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Magnetic anisotropy of transition-metal impurities in metallic hosts

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We show that transition-metal impurities in metallic hosts, which have a high crystalline symmetry, can have appreciable anisotropic magnetic moments and the anisotropy may change sign on varying the transition-metal impurity. Our basic model is a spherically symmetric Friedel-Anderson model, with orbital degeneracy and Hund's-rule couplings. We treat this model in a way which is appropriate to the situation in which an appreciable mixture of ionic configurations exists in the ground state of the impurity. We calculate, in the Hartree-Fock approximation, the effect of the crystalline field and the spin-orbit coupling. The crystalline field acts, in a manner, to quench any orbital magnetic moment present. The spin-orbit interaction is responsible for the reappearance of the orbital magnetic moment, and is, thus, the source of the anisotropic magnetization. We calculate the orbital magnetization induced by the spin-orbit coupling, and the anisotropy energy is calculated to second order in the spin-orbit coupling. We show that the model is capable of generating changes in the sign of the anisotropy energy, as has been observed by the low-field-magnetization measurements on very dilute ZnMn and ZnCr alloys.

I. INTRODUCTION

Recent low-field-magnetization measurements[1] on very dilute ZnMn and ZnCr single-crystal alloys show large anisotropy in the magnetization, at low temperatures. The observed effective spin was much smaller than would be expected from the ionic configurations, even if one takes into account the quenching of the orbital angular momentum. The magnetic anisotropy energy was observed to have opposite sign in the ZnMn and ZnCr samples. Similar behavior has been observed in the electron-spin-resonance spectra[2] of transition-metal impurities in hexagonal hosts.

The interpretation of anisotropic-magnetization measurements has been, hitherto, based on an effective spin Hamiltonian

$$H=-D[S_z^2-\tfrac{1}{3}S(S+1)]+g_{\parallel}H^zS^z+g_{\perp}(H^xS^x+H^yS^y)\ ,$$

where D is known as the anisotropy energy. This type of Hamiltonian has been justified, microscopically, in cases where the impurity ions are in well-defined configurations and have well-defined values for the effective spins.[3] In these cases, the anisotropy has been interpreted as being due to the reintroduction of the quenched orbital magnetic moment by the effect of the spin-orbit coupling. More recently the anisotropy has been explained in terms of the anisotropic exchange interactions between the localized moments and the conduction electrons (Dixon and Dupree),[4] or alternatively, by small or virtual admixtures of other ionic configurations into the ground-state configuration of the transition-metal impurity (Barnes *et al.*,[5] Hirst[6]).

In this paper we take the opposite, extreme, point of view. We assume that the transition-metal ion has an appreciable amount of admixture of ionic configurations occurring in its ground state, as is typical of a system with a large virtual-bound-state width. This model is capable of explaining the nonintegral number of electrons in the transition-metal d shell and the concomitant non-half-integer effective spin. As the ionic model would predict that $S=\frac{5}{2}$ for Mn^{2+} and that $S=2$, $L=2$ for Cr^{2+} rather than the observed effective spin $S\simeq 1$, it is probably a better standpoint to use the Friedel[7]-Anderson[8] virtual-bound-state approach to these systems. On performing a Hartree-Fock calculation on the spherically symmetric Anderson model, we introduce a crystalline-field splitting and include spin-orbit coupling, up to second order. We observe that for hosts with cubic symmetry the spin-orbit coupling does introduce an orbital magnetic moment, but the anisotropy effects are higher than second order in the spin-orbit coupling. In hosts of hexagonal symmetry, we do find that the magnetic moment induced by the spin-orbit coupling is anisotropic and furthermore the second-order contribution of the spin-orbit coupling to the anisotropy energy can be of either sign depending on the density of states at the Fermi level. The change in sign of the anisotropy energy in ZnMn and ZnCr may be due to this effect.

II. THE MODEL HAMILTONIAN

The basic model that we consider is the orbitally degenerate Anderson model,[1] which has been modified to be rotationally invariant in spin space[9] and in coordinate space.[10] The Hamiltonian is written in terms of three components

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_3 \,, \tag{2.1}$$

where $\hat{H}_1$ describes the atomic d orbitals and both the direct and exchange Coulomb interactions between the electrons in the d orbitals, $\hat{H}_2$ describes the conduction-band states, and $\hat{H}_3$ describes the mixing between the conduction band and the localized atomic orbitals.

