and near infrared is due to resonance absorption in the silver particles. A solid continuous specular film of silver reflects most of the light incident on it in the visible and hence has a low quantum yield. Another factor is that most of the silver particles are smaller than the electron scattering length and hence the escape probability of photoelectrons from small particles is higher than from a semi-infinite solid. The resonance absorption, however, appears to be the dominant enhancement mechanism.[17]

Discussions with Dr. A. H. Sommer on the S-1 photocathode have been extremely valuable.

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Proximity-Effect Tunneling in Pd-Pb Sandwiches

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Tunneling characteristics of junctions of the form AlO_x-Pd-Pb are reported. From the thickness dependences of T_c and the induced gaps we find that the total BCS interaction (NV) in Pd is 0 ± 0.05. We find a Fermi velocity of $\sim 0.2 \times 10^8$ cm/sec indicating that the narrow d-band electrons dominate our measurements. Pd phonon structure is not resolved, setting an upper limit of $\lambda \lesssim 0.2$ for the effective electron-phonon interaction. These results indicate that paramagnon effects are substantially less important for superconductivity than was previously envisioned.

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Palladium is a nearly ferromagnetic metal with a strongly exchange-enhanced susceptibility.[1] This has led several authors to suggest that long-lived spin fluctuations (paramagnons) play a fundamental role in preventing Pd from becoming superconducting.[2] Recently interest has grown in related T_c reductions in Nb and V,[3,4] in the possibility of superconductivity in Pd-Ag alloys,[5] and in the possibility of triplet superconductivity in exchange-enhanced metals.[6]

In this Letter we report on a series of proximity-effect studies aimed at evaluating the total effective electron-electron interaction and its electron-phonon component (λ) in pure Pd. Previous studies of induced superconductivity in noble metals have measured NV[7,8] (the BCS coupling parameter, i.e., the density of states at the Fermi energy times the effective electron-electron interaction) from the pair amplitude and energy gap as a function of normal and superconducting met-

al thicknesses and, separately, the electron-phonon interaction from phonon structure in the tunneling density of states at high bias voltages.[9] We find a small electron-phonon interaction for Pd and a total pairing interaction which is essentially zero. The repulsive interaction from virtual exchange of paramagnons is thus weak.

Since this is the first detailed tunneling study of induced superconductivity in a transition metal it is also worth pointing out that the theories used successfully for less complex metals seem to work well here if one accepts a substantially smaller intrinsic normal-superconductor (N-S) coupling. The electron-interference model[10] can be used to evaluate a Fermi velocity and the thickness dependence is well described by the McMillan tunneling model.[11]

The samples were prepared by room-temperature evaporation (at ~1 Å/sec and ~10^{-8} Torr) of Pd on glow-discharge oxidized Al followed by low-temperature (~120 K) evaporation of Pb to avoid interdiffusion. The induced gap as a function of reciprocal thickness is shown in Fig. 1. The gap was measured by pumping the system to 1 K, where the aluminum counter electrode was superconducting, and observing the double-gap structure.[7] The induced gap (Ω_N) falls quite rapidly with Pd thickness but down to $\Omega_N = 40\ \mu V$ (500-Å Pd) the material is still *not* gapless, as evidenced by the double-gap structure and comparison with proximity junctions with magnetic impurities and in magnetic fields.[12]

The induced gap in a normal metal depends on the rate at which its electrons encounter the N-S boundary (v_F/d_N), the transmission coefficient of that barrier (σ), and NV.[11] To get NV we must evaluate the other two parameters in a method used previously by Gray.[7] The transmission coefficient (σ) can be evaluated by studying the T_c's of sandwiches with fixed d_N and varying d_S. Fitting our data to the Rowell-McMillan theory we find $\sigma = 0.027$ from the plot shown as an inset in Fig. 1. This value is an order of magnitude lower than one obtains from clean noble-metal–Pb interfaces.[8] We observe the same transmission coefficient when both films are deposited at low temperature and when the order of deposition is reversed. Moreover, using the same technique we have studied $Pd_{1-x}Ag_x$ alloys which approach the usual value of σ as $x \to 1$.

