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Chemical trends in ground- and excited-state properties of interstitial 3*d* impurities in silicon

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A spin-polarized local-density Green's-function calculation for tetrahedral interstitial 3*d* impurities in silicon reveals a new energy-level scheme that explains the observed chemical trends both in ground-state properties (hyperfine coupling constants and *g* values) and in excited-state properties (donor and acceptor ionization energies).

I. THE ISSUES

More than twenty years ago, Ludwig and Woodbury[1] (LW) proposed what has since become the classical model for explaining the observed electron paramagnetic-resonance (EPR) spectra of interstitial 3*d*-transition (T) atom impurities in silicon. This model has since been extended to magnetic impurities in many other semiconductors.[2]

This classical crystal-field model[1,3] shows that the tenfold degenerate atomic 3*d*-orbital splits in the tetrahedral interstitial symmetry of a silicon lattice into a sixfold degenerate t_2 orbital, separated by a crystal-field (CF) splitting $\Delta_{\rm CF}$ from the fourfold degenerate e orbital above it. These levels are further split by the exchange interactions Δ_x into spin-up (t_+ and e_+) and spin-down (t_- and e_-) components. In complete analogy with the well-studied behavior of substitutional 3*d* impurities in octahedrally coordinated ionic compounds[3] (e.g., MgO), LW postulated[1] that all N-atomic valence electrons of the transition atom (i.e., $d^m s^n$, with $m+n=N$) occupy the t_2 and e levels in a way that produces the maximum possible spin value S (Hund's rule); i.e., the level ordering implied is $t_+ < e_+ < t_- < e_-$. We refer to this strong-field[3] ($\Delta_x > \Delta_{\rm CF}$) ordering as high-spin-like (HSL), to distinguish it from the low-spin-like (LSL) level ordering $t_+ < t_- < e_+ < e_-$ in which the e_+ level does not cross the t_- level. Considerable interest has focused on determining experimentally the actual level ordering.[1,2] This could often be inferred from the measurement of the spin (S) and momentum (J) quantum numbers in EPR experiments. Likewise, observation by Hall effect and deep-level transient spectroscopy (DLTS) of acceptor $E(0/-)$ and donor $E(0/+)$ ionizations from the impurity level to the host band edges have also been used[2] to infer the level structure, since a HSL level ordering predicts a different highest occupied orbital than the LSL level ordering. Such experiments on 3*d* impurities in semiconductors[1,2] have advanced a number of *universal* (i.e., impurity-independent) rules which have since become the paradigms of this field. (i) All 3*d* impurities give rise to a HSL level arrangement. (ii) They all have a (Hund's rule) maximum spin value. (iii) The chemical trends in acceptor and donor transition energies are determined by rules (i) and (ii) above, e.g., a d^5/d^4 ionization energy is larger (i.e., lower in the gap) than a d^6/d^5 ionization energy since the former transition commences from a deeper (exchange-stabilized) e_+ level and the latter from a shallower t_- level. (iv) In analogy with 3*d* impurities in ionic crystals, exchange interactions are envisioned to dominate over covalent hybridization (hence also crystal-field effects). Consequently, the universally observed quenching of the angular momentum part g_L of the g values[1,2] and the reduction in the hyperfine coupling constants[1] A were attributed to unusual new effects (e.g., dynamic Jahn-Teller coupling[4]), rather than to covalency effects.[3]

Theory has not produced a conclusive picture either, largely because no "unified approach" to the problem—i.e., prediction from the same model of *both* wave-function-related ground-state properties (g values, hyperfine coupling constants) and energy-related excited-state properties (donor and acceptor transition energies)—has been attempted. The LW hypothesis continued to be the prevailing working model in the field and remained unchallenged.

We have applied a first-principles self-consistent Green's-function method[5] within the self-interaction corrected[6,7] local-spin-density formalism to study the ground- and excited-state properties of all interstitial 3*d* impurities in silicon in their different charge states. Our results challenge the four concepts [(i)–(iv) above] used in the classical models, yet they produce agreement with the available experimental data, provide predictions for hitherto unobserved transitions, and point to new crucial experiments.

Our method of calculation is identical to what has been previously described.[5] We retain all core and valence electrons of the impurity as spin-polarizable states, and treat them on the same footings (an all-electron approach). We incorporate the self-interaction correction[6,7] (SIC) to the local-spin-density (LSD) formalism. The band structure of Si has been calculated[5] using an empirically adjusted pseudopotential, to assure that the few lowest band gaps are correctly reproduced.

