

more detailed numerical study of the classical anisotropic models is in progress.

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RANGE OF A STATIC SPIN PERTURBATION IN PALLADIUM

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The structure of the large magnetic moments associated with certain first-row transition-metal atoms dissolved in palladium continues to be of interest. These giant moments have been reported by Gerstenberg¹ for Mn, Fe, Co, and Ni dissolved in Pd, by Crangle² for Fe in Pd, and by Bozorth *et al.*³ for Co in Pd. The systematic variation of the size of the moment with electron concentration in the host has been studied by Clogston *et al.* for Fe in Pd-Rh and Pd-Ag alloys.⁴ Geballe *et al.* have studied the magnetic moment found when Fe is dissolved in Pd-Pt solid solutions.⁵ Recently Low and Holden have investigated by inelastic neutron scattering the distribution of magnetic moment in the solvent for Fe and Co dissolved in Pd.⁶

The following general picture has emerged from this work. At the site of each iron atom substitutionally present in the Pd lattice, there exists a magnetic moment of 3-4 μ_B . Surrounding this site, the Pd atoms are polarized for a distance of about 10 Å. The nearest-neighbor atoms to the iron impurity carry a moment of about 0.07 μ_B . This moment falls off exponentially with distance at such a rate that the total moment of the complex is about 10 μ_B . The giant moment thus consists of a rather small spin density spread out over many atoms surrounding the impurity.

In a metal the disturbance in electronic structure created by an impurity atom is generally of very short range, the first zero in the oscillating Ruderman-Kittel-Yosida range function coming approximately at $r/a = 0.36/\nu^{1/3}$ for a spherical Fermi surface containing ν

electron or hole states per atom. Here a is the lattice constant for a fcc metal. In a free-electron approximation this range can be considerably extended by the introduction of a short-range, momentum-independent interaction between the electrons.^{7,8} However, the modified range function can be made to agree with experiment only by assuming unrealistic values of ν or of the interaction strength.⁹

We wish to describe here the effect of considering not only the intra-atomic exchange interaction between electrons on the same atom but also important effects due to interatomic exchange between electrons on nearest-neighbor atoms. We shall assume that the principal response of Pd to a weak spin-dependent perturbation is confined to the heavy-hole band lying at point X in the Brillouin zone and containing approximately 0.18 hole states per atom.¹⁰

For simplicity we consider first the case of a band made up of nondegenerate atomic orbitals and write the Bloch functions in the form

$$\Psi_{\vec{k}}(\vec{r}) = N^{-1/2} \sum_a \exp(i\vec{k} \cdot \vec{r}_a) \theta(\vec{r} - \vec{r}_a). \quad (1)$$

The extension to the case of degenerate orbitals appropriate to Pd has two important effects which will be discussed later. The z component of spin on atom a is written

$$S_{\vec{q}}(a) = (1/N) \sum_{\vec{q}} \exp(-i\vec{q} \cdot \vec{r}_a) S_{\vec{q}}, \quad (2)$$

where in the representation given by Eq. (1) $S_{\vec{q}}$ has the form

$$S_{\vec{q}} = \sum_{\vec{k}, \vec{k}'} \delta_{\vec{k}', -\vec{k}, \vec{q} + \vec{k}} \frac{1}{2} [C_{\vec{k}, \uparrow}^* C_{\vec{k}, \uparrow} - C_{\vec{k}, \downarrow}^* C_{\vec{k}, \downarrow}]. \quad (3)$$

The momenta \vec{k}' , \vec{k} , and q all run over the first Brillouin zone, \vec{K} is a reciprocal lattice vector,

and $C_{\vec{k}\sigma}^*$, $C_{\vec{k}\sigma}$ are creation and destruction operators for state \vec{k} with spin σ . In the random phase approximation it is easy to show that

$$C_{\vec{k}'\uparrow}^* C_{\vec{k}\uparrow} - C_{\vec{k}'\downarrow}^* C_{\vec{k}\downarrow} = -[(\vec{k}|v(\vec{r})|\vec{k}) + \sum_{\vec{l}\vec{l}'} (\vec{k}\vec{l}'|V(\vec{r}_1, \vec{r}_2)|\vec{l}\vec{l}') (C_{\vec{l}'\uparrow}^* C_{\vec{l}\uparrow} - C_{\vec{l}'\downarrow}^* C_{\vec{l}\downarrow})] \frac{f_{\vec{k}'} - f_{\vec{k}}}{E_{\vec{k}'} - E_{\vec{k}}}, \quad (4)$$

