High-field susceptibility and metamagnetism in Pd

T. Jarlborg
Physics Department and Materials Research Center, Northwestern University, Evanston, Illinois 60201

A. J. Freeman
Physics Department, Northwestern University, Evanston, Illinois 60201 and Argonne National Laboratory, Argonne, Illinois 60439

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The electronic structure and the magnetic properties of Pd metal in high magnetic fields have been determined from self-consistent semirelativistic spin-polarized energy-band studies with the applied field included. At low fields our results agree very well with the measured (exchange-enhanced) magnetic susceptibility and observed g-factor behavior. At a high critical field there is a large steplike increase in the magnetization (metamagnetic transition) with a net moment ($0.19\mu_B$) remaining after the field is reduced to ~ 100 T.

Itinerant metamagnetism in high magnetic fields has been a subject of continuing interest since its prediction for Pd and other strongly exchange-enhanced metals.[1] For such a field-induced first-order phase transition from the paramagnetic to the ferromagnetic state, free-energy arguments[1] focused on metals which have a maximum in the temperature dependence of the magnetic susceptibility. While metamagnetic behavior has been inferred or observed for several systems, no first-principles theoretical calculations have been reported in support of such observations. We report the first *ab initio* theoretical study of the electronic band structure, magnetic susceptibility, and magnetization in the presence of external magnetic fields which demonstrates the onset of a metamagnetic transition. At low fields our results for Pd metal agree very well with the measured (exchange-enhanced) susceptibility[2] and the qualitative behavior of the g factors determined recently by de Haas–van Alphen (dHvA) experiments.[3] At a high critical field, H_{crit}, there is a large steplike increase in the magnetization, m. These results indicate that while H_{crit} is too large (~ 300 T) to permit the observation of metamagnetism in pure Pd, its observation at lower critical fields is likely for Pd doped with low concentrations of magnetic impurities such as Ni or in the Au/Pd/Au sandwiches[4] which have been found recently to have enormously enhanced χ values at low temperatures. They also lend support to recent interpretations[5] of the positive deviations at high H from the linear dependence of the magnetization at low H (Ref. 6) as indicating possible metamagnetic behavior in $TiBe_2$.

Self-consistent semirelativistic linear muffin-tin-orbital (LMTO) energy-band calculations[7] were performed using the local-spin-density formalism and the exchange-correlation potential of Gunnarson and Lundqvist[8] as described earlier.[9] For a given applied external magnetic field, the spin-up and spin-down potentials are split by the field energy throughout the iterations until a saturation moment develops self-consistently. This procedure requires that the Fermi surface be well described throughout the self-consistency procedure so that small variations of the density of states (DOS) at E_F and magnetization m do not contain any unphysical "noise." For this reason we used many $\vec{k}$ points, 355 in $\frac{1}{48}$ of the irreducible Brillouin zone, in all calculations and the self-consistent convergence was monitored through the exchange splitting so that it was stable to within 0.1 mRy. The DOS and magnetization were calculated using the analytic tetrahedron scheme and these 355 independent $\vec{k}$ points. The zero-field DOS (34.0 states/Ry) is in good agreement with the value calculated self-consistently using the relativistic augmented plane wave (APW) method.[10]

From the exchange splitting $\xi_{\vec{k}}(H)$ obtained at each $\vec{k}$ point, we calculate the effective g factor, g_{eff}, as an average over the Fermi surface,

$$g_{eff} = \sum_{\vec{k}} \xi_k(H) \frac{\delta(E_F - E_{\vec{k}})}{n(E_F,H)\mu_B H} \quad .$$

