Effect of Spin-Orbit Scattering on the Magnetic and Superconducting Properties of Nearly Ferromagnetic Metals: Application to Granular Pt

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We calculate the effect of scattering on the static, exchange enhanced, spin susceptibility and show that, in particular, spin-orbit scattering leads to a reduction of the giant moments and spin glass freezing temperature due to dilute magnetic impurities. The harmful spin fluctuation contribution to the intragrain pairing interaction is strongly reduced opening the way for BCS superconductivity. We are thus able to explain the superconducting and magnetic properties recently observed in granular Pt as being due to scattering effects in single small grains.

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The recent observation of superconductivity (sc) in Pt grains of $\approx 1\mu$m size at ≈ 1 mK [1] motivated this theoretical study of the superconducting and magnetic properties of small grains taking account of the spin-orbit (s-o) scattering by external and internal surfaces [2]. The importance of the s-o interaction at surfaces has been shown by Meservey and Tedrow [3] from a number of different measurements on superconductors. We show that the interplay between incipient magnetism and superconductivity in Pt is tilted towards BCS superconductivity because s-o scattering is inimical to magnetism and reduces the paramagon effects that inhibit singlet pairing.

In bulk Pt, no sc is observed despite a strong electron-phonon coupling; the BCS parameter is $\lambda_{ph}^{Pt} \approx 0.4$ [4]. The absence of sc is due to the strong exchange interactions between the itinerant 5d electrons. The Pt grains are small enough to have a large surface to volume ratio but are sufficiently large (≥ 100 Å) that the Bloch representation applies and we can ignore the Rashba effect [5]. Although the "lattice softening" near surfaces may enhance λ_{ph}^{Pt}, more importantly, the s-o scattering at rough surfaces strongly reduces the harmful paramagnon effects. In the case of Pt grains, the extremely weak impurity magnetism observed at mK temperatures clearly points to an important role of the changed magnetic behavior for the occurrence of sc [1,6]. Independently of whether the sc extends throughout the grain or is restricted to a surface shell, s-o scattering at surfaces and defects will be important for the sc and magnetic properties. If shells exist in the compacted granules, they may (as in a thin film) consist of small crystallites large enough for bulk superconductivity but sufficiently small to limit the mean free path for s-o scattering. We find that, with reasonable values for the exchange and scattering parameters, sc in granular Pt is possible at the observed temperatures.

We first address the magnetic properties of small grains by calculating the static susceptibility $\chi(q)$ in the presence of ordinary and s-o scattering, taking the exchange enhancement effects into account as in Ref. [7]. Scattering is included by considering the effect on χ_0, the susceptibility without exchange enhancements. We find a significant effect of s-o scattering on χ_0 that affects both the Stoner factor S and the spin correlation range σ. The susceptibility $\chi(r)$ is then calculated to determine how scattering, as well as exchange enhancement, affects the RKKY (Ruderman-Kasuya-Kittel-Yoshida) oscillations in $\chi_0(r)$. The short range and long range parts of $\chi(r)$ determine the two pertinent magnetic properties observed in dilute magnetic systems [8,9], namely, the magnitude of the giant moment μ_{gm} and the scale of the spin glass freezing temperature, T_f/x, in, e.g., $PtFe_x$. The exchange effects suppress the RKKY oscillations at small r yielding the ferromagnetic correlations responsible for μ_{gm}; s-o scattering reduces μ_{gm}. The spin glass transition observed in the bulk $PtFe_x$ system is due to the long range oscillations of $\chi(r)$ relevant for the interaction between two impurity moments at a distance $r \gg a(=$ lattice constant). With scattering $\chi(r)$ at large r is so strongly reduced that spin glass freezing would not be expected in the Pt grains where $x = 4$ ppm [1].

