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## LONG-RANGE POLARIZATION IN HIGH SUSCEPTIBILITY METALS

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Recent electron paramagnetic resonance (EPR) experiments on metals and alloys of high paramagnetic susceptibility (Pd and Ni<sub>3</sub>La)<sup>1-3</sup> have shown an anomalous long range of the spin polarization around magnetic impurities. Wolff<sup>4</sup> has suggested that the exchange interaction between valence electrons in metals will increase the range of the polarization in space. By connecting the enhancement of the polarization in momentum space with the observed uniform susceptibility of the studied metal, we have found that exchange interactions can bring predicted and observed data into agreement.

The susceptibility function of a system is defined by its linear response to an external magnetic field. If the system is homogeneous,

$$\langle \vec{M}(\vec{r}, t) \rangle = \int \chi(\vec{r} - \vec{r}', t - t') \vec{H}(\vec{r}', t') d^3r' dt',$$

or

$$\langle \vec{M}(\vec{q}, t) \rangle = \int \chi(\vec{q}, t - t') \vec{H}(\vec{q}, t') dt',$$

where  $\langle \vec{M}(\vec{q}, t) \rangle$ ,  $\chi(\vec{q}, t)$  are the spatial Fourier transforms of  $\langle \vec{M}(\vec{r}, t) \rangle$ ,  $\chi(\vec{r}, t)$ , respectively.

For an electron gas,  $\chi$  is given by

$$\chi(\vec{q}, t - t') = (2i\mu_B^2 / V\hbar) \theta(t - t') \langle 0 | T \{ \sigma(-\vec{q}, t) \sigma(\vec{q}, t') \} | 0 \rangle,$$

where

$$\sigma(\vec{q}, t) = \rho_{\uparrow}(\vec{q}, t) - \rho_{\downarrow}(\vec{q}, t),$$

and

$$\rho_{\uparrow}(\vec{q}, t) = (1/V) \sum_{\vec{k}} c_{\vec{k}-\vec{q}}^{\dagger} c_{\vec{k}} c_{\vec{r}}(\vec{k}, t);$$

$V$  is the volume of the system,  $|0\rangle$  is the ground state of the isolated system, and  $T$  is the time ordering operator.

EPR measurements of magnetic impurities in metals allow one to get some insight into the shape of this function.

In a series of recent experiments, the shift and the broadening of the EPR lines of 2% Gd (im-

purity  $A$ ) in a matrix formed by 96% of high-susceptibility metals and 2% of additional magnetic impurities ( $B$ ) have been studied.<sup>1</sup> The magnetic moment of rare earth impurities was found to be practically equal to their ionic moment, contrary to transition elements, which show giant moments in solid solution in Pd alloys.<sup>5</sup> The deformation of the EPR line of Gd in the matrix is very sensitive to the shape of the susceptibility function. This can be best understood by thinking first of only one ion of Gd in the host metal: Each magnetic impurity  $B$  will polarize the valence electrons of the host metal and will therefore shift the  $g$  value of the Gd ion. The magnitude of this shift will depend on the value of the susceptibility function of the host metal at the Gd site. Since the magnetic impurities are distributed at random, the statistical average over all Gd ions will give both a displacement and a deformation of the resonance line.

The shift of a resonance line is defined by

$$S = \int (H - H_0) I(H) dH, \quad (1)$$

where  $H_0$  is the center of the nonperturbed line and  $I(H)$  the perturbed intensity line; and the mean square deviation by

$$B = \int (H - H_0)^2 I(H) dH - S^2. \quad (2)$$

One can express  $S$  and  $B$  in terms of  $\chi(\vec{r}) \equiv \int_0^{\infty} \chi(\vec{r}, t) dt$ :

$$S = c_B n_0 a \frac{1}{V} \int \chi(\vec{r}) d^3r, \quad (3)$$

$$B = c_B n_0 a^2 \frac{1}{V} \int \chi^2(\vec{r}) d^3r, \quad (4)$$

where  $c_B$  is the concentration of magnetic impurities in the matrix,  $n_0$  the number of lattice sites per cc, and  $a$  is a constant depending on the characteristics of the system. The value of the ratio of the shift squared to the mean square

deviation is given by

$$\frac{S^2}{B} = R = c_B n_0 \frac{1}{V} \frac{[\int \chi(\vec{r}) d^3 r]^2}{\int \chi^2(\vec{r}) d^3 r}. \quad (5)$$

Note that  $R$  does not depend on  $a$ . The integrals  $\int \chi(\vec{r}) d^3 r$  and  $\int \chi^2(\vec{r}) d^3 r$  are approximations for sums of integrals taken over the lattice sites. The integrals have to be calculated from a lower cutoff  $r_c$  corresponding to the smallest distance between two atomic sites.