(In this case, g_{eff} is isotropic since spin-orbit coupling is not included.) Here $n(E_F,H)$ is the total DOS at E_F in an applied field $\mu_B H$ (in Ry units) and $\delta(E_F - E_{\vec{k}})$ gives the local (at $\vec{k}$) DOS weighting factor. By integrating the difference of spin-up and spin-down DOS up to E_F, we obtain the magnetization as $m(H) = \int_{-\infty}^{E_F} [n_\uparrow(E,H) - n_\downarrow(E,H)]\, dE$ in units of Bohr magnetons per atom. The (exchange-enhanced) magnetic susceptibility $\chi(H)$ is given by $\frac{1}{2}g_{\rm eff}m(H)/\mu_B H$. [This gives $\chi(H)/\mu_B^2$ in units of e/atom Ry; multiplication with 2.21×10^{-8} gives $\chi(H)$ in emu/g.] The $\chi(H)$ values calculated at the two lowest applied fields 0.2 and 0.4 mRy ($\sim$46 and 92 T) are 6.0 and 7.0×10^{-6} emu/g, respectively, and agree very well with the experimental (low-field) value of 6.91×10^{-6} emu/g.[2] This extrapolated result ($\sim6.0\times10^{-6}$) lies between the too-low value of Janak[11] ($\sim3.1\times10^{-6}$) and the too-high value of Poulsen *et al.*[12] ($\sim11.2\times10^{-6}$) obtained using different calculational methods. Quite significantly, our calculated exchange enhancement of the susceptibility (here, $\frac{1}{4}g_{\rm eff}^2$) determined by extrapolating $g_{\rm eff}$ to low H is 7.8—a number in good agreement with an earlier estimate[13] determined from the measured temperature dependence of χ.

Figure 1 shows the Fermi surface (FS) obtained in the 0.4-mRy field (92 T) calculation from a 44-star Fourier fit to 89 $\vec{k}$ points; the line thickness gives the range of the exchange splitting on the spin-up and spin-down FS. The FS agrees well with the paramagnetic ones obtained in other calculations.[14] As seen, the numbers which specify the local g factors, obtained by $\xi_{\vec{k}}(H)$ divided by the 0.4-mRy field, are fairly constant around a value of 6.4. However, the large Γ-centered orbit, which also exhibits small FS splittings due to its higher mass, shows a significant $\vec{k}$ variation of the local g factor. Note especially that on the "knuckle" on the ΓX line, where the state has a large p admixture, the g value is reduced to less than $\frac{1}{2}$ of the average value and rises quickly away from the ΓX line. Recent dHvA studies of Zeeman splittings of the corresponding state in Pt,[3] were interpreted as resulting from a reduced g factor on the

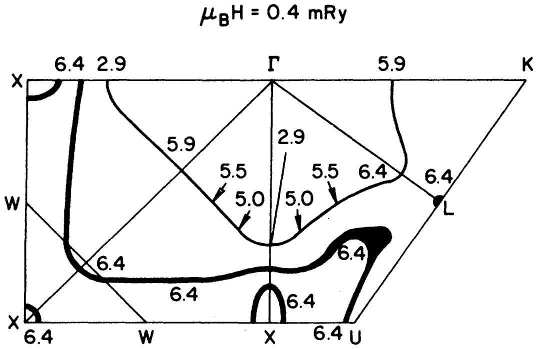

FIG. 1. Exchange-split Fermi surface at a field of 0.4 mRy ($\sim$0.9 MG). The numbers indicate the obtained g factors. Since the g factors are constant around 6.4 (except at the Γ-centered orbit on the ΓX line) the linewidth is inverse to the band mass. At the L point the majority and minority states are on opposite sides of E_F.

"X knuckle." The agreement with experiments for χ and the mentioned FS property gives us confidence that our calculations at higher fields, where no direct experimental data exist, are reliable. In this respect, it is interesting to note that a Fermi-surface plot for fields above 1.3 mRy shows that the "fin"-like structure in Fig. 1 has grown together with the small shaded area at L, giving a large spin-split region around K, U, and L. The merging of these two areas is possibly the triggering mechanism for the system to enter the metamagnetic state and is due to the crossing of the minority saddlelike band (van Hove singularity) with E_F which in the zero-field paramagnetic state lies $\sim$5 mRy below E_F in the WLK region of the zone.

