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 intra-grain 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 due to scattering effects in single small grains.

The recent observation of superconductivity in Pt grains of \( \approx 1 \mu \text{m} \) size at \( \approx 1 \text{mK} \) 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. The importance of the s-o interaction at surfaces has been shown by Merservey and Tedrow from a number of different measurements on superconductors. In Pb, for example, the probability that a conduction electron will change its spin direction in a surface collision is of the order 1. Taking into account s-o scattering, 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 paramagnon effects that inhibit singlet pairing in the late transition metals.

Why can s-o scattering generate superconductivity (sc) in Pt or other nearly ferromagnetic metals? In bulk Pt, no sc is observed despite a strong electron-phonon coupling; the BCS parameter is \( \lambda_{Pt} \approx 0.4 \). The reason for the absence of sc in bulk Pt is due to the strong exchange interactions between the itinerant 5d electrons. The resulting paramagnon effects suppress BCS s-wave sc. The Pt grains are small enough to have a large surface to volume ratio but are sufficiently large (\( \geq 100 \mu \text{m} \)) that the Bloch representation applies and we can ignore the Rashba effect. Although the "lattice softening" near surfaces may enhance \( \lambda_{Pt}^{s-o} \), 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. Independently of whether the sc extends throughout the grain or is restricted to a surface shell of thickness small compared with the grain size, 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. [3]. The Stoner factor \( S \) accounts for the average exchange and the spin correlation range \( \sigma \) measures the spatial range of the inter-atomic exchange. Scattering is included by considering the effect on \( \chi_0 \), the susceptibility without exchange enhancements. We find a significant effect of s-o scattering on \( \chi_0 \) that affects both \( S \) and \( \sigma \).

The susceptibility \( \chi(r) \) is then calculated to determine how scattering as well as exchange enhancement affects the RKKY (Ruderman-Kasuya-Kittel-Yoshida) oscillations occurring 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, namely, the magnitude of the giant moment \( \mu_{gm} \) 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 \( \mu_{gm} \); s-o scattering reduces \( \mu_{gm} \). 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 \( r \gg a (= \text{lattice constant}) \) in the absence of scattering effects. With scattering \( \chi(r) \) at large \( r \) is so strongly reduced that spin glass freezing would not be expected in the Pt grains where \( x = 4 \text{ppm} \).

We consider first the magnetic properties. The static q-dependent, exchange enhanced susceptibility \( \chi(q) \) in the presence of ordinary and s-o scattering is appropriate to describe the giant moments and spin glass freezing.
assume a susceptibility of the RPA form:

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

where $\chi_0(q) = N(0)u(q)$, $N(0)$ is the density of states (DOS) per spin for all three 5d sub bands 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 inter-atomic exchange interaction $J'(q) \equiv J'(0) - (qa)^2 J'_\text{eff}$ where $a$ is the lattice constant. We also define $U = N(0)U/3$, $J_H = N(0)J_H/3$, $J'(q) = N(0)J'(q)/3$, $U_{\text{eff}} = U + 2J_H + 3J'(0)$, and $J'_{\text{eff}} = N(0)J'_{\text{eff}}$ \cite{14}. Now $\chi(0) = 2\mu_B^2 S u_0$, where $S = 1/(1 - U_{\text{eff}} u_0)$ and $u_0 = u(0)$.

To define the spin correlation range, $\sigma$, we first expand Eq. (1) for small $q$. With $u(q) \approx u_0 + u_2(qa)^2$, Eq. (1) becomes

$$\chi(q) = \frac{2\mu_B^2 S u_0}{1 + \sigma^2 q^2}, \quad (2)$$

which yields a factor $\frac{1}{\sigma} e^{-q/\sigma}$ where $\sigma^2 = S\left[u_0 J'_{\text{eff}} - u_2 U_{\text{eff}}\right] - u_2/u_0$, in agreement with Clogston \cite{11}.