The static susceptibility $\chi(q)$ in the presence of ordinary and s-o scattering is appropriate to describe the giant moments and spin glass freezing. We assume the RPA form

$$\chi(q) = \frac{2\mu_B^2\,\chi_0(q)}{1 - \chi_0(q)\frac{1}{3}[U + 2J_H + 3J'(q)]}, \qquad (1)$$

where $\chi_0(q) = N(0)\,u(q)$, $N(0)$ is the density of states (DOS) per spin for all three 5d subbands at the Fermi level, and $u(q)$ reduces to the Lindhard function for free electrons with no impurity scattering. U is the intra-atomic self-exchange, and J_H is Hund's rule exchange. Including up to second nearest neighbors we can define the interatomic exchange interaction $J'(q) \equiv J'(0) - (qa)^2 J'_{\rm eff}$ where a is the lattice constant. We also define $\bar{U} = N(0)U/3$, $\bar{J}_H = N(0)J_H/3$, $\bar{J}'(q) = N(0)J'(q)/3$, $\bar{U}_{\rm eff} = \bar{U} + 2\bar{J}_H + 3\bar{J}'(0)$, and $\bar{J}'_{\rm eff} = N(0)J'_{{\rm eff}s}$. Now $\chi(0) = 2\mu_B^2 S u_0$, where $S = 1/(1 - \bar{U}_{\rm eff}\, u_0)$ and $u_0 = u(0)$.

For small q, with $u(q) \approx u_0 + u_2(qa)^2$, Eq. (1) becomes $\chi(q) = 2\mu_B^2 S u_0 / (1 + \sigma^2 q^2)$ which yields a factor $\frac{1}{r} e^{-r/\sigma}$ where $\sigma^2/a^2 = S[u_0 \bar{J}'_{\rm eff} - u_2 \bar{U}_{\rm eff}] - u_2/u_0$, in agreement with Clogston [10].

For arbitrary q we model the suceptibility with

$$\chi(q) = \frac{2\mu_B^2\, \chi_0(q)}{1 - I(q)\, \chi_0(q)}, \tag{2}$$

where $I(q)$ is a two parameter phenomenological interaction which is determined so that Eq. (1) reduces to the small q form. This yields $\bar{I}(q) = N(0)I(q) = \bar{U}_{\rm eff}/[1 + (qa)^2(\bar{J}'_{\rm eff}/\bar{U}_{\rm eff})]$. $\bar{U}_{\rm eff}$ is determined directly by S. We take $S = 3.8$ for Pt [11] and find $\bar{U}_{\rm eff} = 0.737$. We fix $\bar{J}'_{\rm eff}$ to provide a reasonable value for the spin fluctuation induced effective mass enhancement $\lambda_{\rm SF}$. As in the case of Pd, the problem here is to divide the effective mass enhancement $m^*/m = 1 + \lambda_{\rm SF} + \lambda_{ph}$ between the phonon and spin fluctuation contributions. We assume that λ_{ph} is about the same in Pt as in Pd and take the Pd value of $\lambda_{ph}^{Pd} = 0.41$. Assuming $m^*/m - 1 = 0.63$ for Pt [11] we have $\lambda_{\rm SF}^{Pt} = 0.22$. Employing the standard calculation of $\lambda_{\rm SF}$ [7],

$$\lambda_{\rm SF} = \frac{3}{2}\int_0^{2k_F} \frac{q\, dq}{2k_F^2} \frac{[\bar{I}(q)]^2 u(q)}{1 - \bar{I}(q) u(q)}, \tag{3}$$

we find $\bar{J}'_{\rm eff} = 0.163$ which yields $\sigma = 3.21$ Å. Physically, $\bar{J}'_{\rm eff}$ is a measure of the range of $\bar{I}(r)$ in position space. Increasing $\bar{J}'_{\rm eff}$ increases σ and the range of $\bar{I}(r)$ but decreases the range of $\chi(q)$ in q-space yielding a smaller $\lambda_{\rm SF}$ from Eq. (3).

