Superconductivity in an Ag-Pd-Ag epitaxial metal film sandwich

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Superconductivity is observed in an epitaxial metal film sandwich of Ag-Pd-Ag, with $T_c = 2.15$ K, initially. Room-temperature storage caused T_c to drop to 1.00 K after 180 days, and the T_c decrease was accompanied by development of a resistivity minimum. The large orbital contribution to H_{c2} 70 kOe/K, is comparable to those found in high H_{c2} Chevrel-phase materials.

The possibility of superconductivity in Pd has been considered by many authors.[1-6] In general, s-wave pairing has not been seen[3] because of large paramagnetic fluctuations which prevent Cooper pairing. Whereas, p-wave pairing superconductivity may be possible for highly exchange-enhanced materials, including Pd,[2,7] surface-derived fluctuations may lead to ferromagnetism rather than superconductivity.[5] Superconductivity has been observed in irradiated Pd at 3 K,[4] where it is likely that the induced defects modify the paramagnon repulsions. This Communication reports on the observation of superconductivity in an epitaxial metal film sandwich (EMFS) of Ag-Pd-Ag, with a maximum T_c of 2.13 K.

It has been shown that in Au-Pd-Au EMFS, extremely large exchange enhancements, $S \simeq 10\,000$, can be obtained because of the combination of Pd-lattice stretching and a tetragonal distortion at the Pd-Au interface.[8,9] Furthermore, the spin-fluctuation temperature, T_{sf}, was seen to drop from 260 to 0.1–10 K, i.e., the Pd was very nearly ferromagnetic. Although the Fay and Appel treatment[2] might suggest a finite superconducting transition for the Au-Pd-Au samples with $S \simeq 10\,000$, no such transition was found down to 0.010 K.[8] Since Ag and Au have nearly the same lattice parameters (0.4086 and 0.4078 nm, respectively), it was reasonable to assume that nearly equivalent results might be obtained with Ag-Pd-Ag EMFS. As was noted in Ref. 8, there was a strong time dependence of the large enhancements in the magnetic susceptibility, X, with storage at room temperature, and all of the observable enhancement was lost within four days. Possible interdiffusion of the metals is especially important in the case of Ag-Pd-Ag, where it has been well documented that strong localization of the d band on Pd sites occur in Ag-Pd alloys,[10] and this may lead to local moment behavior, as evidenced by minima in the resistivity temperature, ρ-T, curves.[11]

As before[8] samples were prepared in the (100) orientation by deposition on freshly cleaned NaCl(100) in an UHV system. Base pressures of $< 1 \times 10^{-9}$ torr ($\sim 10^{-7}$ Pa) were always obtained, and during depositions the pressure remained below

2×10^{-8} torr. The first Ag film was deposited at 300 °C, the substrate was cooled to 30 °C in one hour, and the subsequent depositions were carried out at room temperature. Nearly all samples were studied by electrical resistivity along the sheet, with samples that had been floated onto Au leads deposited on sapphire or mica. As samples were floated off the salt, they tended to curl slightly but were mainly flat when dried on the mica or sapphire. One sample, XVIIA 1, curled into a cylinder in the alcohol-water solution and dried as a flattened cylinder. As will be shown below, this was the only one of nine Ag-Pd-Ag samples to become superconducting. Most of one of the depositions was used to measure X as well. Typical film thicknesses, e.g., XVIIA 1 were Ag(170 nm)-Pd(2 nm)-Ag(170 nm).

Figure 1 shows low-temperature ρ-T data for two samples. The curve in the inset of the figure is for sample XVIIA 3 and is typical of all samples measured, except for XVIIA 1 (the sample numbering designation means that both of these samples were
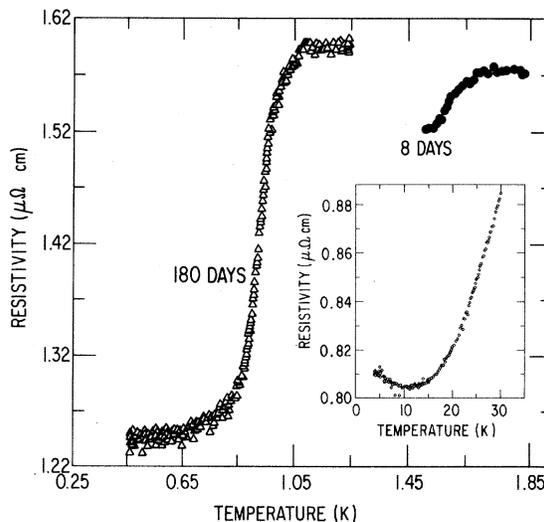