II. ELECTRONIC STRUCTURE

Central to the understanding of the properties of such impurities in covalent semiconductors is the fact that much of the 3*d* character exists as broad, impurity-induced valence-band resonances (missing in classical ionic models[1-3]) and not only as isolated gap levels (the only ones present in ionic systems, e.g., MgO:3*d*). The spin-polarized local density of states of the neutral centers (Fig. 1) shows that these impurities in silicon introduce bonding (b) valence-band resonances of t_2 (t^b_+, and t^b_-) and e (e^b_+ and e^b_-) symmetries in the upper part of the valence bands (shaded areas), and that their antibonding (a) counterparts (t^a_+, t^a_-, e^a_+, and e^a_-), appear in the band gap or inside the conduction band [in addition, deep and nearly impurity-independent resonances (R) t^R_+, t^R_-, a^R_+, and a^R_- appear in the lower part of the valence band[5]]. We find that these VB resonances con-

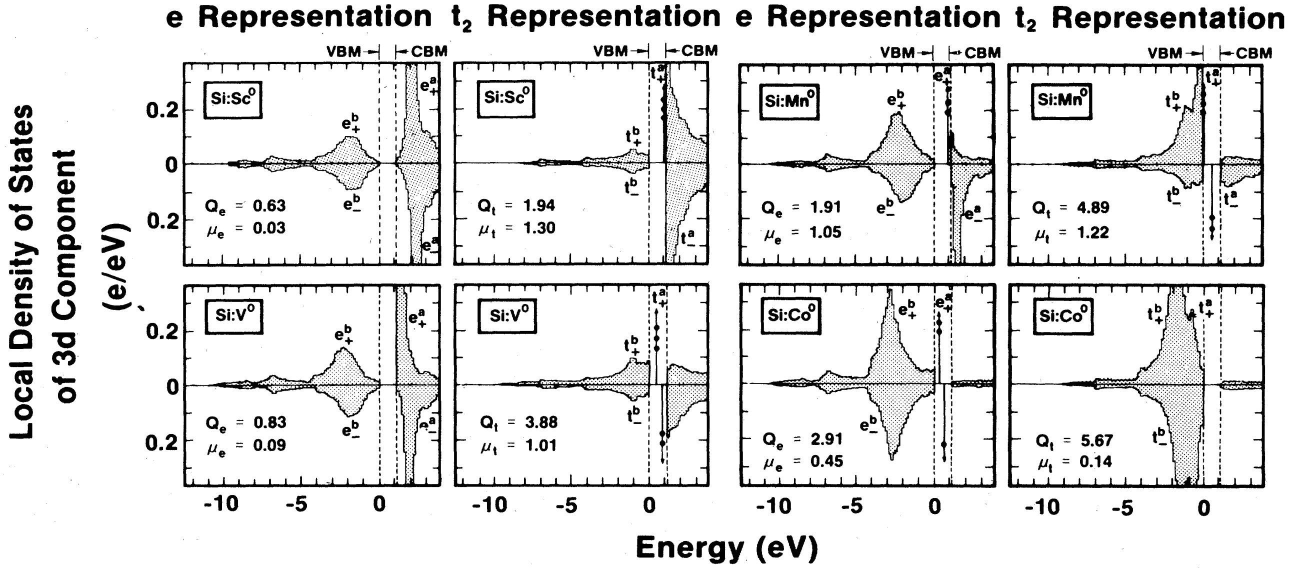

FIG. 1. Calculated local density of states (projected $3d$ component) of neutral interstitial $3d$ impurities in silicon, for spin up (plus sign) and spin down (minus sign). Q_α and μ_α are the charge and local magnetic moment of representation α.

trol the impurity's charge distribution and magnetism. Decomposition[5] of the local magnetic moments μ and the effective impurity charge Q in the impurity subspace into contributions from the occupied VB and the gap (g) levels, shows that much of μ and Q are contributed by the hybridized impurity-induced VB states. For example, out of the 27 electrons of neutral Co [atomic configuration (core)[18] d^7s^2], we find 18e to reside in the core levels, 7.49e to be in VB resonances, and only 1.15e in the $e_+^2 e_-^1$ gap levels (leaving a net formal charge of $+0.36e$ on the impurity ion). These VB electrons contribute to the magnetism ($\mu_{\text{VB}}=0.29$ μ_B) almost as much as the gap electrons do ($\mu_g=0.31\mu_B$). Further examples are given as inserts to Fig. 1. The coexistence of VB resonances with isolated gap levels leads to a remarkable constancy of the net impurity charge (Q_{net} in Fig. 2) in different ionized states[7] (i.e., gap holes are screened effectively by VB resonances, leading to a self-regulating response). It also controls the g values and hyperfine constants, as discussed next.