Figure 2 shows the calculated DOS at E_F, the effective g factor, susceptibility χ, and magnetization m for different fields up to 2.6 mRy (600 T). The total DOS is remarkably flat until $\sim$300 T ($\sim$1.3 mRy), where it undergoes a drop and decreases further with increasing magnetic fields. By contrast $g_{\rm eff}$ and χ first rise slightly and then drop off rapidly until $H_{\rm crit}$ is reached whereas m is roughly linear at low fields and then saturates before the sudden increase at $H_{\rm crit}$. This almost steplike increase in $g_{\rm eff}$, χ, and m indicates the onset of a metamagnetic phase transition in agreement with its prediction[1] but at a considerably higher $H_{\rm crit}$ than estimated[5] using paramagnetic DOS information. Figure 2 also demonstrates a strong hysteresis effect of the magnetization with applied field. Starting with the magnetized state above the metamagnetic transition and gradually *reducing* the strength of H, the self-consistent results show m to be fairly stable at about $0.19\mu_B$/Pd until a low-field value ($\sim$80 T) is reached. Below this value of the supporting field, the system cannot sustain a net magnetization. The appearance of hysteresis in the observed magnetism of $Co(S_xSe_{2-x})_2$ was cited by Wohlfarth[15] as evidence for a metamagnetic transition and arising from tunneling if the free-energy function has a second minimum at a finite value of m which is below that at $m=0$.

While $H_{\rm crit}$ is too large for metamagnetism to be observed in Pd metal, there are conditions that may cause the transition to occur at lower fields and hence make its observation likely. For example, the Pd layers in Au/Pd/Au sandwiches show enormously enhanced[4] susceptibilities over that of bulk Pd. Here the Pd lattice constant, a_0, is stretched by the strain field of the larger a_0 of the Au lattice, the bandwidth narrows and thereby increases the DOS at E_F and produces a giant Stoner enhancement factor. Hence a much reduced critical field is to be expected. Another possible way to reduce $H_{\rm crit}$ is to add dilute amounts of impurities like Ni which provide an internal (exchange) field. Pd becomes an itinerant ferromagnet upon addition of[16] 2.3 at.% Ni and exchange-split de Haas–van Alphen signals have

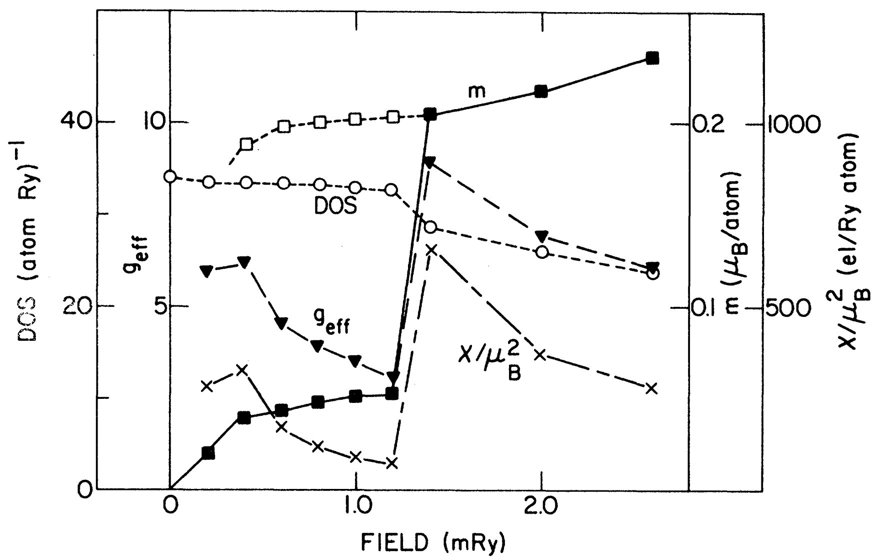

FIG. 2. Density of states n (circles), susceptibility χ (crosses), g_{eff} (triangles), and magnetic moment m (squares) as function of applied field H, given in mRy. The open squares are the moments when the field is reduced from above the metamagnetic transition at ~ 1.4 mRy. One mRy is equal to 2.3 MG or 230 T.

been observed. A crude estimate of the internal exchange field produced by 2.3 at.% Ni impurities, made by scaling the exchange splitting[9] (35–40 mRy at E_F) in Ni metal, yields an average field of 180–200 T (0.8–0.9 mRy) which is of the order of our calculated external H_{crit}.

This demonstration of metamagnetism in Pd provides strong theoretical support for its possible occurrence also in other systems.[5] Thus, for example, Wohlfarth has interpreted the high-field-magnetization data on $TiBe_2$, which show a positive deviation from the linear dependence seen at low H, as indicating possible metamagnetic behavior. Like Pd, this strongly exchange-enhanced (large Stoner factor) material, has strong Fermi-surface nesting features and an E_F that falls close to a very high and narrow DOS peak.[17] Based on the results presented here, metamagnetic behavior also appears likely in $TiBe_2$.

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