We assume the RPA form of Eq. (1) is not changed by scattering. The effect of scattering on χ_0 was first considered by de Gennes [12] for ordinary scattering alone. He showed that $\chi_0(q)$ is not affected for $q = 0$. Fulde and Luther (FL1) [13] calculated $\chi(q, \omega)$ for small q and Jullien [14] extended this work to arbitrary q and ω. Spin-orbit scattering was later added in FL2 [15]. We use the result of FL2 for the effect of s-o scattering on χ_0, but we employ the formalism of Julien [14] which is more suitable for computations. Equation (9) of Jullien for χ_0 with ordinary scattering alone, can be generalized to include s-o scattering by comparison with Eq. (14) of FL2. The result is

$$\chi_0(\mathbf{q}, \omega_0) = \frac{i}{2\pi}\int_0^\infty d\omega\, \frac{Z(\omega)[1 - \pi k_F \gamma_1 Z(\omega)/3]}{1 - \pi k_F \gamma_0 Z(\omega)[1 - \pi k_F \gamma_1 Z(\omega)/3]}, \tag{4}$$

where $Z(\omega) = \int \frac{d^3k}{(2\pi)^3} G(\mathbf{k}, \omega)\, G(\mathbf{k} + \mathbf{q}, \omega + \omega_0)$, $\gamma_0 = 1/k_F \ell_0$, and $\gamma_1 = 1/k_F \ell_1$ with ℓ_0 and ℓ_1 the mean free paths for ordinary and s-o scattering, respectively. The propagator G depends on $\gamma = \gamma_0 + \gamma_1$. We set $\omega_0 = 0$ and consider from now on only $\chi(q)$. In their small-q approximation FL2 set $\chi_0(q)/N(0) = 1$. By doing this they neglected the γ_1 corrections to $\chi_0(0)$ that are crucial in the following considerations. The computation of χ proceeds as in Ref. [14] leading to the results shown in Fig. 1 where we take for Pt, $k_F = 0.642\,\mathrm{cm}^{-1}$ and $a = 3.923$ Å. Figure 1(a) shows the large effect of γ_1 on $\chi_0(0)$. In Fig. 1(b) S, u_0, and σ are shown vs γ_1. S and u_0 do not depend on γ_0 and the dependence of σ on γ_0 arises only through u_2 and is negligible.

We now compute $\chi(r)$. For $\chi(q) \to \chi_0(q)$ the Fourier transform can be done analytically yielding the usual RKKY oscillations. Integrating $\chi(r)$ yields the sum rule,

$$\int d^3r\, \chi(r) = \chi(q = 0) = 2\mu_B^2 N(0) S u_0. \tag{5}$$

χ_0 alone does not provide the necessary short range ferromagnetic correlations. This problem does not occur in our two parameter model for χ, see Fig. 2(a). Here we plot $\bar{\chi}(r)$ which is defined by $\chi(r) = 2\mu_B^2 N(0)(\Omega/a^3)\, \bar{\chi}(r)$, where Ω is $a^3/4$ for the fcc lattice. The first effect of $U_{\rm eff}$ is to shift the curve to larger r increasing the spin correlation range σ, an effect discussed previously by [16]. Further increasing $U_{\rm eff}$ pushes the curve above the axis for small r. Increasing $\bar{J}'_{\rm eff}$ has a similar effect. The solid curve for the Pt parameters provides both the ferromagnetic short range correlations and the long range oscillations. The effect of scattering at small r is shown in Fig. 2(b). Ordinary scattering (upper dash curve) tends to smooth out the oscillations with little

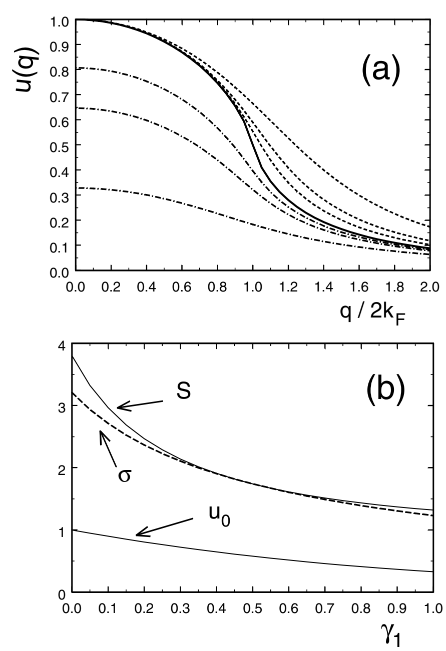

FIG. 1. (a) Solid curve: Lindhard function $u(q)$ without scattering. Dashed curves: Ordinary scattering alone, $\gamma_1 = 0$, $\gamma_0 = 0.2, 0.4, 1.0$. Dot-dash curves: s-o scattering alone, $\gamma_0 = 0$, $\gamma_1 = 0.2, 0.4, 1.0$. (b) Stoner factor, spin correlation range, and $u_0 = u(0)$ as a function of s-o scattering.

