with which charge can be exchanged without surpassing an excitation barrier is the key to the remarkable stability of various charge states.

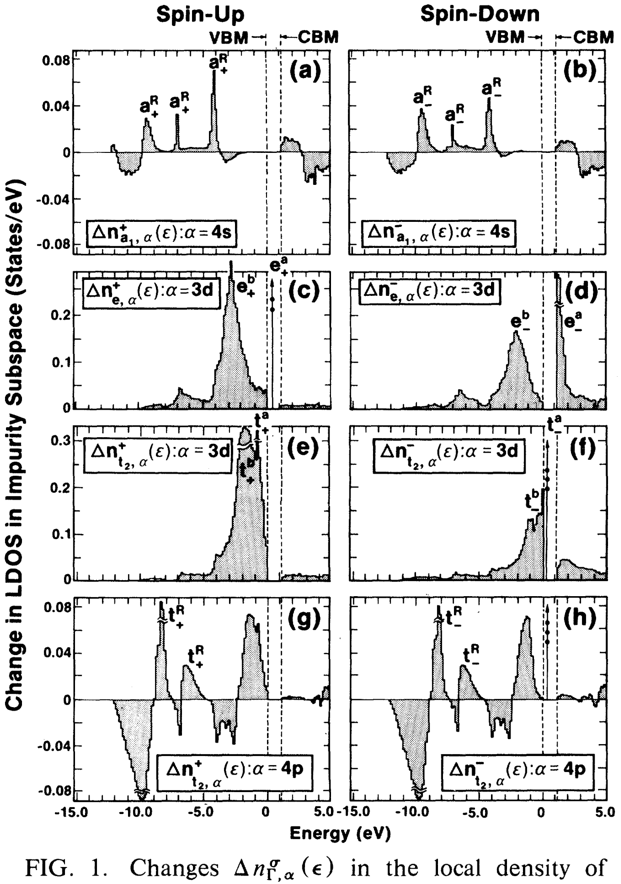

FIG. 1. Changes $\Delta n^{\sigma}_{\Gamma,\alpha}(\epsilon)$ in the local density of states (LDOS) for spin σ (+ or −) and representation $\Gamma = a_1$, e, and t_2. We show only the major orbital components: $\alpha = 4s$ for a_1, 3*d* for *e*, and 3*d* and 4*p* for t_2.

A few conclusions can be drawn from the results on Si:Fe^0. First, whereas the *total* magnetic moment (calculated from the phase shifts) is $2.0\mu_B$, much like in the d^8 free atom, the *local* magnetic moment in the impurity orbital subspace is only $1.42\mu_B$, and the remaining $(1 - 1.42/2.0) \times 100 = 29\%$ of the spin density (as indicated by ENDOR[6]) is delocalized through the crystal, showing substantial covalency. This shows that the perturbation potential is localized but the impurity wave functions are not. A population analysis of the magnetic moment shows it to evolve primarily from the valence *d* orbitals [moment distribution of $(\text{core})^{0.00}$, $4s^{0.00}$, $4p^{0.01}$, $3d^{1.29}$, $4d^{0.100}$, $4f^{0.02}$], and to be shared in a 5:1 proportion between the *e* and t_2 valence representations [moment distribution of $(\text{core})^{0.00}$, $a_1^{0.01}$, $e^{1.17}$, $t_2^{0.24}$]. Second, in contrast to the dominant role of the *valence-band states* in determining the local moment, the hyperfine field H_{hf} is determined largely by the *core states.* The contribution to the Fermi contact interaction (both direct and core polarization) from the core states is $-24.50 - 278.52 + 179.70 = -123.32$ kG for the 1*s*, 2*s*, and 3*s* states, respectively, and that from the 4*s* valence-band states is only $+8.18$ kG, yielding a total contact term of -115.14 kG. The contribution from the interaction with the electron orbital magnetic moment is estimated from the *g* shift[3] to be $+9.93$ kG. With neglect of the small dipolar term, the total calculated H_{hf} of -105.21 kG is reasonably close to the observed values[3,4] (only the absolute value is known from experiment) of $|H_{\text{hf}}|$