A simple interpretation of  $R$  can be given by considering the following susceptibility function:

$$\begin{aligned} \chi(\vec{r}) &= cte, & |\vec{r}| < r_0, \\ &= 0, & |\vec{r}| > r_0. \end{aligned}$$

One gets then

$$R = c_B n_0 \frac{1}{V} \frac{4\pi}{3} (r_0^3 - r_c^3). \quad (6)$$

The value of  $R$  is therefore connected with the range of the susceptibility function. The experimental values of  $R$  for the system considered are of the order of unity; for instance in the specific case whereby the matrix is formed by 96% of Pd and 2% of Tb, we obtain  $R = 0.96$ , whereas a free electron picture applied to the 0.6 residual  $d$  holes in Pd gives  $R < 10^{-3}$ . This discrepancy cannot be explained by exchange narrowing, because the exchange energy between the Gd ions is of the same order of magnitude as the exchange energy which produces the broadening.

Since the high electronic susceptibility of Pd can be related to a high exchange interaction between  $d$  electrons, we were led to consider the exchange correction to the Ruderman-Kittel-Yosida potential. There are several qualitative effects to consider: (1) The "s" electrons screen the long-range part of the Coulomb interaction between  $d$  electrons; (2) since the  $d$  band is narrow, there are strong correlations which keep  $d$  holes apart, regardless of their relative spin orientation; (3) the Fermi surface is likely to be very complicated for Pd. To handle the first two effects, we assume that there exists a pseudopotential  $-\bar{v}$  for particle-hole scattering which includes screening and correlation effects. Due to the strong screening and the narrowness of the  $d$  band, it is natural to assume that  $\bar{v}$  is roughly a constant for the virtual transitions involved in obtaining  $\chi(q)$ . The third effect is more difficult to handle and we are reduced to making an effective mass approximation for the

$d$ -band holes. One then obtains Wolff's form

$$\tilde{\chi}(q) = \left( \mu \frac{g}{B} \right)^2 \frac{2\eta(0)U(q/2k_F)}{1 - \bar{v}\eta(0)U(q/2k_F)}, \quad (7)$$

where

$$U(x) = \frac{1}{2} \left\{ 1 + \frac{1-x^2}{2x} \ln \left| \frac{1+x}{1-x} \right| \right\}; \quad (8)$$

$\eta(0)$  = density of states at the Fermi surface. A simple estimate of  $\bar{v}\eta(0)$  can in principle be obtained from the uniform susceptibility in undoped Pd,<sup>6</sup>  $\tilde{\chi}(0)$ :

$$\tilde{\chi}(0) = \frac{g^2 \mu_B^2 \eta(0)/2}{1 - \bar{v}\eta(0)} = \frac{\frac{1}{4} g^2 \mu_B^2}{k_B^2 \pi^2} \frac{3\gamma_{\text{obs}}}{1 - \bar{v}\eta(0)}, \quad (9)$$

where  $\gamma_{\text{obs}}$  = experimental value of the coefficient of the electronic specific heat corrected for the  $s$ -electron contribution;  $k_B$  = Boltzmann constant.

The uniform susceptibility of Pd is very sensitive to the amount of impurity present.<sup>7</sup> Pure Pd has a susceptibility of  $7.3 \times 10^{-6}$  emu/g [ $\eta(0) = 6.8 \times 10^{33}$  erg<sup>-1</sup> g<sup>-1</sup>]. Addition of 5% Rh brings the susceptibility to  $12.7 \times 10^{-6}$  emu/g [ $\eta(0) = 7.4 \times 10^{33}$  erg<sup>-1</sup> g<sup>-1</sup>]. Comparison of the  $g$  shift of Gd in alloys of the Pd series with the uniform susceptibility of these alloys<sup>8</sup> leads to some uncertainty as to the background susceptibility one has to attribute to the Pd-Gd alloy. It is therefore difficult to give an accurate figure for the background susceptibility in the system considered, and we calculated  $\bar{v}\eta(0)$  and the values obtained for  $R$  for different values of  $\tilde{\chi}(0)$  (Table I). The values obtained for  $\bar{v}$  by this method have about one half of the value one would obtain by spectroscopic data. One expects  $\bar{v}$  to be reduced

Table I. Calculated values of the ratio  $R$  [defined by Eq. (5)] and the shift to half half-width ratio  $L$  for several values of the valence electron exchange interaction strength  $\bar{v}\eta(0)$ . The factor  $\alpha$  is the ratio of the effective exchange interaction of the magnetic impurity with the valence electrons as given by the present theory to that given by Shaltiel *et al.*<sup>a</sup> and Peter *et al.*<sup>b</sup> The uniform susceptibilities  $\tilde{\chi}(0) = 7.3 \times 10^{-6}$  and  $12.7 \times 10^{-6}$  give  $\bar{v}\eta(0) = 0.835$  and  $0.9$ , respectively.

