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Observation of a Strongly Enhanced Magnetic Susceptibility of Pd in Au-Pd-Au Sandwiches

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Exceptionally large increases in the magnetic susceptibility (indicating nearly magnetic ordering) of thin films of Pd sandwiched between thicker Au films have been observed at low temperatures—presumably due to the expansion of the Pd average lattice constant by the Au. The large resultant Stoner factors and the modified paramagnon model of Levin and Valls indicate the possibility of observing p-wave superconductivity in Pd structures with reduced proximity effects.

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Magnetism has been sought in Pd metal since the first recognition of its "incipient ferromagnetic" nature and the large effects of spin fluctuations.[1,2] With its high density of states at the Fermi energy and large Stoner exchange enhancement ($S \simeq 10$), it is easily polarized by dilute magnetic impurities leading to giant magnetic moments, and often to ferromagnetism at relatively high temperatures. More recently, interest in p-wave superconductivity has focused on Pd as a most likely candidate[3,4] because it has the largest value of S for pure metals; however, experimental studies[5] with very pure samples yield no superconductivity down to 1.7 mK. The observation of superconductivity[6] in irradiated Pd at $T_c \leq 3.2$ K demonstrates that drastic changes in the electronic and magnetic properties of a metal with large S may be expected with changes in its structure, presumably in this case because the disorder suppresses the spin fluctuations.

It is well known that changes in the properties of materials are often caused by application of high pressures which decrease the lattice parameter, a_0, but do not otherwise affect their basic structure. Obviously, the common use of alloying methods to *increase* a_0 is not satisfactory for studying intrinsic magnetism/superconductivity in Pd. Instead, we have prepared thin films of Pd, presumably with expanded lattice parameters, sandwiched between thicker Au films. We hoped to obtain large increases in the Stoner factor and hence to increase the possibility of producing either ferromagnetism or p-wave superconductivity in pure Pd.[7] This Letter reports the first successful observation of exceptionally large increases in the magnetic susceptibility, χ, of pure Pd in these sandwiches at low T. The films do not show magnetic order ($T \geqslant 2.2$ K) or superconductivity ($T \leqslant 0.05$ K). From the results of band calculations on Pd at negative pressure[8] and our measured χ values at low T we derive very large values of S (~350–25 000) for the sandwiches. Since large S values in the modified paramagnon model of Levin and Valls[4] for superfluid ^{3}He yield sizable values of T_c from p-wave pairing superconductivity in the absence of magnetic ordering, we suggest the possibility of superconductivity in similar expanded Pd systems.

During deposition of metal A on a single crystal of an isostructural metal B, the initial layers of A form with an a_0 between those of A and B.[9,10] As the A layer thickens, its a_0 relaxes towards the normal value; thus there is a limit to the thickness of the modified a_0. The results reported here are for Pd ($a_0 = 0.3890$ nm) deposited on the (001) face of Au films ($a_0 = 0.4078$ nm). The large misfit, 4.72%, leads to an expanded a_0(Pd), calculated to be $\lesssim 2.5\%$, and to relaxation within several layers.[10] In order to stretch as many Pd layers as possible, the samples were prepared as Au-Pd-Au sandwiches to lock the expanded Pd lattice from both sides. Of course, since each layer of Pd atoms has a different a_0 and tetragonal distortion, the experimental data result from an averaging process. Transmission electron microscopy of a single Au-Pd-Au sandwich shows the layers to be epitaxial. Moiré fringe patterns from (200), (220), and (311) give $\Delta a_0/a_0$ of (0.4–2.5)%, with an average of 1.8%, for Pd on Au.

Au-Pd-Au films were vaporized onto cleaved NaCl(001) crystals at rates of 0.1–0.3 nm/sec. Although pressure rises up to 5×10^{-7} Torr (~5×10^{-5} Pa) were observed during some evaporations, oxygen partial pressures were always below 1×10^{-8} Torr. Typically, samples consisted of up to twelve sandwiches of 1–1.5-nm-thick Pd (3–4 atom layers) and 10-nm layers of Au. The total Pd mass in a sample ranged from 3 to 193 μg. Sample thicknesses were followed with quartz monitors, and verified by weighing standard area targets. Standard Faraday measurements of χ were made between 2.2 and 300 K, usually only at 1.45 T, with a sensitivity of 0.001 (and 0.03) emu/(g-atom) for multiple (and single) Pd sandwiches. The results, summarized in Table I, are to be compared to $\chi(\mathrm{Pd}) = 0.0007$ emu/(g-atom) at 2 K. For seven out of nine Pd-Au samples, χ is well in excess of the value for normal Pd. The largest χ's were obtained with samples IV and XIII, for which the first Au layer was deposited epi-

TABLE I. Properties of Pd sandwich films.