III. *g* VALUES AND HYPERFINE COUPLING CONSTANTS

The phenomena of quenching of the angular-momentum part g_L of the g value which occurs for $3d$ impurities in semiconductors[1,2] has long been familiar in inorganic chemistry of coordination compounds,[3] where it has been interpreted[3] in terms of a hybridization-induced partial cancellation between p- and d-orbital effects. The early notion[1,4]

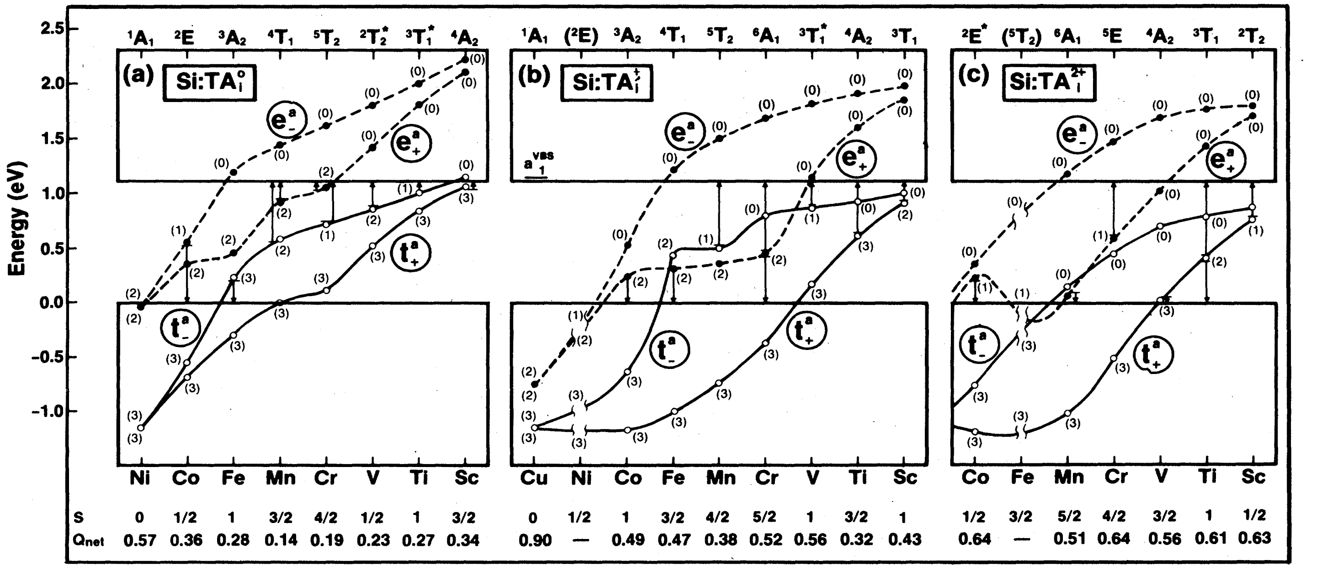

FIG. 2. Calculated ground-state energy levels for (a) neutral, (b) singly positive, and (c) doubly positive interstitial $3d$ impurities in Si. Occupation numbers are given in parentheses. S is the spin, Q_{net} is the net impurity charge (Ref. 5). An asterisk on the multiplet denotes a predicted low-spin state.

that no such hybridization could exist universally for $3d$ impurities in semiconductors has led to the suggestion (and indeed, the discovery) of a new mechanism for quenching g_L—the dynamic Jahn-Teller effect.[4] While this has been subsequently demonstrated to be the case in other systems, no proof (theoretical, or experimental) has been advanced to show that this is a viable effect for $3d$ impurities in semiconductors, and what its measurable distinguishing features are relative to the p-d hybridization effect. The hitherto unrecognized universal occurrence of hybridized valence resonances for all $3d$ impurities which we find (Fig. 1) led us to reconsider the classical p-d hybridization effect. Calculating[8-10] g from the impurity wave functions, with no adjustable parameters (Table I), we find that the hybridization effect explains the quenching of g_L and the chemical trends in g both along the $3d$ series and for different ionized impurity states. The same effect (through a covalent reduction of the s-d repulsion) also explains the trends in the hyperfine coupling constant[9] A (Table I). Table I includes a number of predictions. In particular, the parameters of Si:Ti$^+$ ($A = +4.727\times10^{-4}$ cm^{-1}, $g = 1.9912$), not observed by LW, are in excellent agreement with the data [$A = (\pm5.224\pm0.010)\times10^{-4}$ cm^{-1}, $g = 1.998\,06\pm0.000\,04$] observed very recently by Van Wesep and Ammerlaan.[11]