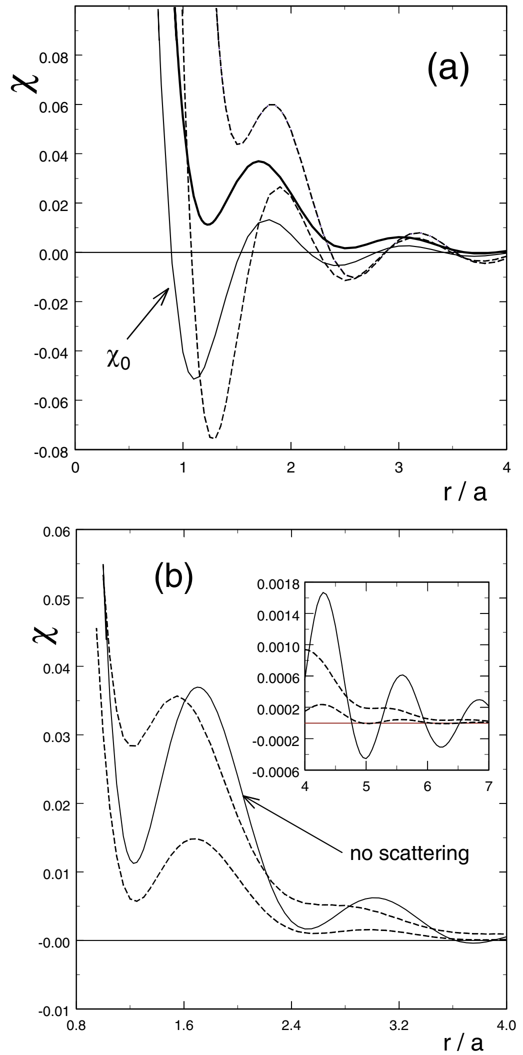

FIG. 2. Dimensionless susceptibility $\bar{\chi}(r)$ without scattering vs r/a. (a) Lower dash curve: $\bar{U}_{\rm eff} = 0.737$, $\bar{J}'_{\rm eff} = 0$; upper dash curve: $\bar{U}_{\rm eff} = 0.92$, $\bar{J}'_{\rm eff} = 0$; thick solid curve: Pt parameters, $\bar{U}_{\rm eff} = 0.737$, $\bar{J}'_{\rm eff} = 00.163$. (b) $\bar{\chi}(r)$ with and without scattering for Pt parameters. Solid curve: no scattering; upper dash curve: ordinary scattering, $\gamma_0 = 0.2$, $\gamma_1 = 0$; lower dash curve: s-o scattering, $\gamma_0 = 0$, $\gamma_1 = 0.2$.

change in the area under the curve consistent with the sum rule, Eq. (5). S-o scattering (lower dash curve), on the other hand, reduces the magnitude of $\chi(r)$.

The giant moments observed in the bulk $PtFe_x$ [8] are not seen in the Pt powders [1] although the granules contain $x = (4 \pm 1)$ ppm of magnetic impurities. The giant moment consists of two parts, $\mu_{gm} = \mu(i) + \mu(h)$, where $\mu(i = \text{impurity})$ is the local moment of the 3d electrons of the Fe impurity atom and $\mu(h = \text{host})$ is the spin polarization of the Pt host matrix. We assume that $\mu(i)$ of Fe in Pt has approximately the same value as in Pd and take $\mu(i) \simeq 3\,\mu_B$. Using the experimental susceptibility value [8], $\mu_{gm} \simeq 8\,\mu_B$, leads to $\mu(h) \simeq 5\,\mu_B$. We have