The form of $\hat{H}_1$ is such that the Coulomb exchange interaction, which is responsible for the tendency of the spins to align in parallel, is rotationally invariant in both spin and coordinate space.[3] Thus H_1 is given by

$$\hat{H}_1 = \sum_{m\sigma} e_{dm\sigma} d^{\dagger}_{m\sigma} d_{m\sigma} + \sum_{\substack{m,m' \\ \sigma,\sigma'}} \frac{U_{dd} - J_{dd}\delta_{\sigma\sigma'}}{2} d^{\dagger}_{m\sigma} d_{m\sigma} d^{\dagger}_{m'\sigma'} d_{m'\sigma'} - \sum_{\substack{m'm' \\ \sigma}} \frac{J_{dd}}{2} d^{\dagger}_{m\sigma} d_{m\,-\sigma} d^{\dagger}_{m'\,-\sigma} d_{m'\sigma} + \sum_{m\sigma} \frac{J_{dd}}{2} d^{\dagger}_{m\sigma} d_{m\sigma} d^{\dagger}_{m\,-\sigma} d_{m\,-\sigma} \,, \tag{2.2}$$

where $d^{\dagger}_{m\sigma}$ and $d_{m\sigma}$ are, respectively, the creation and destruction operators for an electron, with spin σ, in an $l=2$ orbital with azimuthal quantum number m.

The Coulomb interaction strengths U and J have been defined, as in Ref. 10, such that the Slater sum rules

$$\sum_{m} U_{mm'} = 5F^{(0)} \equiv 5U + J$$

and

$$\sum_{m} J_{mm'} = F^{(0)} + \tfrac{2}{7}F^{(2)} + \tfrac{2}{7}F^{(4)} \equiv U + 5J$$

are satisfied. As Dworin and Narath[10] found, these definitions of U and J for the spin and rotationally invariant Hamiltonian do have the advantage that the other Slater sum rules are more closely satisfied than in the nonrotationally invariant Hamiltonian. For this reason, we shall neglect the complications of the full ionic Hamiltonian,[11] and use the above simplified model of the interaction.

The conduction-band Hamiltonian is expressed as

$$\hat{H}_2 = \sum_{\vec{k}\sigma} e_{\sigma}(\vec{k}) c^{\dagger}_{\vec{k}\sigma} c_{\vec{k}\sigma} \,, \tag{2.3}$$

where $c^{\dagger}_{\vec{k}\sigma}$ and $c_{\vec{k}\sigma}$ are the creation and destruction operators of an electron, with spin σ, in the conduction-band density of states with Bloch wave vector $\vec{k}$.

The mixing between the atomic orbitals and the conduction-band states is described by a one-electron mixing term,

$$\hat{H}_3 = \sum_{\substack{\vec{k}m \\ \sigma}} V_{\vec{k}m} d^{\dagger}_{m\sigma} c_{\vec{k}\sigma} + V^{*}_{\vec{k}m} c^{\dagger}_{\vec{k}\sigma} d_{m\sigma} \,. \tag{2.4}$$

In the absence of a crystal field, the Hartree-Fock solution does exhibit a magnetic moment due to the aligning of the electron spins,[10] whenever

$$\tfrac{1}{5}(U_{dd} + 5J_{dd})\rho_d(\mu) > 1 \,.$$

In this $\rho_d(\mu)$ is the d-electron density of states of the Fermi level. Similarly, the orbital magnetic moment is expected[10] to appear when

$$(U_{dd} - J_{dd})\rho_d(\mu) > 1 \,.$$

This condition for the existence of a nonzero orbital magnetic moment is more stringent than that for the appearance of spin magnetism. The effect of a crystal field on these conditions has been discussed in Ref. 10. A more detailed investigation of the effects of crystal field for the nonrotationally invariant Hamiltonian has been given in the extensive review article of Coqblin and Blandin.[11] We shall use values of the parameters U and J, and the width of the density of states which allows for the appearance of a magnetic moment due to the electronic spin, but does not allow for an orbital magnetic moment. The electronic contribution to the magnetic moment is plotted in Fig. 1. We shall consider the additional features of a crystalline-field and spin-orbit coupling. We consider the hexagonal closed-packed structures, in which the

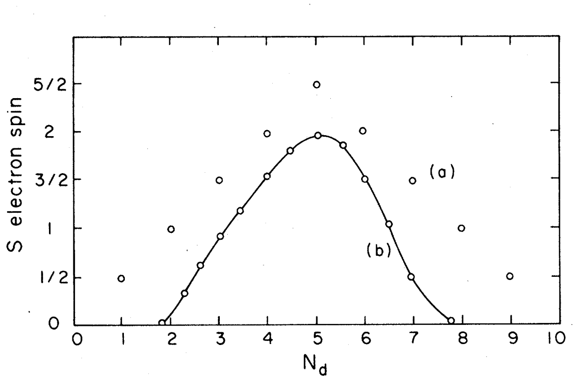

FIG. 1. Magnetization due to electron spin, as a function of the number of d electrons N_d. The upper curve (a) is the free-ionic spin. The lower curve (b) is calculated in the Hartree-Fock approximation.