TABLE I. Calculated (Refs. 8 and 9) and observed (Refs. 1 and 11) g values and hyperfine coupling constants A of interstitial $3d$ impurities in Si. Asterisks denote calculated values of contact interaction alone. A is in unit of 10^{-4} cm^{-1}. Error bars (Ref. 11) are given only in the case of Si:Ti$^+$ [$g = 1.998\,06\pm0.000\,04$, $A = (\pm5.224\pm0.010)\times10^{-4}$ cm^{-1}].

	Impurity	S	J	g_{calc}	g_{expt}	A_{calc}	A_{expt}
d^3	$^{45}\text{Sc}^0$	$\frac{3}{2}$	$\frac{3}{2}$	1.9885	· · ·	−13.6	· · ·
	$^{47}\text{Ti}^+$	$\frac{3}{2}$	$\frac{3}{2}$	1.9912	1.9986	+4.7	5.224
	$^{51}\text{V}^{2+}$	$\frac{3}{2}$	$\frac{3}{2}$	1.9731	1.9892	−33.0	−42.10
d^5	$^{53}\text{Cr}^+$	$\frac{5}{2}$	$\frac{5}{2}$	1.9986	1.9978	+11.0	+10.67
	$^{55}\text{Mn}^{2+}$	$\frac{5}{2}$	$\frac{5}{2}$	2.0047	2.0066	−41.0	−53.47
d^6	$^{53}\text{Cr}^0$	2	1	3.0828	2.97	+14.0*	15.9
	$^{53}\text{Cr}^0$	2	2	1.6393	1.72	+8.3*	· · ·
	$^{53}\text{Cr}^0$	2	3	1.2764	· · ·	+6.4*	· · ·
	$^{55}\text{Mn}^+$	2	1	3.1069	3.01	−68.3*	73.8
	$^{55}\text{Mn}^+$	2	2	1.6390	1.68	−38.1*	46.1
	$^{55}\text{Mn}^+$	2	3	1.2758	1.34	−30.4*	· · ·
d^7	$^{55}\text{Mn}^0$	$\frac{3}{2}$	$\frac{1}{2}$	3.5265	3.362	−42.4	92.5
	$^{55}\text{Mn}^0$	$\frac{3}{2}$	$\frac{3}{2}$	1.4051	1.46	−35.6*	· · ·
	$^{57}\text{Fe}^+$	$\frac{3}{2}$	$\frac{1}{2}$	3.5582	3.524	−3.9	2.99
	$^{57}\text{Fe}^+$	$\frac{3}{2}$	$\frac{3}{2}$	1.4072	· · ·	−3.8*	· · ·
d^8	$^{55}\text{Mn}^-$	1	1	2.0430	2.0104	−49.1	−71.28
	$^{57}\text{Fe}^0$	1	1	2.0210	2.0699	−5.2	6.98
	$^{59}\text{Co}^+$	1	1	2.0600	· · ·	−13.8	· · ·

IV. HSL VERSUS LSL LEVEL ORDERING AND THE TOTAL SPIN

The calculated one-electron configurations of the interstitial $3d$ impurities in the T^0, T^+, and T^{2+} charge states in Si leading to the results of Table I are depicted in Fig. 2. We see that for the neutral centers T^0, contrary to the classical model,[1] the e_+^a level lies *above* the t_-^a level; i.e., we have a LSL level arrangement. For the charged centers T^+ and T^{2+}, the same is true for both the high-Z and low-Z ends of the $3d$ series. A LSL level arrangement at both ends of the $3d$ series has been also recently predicted[12] for substitutional $3d$ impurities in GaP. It reflects the fact that $\Delta_x > \Delta_{\text{CF}}$ is not universally true. In contrast, small-cluster calculation with spherical potentials[13] leads to an underestimation[7] of directional covalency effects (hence Δ_{CF}), rendering the exchange coupling as the only "strong interaction;" hence $\Delta_x >> \Delta_{\text{CF}}$. This resulted in a *universal* HSL level arrangement for all $3d$ impurities.[13] We find in our LSD-SIC calculation that the ground-state spin values and multiplets (Fig. 2) conform with those suggested[1] by LW (i.e., Hund's rule) for all impurities but Ti^0, Ti$^-$, V^0, V$^+$, and Co^{2+} for which we predict the low-spin multiplets $^3\text{T}_1$, $^2\text{T}_2$, $^2\text{T}_2$ and $^3\text{T}_1$, and ^2E, respectively, indicated in Fig. 2 by asterisks. No experimental data exist for these centers as yet; these would surely be critical experiments.