For arbitrary $q$ we model the susceptibility with

$$\chi(q) = \frac{2\mu_B^2 \chi_0(q)}{1 - I(q) \chi_0(q)}, \quad (3)$$

where $I(q)$ is a two parameter phenomenological interaction which is determined so that Eq.(1) reduces to Eq.(2) for small $q$. This yields $I(q) = N(0)I(q) = U_{\text{eff}} \left[1 + (qa)^2 J'_{\text{eff}}/U_{\text{eff}}\right]$. $U_{\text{eff}}$ is determined directly by $S$. We take $S = 3.8$ for Pt \cite{12} and find $U_{\text{eff}} = 0.737$. We fix $J'_{\text{eff}}$ to provide a reasonable value for the spin fluctuation induced effective mass enhancement $\lambda_{\text{SF}}$. As in the case of Pd, the problem here is to divide the effective mass enhancement $m^*/m = 1 + \lambda_{\text{SF}} + \lambda_{\text{ph}}$ between the phonon and spin fluctuation contributions. We assume that $\lambda_{\text{ph}}$ is about the same in Pt as in Pd and take the Pd value of $\lambda_{\text{ph}}^\text{Pd} = 0.41$. Assuming $m^*/m - 1 = 0.63$ for Pt \cite{12} we have $\lambda_{\text{SF}} = 0.22$. Employing the standard calculation of $\lambda_{\text{SF}}$ \cite{7},

$$\lambda_{\text{SF}} = \frac{3}{2} \int_{0}^{2k_F} q \, dq \frac{\left[I(q)\right]^2 u(q)}{2k_F^2 \left[1 - I(q) u(q)\right]}, \quad (4)$$

we find $J'_{\text{eff}} = 0.163$ which yields $\sigma = 3.21\text{Å}$. Physically, $\bar{r}_{\text{eff}}$ is a measure of the range of $\bar{I}(r)$ in position space. Increasing $J'_{\text{eff}}$ increases $\sigma$ and the range of $\bar{I}(r)$ but decreases the range of $\chi(q)$ in q-space yielding a smaller $\lambda_{\text{SF}}$ from Eq. (4).

Assuming the RPA form of Eq. (1) is not changed by the presence of scattering centers, one need only consider the effect of scattering on $\chi_0$. This was first done by de Gennes \cite{13} for ordinary scattering alone. He showed that $\chi_0(q)$ is not affected for $q = 0$. Fulde and Luther (FL1) \cite{14} calculated $\chi(q, \omega)$ for small $q$ and Julien \cite{15} extended this work to arbitrary $q$ and $\omega$. Spin-orbit scattering was later added to the ordinary scattering in FL2 \cite{16}. We use the result of FL2 for the effect of s-o scattering on $\chi_0$. As FL2 were primarily interested in obtaining approximate analytic expressions for the $\omega$-dependent susceptibility we employ however the formalism of Julien \cite{15} which is more suitable for computations. Equation (9) of Julien for $\chi_0$ with ordinary scattering alone, can be generalized to include s-o scattering by comparison with Eq.(14) of FL2. The result is

$$\chi_0(q, \omega) = \frac{i}{2\pi} \int_{0}^{\infty} d\omega \frac{Z(\omega) \left[1 - \pi k_F \gamma \gamma_1 Z(\omega)/3\right]}{1 - \pi k_F \gamma \gamma_1 Z(\omega)/3}, \quad (5)$$

