Orbital Paramagnetism of Localized Nonmagnetic Impurities in Metals*

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The importance of orbital paramagnetism in a weakly exchange-enhanced dilute solution of transition-metal impurities in a nonmagnetic host metal is demonstrated both theoretically and experimentally. It is shown that the orbital and spin contributions to the nuclear resonance shift and relaxation rate separately satisfy a Korringa-like relation. These relations may be used to determine uniquely the individual contributions. The sensitivity of the analysis to crystal-field effects is discussed.

Discussions of the magnetic properties of paramagnetic impurities in metals have traditionally focused attention on the locally exchange-enhanced spin susceptibility. In this Letter we demonstrate theoretically as well as experimentally that the orbital paramagnetism is, in many cases, of comparable magnitude. This result is of particular importance for the interpretation of impurity nuclear-magnetic-resonance (NMR) experiments because of the relatively large magnitude of the d-orbital hyperfine fields $(H_{\mathrm{hfs}}^{(\mathrm{orb})})$ relative to the d-spin (core-polarization) hyperfine fields $(H_{\mathrm{hfs}}^{(d)})$. We consider the nonmagnetic regime where the impurity can be discussed in terms of a Hartree-Fock treatment of the equilibrium properties and a random-phase approximation (RPA) treatment of the transport properties. This leads to the conclusion that a measurement of the nuclear resonance shift K and the spin-lattice relaxation rate $(T_1 T)^{-1}$ is sufficient to determine both the orbital and spin contributions. Moreover, this separation is invariant to first order in the cubic crystal-field splitting. Our principal conclusions are supported by results of NMR measurements on ^{61}Ni impurities on copper and gold.

We shall base our discussion on the following (modified) Anderson Hamiltonian[1]:

$$\mathcal{H} = \sum_{k,\sigma} \epsilon_{k\sigma} c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_{m,\sigma} \epsilon_{m\sigma} n_{m\sigma} + \sum_{k,m,\sigma} (V_{km} c_{k\sigma}^{\dagger} c_{m\sigma} + \mathrm{c.c.}) + \frac{U}{2} \sum_{m,m',\sigma} n_{m\sigma} n_{m'-\sigma} + \frac{U-J}{2} \sum_{m \neq m',\sigma} n_{m\sigma} n_{m'\sigma}$$

$$- \tfrac{1}{2} J \sum_{m \neq m',\sigma} c_{m\sigma}^{\dagger} c_{m-\sigma} c_{m'-\sigma}^{\dagger} c_{m'\sigma} + \tfrac{1}{2} J \sum_{m,\sigma} n_{m\sigma} n_{m-\sigma} + \text{crystal field}, \tag{1}$$

where, for the case $l = 2$ (the only case we shall consider in detail), the sums over m and m' go from -2 to 2. This Hamiltonian, with the exception of the last three terms, is the one suggested by Anderson. It was recognized by Caroli, Caroli, and Fredkin[2] that the Anderson Hamiltonian is not invariant under a rotation in spin space, and to correct this they added the sixth term in the Hamiltonian. This term, however, is not invariant under a rotation in coordinate space, and we have therefore added the seventh term to restore full rotational invariance.

The orbital susceptibility at frequency Ω may be expressed in terms of an effective orbital density matrix $\tilde{S}(m_1, m_2; \Omega)$, just as the transverse spin susceptibility was expressed in terms of an effective spin density matrix $S(m_1, m_2; \Omega)$ in Ref. 2:

$$\chi_{\mathrm{orb}}(\Omega) = \mu_B^2 \sum_{m_1, m_2} |\langle m_2 | L^+ | m_1 \rangle|^2 \tilde{S}(m_1, m_2; \Omega), \tag{2}$$

where $\tilde{S}(m_1, m_2; \Omega)$ satisfies the Bethe-Salpeter equation,

$$\tilde{S}(m_1, m_2; \Omega) = \chi^0(m_1, m_2; \Omega)[1 + (U-J)\tilde{S}(m_1, m_2; \Omega)]. \tag{3}$$