FIG. 1. Low-temperature resistivity-temperature curve for sample XVIIA 1 taken after 8 and 180 days at room temperature. The inset shows data for sample XVIIA 3.

deposited at the same time, onto the same piece of NaCl, but were demounted and remounted at different times). That is, there is a minimum near 10 K in the ρ-T curve, and measurements down to 0.4 K still show a negative $d\rho/dT$.

Conversely, the data for XVIIA 1 show a residual resistivity at about 4 K, and a subsequent drop of 6% in the ρ below 2.15 K. As is shown in Fig. 1, after 8 days at room temperature (and several thermal cycles between 300 and 1.4 K), the ρ drop occurred at 1.65 K, and was 3.5% of the total ρ. After 10.5 days at room temperature, no ρ drop was seen down to 1.46 K. Measurements made much later in a ^{3}He cryostat showed that the ρ drop now occurred at 1.05 K, was 22% of the total ρ, and clearly showed a residual ρ. The data in Fig. 1 are after 180 days at room temperature. After sample XVIIA 1 had been stored at room temperature for 58 days, a shallow minimum was seen at 12 K.

Measurements of χ on sample XXVII yielded 0.07 ± 0.02 emu/(g atom), with no discernible temperature dependence between 2.5 and 6.7 K. This corresponds to $\Delta\chi/\chi \simeq 100$ and $S \simeq 1000$. Thus S for this sample is comparable to those of the Au-Pd-Au samples discussed before,[8] indicating a strengthening of the paramagnons. However, the probable lack of a temperature dependence is indicative of the uniform enhancement discussed by Béal-Monod[5] as a necessity for p-wave superconductivity.

Figure 2 shows the low-temperature ρ-T data with magnetic fields applied perpendicularly to the sample. As is seen in the figure, only relatively low fields are needed to shift the ρ drop to lower temperatures, and ultimately to prevent its observation at 0.40 K. Parallel magnetic fields have a similar effect, but higher fields are needed for a comparable shift in the "transition temperature." These are plotted in Fig. 3 as critical field versus critical temperature (taken as the temperature at which ρ drops by 10% of the total drop at $H = 0$). These curves are clearly the signature of a superconducting transition. The lack of a zero ρ at low temperatures may be due to a large normal-state proximity effect, or to incomplete connectivity of the 2-nm-thick Pd film. Normal-state proximity effects have yielded nonzero ρ's in earlier studies on superconductors also.[12]

As was shown by Tinkham,[13] $H_{\parallel}/H_{\perp} = 2\lambda\sqrt{3}/d\kappa$. We find $H_{\parallel}/H_{\perp} = 8.05$, where λ is the penetration depth, κ the Ginzburg-Landau parameter, and d the Pd film thickness. Thus, for $d = 2.0$ nm, the coherence length, $\xi = \lambda/\kappa = 4.6$ nm and $d < \xi$. Therefore, the system is in the mixed state even for $H = 0$, and the data in Fig. 3 are representative of $H_{c2\parallel}$ and $H_{c2\perp}$. There is no hysteresis in heating and cooling curves, and therefore the transitions appear to be of second order. Thus, $\lambda > d/\sqrt{5}$, and $\kappa > 0.19$. There is an apparent curvature in $H_{c2\parallel}$ near $T_c(0)$. which is similar to results for layered Al-Ge samples.[14] Curvature
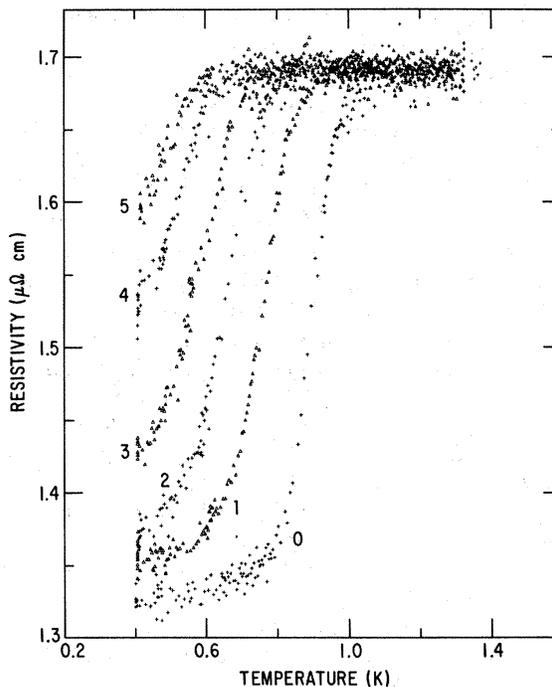