group theory shows that the *d* orbitals split into a nondegenerate *a* level and two doubly degenerate levels ϵ_1 and ϵ_2. The basis operators for these states are

$$a_1\colon\ \Phi^\dagger_{1\sigma} = d^\dagger_{m=0\sigma}$$

$$\epsilon_1\colon\ \Phi^\dagger_{2\sigma} = \frac{1}{2^{1/2}}\left(d^\dagger_{m=1\sigma} - d^\dagger_{m=-1\sigma}\right) ,$$

$$\Phi^\dagger_{3\sigma} = \frac{1}{2^{1/2}}\left(d^\dagger_{m=-1\sigma} + d^\dagger_{m=-1\sigma}\right) ,$$

$$\epsilon_2\colon\ \Phi^\dagger_{4\sigma} = \frac{1}{2^{1/2}}\left(d^\dagger_{m=2\sigma} - d^\dagger_{m=-2\sigma}\right) ,$$

$$\Phi^\dagger_{5\sigma} = \frac{1}{2^{1/2}}\left(d^\dagger_{m=2\sigma} + d^\dagger_{m=-2\sigma}\right) .$$

The point-charge model indicates that the *a* orbital is the highest followed by the ϵ_2 and then the ϵ_1 orbitals (see Hirst[6]). The spin-orbit coupling is expressed as

$$H_{\mathrm{so}} = \lambda \sum_{\substack{mm'\\ \sigma\sigma'}} \langle m\sigma|\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|m'\sigma'\rangle d^\dagger_{m\sigma} d_{m'\sigma'} , \tag{2.5}$$

where λ is the spin-orbit coupling strength and the matrix elements $\langle m\sigma|\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|m'\sigma'\rangle$ are the scalar products of the electron spin and the orbital angular momentum.

In Sec. III, we shall calculate the Green's function for this model, in the Hartree-Fock approximation. From this we shall calculate the *g* shift and the magnetic anisotropy energy. The calculation is separated into three stages. The first step is that of solving the Hartree-Fock equations for the Anderson model, in which we have included the crystal fields. The spin-orbit coupling is introduced as a perturbation on the Hartree-Fock solutions. This is not treated as a simple perturbation, as it does have the effect of displacing the minima of the approximate energy functional. We take into account the effect that the perturbation has on the Hartree-Fock self-consistency equations. The last step of the calculation is that of calculating the energy of the perturbed solution. A comparison with the effective spin Hamiltonian, allows us to extract the *g* shift and the anisotropy parameter.

III. ONE-PARTICLE GREEN'S FUNCTION

We shall evaluate the one-particle Green's function in the Anderson,[1] Hartree-Fock approximation scheme. The Green's function is defined by

$$\langle\langle \Phi_{m\sigma};\Phi_{m^\bullet\sigma^\bullet}\rangle\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} \epsilon^{i\omega t}\langle \hat{T}[\Phi_{m\sigma}(t);\Phi^\dagger_{m^\bullet\sigma^\bullet}(0)]\rangle_T\, dt , \tag{3.1}$$

where $\hat{T}$ is the time-ordering operator and the brackets $\langle\ \rangle_T$ denote thermal averaging. In the Hartree-Fock approximation, the Coulomb interaction terms in $\hat{H}_1$ are replaced by the form

$$\begin{aligned}
\hat{H}_1 = {} & \sum_{\substack{mm'\\ \sigma}} \frac{U_{dd}}{2}\Big(\langle \Phi^\dagger_{m'\sigma}\Phi_{m'\sigma}\rangle_T \Phi^\dagger_{m\,-\sigma}\Phi_{m\,-\sigma} + \langle \Phi^\dagger_{m\,-\sigma}\Phi_{m\,-\sigma}\rangle_T \Phi^\dagger_{m'\sigma}\Phi_{m'\sigma} \\
& \qquad + \langle \Phi_{m'\sigma}\Phi^\dagger_{m\,-\sigma}\rangle_T \Phi^\dagger_{m'\sigma}\Phi_{m\,-\sigma} + \langle \Phi^\dagger_{m'\sigma}\Phi_{m\,-\sigma}\rangle_T \Phi_{m'\sigma}\Phi^\dagger_{m\,-\sigma}\Big) \\
& + \sum_{\substack{m\neq m'\\ \sigma}} \frac{U_{dd}-J_{dd}}{2}\Big(\langle \Phi^\dagger_{m'\sigma}\Phi_{m'\sigma}\rangle_T \Phi^\dagger_{m\sigma}\Phi_{m\sigma} + \Phi^\dagger_{m\sigma}\Phi_{m\sigma}\langle \Phi^\dagger_{m'\sigma}\Phi_{m'\sigma}\rangle + \langle \Phi_{m'\sigma}\Phi^\dagger_{m\sigma}\rangle_T \Phi^\dagger_{m'\sigma}\Phi_{m\sigma} + \Phi_{m'\sigma}\Phi^\dagger_{m\sigma}\langle \Phi^\dagger_{m'\sigma}\Phi_{m\sigma}\rangle\Big) \\
& - \sum_{\substack{m\neq m'\\ \sigma}} \frac{J_{dd}}{2}\Big(\langle \Phi^\dagger_{m\sigma}\Phi_{m\,-\sigma}\rangle_T \Phi^\dagger_{m'\,-\sigma}\Phi_{m'\sigma} + \Phi^\dagger_{m\sigma}\Phi_{m\,-\sigma}\langle \Phi^\dagger_{m'\,-\sigma}\Phi_{m'\sigma}\rangle_T \\
& \qquad + \Phi^\dagger_{m\sigma}\Phi_{m'\sigma}\langle \Phi_{m\,-\sigma}\Phi^\dagger_{m'\,-\sigma}\rangle_T + \langle \Phi^\dagger_{m\sigma}\Phi_{m'\sigma}\rangle_T \Phi_{m\,-\sigma}\Phi^\dagger_{m'\,-\sigma}\Big) \\
& + \sum_{m\sigma} J_{dd}\Big(\Phi^\dagger_{m\sigma}\Phi_{m\sigma}\langle \Phi^\dagger_{m\,-\sigma}\Phi_{m\,-\sigma}\rangle_T + \langle \Phi^\dagger_{m\sigma}\Phi_{m\sigma}\rangle_T \Phi^\dagger_{m\,-\sigma} + \Phi^\dagger_{m\sigma}\Phi_{m\,-\sigma}\langle \Phi_{m\sigma}\Phi^\dagger_{m\,-\sigma}\rangle_T + \Phi_{m\sigma}\Phi^\dagger_{m\,-\sigma}\langle \Phi^\dagger_{m\sigma}\Phi_{m\,-\sigma}\rangle_T\Big) .
\end{aligned} \tag{3.2}$$