Equation (2) is valid for any crystal-field representation such that the orbital angular momentum operator L^+ has vanishing diagonal matrix elements. $\chi^0(m_1, m_2; \Omega)$ is the generalized unenhanced susceptibility given by

$$\chi^0(m_1, m_2; \Omega) = (2\pi i)^{-1} \int_{-\infty}^{\infty} d\omega f(\omega) \{ [G^>(m_1; \omega) - G^<(m_1; \omega)] G^>(m_2; \omega + \Omega)$$

$$+ G^<(m_1; \omega - \Omega)[G^>(m_2; \omega) - G^<(m_2; \omega)] \}, \tag{4}$$

where $f(\omega)$ is the Fermi function and $G^{>(<)}(m_i; \omega)$ are the Hartree-Fock Green's functions:

$$G^{>(<)}(m_i; \omega) = [\hbar\omega - E(m_i) \pm i\Delta(m_i)]^{-1} \qquad (5)$$

[where $E(m_i)$ and $\Delta(m_i)$ are the resonance energy and width of the ith orbital state, respectively], from which the occupation probabilities may be obtained:

$$\langle n(m_i)\rangle = (i/2\pi) \int_{-\infty}^{\infty} d\omega\, f(\omega)[G^{>}(m_i; \omega) - G^{<}(m_i; \omega)]. \qquad (6)$$

The corresponding expression obtained in Ref. 2 for the transverse spin susceptibility is

$$\chi_d(\Omega) = 2\mu_B^2 \sum_{m_1, m_2} S(m_1, m_2; \Omega), \qquad (7)$$

where $S(m_1, m_2; \Omega)$ satisfies the Bethe-Salpeter equation

$$S(m_1, m_2; \Omega) = \chi^0(m_1, m_1; \Omega)[\delta_{m_1, m_2} + US(m_1, m_2; \Omega) + J\sum_{m_1'}S(m_1', m_2; \Omega)]. \qquad (8)$$

We may solve Eqs. (3) and (8) and substitute the results into Eqs. (2) and (7):

$$\chi_{\mathrm{orb}}(\Omega) = \mu_B^2 \sum_{m_1, m_2} \frac{|\langle m_2|L^+|m_1\rangle|^2 \chi^0(m_1, m_2; \Omega)}{1 - (U-J)\chi^0(m_1, m_2; \Omega)} \qquad (9)$$

and

$$\chi_d(\Omega) = 2\mu_B^2 A(\Omega)/[1 - JA(\Omega)], \qquad (10)$$

where

$$A(\Omega) = \sum_{m_1} \chi^0(m_1, m_1; \Omega)[1 - U\chi^0(m_1 m_1; \Omega]^{-1}. \qquad (11)$$

In the absence of crystal-field effects $[E(m_i) = E;\ \Delta(m_i) = \Delta$ for all $i]$ we find, from Eqs. (9) and (10),

$$\lim_{\Omega \to 0} \mathrm{Re}\chi_{\mathrm{orb}}(\Omega) = 4\rho_d\mu_B^2/[1 - \tfrac{1}{5}(U-J)\rho_d], \qquad (12)$$

$$\lim_{\Omega \to 0} \mathrm{Im}\chi_{\mathrm{orb}}(\Omega)/\hbar\Omega = 4\pi\rho_d^2\mu_B^2/5[1 - \tfrac{1}{5}(U-J)\rho_d]^2, \qquad (13)$$

and

$$\lim_{\Omega \to 0} \mathrm{Re}\chi_d(\Omega) = 2\rho_d\mu_B^2/[1 - \tfrac{1}{5}(U + 5J)\rho_d], \qquad (14)$$

$$\lim_{\Omega \to 0} \mathrm{Im}\chi_d(\Omega)/\hbar\Omega = 2\pi\rho_d^2\mu_B^2/5[1 - \tfrac{1}{5}(U + 5J)\rho_d]^2, \qquad (15)$$

where $\rho_d \equiv 5(\Delta/\pi)(E^2 + \Delta^2)^{-1}$ is the total impurity-state density at the Fermi surface per spin. {The orbital enhancement factor $[1 - \tfrac{1}{5}(U-J)\rho_d]^{-1}$ has also appeared in the work of Anderson[1] and of Yosida, Okija, and Chikazumi.[3]} It is interesting to note that the static orbital susceptibility [Eq.(12)] is directly proportional to the density of states ρ_d as is the case for the spin susceptibility. This similarity between $\chi_{\mathrm{orb}}(0)$ and $\chi_d(0)$ is a unique property of an isolated paramagnetic impurity in a metal. In pure metals the translational invariance completely removes the orbital degeneracy except at certain symmetry points in the Brillouin zone; the resulting Van Vleck susceptibility is, of course, unrelated to ρ_d. Another interesting feature of our results is the appearance of the term $(U + 5J)$ rather than the usual $(U + 4J)$ in the spin-enhancement factor [Eqs. (14) and (15)]. This difference is a direct consequence of the last term in our Hamiltonian and can be eliminated by redefining our interaction parameters according to $U \to \overline{U} - (\overline{J}/6)$ and $J \to 5\overline{J}/6$. However, our formulation of the problem has the advantage that if U and J are required to satisfy the Slater sum rules,[4]