Sample	No. of Pd layers	Largest χ [emu/(g-atom)]	θ_{CW} (°K)	p_{eff} (μ_B/Pd)
II-1	5	0.029	b	b
II-2	5	0.10	−3.4	2.2
III	5	0.020	−4.6	1.0
IV[a]	1	0.36	−7.6	5.4
V	12	0.006	b	b
VIII	1	0.07	b	b
XIII[a]	1	0.20	−0.1	1.8
VI	5	0	...	...
VII	1	0	...	...
IX-Al-Al	0	0	...	...
X-Pt-Pd-Pt	1	0	...	...
XIV-Au-Au[a]	0	0	...	...

[a] Grown epitaxially.
[b] Temperature dependence not obtained.

taxially.[10] Samples IX (Al-Al) and XIV (Au-Au), both made *without* Pd, showed no magnetic effect. Also, sample X, made with Pt-Pd-Pt, whose mismatch in a_0 is only 0.9%, yielded no observable magnetism. Apparently this small expansion of the Pd lattice is not sufficient to yield a measurable effect. Over the limited T range of useful measurements, the data fit a Curie-Weiss law,[11] $\chi = C/(T-\theta)$ (see Fig. 1). The least-squares results are given in Table I. The small negative θ's and large χ's are indicative of the samples becoming nearly ferromagnetic. Within a spin fluctuation model,[2] T_{sf} ($\simeq -\theta$) has decreased to $\simeq 1-8$ K from $\simeq 320$ K for normal Pd.

The fragility of the expanded Pd films was seen when sample VII was crumpled during mounting and there was no observable paramagnetism. Presumably, the dislocation motion relieved the strain, i.e., expansion, in the Pd film and/or enhanced interdiffusion. A further example of the effect of wrinkling on the stability of expanded Pd is seen for sample II-1 vs II-2. Both were taken from the same deposition but II-1 was wrinkled during mounting, and a larger effect (~a factor of 4) is seen for II-2. Since the data for II-2 were taken one day later than for II-1, the decay with time (see below) may have masked an even larger difference. All samples showed a decrease of χ with storage time, presumably due to the effect of mutual Pd-Au solid solution formation. In some cases, Pd color could be seen after deposition because the Au and Pd beams were not perfectly aligned. In all such cases, only the gold color was seen after two weeks, indicating alloying due to diffusion. The decrease in χ was a factor of 2 after one day for II-2, and total disappearance of the enhancement occurred after two weeks. Storage at $\lesssim 100$ K was an effective retardant of the decay. The use of multiple layers did not yield a larger measurable effect. It is likely that the very low energy needed to convert a 3–4 atom layer of expanded Pd to normal Pd could be easily obtained from the subsequent atom beams. An additional advantage of the sandwich technique used here is shown with VII, prepared as Au(115 nm)-Pd(1 nm) with an epitaxial Au film, but with no covering Au layer. The sample curled severely when floated off the NaCl because of the marked difference in surface tension of the two surfaces and it was impossible to mount VII without wrinkling the films. Thus, the measured $\chi \simeq 0$ is not surprising.

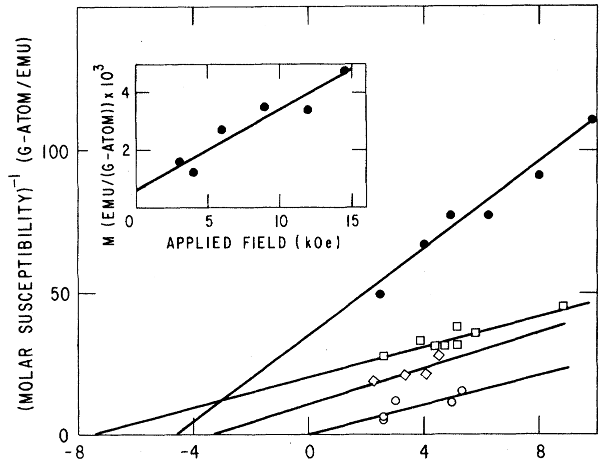

FIG. 1. χ^{-1} vs T for samples II-2 (diamonds, $\chi^{-1}\times 2$), III (closed circles), IV (squares, $\chi^{-1}\times 10$) and XIII (open circles). Inset shows magnetization vs applied field for sample IV at 2.60 K.