We shall see that the factors $\langle \Phi^\dagger_{m'\sigma}\Phi_{m\,-\sigma}\rangle$ are nonzero, only by virtue of the spin-orbit coupling. Thus we have replaced the interaction by one which is quadratic in the fermion operators, and so the Hamiltonian H_1 is composed of two types of terms; the one-electron Hamiltonians describing the up and down spin electron states; and the terms which scatter the electrons between the various localized electronic states. The coefficients of these terms have to be evauated self-consistently. We shall show, however, that the coefficients of the scattering terms are only of the order of magnitude of λ, the spin-orbit coupling matrix elements.

The above type of approximation is known to give misleading predictions about the magnetic phase diagram,[8] in particular the sharpness of the transition from magnetic to nonmagnetic behavior. Despite the inadequacies of the Hartree-Fock approximation, it does give a good description of the low-temperature physics. Therefore, we shall use this approximation as a guideline to the true behavior of the system at $T=0$. We calculate the single-particle Green's function from the Fourier transform of the equations of motion

$$i\frac{\partial}{\partial t}\langle \hat{T}A(t)B(t')\rangle_\beta=\delta(t-t')\langle [A(t),B(t')]_-\rangle_\beta+i\langle \hat{T}[A(t),\hat{H}(t)]_-B(t')\rangle_\beta\ . \tag{3.3}$$

To second order in λ, the spin-orbit coupling strength, we find the Green's function to be given by

$$\langle\langle \Phi_{m\sigma},\Phi^\dagger_{m\sigma}\rangle\rangle=\frac{1}{\omega-\epsilon_{m\sigma}-\Sigma_{m\sigma}-\lambda\langle m\sigma|\vec{L}\cdot\vec{S}\,|m\sigma\rangle}\times\left(1+\sum_{m\neq m'}\frac{[\lambda\langle m\sigma|\vec{L}\cdot\vec{S}\,|m'\sigma'\rangle-(U_{dd}-J_{dd}\delta_{\sigma\sigma'})\langle\Phi^\dagger_{m\sigma}\Phi_{m'\sigma'}\rangle+J_{dd}\delta_{\sigma\sigma'}\langle\Phi^\dagger_{m\;-\sigma}\Phi_{m'\sigma}\rangle]^2}{(\omega-\epsilon_{m\sigma}-\Sigma_{m\sigma}-\lambda\langle m\sigma|\vec{L}\cdot\vec{S}\,|m\sigma\rangle)(\omega-\epsilon_{m'\sigma'}-\Sigma_{m'\sigma'}-\lambda\langle m'\sigma|\vec{L}\cdot\vec{S}\,|m\sigma\rangle)}\right)\ , \tag{3.4}$$

in which the Hartree-Fock self-energy $\Sigma_{m\sigma}$ is given by

$$\Sigma_{m\sigma}=\sum_{m''}U_{dd}N_{m''\;-\sigma}+\sum_{m''\neq m}(U_{dd}-J_{dd})N_{m''\sigma}+J_{dd}N_{m\;-\sigma}+\sum_{\vec{k}}\frac{V_{m\vec{k}}V^*_{m'\vec{k}}}{\omega-\epsilon_\sigma(\vec{k})}$$

and $N_{m\sigma}$ are the occupation numbers of the localized orbitals. The thermal equilibrium expectation values $N_{m\sigma}$ and $\langle\Phi^\dagger_{m\sigma}\Phi_{m'\sigma'}\rangle_\beta$ are found self-consistently. The occupation number of the localized orbitals are given by