$$\sum_m U_{mm'} = 5F^{(0)}(\equiv 5U + J), \qquad (16)$$

$$\sum_m J_{mm'} = F^{(0)} + (2/7)F^{(2)} + (2/7)F^{(4)}(\equiv U + 5J), \qquad (17)$$

we find that the additional sum rules

$$\sum_m U_{mm} = 5F^{(0)} + (2/7)F^{(2)} + (10/63)F^{(4)},$$

and

$$\sum_{m>m'} U_{mm'} = 10F^{(0)} - (1/7)F^{(2)} - (5/63)F^{(4)},$$

are much more closely satisfied than is the case for the Hamiltonian used in Ref. 2. Incidentally, if this method is used to define $\bar{U}$ and $\bar{J}$, we obtain $U + 5J \equiv \bar{U} + 4\bar{J}$ and $U - J \equiv \bar{U} - \bar{J}$. Finally, we note that in the limit of zero enhancement $\chi_{\text{orb}}(\Omega) = 2\chi_d(\Omega)$. However, since $U + 5J$ is always greater than $U - J$, the ratio $\chi_d(\Omega)/\chi_{\text{orb}}(\Omega)$ can presumably become quite large as magnetic instability is approached.

The nuclear Knight shift and relaxation rates may now be obtained[5]:

$$K = K_{(d)} + K_{(\text{orb})}, \tag{18}$$

$$T_1^{-1} = T_{1(d)}^{-1} + T_{1(\text{orb})}^{-1}, \tag{19}$$

where, for $i \equiv d$ or orb,

$$K_{(i)} = (\mu_B)^{-1} H_{\text{hfs}}^{(i)} \lim_{\Omega \to 0} \text{Re}\chi_i(\Omega), \tag{20}$$

$$(T_1 T)_{(i)}^{-1} = 2(\mu_B)^{-2} \gamma_n^2 k_B H_{\text{hfs}}^{(i)2} \lim_{\Omega \to 0} \text{Im}\chi_i(\Omega)/\Omega. \tag{21}$$

We note that K_d is typically negative, whereas K_{orb} is always positive. From Eqs. (12)-(15) we see that the spin and orbital hyperfine mechanisms separately obey Korringa-like relations[6]

$$(K^2 T_1 T)_{\text{orb}} = 10S, \tag{22}$$

$$(K^2 T_1 T)_d = 5S, \tag{23}$$

where

$$S \equiv (\gamma_e/\gamma_n)^2 (\hbar/4\pi k_B). \tag{24}$$

Before proceeding with a consideration of the relevant NMR data we wish to examine the sensitivity of the above results to cubic crystal-field effects[7,8] which we characterize by an energy splitting $10D$ as well as a difference in the resonance widths $\delta\Delta$. Thus

$$n(e_g) = \tfrac{1}{10}N - \tfrac{3}{5}x, \quad n(t_{2g}) = \tfrac{1}{10}N + \tfrac{2}{5}x; \tag{25}$$

$$E(e_g) = E + \tfrac{3}{5}R, \quad E(t_{2g}) = E - \tfrac{2}{5}R; \tag{26}$$

$$\Delta(e_g) = \Delta + \tfrac{3}{5}\delta\Delta, \quad \Delta(t_{2g}) = \Delta - \tfrac{2}{5}\delta\Delta; \tag{27}$$

where N is the total occupation number and

$$R \equiv E(e_g) - E(t_{2g}) = 10D + (U - 2J)x. \tag{28}$$

Equations (25)-(27) may be solved, to lowest order, by differentiating Eq. (6) with respect to $E(m_i)$ and $\Delta(m_i)$ and solving Eq. (28) for x. We find

$$x = n(e_g) - n(t_{2g}) = \rho_d [10D - \delta\Delta \cot(\tfrac{1}{10}N\pi)]/5[1 - \tfrac{1}{5}(U - 2J)\rho_d]. \tag{29}$$