Sources of enhanced magnetism other than expanded Pd that must be considered are the following:

(1) *Accidental impurities (e.g., Fe).*—Because the paramagnetism disappears with time or with mechanical working, the large measured χ cannot be caused by magnetic impurities in the Au-Pd-Au sandwiches. The process of mounting the films for study does entrap some NaCl, which is diamagnetic.

(2) *Entrapped O_2.*—The strongest argument against O_2 being the source of the effect observed here is seen for samples XIII (Au-Pd-Au) and XIV (Au-Au). These were prepared one after the other and studied immediately. The oxygen partial pressure during the evaporation of XIII was never above 1.4×10^{-10} Torr, and during the evaporation of XIV was $\leqslant 2.4\times10^{-10}$ Torr. No measurable effect is seen for XIV (no Pd) while the data for XIII behave similarly to those for II, III, and IV. For sample III, the susceptibility system was evacuated at 325 K and recooled to 2.4 K, again yielding the enhanced paramagnetism. Furthermore, no correlation was observed between the magnitude of χ with oxygen pressure during the various evaporations, with the number of separate films deposited, or with the total amount of Au and Pd deposited. In addition, the lack of an observable effect for samples IX (Al-Al) and X (Pt-Pd-Pt) is also a strong argument against O_2 as the source of the enhanced magnetism.

Enhanced magnetism for expanded Pd is not surprising since it is known experimentally that Pd becomes less magnetic when compressed. Energy band calculations[8] on expanded Pd yield an 8.4% increase in $N(E_F)$ for a 2.3% increase in lattice parameter. Since the Pd in the Au-Pd-Au sandwich undergoes a tetragonal strain it may not have the same increase in $N(E_F)$ as normal Pd. With $\chi = S\chi_0 = \chi_0[1 - VN(E_F)]^{-1}$, where χ_0 is the noninteracting or band susceptibility and V the electron-electron interaction, changes in $N(E_F)$ and/or V will produce large changes in χ. The extreme sensitivity of S to changes in $N(E_F)$ is well known. For pure Pd, with $VN(E_F) = 0.9$, $S = 10$, and V constant, a 10% (or 11%) increase in χ_0 yields $VN(E_F) = 0.99$ (or 0.999) and $S = 100$ (or 1000). The sensitivity of S to changes in V is seen if one uses the calculated increased[8] $N(E_F)$, now held constant. For $\Delta V/V = 2.5\%$, S becomes enormous (10^5). Thus, very slight changes in the weighted average of a_0, χ_0, or V for the expanded Pd films lead to dramatic variations in the observed values of S.

Two methods may be used to give crude estimates of the magnitude of S from the present data. Since $\Delta\chi_0/\chi_0$ is small,[8] $\Delta\chi/\chi \approx \Delta S/S$. The value of $\Delta\chi/\chi$ at 0 K obtained from the least-squares fits in Fig. 1 yields a range of S values from 350 to 25 000. Alternatively,[2] the definition of S is $S = T_0/T_{sf}$; T_0 is the degeneracy temperature, taken here as the difference between the top of the d band and E_F. A value of $T_0 = 2800$ K for the present case, 2.3% expansion, seems reasonable.[2,8] As before, we take $T_{sf} \simeq -\theta$, which yields S values ranging from 370 to 28 000. Since neither of these estimates is rigorous and because the inhomogeneity of the Pd films may project differently in the two calculations, the two sets of S values may not agree. However, as shown in Fig. 2, there is a general correspondence between the two sets of S values.