$$N_{m\sigma}=\frac{1}{\pi}\int f(\omega-\mu)\,\mathrm{Im}\,\langle\langle\Phi_{m\sigma};\Phi^\dagger_{m\sigma}\rangle\rangle\,d\omega\ ,$$

where $f(\omega-\mu)$ is the Fermi-Dirac distribution function. The off-diagonal matrix element $\langle\Phi^\dagger_{m\sigma}\Phi_{m'\sigma'}\rangle$ is first order in the spin-orbit-coupling matrix elements

$$\begin{aligned}\langle\Phi^\dagger_{m\sigma}\Phi_{m'\sigma'}\rangle_\beta=&\Bigg[\Bigg[\left(1+(U-J)\delta_{\sigma\sigma'}\frac{N_{m-\sigma}-N_{m'-\sigma'}}{\epsilon_{m\sigma}+\Sigma_{m\sigma}-\epsilon_{m'\sigma'}-\Sigma_{m'\sigma'}}\right)\frac{\lambda\langle m\sigma|\vec{L}\cdot\vec{S}\,|m'\sigma'\rangle(N_{m\sigma}-N_{m'\sigma'})}{\epsilon_{m\sigma}+\Sigma_{m\sigma}-\epsilon_{m'\sigma'}-\Sigma_{m'\sigma'}}\\&+J(1-\delta_{mm'})\delta_{\sigma\sigma'}\frac{N_{m\sigma}-N_{m'\sigma'}}{\epsilon_{m\sigma}+\Sigma_{m\sigma}-\epsilon_{m'\sigma}-\Sigma_{m'\sigma'}}\;\frac{\lambda\langle m-\sigma|\vec{L}\cdot\vec{S}\,|m'-\sigma'\rangle(N_{m\sigma}-N_{m'\sigma'})}{\epsilon_{m\sigma}+\Sigma_{m\sigma}-\epsilon_{m'\sigma'}-\Sigma_{m'\sigma'}}\Bigg]\\&\times\Bigg[\left(1+(U-J\delta_{\sigma\sigma'})\frac{N_{m\sigma}-N_{m'\sigma'}}{\epsilon_{m\sigma}+\Sigma_{m\sigma}-\epsilon_{m'\sigma'}-\Sigma_{m'\sigma'}}\right)\left(1+(U-J\delta_{\sigma\sigma'})\frac{N_{m\;-\sigma}-N_{m\;-\sigma'}}{\epsilon_{m\;-\sigma}+\Sigma_{m\;-\sigma}-\epsilon_{m'\;-\sigma'}+\Sigma_{m'\;-\sigma'}}\right)\\&-J^2\left(\frac{N_{m\sigma}-N_{m'\sigma'}}{\epsilon_{m\sigma}+\Sigma_{m\sigma}-\epsilon_{m'\sigma'}-\Sigma_{m'\sigma'}}\right)\left(\frac{N_{m\;-\sigma}-N_{m'\;-\sigma}}{\epsilon_{m\;-\sigma}+\Sigma_{m\;-\sigma}-\epsilon_{m'\sigma'}-\Sigma_{m'\;-\sigma'}}\right)\Bigg]\Bigg]^{-1}\ .\end{aligned} \tag{3.5}$$

In the absence of the spin-orbit coupling, the crystal field quenches the orbital magnetic moment. The introduction of spin-orbit coupling reintroduces an extra magnetic moment which is orbital in origin. To first order in the spin-orbit coupling, we find that

$$\delta\vec{M}=\sum_{\substack{m\sigma\\m'\sigma'\\m\neq m'}}\langle\Phi^\dagger_{m\sigma}\Phi_{m'\sigma'}\rangle_\beta\langle m'\sigma'|\vec{L}\,|m\sigma\rangle+\sum_{m\sigma}\frac{\lambda\rho_{m\sigma}\langle m\sigma|\vec{L}\cdot\vec{S}\,|m\sigma\rangle\langle m\sigma|\vec{L}\,|m\sigma\rangle}{[1-(U-J)\rho_{m\sigma}][1-(U-J)\rho_{m\;-\sigma}]-J^2\rho_{m\sigma}\rho_{m\;-\sigma}}\ , \tag{3.6}$$

where $\rho_{m\sigma}$ is the density of states at the Fermi level. The first term of this expression is just the form of $\delta\vec{M}$ that one would expect for an insulator. There, with m referring to spherical harmonics one would have $\langle m'\sigma'|\vec{L}\,|m\sigma\rangle=0$ for $m'=m$. While for $m\neq m'$, we have $\langle\Phi^\dagger_{m\sigma}\Phi_{m\sigma}\rangle$ to be first order in λ. The last term in this expression is a purely metallic contribution. It depends on the density of states at the Fermi level $\rho_{m\sigma}$, and vanishes when $\rho_{m\sigma}=0$. The density of states at the Fermi level behaves as $\rho_{m\sigma}=\mathrm{Im}\Sigma/(\epsilon_{m\sigma}-\mu)^2$ so the last term is negligible when the virtual bound state is far from the Fermi level. When the virtual bound state lies near the Fermi level the last term becomes of comparable magnitude to the first. Thus the orbital magnetic moment is unquenched due to the spin-orbit coupling, and is enhanced by the orbital enhancement factor

$$\{[1-(U-J)\rho_{m\sigma}][1-(U-J)\rho_{m\,-\sigma}]-J^2\rho_{m\sigma}\rho_{m\,-\sigma}\}^{-1} .$$