where $-v(\vec{r})\sigma_z$ is some spatially varying spin-dependent potential, $V(\vec{r}_1, \vec{r}_2)$ is the screened Coulomb interaction, and $f_{\vec{k}}$ is the Fermi function for energy $E_{\vec{k}}$. Using Eq. (1) we have approximately

$$(\vec{k}|v(\vec{r})|\vec{k}') = \frac{1}{N} \sum_a \exp[-i(\vec{k}-\vec{k}')\cdot\vec{r}_a] \int \theta^*(\vec{r}-\vec{r}_a) v(\vec{r}) \theta(\vec{r}-\vec{r}_a) d\vec{r} \quad (5)$$

$$= \frac{1}{N} v_{\vec{k}'-\vec{k}}. \quad (6)$$

We also have

$$(\vec{k}\vec{l}'|V(\vec{r}_1, \vec{r}_2)|\vec{l}\vec{l}') = \frac{1}{N} \delta_{\vec{l}'-\vec{l}, \vec{k}'-\vec{k}+\vec{K}} \sum_{abc} \exp[-i\vec{k}\cdot(\vec{r}_a-\vec{r}_d)] \exp[-i\vec{l}'\cdot(\vec{r}_b-\vec{r}_d)] \exp[i\vec{l}\cdot(\vec{r}_c-\vec{r}_d)] \\ \times \int \theta^*(\vec{r}_1-\vec{r}_a) \theta^*(\vec{r}_2-\vec{r}_b) V(\vec{r}_1, \vec{r}_2) \theta(\vec{r}_1-\vec{r}_c) \theta(\vec{r}_2-\vec{r}_d) d\vec{r}_1 d\vec{r}_2. \quad (7)$$

From the wide variety of terms included in (7) we retain those for which $a=d$ and $c=b$. We have then

$$(\vec{k}\vec{l}'|V(\vec{r}_1, \vec{r}_2)|\vec{l}\vec{l}') = \frac{1}{N} \delta_{\vec{l}'-\vec{l}, \vec{k}'-\vec{k}+\vec{K}} \sum_b \exp[-i(\vec{l}'-\vec{l})\cdot(\vec{r}_b-\vec{r}_d)] \\ \times \int \theta^*(\vec{r}_1-\vec{r}_d) \theta^*(\vec{r}_2-\vec{r}_b) V(\vec{r}_1, \vec{r}_2) \theta(\vec{r}_1-\vec{r}_b) \theta(\vec{r}_2-\vec{r}_d) d\vec{r}_1 d\vec{r}_2 \quad (8)$$

$$= \frac{1}{N} \delta_{\vec{l}'-\vec{l}, \vec{k}'-\vec{k}+\vec{K}} J_{\vec{l}'-\vec{l}}. \quad (9)$$

We can expand $J_{\vec{l}'-\vec{l}}$ in the form $J+J'Z_{\vec{l}'-\vec{l}}$, where J is the intra-atomic exchange energy, J' is the interatomic exchange energy, and $Z_{\vec{q}} = \sum \exp(i\vec{q}\cdot\vec{r}_a)$ with the sum on \vec{r}_a running over near neighbor sites to $\vec{r}_0=0$. For small \vec{q} , $Z_{\vec{q}} = Z - (aq)^2$, where Z is the number of nearest neighbors. This choice includes terms of order $I^{(00)}$ and $I^{(2)}$ in Herring's notation.¹¹ We omit terms of order $I^{(0)}$ obtained with $c=a$ and $b=d$, and terms of order $I^{(1)}$ obtained with $b=c=d$, which do not depend explicitly on the momentum transfer $\vec{l}'-\vec{l}$. Although these terms give important contributions to the $\vec{q}=0$ component of the exchange interaction, we have been able to show in simple cases that their momentum dependence is strongly suppressed. We will assume, therefore, that these terms do not make a large contribution to the momentum-dependent exchange enhancement discussed below.

From Eqs. (3), (4), and (9) we obtain

$$S_{\vec{q}} = \left[\frac{1}{2} v_{\vec{q}} + J_{\vec{q}} S_{\vec{q}} \right] \xi_{\vec{q}}, \quad (10)$$

where

$$\xi_{\vec{q}} = - \frac{1}{N} \sum_{\vec{k}\vec{k}'} \delta_{\vec{k}'-\vec{k}, \vec{q}+\vec{K}} \frac{f_{\vec{k}'} - f_{\vec{k}}}{E_{\vec{k}'} - E_{\vec{k}}}. \quad (11)$$

These are the usual equations for the momentum-dependent susceptibility $\xi_{\vec{q}}$ and the exchange-enhanced spin density $S_{\vec{q}}$, except that we have now in effect introduced a momentum-dependent exchange interaction $J_{\vec{q}}$.