In all estimates of p-wave pairing induced superconductivity, a large (but not too large) value of S is favorable for superconductivity. For example, Fay and Appel[3] calculate a maximum $T_c = 0.5$ K at $S = 70$ for Pd within the paramagnon model. Using a modified paramagnon model in conventional strong coupling theory for superfluid ^{3}He, Levin and Valls[4] showed that T_c reaches a maximum ($\simeq 8 \times 10^{-4}\ T_0$) for $S = 200$, and is reduced to $\sim(\pm 0.5) \times 10^{-4}\ T_0$ for $S = 10^4$. While not quantitatively applicable to our Au-Pd-Au sandwiches because of large solid-state effects not found in ^{3}He, these theoretical estimates and our large calculated S values indicate the possibility of observing p-wave pairing superconductivity in these systems at finite temperatures. However, since the proximity effect (if not possible microscale magnetic ordering at temperatures below those obtained in the present work) will reduce T_c to zero in our thick layer Au sandwiches, measurable superconductivity may occur only for thin sandwiches.

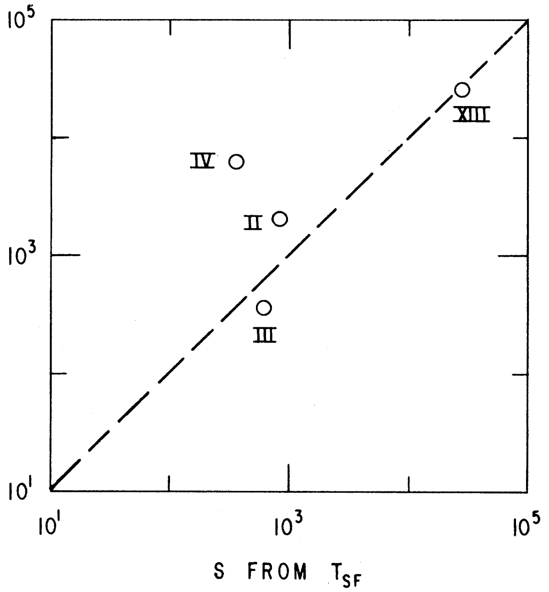

FIG. 2. Stoner factor calculated by the two methods described in the text.

The possibility of expanding the Pd still further, e.g., with[9] Ag-Pd-Ag ($\Delta a_0/a_0 = 0.0491$ vs $\Delta a_0/a_0 = 0.0472$ for Au-Pd-Au) is being explored. More stable films may be obtained by depositing Pd on bcc substrates, where there is no mutual solubility.[12] In the latter case, it would also be possible to examine the effects of the Pd films on superconducting bcc films via the proximity effect.

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Four-Spin Exchange Model and ^{3}He Magnetism

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A two-parameter model based on three-spin exchange and planar four-spin exchange gives at low field a first-order transition to the ordered phase suggested by Osheroff, Cross, and Fisher and at high field gives a second-order phase agreeing with the experiments of Godfrin *et al*. and Adams *et al*. It also fits well the high-temperature expansion coefficients and the susceptibility of the low-field phase.

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Four experiments[1-4] have recently been reported which clarify the nature and location of the magnetic phases of solid ^{3}He. Figure 1 summarizes their contributions. The work of Adams *et al.*[3] has confirmed that the high-field branch of the phase diagram is a second-order phase transition and has given information about possible phase structures below the transition temperatures. Godfrin *et al.*[4] have followed a feature which seems to correspond to this phase line to the region of 7 T and 3 mK. The work of Prewitt and Goodkind[2] has confirmed the first-order nature of the transition below 0.41 T and discovered another phase transition line below the second-order transition at about 0.42 T.

Finally and most remarkably the experiment of Osheroff, Cross, and Fisher[1] on single crystals of ^{3}He below the phase transition and at low field indicates that the magnetic structure of that phase is probably of the 100 up-up-down-down (uudd) form, and in any case the sublattice structure is not cubic and is characterized by a vector along the 100 direction.

Of the theories put forward to explain the magnetic properties of solid ^{3}He magnetism[5] only the idea that four-particle ring exchanges are large enough to induce first-order transitions[6-8] still seems viable. We show that this theory can explain all the measured high-temperature coefficients and give an approximate phase diagram.

The kinds of exchanges which we might have considered include (i) nearest-neighbor exchange $J(nn)$, (ii) three-particle ring exchange J_t, (iii) four-particle planar ring exchange K_P, (iv) four-particle folded ring exchange K_F. K_F and K_P lead to four-spin terms in the Hamiltonian.[9] Other exchanges such as two-particle second-neighbor exchange or five-particle ring exchange are expected to be smaller.[8,10] Early calculations[11] indicated that the four-spin exchange terms were very small but those calculations were based on variational wave functions which could not be correct on the tunneling path. Estimates of the wave function inside the tunnel indi-