FIG. 2. Field dependence of the ρ-T results for sample XVIIA 1, taken after 180 days at room temperature. The magnetic field is perpendicular to the plane of the sample and applied fields in kOe are indicated.
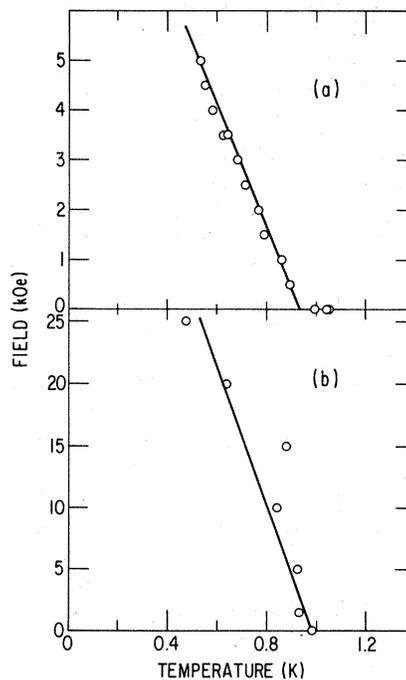

FIG. 3. Critical field vs temperature for sample XVIIA 1; (a) H perpendicular to film and (b) H parallel to film.

in H_{c2}-T_c plots for layered compounds are seen in both $H_{c2\parallel}$ and $H_{c2\perp}$.[15] However, the source of the curvature is not understood. In the present case, the curvature could be attributed to a varying critical behavior as a function of lattice plane (and, therefore a_0) but this would be expected to occur in $H_{c2\perp}$, also.

It should now be possible to estimate the orbital contribution to H_{c2}, $(dH^*_{c2\perp}/dT_c)_{T_c}$. It is expected, as in the case of Au-Pd-Au where $\Delta a_0/a_0$ is essentially the same, that $N(E_F)$ is increased by 8.4% because of the stretched lattice.[8] Further, Gyorffy et al.[6] have shown that the total mass enhancement factor, made up of the electron-phonon and spin-fluctuation contributions ($\lambda_T = \lambda_{ep} + \lambda_{sf}$), is a strong function of composition in Pd-Ag alloys, and thus of $N(E_F)$. Whereas Gyorffy et al.[6] obtain $\lambda_T = 0.72$ for bulk Pd, an extrapolated value of 1.1 is obtained when λ is scaled with $N(E_F)$ using Fig. 2 of Ref. 6. Thus the electronic specific-heat term, $\gamma = \gamma_0/(1+\lambda)$, becomes 12.6 mJ/(g atom K^2) for the stretched Pd films versus 9.4 in the bulk.

The calculation of ρ_{Pd} is not straightforward for these thin film samples. It has been found in Au-Cr-Au EMFS (Ref. 16) that the mean free path, $l \simeq d$. From this, and the measured total ρ above T_c, it is possible to determine a range of ρ_{Ag} values in the sample which yield physical results for ρ_{Pd}. These are $\rho_{Ag} > 1.590$ $\mu\Omega$ cm, and ρ_{Pd} grows very rapidly as ρ_{Ag} approaches this limit. At 20 K, Meaden[17] gives $\rho_{Pd}/\rho_{Ag} = 9.5$, which is nearly the ratio of the respective $N(E_F)$'s (8.6). Scaling this with the increased $N(E_F)$ for the stretched Pd, yields $\rho_{Pd}/\rho_{Ag} = 10.3$, or $\rho_{Pd} \simeq 16$ $\mu\Omega$ cm. Such a large ρ, compared to bulk Pd, means that $d/l \ll 1$.