For host materials which have hexagonal symmetry we find that the induced orbital magnetic moment is anisotropic and can be large. The derivation of the g factor from 2, the g shift, along the principal axis of the crystal $\Delta g_{\parallel}$ is calculated as

$$\Delta g_{\parallel}=\frac{2\lambda}{S}\left(\frac{4(\rho_{\epsilon_2\uparrow}-\rho_{\epsilon_2\downarrow})}{[1-(U-J)\rho_{\epsilon_2\uparrow}][1-(U-J)\rho_{\epsilon_2\downarrow}]-J^2\rho_{\epsilon_2\uparrow}\rho_{\epsilon_2\downarrow}}+\frac{\rho_{\epsilon_1\uparrow}-\rho_{\epsilon_1\downarrow}}{[1-(U-J)\rho_{\epsilon_1\uparrow}][1-(U-J)\rho_{\epsilon_1\downarrow}]-J^2\rho_{\epsilon_1\uparrow}\rho_{\epsilon_1\downarrow}}\right) . \tag{3.7}$$

We calculate the anisotropy energy from the difference of the energies (3.2) of the Hartree-Fock solutions which have the spin polarization parallel and perpendicular to the principal axis. The anisotropy energy D is proportional to λ^2 and consists of two types of terms, those involving the diagonal matrix elements of the spin-orbit interaction and those involving the nondiagonal matrix elements. We find that the anisotropy energy is given by

$$\begin{aligned}D=&-\lambda^2\sum_{\sigma}\frac{4\rho_{1\sigma}\{(1-U\rho_{2\,-\sigma})[1+(U-J)\rho_{2\sigma}(1-5U\rho_{2\sigma})]-4U^2J^2\rho_{2\sigma}^2\rho_{2\,-\sigma}^2\}}{[1-(U-J)\rho_{2\sigma}][1-(U-J)\rho_{2\,-\sigma}]-J^2\rho_{2\sigma}\rho_{2\,-\sigma}}\\&-\lambda^2\sum_{\sigma}\frac{\rho_{1\sigma}\{(1-U\rho_{1\,-\sigma})[1+(U-J)\rho_{1\sigma}-J\rho_{1\,-\sigma}]-J^2\rho_{1\sigma}\rho_{1\,-\sigma}\}}{[1-(U-J)\rho_{1\sigma}][1-(U-J)\rho_{1\,-\sigma}]-J^2\rho_{1\sigma}\rho_{1\,-\sigma}}\\&-\frac{2\lambda^2(N_{2\sigma}-N_{1\sigma})}{\epsilon_{2\sigma}+\Sigma_{2\sigma}-\epsilon_{1\sigma}-\Sigma_{1\sigma}}F_{2\sigma1\sigma}-\frac{3\lambda^2(N_{1\sigma}-N_{0\sigma})}{\epsilon_{1\sigma}+\Sigma_{1\sigma}-\epsilon_{0\sigma}-\Sigma_{1\sigma}}F_{1\sigma0\sigma}+\frac{2\lambda^2(N_{1\uparrow}-N_{1\downarrow})}{\epsilon_{1\uparrow}+\Sigma_{1\uparrow}-\epsilon_{1\downarrow}-\Sigma_{1\downarrow}}F_{1\uparrow1\downarrow}\\&+\frac{8\lambda^2(N_{2\uparrow}-N_{2\downarrow})}{\epsilon_{2\uparrow}-\Sigma_{2\uparrow}-\epsilon_{2\downarrow}-\Sigma_{2\downarrow}}F_{2\uparrow2\downarrow}-\frac{2\lambda(N_{2\uparrow}-N_{1\downarrow})}{\epsilon_{2\uparrow}+\Sigma_{2\uparrow}-\epsilon_{1\downarrow}-\Sigma_{1\downarrow}}F_{2\uparrow1\downarrow}-\frac{3\lambda^2(N_{1\uparrow}-N_{0\downarrow})}{\epsilon_{1\uparrow}+\Sigma_{1\uparrow}-\epsilon_{0\downarrow}-\Sigma_{0\downarrow}}F_{1\uparrow0\downarrow}\\&-\frac{2\lambda^2(N_{1\uparrow}-N_{2\downarrow})}{\epsilon_{1\uparrow}+\Sigma_{1\uparrow}-\epsilon_{2\downarrow}-\Sigma_{2\downarrow}}F_{1\uparrow2\downarrow}-\frac{3\lambda^2(N_{0\uparrow}-N_{1\downarrow})}{\epsilon_{0\uparrow}+\Sigma_{0\uparrow}-\epsilon_{1\downarrow}-\Sigma_{1\downarrow}}F_{0\uparrow1\downarrow} ,\end{aligned} \tag{3.8}$$