Likewise, by differentiating Eq. (4) with respect to $E(m_i)$ and $\Delta(m_i)$ and integrating the resulting expression by parts, we find, using Eq. (29), the first-order contributions $(i, j \equiv e_g, t_{2g})$

$$\lim_{\Omega \to 0} \text{Re}\delta\chi^0(i, j; \Omega) = \rho_d / 10\Delta [1 - \tfrac{1}{5}(U - 2J)\rho_d] \{[1 - 2\sin^2(\tfrac{1}{10}N\pi) + \tfrac{1}{5}(U - 2J)\rho_d](\delta\Delta_i + \delta\Delta_j)$$
$$- 2\sin(\tfrac{1}{10}N\pi)\cos(\tfrac{1}{10}N\pi)(\delta\epsilon_i + \delta\epsilon_j)\} \tag{30}$$

and

$$\lim_{\Omega \to 0} \text{Im}\frac{\delta\chi^0(i, j; \Omega)}{\hbar\Omega} = \tfrac{1}{5}\pi\rho_d \lim_{\Omega \to 0} \text{Re}\delta\chi^0(i, j; \Omega), \tag{31}$$

where $\delta\epsilon(e_g) = \tfrac{3}{5}(10D)$, $\delta\Delta(e_g) = \tfrac{3}{5}(\delta\Delta)$, etc. Inserting these expressions into the equation

$$\delta\chi_{\text{orb}}(\Omega) = 4\mu_B^2 [4\delta\tilde{S}(e_g, t_{2g}; \Omega) + \delta\tilde{S}(t_{2g}, t_{2g}; \Omega)], \tag{32}$$

obtained by explicit evaluation of the matrix elements of L^+, we find

$$\lim_{\Omega \to 0} \mathrm{Re}\delta\chi_{\mathrm{orb}}(\Omega) = \lim_{\Omega \to 0} \mathrm{Im}\delta\chi_{\mathrm{orb}}(\Omega)/(\hbar\Omega) = 0. \quad (33)$$

Similarly, we find $\delta A = 0$. Thus, to first order in a cubic crystal field, represented by an energy splitting and a difference in widths, both the orbital and spin susceptibilities are unchanged.

For very strong cubic crystal fields the analysis is very simple for the two cases of pure e_g or t_{2g} character at the Fermi level [i.e., $\Delta(t_{2g})$ or $\Delta(e_g) \to 0$]. The e_g solutions for the orbital and spin Korringa relations, Eqs. (22) and (23), are ∞ and $2S$, respectively; the corresponding t_{2g} solutions are $2S$ and $3S$. For intermediate values of the e_g/t_{2g} admixture ratio both the spin and orbital Korringa relations are dependent upon U and J; however, as either spin or orbital instability is approached, the corresponding Korringa product approaches one of the limiting values discussed above. Thus, strong cubic crystal fields can in principle have a large effect only on the orbital Korringa relation. Since crystal-field splittings for impurities in simple metals are believed to be small compared with typical level widths,[8] this complication can presumably be ignored in most instances.

Examples of dilute alloys in which the orbital hyperfine interaction plays a dominant role are provided by Cu:Ni and Au:Ni. The nickel d states in these alloys are believed to form narrow virtual levels containing ~9 electrons. That the levels are almost fully occupied is supported by the relatively small electronic specific heat of Cu:Ni ($\gamma = 2.9$ mJ/g atom °K^2).[9] Exchange-enhancement effects are therefore most likely also small. The orbital mechanism is further favored by the large orbital hyperfine field of nickel, whose free-atom value of 716 kOe/μ_B may be compared with the usual d-spin hyperfine field of only ~-100 kOe/μ_B. We have studied the ^{61}Ni NMR in these alloys in the temperature range 1 to 4°K and in external fields near 60 kOe using a phase-coherent spin-echo spectrometer. The experimental resonance