where $Z(\omega) = \int \frac{d^3k}{(2\pi)^3} G(k, \omega) G(k + q, \omega + \omega_0)$, $\gamma_0 = 1/k_F \ell_0$ and $\gamma_1 = 1/k_F \ell_1$ with $\ell_0$ and $\ell_1$ the mean free paths for ordinary and s-o scattering, respectively. The single particle propagator $G$ contains the scattering rates in the combination $\gamma = \gamma_0 + \gamma_1$. 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 $\gamma_1$ corrections to $\chi_0(0)$ that are crucial in the following considerations. The computation of $\chi$ proceeds as in Ref. \cite{13} leading to the results shown in Fig. (1) where we take for Pt, $k_F = 0.642$ cm$^{-1}$ and $a = 3.923\text{Å}$. Fig. (1a) shows the large effect of s-o scattering on $\chi_0(0)$. In Fig. (1b) $S$, $u_0$, and $\sigma$ are shown vs $\gamma_1$. $S$ and $u_0$ do not depend on $\gamma_0$ and the dependence of $\sigma$ on $\gamma_0$ arises only through $u_2$ and is negligible.
We need the Fourier transform of $\chi(r)$ at small $r$ to calculate the induced spin polarization around an impurity moment and at large $r$ for the RKKY interaction responsible for spin glass transition. For $\chi(q) \to \chi_0(q)$ the Fourier transform can be done analytically yielding the usual RKKY oscillations. Integrating $\chi(r)$ over $d^3r$ leads directly to the sum rule

$$
\int d^3r \chi(r) = \chi(q = 0) = 2\mu_B^2 N(0) S u_0.
$$

(6)

$\chi_0$ alone does not provide a reasonable induced moment since the RKKY oscillations do not yield the necessary short range ferromagnetic correlations. This problem does not occur in our two parameter model for $\chi$ as can be seen from Fig. (2a). Here we plot the dimensionless susceptibility $\bar{\chi}(r)$ which is defined by $\chi(r) = 2\mu_B^2 N(0)/\hbar^2 a^3 \bar{\chi}(r)$, where $\hbar$ is the atomic volume ($a^3/4$ for the fcc lattice). The first effect of $U_{eff}$ is to shift the curve to larger $r$ increasing the spin correlation range $\sigma$, an effect discussed by Giovannini, Peter, and Schrieffer [7]. Further increasing $U_{eff}$ pushes the curve above the axis for small $r$. Increasing $J_{eff}$ has a similar effect. The solid curve for the Pt parameters provides both the ferromagnetic short range correlations and the long range oscillations necessary for spin glass freezing. The effect of scattering at small $r$ is shown in Fig. (2b). Ordinary scattering (dash curve) tends to smooth out the oscillations with little change in the area under the curve consistent with the sum rule, Eq. (6). Spin orbit scattering (dot-dash curve) on the other hand reduces the magnitude of $\chi(r)$.

The giant moments observed in the bulk PtFe [8] are not seen in the Pt powders [9] although, according to susceptibility measurements, 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 5d electrons 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

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

(7)

where $r_{gm}$ is the giant moment radius and $\sigma_s(r)$ is the isotropic spin polarization induced by the Fe moment at $r = 0$ due to the exchange interaction $V_{ex}$ between the 3d electrons of the impurity and the 5d electrons of the Pt host, $\sigma_s(r) = (V_{ex}/4) N(0) \mu_B \bar{\chi}(r)$ [4]. $N(0)$ is the DOS per spin and eV cm$^{-3}$. In order 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. (8): 

$$
\mu(h) \mid_{r_{gm} \to \infty} = V_{ex} N(0) a^3 \frac{\mu_B}{4}.
$$

We take $r_{gm} \sim 2.5 \mu \sim 10\text{Å}$ as in Pd and then fix the value of the local exchange coupling $V_{ex}$ by requiring that Eq. (8) yield $\mu(h) = 5 \mu_B$. We find $V_{ex} = 2.504\text{eV}$ which is somewhat large but still seems reasonable. Here we have used $N(0) = 0.386 (m^*_s/m)$ states/eV/atom with band mass $m^*_s/m = 3.36 [4]$. The effect of s-o scattering on $\mu(h)$ is shown in Fig. (3), where $\mu(h)$ from Eq. (8) (solid curve) and for $r_{gm} \to \infty$ (dash curve) are shown versus the s-o scattering parameter $\gamma_1$. It turns out that $\mu(h)$ is practically independent of ordinary scattering, $\gamma_0$. This can be seen from the sum rule result, $r_{gm} \to \infty$, since $S$ and $u_0$ are only affected by s-o scattering. Due to 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. (2b) 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 $T_f$ in dilute impurity systems 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 $\cos(2k_F r)/r^3$. 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 $<\bar{\chi}(r_{avg})>$ we take for Fe impurities in Pt