For Cr^0 and Mn^0 we find an interesting level arrangement. The possible ground-state configurations are Cr^0 $t_+^3 t_-^{1+n} e_+^{2-n}$ with spin $S = 2 - n$, and Mn^0 $t_+^3 t_-^{2+n} e_+^{2-n}$ with spin $S = 3/2 - n$, where n is an integer $\geqslant 0$. Normally,[1] one associates a maximum spin value (i.e., $n = 0$ above) with a HSL level ordering (e_+ below t_-). Rather than assuming this, we have searched first for an integer n that produces the lowest total energy, letting the level ordering be determined by the self-consistent solution. In agreement with experiment,[1] we find for Cr^0 and Mn^0 that the minimum energy solution corresponds to the maximum spin value (i.e., $n = 0$). Interestingly, however, these stable solutions have a LSL level arrangement [Fig. 2(a)]. This is so because both $n = 0$ [cf. Fig. 2(a)] yield t_-^1 below e_+^2, whereas the excited state $n = 1$ gives an e_+^1 level below t_-^2. This is a statement of the fact that we find a delicate, occupation-dependent balance between two competing effects: $\Delta_x < \Delta_{\text{CF}}$ for $n = 0$, but $\Delta_x > \Delta_{\text{CF}}$ for $n = 1$. Notice that the latter result shows that the total energy of ($S = 2$, $n = 0$) is lower than that of ($S = 0$, $n = 2$) since the configuration $e_+^1 t_-^2$ is the transition-state configuration for an $S = 0 \rightarrow S = 2$ excitation. Using *fractional* occupating numbers n, we find that $n = 0.35$ for Cr^0 and $n = 0.45$ for Mn^0 yield the (absolute) lowest total energy (and degenerate e_+ and t_- orbitals). This "Fermi statistics problem" is natural for the LSD model, and is familiar from atomic calculations[6] on Fe and Co: if *integer* occupation numbers n are used for Fe, the $d_+^5 d_-^{1+n} s_+^1 s_-^{1-n}$ configuration shows the experimentally observed ground state for $n = 0$. Both choices $n = 0$ and $n = 1$ produce an unoccupied level lower in energy than the highest occupied level; $n \simeq 0.4$ yields the absolute minimum in total energy, with degenerate s_- and d_- orbitals.

V. ELECTRICAL LEVELS

The vertical arrows in Figs. 2(a)–2(c) denote the one-electron levels that can be ionized in the lowest-energy sin-

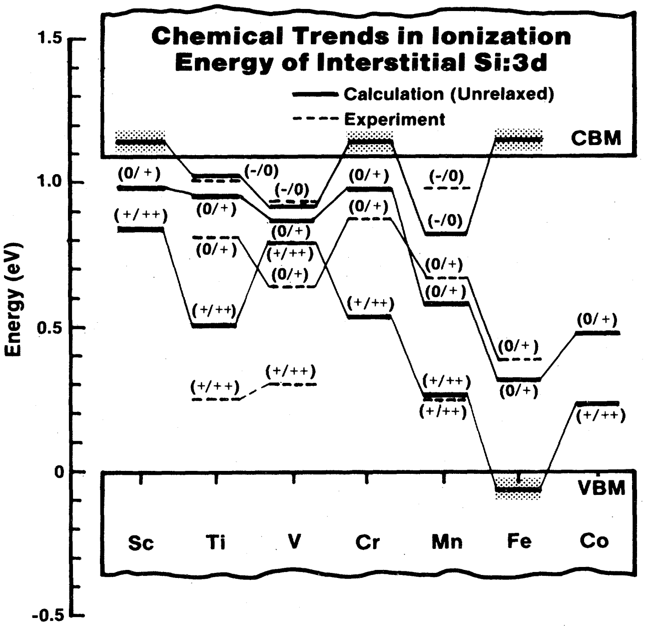

FIG. 3. Calculated and observed (Ref. 2) donor and acceptor ionization energies for interstitial $3d$ impurities in Si. Transitions inside the host bands are shown schematically by shaded areas.