in which $F_{m\sigma m'\sigma'}$ is given by

$$\begin{aligned}F_{m\sigma m'\sigma'}=&\left\{\left(1-U\frac{N_{m\,-\sigma}-N_{m'\,-\sigma'}}{\epsilon_{m\,-\sigma}-\Sigma_{m\,-\sigma}-\epsilon_{m'\,-\sigma'}-\Sigma_{m'\,-\sigma'}}\right)\left[1+\frac{(U-J)(N_{m\sigma}-N_{m'\sigma'})}{\epsilon_{m\sigma}-\Sigma_{m\sigma}-\epsilon_{m'\sigma'}-\Sigma_{m'\sigma'}}-\frac{J(N_{m\,-\sigma}-N_{m'\,-\sigma'})}{\epsilon_{m\,-\sigma}+\Sigma_{m\,-\sigma}-\epsilon_{m'\,-\sigma'}-\Sigma_{m'\,-\sigma'}}\right.\right.\\&\left.\times\left(1-\frac{5U(N_{m\sigma}-N_{m'\sigma'})}{\epsilon_{m\sigma}+\Sigma_{m\sigma}-\epsilon_{m'\sigma'}-\Sigma_{m'\sigma'}}\right)\right]\\&\left.-\frac{4U^2J^2(N_{m\sigma}-N_{m'\sigma'})}{\epsilon_{m\sigma}+\Sigma_{m\sigma}-\epsilon_{m'\sigma'}-\Sigma_{m'\sigma'}}\,\frac{(N_{m\,-\sigma}-N_{m'\,-\sigma'})}{\epsilon_{m\,-\sigma}+\Sigma_{m\,-\sigma}-\epsilon_{m'\,-\sigma}-\Sigma_{m'\,-\sigma'}}\right\}\\&\times\left[\left(1-\frac{(U-J)(N_{m\sigma}-N_{m'\sigma'})}{\epsilon_{m\sigma}+\Sigma_{m\sigma}-\epsilon_{m'\sigma'}+\Sigma_{m'\sigma'}}\right)\left(1-\frac{(U-J)(N_{m\,-\sigma}-N_{m'\,-\sigma'})}{\epsilon_{m\,-\sigma}+\Sigma_{m\sigma}-\epsilon_{m'\,-\sigma'}-\Sigma_{m'\,-\sigma'}}\right)\right.\\&\left.-\frac{N_{m\sigma}-N_{m'\sigma'}\quad N_{m\,-\sigma}-N_{m'\,-\sigma'}}{(\epsilon_{m\sigma}+\Sigma_{m\sigma}-\epsilon_{m'\sigma'}-\Sigma_{m'\sigma'})(\epsilon_{m\sigma}+\Sigma_{m\,-\sigma}-\epsilon_{m'\,-\sigma'}-\Sigma_{m'\,-\sigma'})}\right]^{-1} .\end{aligned}$$

Again, this has a form of insulating nature and terms which are purely metallic. It is seen that the diagonal terms, which involve the density of states at the Fermi level, are of the same form as the nondiagonal terms, which involve $F_{m\sigma m'\sigma'}$. These terms have both signs, and each term is enhancement factor. Each enhancement factor becomes smallest for a different value of the total number of d electrons $N_d=\sum_{m\sigma}N_{m\sigma}$. Thus the anisotropic part of the energy may change sign, as the total number of d electrons is varied, in agreement with experiments on $3d$ impurities in hexagonal hosts. The calculated behavior of the anisotropy energy is shown in Fig. 2. In this graph, we have taken the parameter to have the values $U=2.5$ eV, $J=1$ eV, $\mathrm{Im}\Sigma=1$ eV, crystal-field splitting $\Delta E=0.125$ eV, and $\lambda=0.01$ eV.

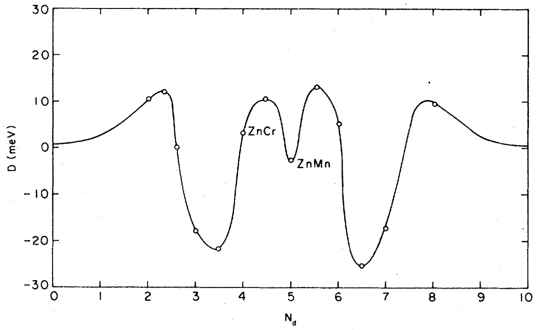

FIG. 2. Anisotropy energy D plotted against the number of electrons in the d-shell N_d. The points mark the calculated values, the curves are obtained by interpolation.