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

(8)

where $\mu_{Fe}$ is the bare Fe moment. Without scattering, $k_B T_f = \mu_{Fe}^2 (V_{ex}/2\mu_B)^2 2N(0) \sqrt{x}/4\pi$, where $x = n_{Fe}/n_{Pt}$ with $n_{Fe} = 1/r_{avg}^3$ and $n_{Pt} = 4/a^3$. Using this equation with $x \approx 5$ ppm and $\mu_{Fe} = 3 \mu_B$, we obtain for bulk Pt a value for $T_f$ ($2.1 \text{mK/ppm}$) 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 discrepancy. Here however, we are concerned with the effect of scattering on $T_f$, Eq. (8). In the presence of either ordinary or s-o scattering, $\bar{\chi}(r)$ falls off rapidly at large $r$. A rough numerical fit gives $\bar{\chi}(r) \sim \exp(-\gamma_i r/a)$ for $r/a > 1/\gamma_i$ where $\gamma_i = \gamma_0$ or $\gamma_1$. 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 χ(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. [8] it was shown that these contributions are exponentially small in the presence of s-o scattering. Thus it seems quite reasonable that no spin glass transition was observed in the Pt granules.

The single grain superconducting transition temperature T_c is affected by scattering only through the indirect effect on the spin fluctuation part pair interaction, λ_{SF}. There is no direct effect for ordinary scattering due to Anderson’s theorem which also holds for s-o scattering [11], for other scattering processes that obey time-reversal symmetry, and in zero magnetic field. In order to estimate the indirect effect we calculate T_c for s-wave pairing with the standard weak-coupling equation [7,20]:

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

Here λ_{SF} is given by Eq. [4] but now with scattering included. We take Θ_D(Pt) = 234 K and μ* = 0.1 which is a standard estimate. We assume λ_{ph} ≈ 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 γ_0 = 0.01. It is seen that the T_c’s observed in Pt powders [3] 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 affect the exchange enhanced magnetic properties of the itinerant d electrons so that μ_{gm} and T_f of PtFe_x, e.g., are reduced. On the other hand, s-o scattering weakens the spin fluctuations to the extent that the phonons dominate and superconductivity with T_c ≈ 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 [21]. 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 films one must distinguish between thick (> 100 Å) films where s-o scattering accounts for the surface effects on the 3D electron states and thin films with smooth surfaces where the Rashba s-o splitting occurs throughout the film thickness. How the spin fluctuations in very thin 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 surface roughness suppresses the Rashba effect and s-o scattering reduces λ_{SF}. Finally, the films can become so thin, or the grains so small, that size quantization of electron states occurs that may lead to new effects in the interplay between magnetism and superconductivity.

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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. 2a
FIG. 2. Dimensionless susceptibility $\bar{\chi}(r)$ without scattering vs. $r/a$. (a) Lower dash curve: $\bar{U}_{\text{eff}} = 0.737, \bar{J}'_{\text{eff}} = 0$; upper dash curve: $\bar{U}_{\text{eff}} = 0.92, \bar{J}'_{\text{eff}} = 0$; thick solid curve: Pt parameters, $\bar{U}_{\text{eff}} = 0.737, \bar{J}'_{\text{eff}} = 0.163$. (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, $\gamma_0 = 0, \gamma_1 = 0.2$. 
Fig. 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 $\gamma_1$. The dashed curve is the exact rule result for infinite giant moment radius.