shifts and spin-lattice relaxation times are summarized in Table I. The shift and normalized relaxation rate $(\gamma_n^2 T_1 T)^{-1}$ exceed the pure copper values by factors of ~5 and ~9, respectively. It is obvious that the direct s-contact interaction cannot account for these results. In fact, on general grounds one expects this mechanism to be unimportant for paramagnetic impurities relative to the d-electron mechanisms. Since the observed shift is positive we must attribute it to orbital paramagnetism. By using Eqs. (22) and (23) we are able to partition the shift in Cu:Ni into d-orbital ($K_{\mathrm{orb}} = +1.6\%$) and d-spin ($K_d = -0.3\%$) contributions. Furthermore, assuming the $H_{\mathrm{hfs}}^{(\mathrm{orb})}$ given above, we conclude that a susceptibility $\chi_{\mathrm{orb}} = 1.2 \times 10^{-4}$ emu/g atom is required to account for the $+1.6\%$ orbital shift. This compares with the specific heat value $\chi_{\mathrm{orb},\gamma} = 0.8 \times 10^{-4}$ emu/g atom. Thus, provided that mass-renormalization effects are unimportant, an orbital enhancement factor of 1.6 is indicated which in turn implies $U-J \approx 3$ eV. Similarly, assuming $H_{\mathrm{hfs}}^{(d)} = -100$ kOe/μ_B, we obtain $U + 5J \approx 6$ eV. We note that the same analysis can account for the ^{59}Co NMR data in Cu:Co, for which Asayama, Wada, and Oda[10] observed positive resonance shifts and rapid relaxation rates. Although the Au:Ni data again indicate the importance of the orbital hyperfine mechanism, the relaxation rate appears to be somewhat slower than predicted by Eq. (22). This may indicate an enhanced e_g admixture at the Fermi level. Unfortunately, the experimental uncertainty in the Au:Ni relaxation rate is too large to allow more definite conclusions to be drawn at this time.

We conclude that orbital paramagnetism plays an essential role in weakly exchange-enhanced dilute alloys. Furthermore, since the limiting values of the orbital and spin Korringa relations are independent of U and J, it appears likely that their validity extends over a much wider range of exchange enhancements than is the case for the RPA susceptibilities from which they were derived. The present work therefore provides the necessary basis for obtaining reliable estimates

Table I. Summary of ^{61}Ni NMR data for concentrations c as indicated. The shifts are defined relative to the reference $\nu/H = 0.380\,48$ kHz/Oe.

	c (at.%)	$T_1 T$ (sec°K)	K (%)
Cu:^{61}Ni	0.5, 1.0, 2.0	1.2(1)	+1.28(2)
Au:^{61}Ni	1.0	1.0(3)	+2.55(2)

of the relative magnitudes of d-orbital and d-spin hyperfine interactions in dilute paramagnetic alloys.

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Electron Transport and Lorenz Number in Iron*

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Measurements of the electrical and thermal resistivity in longitudinally saturated ⟨111⟩ iron crystals provide evidence that the temperature-dependent transport is dominated by electron-electron scattering from 0.28 to 20°K. The ideal Lorenz number is nearly constant below 40°K and has a value of 1.09×10^{-8} W Ω/deg^2 from 40 to 6°K and a value of 1.16×10^{-8} W Ω/deg^2 below 6°K.

We have measured both the electrical and thermal resistivity of iron single crystals in the range 2 to 77°K. In addition, electrical resistivity has been measured down to a temperature of 0.28°K. Measurements have been carried out in zero magnetic fields and in applied longitudinal magnetic fields up to values sufficient to saturate the specimen as a single domain along the measuring length. Specimens with both ⟨100⟩ and ⟨111⟩ axial orientations have been used with ratios $R(295°K)/R(4.2°K)$ between 700 and 2000. The data reported here are limited mainly to the ⟨111⟩ axial orientation in the single-domain saturated state.

Our measurements have indicated that the single-domain ⟨111⟩ crystals give the most reproducible results on the temperature dependence of electrical and thermal resistivity. Measurements in the multidomain state show large magnetic contributions which alter substantially both the magnitude and temperature dependence of the transport and make the interpretation of results complex.

Herring[1] has given a theoretical analysis which suggests that for transition metals with complex Fermi surfaces and in which electron-electron scattering dominates the temperature-dependent transport at low temperature, the ideal Lorenz number ($L_i = \rho_i/W_i T$) should reach a constant value at low temperature equal to 1.58×10^{-8} W Ω/deg^2. (This number is the corrected number; see Erratum, Ref. 1.) ρ_i and W_i are the intrinsic electrical and thermal resistivities, respectively. White and Tainsh[2] have reported data on nickel which tend to support this prediction for a magnetic transition metal. A number of experiments[3,4] on nonmagnetic transition metals also provide evidence that this prediction may have general validity although the exact value of the Lorenz number may depend somewhat on the particular metal.[5]

The data reported here for single-domain longitudinally saturated ⟨111⟩ iron crystals appear to indicate that Herring's prediction may