$\bar{v}\eta(0)$	$R$	$L$	$\alpha$
0.83	0.13	0.5	5.8
0.86	0.2	0.8	4.4
0.894	0.31	1.2	3.1

<sup>a</sup>See reference 1.

<sup>b</sup>See reference 2.

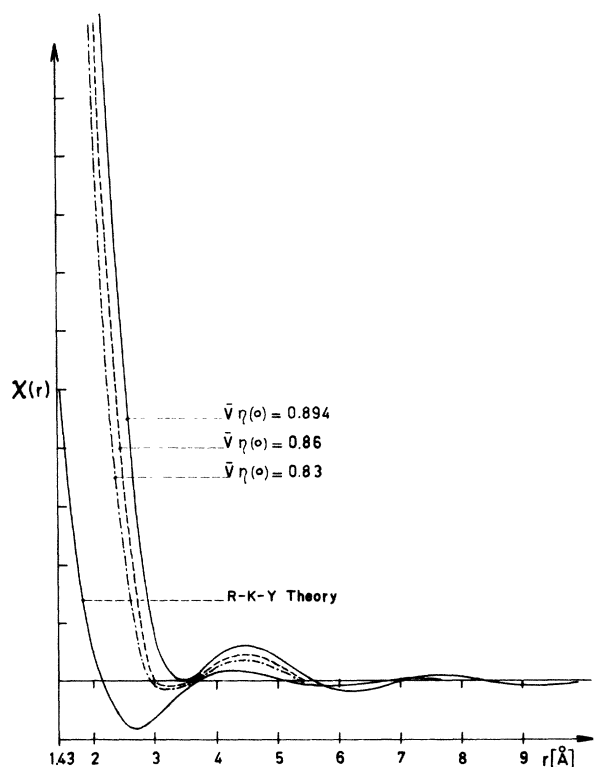


FIG. 1. Upper curves:  $\chi(r)$  for different values of the parameter  $\bar{v}\eta(0)$ . Lower curve: Ruderman-Kittel-Yosida potential.

both by  $s$ -electron screening and by  $d$ -band correlation effects. Figure 1 shows the corresponding functions  $\chi(r)$ , along with the result of the Ruderman-Kittel-Yosida theory.

Since the maximum density of  $f$  electrons in Gd occurs at about  $0.3 \text{ \AA}$  from the nucleus<sup>9</sup> and since the distance between nearest neighbors in Pd is  $1.75 \text{ \AA}$ , we choose  $r_C = 2 \text{ \AA}$ . The value obtained for  $R$  is not much different from the value obtained for  $r_C = 0$ , and it is little sensitive to the possible values one can choose for  $r_C$ . This is not true if we use the Ruderman-Kittel-Yosida free-electron potential. We note that the present theory increases the predicted values of the effective exchange interaction of the magnetic impurity with the valence electrons by a factor  $\alpha$  (see Table I) relatively to the values given by Shaltiel *et al.*<sup>1</sup> and Peter *et al.*<sup>2</sup>

The "half half-width" of a resonance line is only equal to the square root of its second moment if the line is Gaussian. This is not the case within our model, which gives for the fourth moment of

Table II. Observed values<sup>a</sup> of the shift to half half-width ratio  $L_{\text{obs}}$  for several rare earth impurities.

R. E.	$L_{\text{obs}}$
Tb	0.98
Ho	1.6
Er	0.52

<sup>a</sup>See reference 1.

the line a value 25 times larger than the second moment squared. This means that the calculated ratio of the shift to the "half half-width,"  $L$ , which is the quantity directly related to experiments, is larger than  $R^{1/2}$  by a factor  $\beta$ . Two line shapes taken as model, a Lorentzian with cutoff and a Lorentzian with Gaussian wings,<sup>10</sup> gave about the same result,  $\beta \cong 4$ . Table II shows some typical observed values; they are of the same order as the calculated values given in Table I.

In conclusion we see that valence electron exchange interactions strongly modify the form of the induced polarization surrounding a localized moment in Pd. The main effect is to increase the polarization on the sites neighboring the localized moment.

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