$$\mu(h) = 4\pi \int_0^{r_{gm}} r^2\, dr\, \sigma_s(r), \tag{6}$$

where r_{gm} is the giant moment radius and $\sigma_s(r)$ is the isotropic spin polarization induced by the Fe moment at $\mathbf{r} = 0$ due to the exchange interaction V_{ex} between the 3d electrons of the impurity and the 5d electrons of the Pt host, $\sigma_s(r) = (V_{ex}/4)\, N(0)\, \mu_B\, \bar{\chi}(r)$ [10]. N(0) is the DOS per spin and $\mathrm{eV} \cdot \mathrm{cm}^3$. To calculate $\mu(h)$ we need the parameters r_{gm} and V_{ex}. $\mu(h)$ is not particularly sensitive to r_{gm} and an upper limit can be obtained from the sum rule, Eq. (5): $\mu(h)\,|_{r_{gm}\to\infty} = V_{ex}\, N(0)\, a^3\, S\, u_0\, \mu_B\,/4$. We take $r_{gm} \sim 2.5\,a \sim 10$ Å as in Pd and then fix the value of V_{ex} by requiring that Eq. (6) yield $\mu(h) = 5\,\mu_B$. We find $V_{ex} = 2.504$ eV which is somewhat large but still seems reasonable. Here we have used $N(0) = 0.386(m_b^*/m)$ states/eV/atom with band mass $m_b^*/m = 3.36$ [11]. The effect of s-o scattering on $\mu(h)$ is shown in Fig. 3, where μ(h) from Eq. (6) (solid curve) and for $r_{gm} \to \infty$ (dash curve) are shown versus γ_1. It turns out that $\mu(h)$ is practically independent of γ_0. This can be seen from the sum rule result, $r_{gm} \to \infty$, since S and u_0 are affected only by s-o scattering. Because of the rapid decrease of $\chi(r)$ in the presence of scattering the sum rule is approximately exhausted for the experimental r_{gm}. The decrease of $\chi(r)$ at small r seen in Fig. 2(b) leads to a reduction of $\mu(h)$ by a factor 2 for $\gamma_1 \simeq 0.2$ and can explain why giant moments are not observed in the Pt granules.

The spin glass freezing temperature T_f is determined by the long range spin polarization that provides the RKKY coupling between two magnetic impurities. At large r and in the absence of scattering, $\chi(r)$ and $\chi_0(r)$ are nearly the same and proportional to $\cos(2\,k_F\, r)/r^3$.

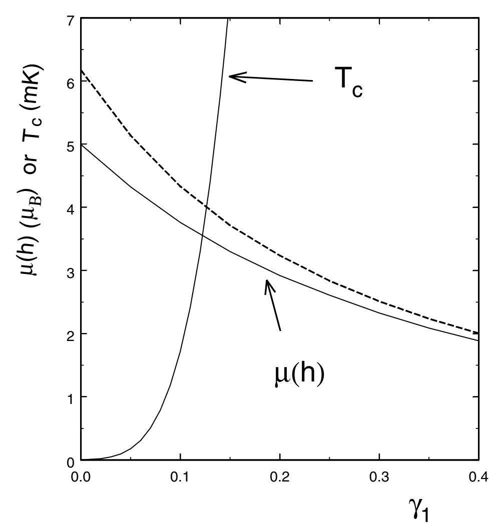

FIG. 3. Superconducting transition temperature T_c and the Pt host contribution to the giant moment $\mu(h)$ as functions of the s-o scattering rate γ_1. The dashed curve is the exact rule result for infinite giant moment radius. The curves are continued in the inset.