For the more realistic case of λ degenerate orbitals appropriate to Pd, Eq. (10) should be replaced by the expression

$$S_{m\vec{q}} = \left[\frac{1}{2} v_{m\vec{q}} + \sum_{m'} J_{mm'\vec{q}} S_{m'\vec{q}} \right] \xi_{m\vec{q}}, \quad (12)$$

where m refers to sections of the Brillouin zone where the wave functions are composed of atomic orbitals of predominately one symmetry type m . For small \vec{q} as required later we take $\xi_{m\vec{q}} \equiv \lambda \xi_{m\vec{q}}$ to be independent of m . This would be true for instance of spherical or cy-

lindrical Fermi surfaces. We also make the reasonable assumption that $\sum m' J_{mm'q} = \lambda J_{q}^{\rightarrow}$ independent of m' . J_{q}^{\rightarrow} thus includes Hund's rule exchange terms which are smaller than the exchange self-energy terms.¹² If we now chose $v_{m\vec{q}} = v_{\vec{q}}$, we return to Eq. (10) with $S_{\vec{q}} = \sum m S_{m\vec{q}}$.

For a uniform applied magnetic field H , $v(\vec{r}) = g\mu_B H$ and the susceptibility per atom is given by

$$\chi = \frac{\frac{1}{2} g^2 \mu_B^2 \rho(E_F)}{1 - (J + J'Z)\rho(E_F)}, \quad (13)$$

since

$$\lim_{\vec{q} \rightarrow 0} \xi_{\vec{q}} = \rho(E_F),$$

the density of states of one spin at the Fermi energy. The susceptibility is enhanced by the factor $\alpha = [1 - (J + J'Z)\rho(E_F)]^{-1}$. In Pd metal the low-temperature susceptibility is about 12 states/eV atom.¹³ Judging by the augmented-plane-wave calculation of Freeman, Furdyna, and Dimmock,¹⁴ the unrenormalized state density is about 1 state/eV atom. Very approximately, therefore, $\alpha = 10$.

If the system is perturbed by a potential limited to the atom at $\vec{r}_0 = 0$, $v_{\vec{q}} = v(0)$ and we have

$$S(a) = \frac{1}{2} v(0) \Omega \int \frac{d\vec{q}}{(2\pi)^3} \exp(-i\vec{q} \cdot \vec{r}_a) \frac{\xi_{\vec{q}}}{1 - J_{\vec{q}} \xi_{\vec{q}}}, \quad (14)$$

where Ω is the atomic volume. For \vec{r}_a greater than a lattice constant, the integral in Eq. (14) depends principally upon small values of \vec{q} . For strong exchange enhancement, the integral can be evaluated approximately to give

$$S(a) = v(0) \frac{\Omega}{8\pi} \alpha \rho(E_F) \frac{1}{\sigma^2 r_a} \exp(-r_a/\sigma), \quad (15)$$

where

$$\left(\frac{\sigma}{a}\right)^2 = \alpha \left[\rho(E_F) J' - \frac{1}{2a^2} \left(\frac{d^2 \xi_{\vec{q}}}{dq^2} \right)_0 (J + ZJ') \right]. \quad (16)$$

For Fe dissolved in Pd, the neutron diffraction measurements can be fitted approximately with $\sigma = 3.3 \text{ \AA}$. With the lattice constant $a = 3.88 \text{ \AA}$, $(\sigma/a)^2 = 0.72$. For a spherical band

of holes,

$$\begin{aligned} \frac{1}{2a^2} \left(\frac{d^2 \xi_{\vec{q}}}{dq^2} \right)_0 &= -\rho(E_F) \frac{1}{12(ak_F)^2} \\ &= -\rho(E_F) \frac{1}{460\nu^{2/3}}. \end{aligned} \quad (17)$$

Vuillemin and Priestly find $\nu \approx 0.06$ hole states in each heavy-hole pocket at the three nonequivalent points X of the Brillouin zone. If $J' = 0$ and $\alpha = 10$, this corresponds to $(\sigma/a)^2 = 0.14$ or $\sigma = 1.5$, much smaller than the observed value. To fit the experimental value we require $\rho(E_F) J' = 0.058$. This is a large value of J' in the sense that $Z\rho(E_F) J' = 0.7$ is the largest contribution to the exchange enhancement factor α . If $\rho(E_F) \approx 1$ state/eV atom, $J' \approx 0.06$ eV, a value compatible with the magnitudes of the integrals $I^{(2)}$ quoted by Herring for 3d atomic orbitals.¹¹ If the actual energy surfaces of Pd in the vicinity of X could be represented by a set of concentric cylinders, $(d^2 \xi_{\vec{q}}/dq^2)_0 = 0$ and $\rho(E_F) J' = 0.072$ to fit the experimental range parameter.