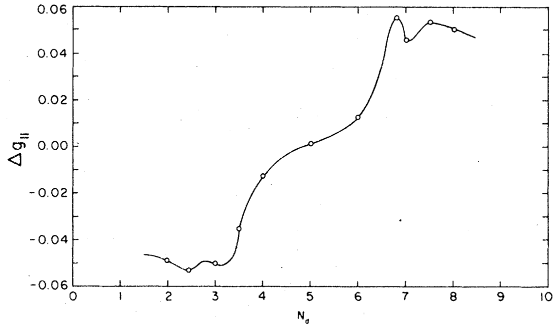

FIG. 3. g shift parallel to the axis of hexagonal symmetry, as a function of N_d.

It is seen that two transition-metal impurities, that occupy adjacent positions in the rows of the Periodic Table, may exhibit completely different anisotropy when they are placed in the same hexagonal host metal. There is some limited experimental evidence for this type of behavior, for measurements on ZnCr and ZnMn alloys. In Fig. 3 we plot the calculated variation of the g shift, $\Delta g_{\parallel}$, as the number of d electrons is varied. We have used the same parameters as in Fig. 1. The dominant feature of this curve is the minima of Δg at $N_d = 5$. The small value of the g shift at $N_d = 5$ is due to the change in the dominant spin character of the density of states at the Fermi level. This minima of the g shift is in accord with Hund's rules, which predict that for an isolated S-state ion ($3d^5$) the g shift vanishes. The general trends seen in Figs. 2 and 3 have not been verified experimentally. No systematic investigations have been made on how the magnetic anisotropy of an impurity, in the same hexagonal host metal, depends on the number of electrons in the impurities d shell. We may compare our results with the experimental data on Mn and Cr impurities in Zn hosts. In the electron-spin-resonance measurements on ZnMn, Devine and Moret find that the g factor is close to the value for free electrons. However, the g factor does show a small anisotropy. The g factor for the magnetic field along the principal axis $g_{\parallel}$ is measured as 2.0065, while the g factor perpendiocular to the principal axis is 2.0015. They estimate the anisotropy to be $D = -7$ meV. Our calculation does give the result that for $N_d = 5$, the g shift and its anisotropy will be small. We also find that the anisotropy energy D is negative. Electron-spin-resonance data on ZnMn does not exist, so we do not have any accurate information on the g factor. However, we do have accurate information on the anisotropy energy D from Symko's low-field-magnetization data. Symko *et al.* give the anisotropy energy of ZnCr to be positive $D = +6.8$ meV, which is of similar magnitude but of opposite sign to that which he finds for ZnMn $D = -6$ meV. As can be seen from Fig. 2, we do have a change in sign in the anisotropy energy occurring between $N_d = 4$ and $N_d = 5$. At the values of $N_d = 4$ corresponding to Cr^{2+} and $N_d = 5$ corresponding to Mn^{2+} we do have the magnitudes of D to be similar. Although this calculation does not deal with the effects of changing the host material, we do predict that the variation in the anisotropy effects should be larger for materials with wide conduction bands, as has been implied by Moret and Devine. Thus, we conclude that the Friedel-Anderson model provides an adequate description of the magnetic anisotropy of transition-metal impurities in hexagonal metallic hosts. The model describes the manner in which the anisotropy energy D varies and changes sign, as the number of electrons in the d shell is varied. The calculation is in agreement with the experimental results on ZnMn and ZnCr alloys. We have also calculated the anisotropic g factor. This exhibits trends that are expected on the basis of Hund's rule for isolated ions, though one must include the coupling between the conduction electrons and the d orbitals to obtain meaningful results.

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[1] S. F. Kral, L. A. Moberly, T. Steelhammer, and O. G. Symko (unpublished); L. A. Moberly and O. G. Symko, in Proceedings of the Conference on Magnetism and Magnetic Materials, Cleveland, 1978 (unpublished); F. T. Hedgcock, S. Lenis, P. L. Li, J. O. Strom-Olson, and E. F. Wassermann, Can. J. Phys. 52, 1759 (1974).

[2] R. A. B. Devine and J. M. Moret, Solid State Commun. 14, 1287 (1974).

[3] K. W. H. Stevens, Rep. Prog. Phys. 30, 189 (1967).

[4] J. M. Dixon and R. Dupree, Solid State Commun. 16, 1301 (1975).

[5] S. E. Barnes, V. Baberschke, and M. Hardiman (unpublished).

[6] L. L. Hirst, Z. Phys. 9, 241 (1971).

[7] J. Friedel, Nuovo Cimento Suppl. 7, 287 (1958), Can. J. Phys. 34, 1190 (1956).

[8] P. W. Anderson, Phys. Rev. 178, 599 (1969).

[9] B. Caroli, C. Caroli, and D. R. Fredkin, Phys. Rev. 178, 599 (1969).

[10] Lowell Dworin and Albert Narath, Phys. Rev. Lett. 25, 1287 (1970).

[11] B. Coqblin and A. Blandin, Adv. Phys. 17, 281 (1968).