The scale of T_f is set by the average RKKY coupling energy of a typical impurity atom pair. Although a correct calculation of T_f requires evaluation of the second moment of the distribution of the couplings, an estimate can be obtained from the envelope of $\chi(r)$ determined by the peaks of the oscillations. Denoting this quantity by $\langle\bar{\chi}(r_{\text{avg}})\rangle$ we take for Fe impurities in Pt

$$k_B T_f \approx \mu_{\text{Fe}}^2 \left(\frac{V_{ex}}{2\mu_B}\right)^2 2N(0)\,\frac{\Omega}{a^3}\langle\bar{\chi}(r_{\text{avg}})\rangle, \qquad (7)$$

where μ_{Fe} is the bare Fe moment. Without scattering, $k_B T_f = \mu_{\text{Fe}}^2 (V_{ex}/2\mu_B)^2\, 2N(0)x/4\pi$, where $x = n_{\text{Fe}}/n_{\text{Pt}}$ with $n_{\text{Fe}} = 1/r_{\text{avg}}^3$ and $n_{\text{Pt}} = 4/a^3$. With $x \approx 5$ ppm and $\mu_{\text{Fe}} = 3\mu_B$, we obtain for bulk Pt a value for T_f (2.1 mK/ppm) that is almost an order of magnitude greater than the observed 0.26 mK/ppm. Our rather large value of V_{ex} presumably contributes to this discrepency. Here, however, we are concerned with the effect of scattering on T_f, Eq. (7). In the presence of either ordinary or s-o scattering, $\bar{\chi}(r)$ falls off rapidly at large r. A rough numerical fit gives $\bar{\chi}(r) \sim \exp(-5\gamma_i r/a)$ for $r/a > 1/\gamma_i$ where $\gamma_i = \gamma_0$ or γ_1. Although a power law cannot be ruled out, the decrease is in any case much faster than $1/r^3$. We can thus conclude that the contributions to $\chi(r)$ we have calculated do not lead to a measurable T_f in the presence of scattering in granular Pt. However, at large r, diffusion-type diagrams for χ may be dominant leading to a contribution proportional to $1/r^3$ and independent of ordinary scattering. In Ref. [17] it was shown that these contributions are exponentially small in the presence of s-o scattering.

The single grain superconducting transition temperature T_c is affected by scattering only through the indirect effect on the spin fluctuation part of the pair interaction, λ_{SF}. There is no direct effect for ordinary or s-o scattering due to Anderson's theorem [18], for other scattering processes that obey time-reversal symmetry, and in zero magnetic field. To estimate the indirect effect we empoy the standard equation [7,19]:

$$T_c = \Theta_D \exp\left[-\frac{1 + \lambda_{ph} + \lambda_{\text{SF}}}{\lambda_{ph} - \lambda_{\text{SF}} - \mu^*}\right]. \qquad (8)$$

Here λ_{SF} is given by Eq. (3) but now with scattering included. We take $\Theta_D(Pt) = 234$ K and $\mu^* = 0.1$ which is a standard estimate. We assume $\lambda_{ph} \approx 0.41$ is not affected by scattering and it turns out that λ_{SF} is practically independent of γ_0, yielding a decrease of only a few percent in T_c. In Fig. 3 we plot T_c versus γ_1 for $\gamma_0 = 0.01$. The T_c's observed in Pt powders [1] are reached for a s-o scattering rate γ_1 less than 0.1 and that T_c increases strongly with increasing γ_1.

In conclusion, we have shown that ordinary and s-o scattering reduce μ_{gm} and T_f. On the other hand, s-o scattering weakens the spin fluctuations to the extent that the phonons dominate and superconductivity with $T_c \approx$ 1 mK can occur in single Pt granules. This is possible with moderate s-o scattering since the effective electron-electron interaction in bulk Pt is very close to zero [20]. Of the effects not considered here that could change T_c, phonon softening is probably the most important. To control surface phonon effects and to complement the studies of grains an experimental search for superconductivity in thin films of Pt is of interest. In very thin films (< 50 Å) with smooth surfaces the Rashba s-o splitting occurs throughout the film thickness and how the spin fluctuations in films of nearly ferromagnetic metals affect (spoil?) the Rashba effect is an open question. It would also be interesting to investigate thin films where the random surface roughness suppresses the Rashba effect and s-o scattering reduces λ_{SF}. Finally, in very small grains size quantization can influence the interplay between magnetism and superconductivity. We also have not discussed intergranular effects which may affect, e.g., the dependence of T_c on the packing fraction.

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