$=147.6$–152.2 kG. We find a spin density at the Fe nucleus of $\delta\rho(0) = -0.220$ a.u.$^{-3}$, in reasonable agreement with the observed values[3,4] of $|\delta\rho(0)| = 0.282$–0.299 a.u.$^{-3}$. The negative H_{hf} and $\delta\rho(0)$ result from the preferred expulsion of spin-up density from the core region by the Coulomb repulsion between the core electrons and the unpaired $3d$ electrons. Third, we find for Si:Fe^0 that the crystal-field splitting exceeds the exchange splitting ($\Delta_x/\Delta_{\mathrm{CF}} = 0.88$), and hence the t_- gap level is *below* the e_+ level which is the highest occupied state. This level arrangement is characteristic of a strong-field (covalent) situation unlike that postulated by Ludwig and Woodbury.[3] For Si:Fe^0, both the strong-field and the weak-field configurations give the observed[3,4] spin value $S = 1$. Finally, in agreement with the nonmagnetic calculation[14b] and with Ludwig and Woodbury,[3] a population analysis of the orthogonalized states reveals that the s electrons are largely transferred into d orbitals [effective configuration: (core)$^{18.0}$, $4s^{0.06}$, $4p^{-0.13}$, $3d^{8.18}$, $4d^{-0.386}$, $4f^{-0.00}$] and that in the impurity subspace, iron has a small positive net charge (nuclear charge minus electronic charge) of $Q_{\mathrm{net}} = 0.276e$, indicating a small Fe-to-Si ionic charge transfer. This $s \rightarrow d$ population inversion decreases the effective size of the atom (as extended s are converted to more localized d states) without converting it into an ion. It therefore suggests a simple chemical reason for its fast diffusivity and low solubility[1]—the occurrence of a rather small diffusing species. Our results for Si:Fe^0 are hence consistent with the covalently delocalized model.

Si:Fe$^+$ has different characteristics. We describe it using Slater's transition-state approximation: We remove half an electron from either the e_+ or the t_- gap levels, placing the ionized charge in the conduction-band minimum, and seek a new self-consistent solution. We find that although the highest occupied orbital of the neutral system is the e_+ state, the lowest energy ionization proceeds instead from the t_- orbital. Remarkably, upon ionizing t_-, the e_+ orbital moves down in energy, exposing the t_- as the highest occupied state of the ion, and producing thereby the observed $S = \frac{3}{2}$ high-spin (weak-field) configuration as $\Delta_x/\Delta_{\mathrm{CF}}$ switches from below unity for Si:Fe^0 to above unity (1.4) for Si:Fe$^+$. It is important to emphasize that without the self-interaction correction, the correct high-spin ground state is not obtained[14a] (unless the spherical approximation to the potential is involved[13]). We find a donor energy $\epsilon(t_-) - \epsilon_{\mathrm{VBM}} = E_v + 0.32$ eV, in good agreement with the observed value[2,5] of $E_v + 0.385 \pm 0.01$ eV. In agreement with experiment,[2] no stable acceptor state (Fe^0/Fe$^-$) exists in the gap, as the empty e_- level that would accommodate the next electron is in the conduction band [Fig. 1(d)]. The reason for this e_+-t_- level reversal is that upon ionizing a spin-down orbital, the highly localized (bonding) spin-up resonances in the valence band are relieved from their Coulomb repulsion with the ionized orbital and move to more negative energies (i.e., an orbital relaxation effect). Becoming thereby more localized, their exchange splitting Δ_x increases (suppressing thereby Jahn-Teller distortions) and the antibonding spin-down orbital t_- is repelled to a higher energy. The increased localization of the valence-band resonances upon removal of a gap electron means that their wave functions penetrate the impurity region better, making up for most of the charge that was removed from this region by ionization of the gap level. Stated simply, whereas Fe^0 has much of its charge density delocalized on the ligands (whereas most of the spin density is localized within the central cell), when converted to Fe$^+$, charge flows from the ligands to the impurity, making both Fe^0 and Fe$^+$ have comparable ionic charge. We find indeed that the *net* impurity charge Q_{net} increases in the impurity subspace only by $0.1e$ upon ionization. This mechanism suggests that the charge density on the *impurity site* (as could be measured by the Mössbauer isomer shift) will change only little by ionization of the impurity (we estimate the change to be at least one order of magnitude smaller than in the Fe^0/Fe$^+$ free ions), whereas the largest change in density would occur on the *ligands* (as could be measured by comparing the ENDOR of Si:Fe^0 to that of Si:Fe$^+$). Unfortunately, while existing Mössbauer data[8] show a vanishing change in the isomer shift upon ionization, the data available to date are clouded by the occurrence of complexes.[9] This self-regulating response[20] of the valence band to excitations of the "outer" gap electrons means that the *effective* Coulomb repulsion U^{dd} is substantially smaller than what a linear dielectric-screening mechanism would grant us, and even an "overcrowded" d^8 configuration can be stabilized. We suspect that a similar self-regulating (Le Chatelier) response is the reason why Fe^{2+}/Fe^{3+} redox ionizations in heme proteins and electron-transporting biological systems take so little energy,[21] despite the fact that the molecule is not severely distorted. In contrast, this excitationless coupling of $3d$ resonances with the host states is not available in ionic media where the impurity levels are isolated in the gap. There, external perturbations (e.g., ionizations) could be accommodated only through massive lattice relaxations.

The resolution to the apparent dichotomy between the covalently delocalized and atomically localized models for Si:Fe lies therefore in this self-regulating response and in the fact that different orbitals are responsible for the different aspects of the localization (duality): The contact spin density and hyperfine field are decided by the hyperlocalized *core states,* the magnetism is largely contributed by the localized *valence-band resonances,* and the donor ionization, with its attendant high-spin configuration, and the consistancy of the isomer shift are decided by a combination of *delocalized gap states* and the feedback (self-regulating) response of the valence-band resonances to excitations of the outer states.

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