gle, double, and triple donor transitions, respectively. Notice that in principle impurities with two gap levels (e.g., Fe^0 with a t_+ level below e_+) could exhibit a photoluminescence transition (from the higher level to the CB) different from a DLTS transition (from the lower level to the VB). This idea awaits experimental testing. We predict that, whereas the first donor transition in Ti, V, and Fe commence from the t^a_- level, the same transitions in Sc, Cr, Mn, and Co commence from the t^a_+, e^a_+, e^a_-, and e^a_+ levels, respectively. The corresponding transition energies have been calculated as total energy differences between the final and initial states, using Slater's transition-state construct. Their trends follow those of the different one-electron levels shown in Fig. 2. The calculated transition energies (Fig. 3) display the chemical trends apparent in the experimental data[2] in contrast with models[13] that embody a universal HSL level ordering for all impurities. For instance, we find the occurrence of local minima (maxima) in the first donor energy of V d^4/d^5 (Cr d^5/d^6) to be a consequence of switching the initial state from t^a_- (in V) to e^a_+ (in Cr), and the relative ease of ionizing in Cr^0 the sixth electron, producing the exchange-stabilized half-filled shell of Cr^+ (d^5). On the other hand, the classical argument assuming a universal HSL ordering will predict the first acceptor of $\mathrm{Ti}(d^4/d^5)$ to likewise be lower in the gap than the first acceptor of $\mathrm{V}(d^5/d^6)$, in contrast with the reversed trend observed.[2] This reversal is naturally accounted for in our model (Fig. 3) in terms of the *low-spin ground states* of Ti^0 and V^0. Note that since the calculated values correspond to an unrelaxed lattice (i.e., Frank-Condon optical transitions), they are higher in energy than the experimental values depicted in Fig. 3, which were obtained under equilibrium-relaxed conditions (thermal excitations). Figure 3 contains a number of predictions for hitherto unobserved transitions. The overall agreement between theory and experiment for both ground-state and excited-state properties lends support to this new microscopic model for deep $3d$ impurities in silicon.

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[8] The g values are calculated from $g = g_S + g_L + \Delta g_{LS}$, where g_S and g_L are the electron spin and orbital angular-momentum parts (Ref. 9), respectively. The contribution of the spin-orbit interaction Δg_{LS} is calculated (Ref. 10) from the effective crystal-field splitting Δ_{eff} (obtained from a transition-state calculation) and the spin-orbit (SO) coupling constant (Ref. 10) λ; i.e., $\Delta g_{LS} = (n/m)(\lambda k/\Delta_{\mathrm{eff}})$. The SO reduction factors k in the solid are given in Ref. 9.

[9] The hyperfine coupling constant A is obtained as a sum of the contact interaction A_c and the contribution A_L from the orbital magnetic moment. A_c is given by (Ref. 1)

$$A_c = (8\pi/3) g \mu_B g_N \beta_N \delta\rho(0)/2S \ ,$$

where g and g_N are the electron and nuclear g values, μ_B and β_N are the electron and nuclear Bohr magneton, S is the electron spin, and $\delta\rho(0)$ is the calculated net spin density at the impurity nucleus. For $L = 0$, A_L is given by $A_L = 2\mu_B g_N \beta_N \Delta g \langle r^{-3} \rangle$, where the g shift is $\Delta g = g - 2.0023$ and $\langle r^{-3} \rangle$ is the average of r^{-3} over the impurity orbital at the Fermi energy. In the case of $L = 1$, $S = 3/2$, and $J = 1/2$, A_L is given by (Ref. 10)

$$A_L = g \mu_B g_N \beta_N \langle r^{-3} \rangle [g_L - (k/2) g_S] \ ,$$

where $g_S = 2.0023(S \cdot J/J \cdot J)$, $g_L = \gamma(L \cdot J/J \cdot J)$, $J = L + S$, and the covalency factor is $\gamma = \langle \phi_t(r) | L | \phi_t(r) \rangle$. Here, $\phi_t(r)$ denotes the impurity wave function of the t_2 level, and k denotes the spin-orbit reduction factors in the solid (calculated from the ratio $k = \langle r^{-3} \rangle_{\mathrm{solid}} / \langle r^{-3} \rangle_{\mathrm{atom}}$). We find the covalency factor γ to be very small ($\gamma \approx 0$) because of an effective cancellation between the contributions of d and p orbitals to the matrix elements of L.

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