We conclude that the interatomic exchange J' in Pd is an important source of exchange enhancement of the spin susceptibility and of the long-range spin polarization produced by an Fe or Co impurity.

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EXACT SOLUTION OF A MODEL OF TWO-DIMENSIONAL FERROELECTRICS IN AN ARBITRARY EXTERNAL ELECTRIC FIELD

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We generalize the recent solution of a model of two-dimensional ferroelectrics to include the addition of an arbitrary horizontal and an arbitrary vertical electric field and show that the general problem when all six vertex configurations have different energies, and when arbitrary horizontal and vertical electric fields are present is mathematically equivalent to the above problem.

Recently Lieb¹ solved the two-dimensional ice problem exactly. There have been three²⁻⁴ further papers generalizing this solution, of which Sutherland's problem³ includes all the others as special cases. We show in this paper a further generalization to include a horizontal electric field.

Consider a two-dimensional, cyclic $N \times N$ square lattice with periodic boundary conditions. Two hydrogen atoms are bonded to each site. These bonds are represented by arrows. The ice condition is imposed which demands that two and only two arrows must point away from (and toward) each lattice site. We then assume that there are configurational energies at each site as in Fig. 1.

We further assume that each bond has a unit electric dipole moment, and that there are present a vertical electric field v and a horizontal electric field h . Each vertical arrow contributes an energy $-v(+v)$ if it points upward (downwards). Each horizontal arrow contributes $-h(+h)$ if it points to the right (left).

First, consider the case

$$\epsilon_1 = \epsilon_2 = +\epsilon, \quad \epsilon_5 = \epsilon_6 = -\epsilon_3 = -\epsilon_4 = -\frac{1}{2}\delta. \quad (1)$$

Define

$$\xi = \exp[2\epsilon/kT], \quad \eta = \exp[\delta/kT],$$

$$H = \exp[2h/kT], \quad V = \exp[2v/kT], \quad (2)$$

$$y = 1 - 2[\text{fraction of vertical spin pointing downwards}],$$

$$y = \text{vertical polarization.} \quad (3)$$

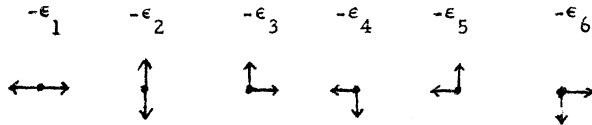


FIG. 1. The six configurations at each lattice site. Inward-pointing arrows are omitted in this figure.

Lieb¹ has shown that the value of y defined for each horizontal row of vertical spins is the same for all rows, because of the ice condition. We consider first the problem of fixed y with no vertical field. Denote by

$$F_{hy}(h, y) = -NkT \ln(\text{partition function}) \quad (4)$$

the free energy for such a system. In exactly the same way as in Refs. 1-4, the present partition function can be formulated in terms of the trace of a transfer matrix.

The largest eigenvalues of the matrix can be found in the same way as in these references, following Lieb's method.¹ We thus obtain

$$F_{hy}(h, y) = -NkT \ln \lambda, \quad (5)$$

where

$$\lambda = (H\eta)^{\frac{1}{2}m} \prod_{j=1}^m \left(\eta^{-1} - \frac{\xi}{1 - H\eta \exp[ip_j]} \right)$$

$$+ (H\eta)^{-\frac{1}{2}m} \prod_{j=1}^m \left(\eta - \frac{\xi}{1 - H^{-1}\eta^{-1} \exp[-ip_j]} \right). \quad (6)$$

The conditions that are satisfied by (p_i) are

$$\exp(inp_i) = \prod_{j \pm i} \left(\frac{1 + H^2 \exp[i(p_i + p_j)] - 2\Delta H \exp(ip_i)}{-1 + H^2 \exp[i(p_i + p_j)] - 2\Delta H \exp(ip_j)} \right) \quad (i = 1, 2, \dots, m), \quad (7)$$