In the case of dirty superconductors,[18] $\xi \sim l$, $(dH^*_{c2}/dT)_{T_c} = 4.44 \times 10^4 \rho\gamma$ or 10.1 kOe/K for the Pd in sample XVIIA1, where H^*_{c2} is the orbital contribution to H_{c2} and ρ and γ are given above. The ratio of H^*_{c2}(clean)/H^*_{c2}(dirty) $\simeq l/\xi_0$. Working backwards as has been done for the Chevrel-phase compound PbMo$_6$S$_8$,[18] the ratio of the measured slope of Fig. 3 (71.0 kOe/K) and the calculated value, coupled with $\xi = 4.6$ nm yields $l = 32$ nm. Thus, $d/l \ll 1$, as was derived above. Also, from Ref. 18,
$$H^*_{c2}(0) = 3.06 \times 10^4 \rho\gamma T_c = 48.9 \text{ kOe for sample}$$
XVIIA1, with $T_c = 1.00$ K as for the data in Figs. 2 and 3. The Maki parameter, α, may also be obtained from the slope of $H_{c2\parallel}$ vs T_c,[18] yielding $\alpha = 3.7$. With data only down to $0.4 T_c$, it is difficult to get a reliable estimate for λ_{so}, the spin-orbit coupling parameter. However, a value of $\lambda_{so} \gtrsim 4$ is necessary in order to have $H^*_{c2}(0)$ below the paramagnetic limit, $H_p = 1.33 H_{p0}\sqrt{\lambda}$, where H_{p0} is the Clogston limit ($H_{p0} = 18.4 T_c$). A comparison of the apparently straight line of $H_{c2\parallel}$ vs T down to $0.4 T_c(0)$ to data for Chevrel-phase compounds shows similar

behavior, i.e., nearly straight lines until $T \lesssim 0.3 T_c$, and $\lambda_{so} > 4$.

The very large H_{c2} vs T slope of 71 kOe/K is comparable to that of LaMo$_6$Se$_8$ but with $T_c = 10.8$ K and $H_{c2}(0) = 445$ kOe, which is surprising considering the much lower T_c and $H_{c2}(0)$ estimates for Ag-Pd-Ag. Part of the answer must lie in the proximity effect due to the relatively large normal-state Ag thicknesses. Using the de Gennes equation[19] and the BCS pairing potential of bulk Pd, the reverse result is obtained, i.e., thinner layers of Ag yield lower T_c's. This is probably a result of V_{Pd} being too low for stretched Pd. Lacking the value for stretched Pd, the estimate of the proximity effect cannot be carried out.

If the Pd superconductivity observed here is simply due to s-wave pairing, then in the spirit of Refs. 4 and 6, it may be argued that a slight amount of Pd-Ag intermixing has caused the reduction of the spin-fluctuation effect on Cooper-pair production. The $N(E_F)$ may still be higher than in bulk Pd due to stretching and lattice distortion at the Pd-Ag interface. The drop in T_c with time and the development of a ρ minimum with time for sample XVIIA1, and the existence of the ρ minimum in the nonsuperconducting samples is probably related to further intermixing. This leads to alloy formation. It is well known that ρ minima in Pd-Ag are related to localization of the d states.[11] Thus the strongly intermixed samples still have strong spin fluctuations, a reduced $N(E_F)$ and, therefore, no observable superconductivity.

In view of the $S \simeq 1000$ obtained for sample XXVII, it might be argued that the superconductivity, here, is due to p-wave pairing. This is especially tempting since this value for S is near the value which yields the maximum T_c,[2,7] and since no temperature-dependent[5] χ was observed for sample XXVII, conversely to the results for Au-Pd-Au.[8] Within this model, the time-dependent effects are again due to intermixing, and disorder is known to have very strong effects on p-wave superconductivity. The question of s- versus p-wave pairing, cannot be resolved until more superconducting samples can be prepared, and characterized by tunneling studies.[20]

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