Pd has a complicated Fermi surface with both s and d bands contributing. However, in performing tunneling measurements on these samples we

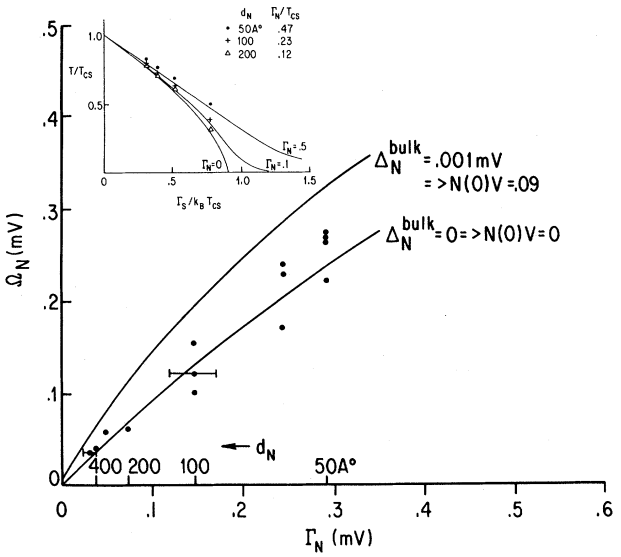

FIG. 1. Induced gap in Pd as a function of inverse thickness or coupling energy to a 3000-Å Pb film. The inset is the reduced transition temperature of Pd-Pb sandwiches as a function of coupling energy compared to the Rowell-McMillan theory (Ref. 10), used to determine the barrier transmission coefficient.

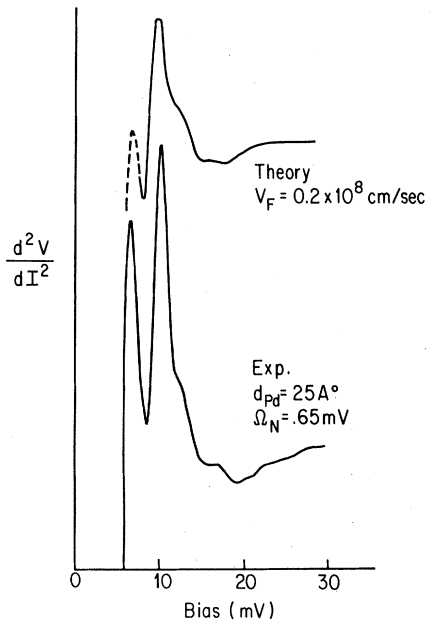

FIG. 2. Second derivative tunneling characteristic of Pd-Pb (arbitrary units) as a function of bias voltage. The dominant structures are related to the gap function in Pb as modified by an electron interference effect (Ref. 10). The dashed region is too close to the Pb gap for the perturbation theory to accurately predict amplitude.

were able to observe an electron interference phenomenon, often seen in s-band metals in proximity,[10] which allows us to determine v_F. In Fig. 2 we show the second derivative tunneling characteristic of a junction with $d_N = 25$ Å. (Electron micrographs of 25-Å Pd films deposited on carbon show uniform thickness with some thin cracks. The films are electrically continuous to less than 20 Å.) Also shown in Fig. 2 is the prediction of the Rowell-McMillan[10] model for the second derivative of a 25-Å normal metal with a Fermi velocity of 0.2×10^8 cm/sec. Electron interference gives a term proportional to the square of the gap function of the superconductor (S) times an oscillating function of period $\hbar v_F/4d$ (~70 mV for our case). The bias voltages where peaks and dips occur is very sensitive to the Fermi velocity and these positions agree quite well. However, since our measurements cover only $\sim\frac{1}{3}-\frac{1}{2}$ of a period we are only able to determine v_F to ~20%. The value of 0.2×10^8 cm/sec is a factor of 5–10 less than one finds in s-band metals and clearly indicates that the electrons we are seeing, which are being induced superconducting, are predominantly the d electrons in Pd. Recent de Haas–van Alphen experiments also give a value of 0.2×10^8 cm/sec for most of the d-like Fermi surface.[13] For thicknesses greater than ~60 Å the interference effect (whose amplitude decreases as Ω_N^2) is too small for evaluation of v_F. Up to ~50 Å we find the same v_F.

From our values of σ and v_F we can calculate the coupling energy (Γ_N) between electrons in N and S as a function of thickness as[11]

$$\Gamma_N = h v_{FN} \sigma / 2 d_N . \quad (1)$$

The induced gap as a function of Γ_N is plotted in Fig. 1. The theoretical curves for two values of NV are also plotted as calculated from the Rowell-McMillan theory. This theory, which involves a perturbative treatment of the N-S coupling, is appropriate in our case because of our small value of σ. The dependence of the induced gap on Γ_N or the normal-metal thickness is very sensitive to the pairing interaction in the normal metal, given in terms of Δ_N^{bulk}, the pair potential in the normal metal at $T=0$ with no proximity. We have plotted values for $\Delta_N^{\text{bulk}}=0$ and $\Delta_N^{\text{bulk}}=1$ μV which for Pd with $\omega_0 \approx 290$ K (Ref. 14) would give an NV of 0 or 0.09, respectively.

The horizontal error bars on the data in Fig. 1 represent our uncertainty in assigning Γ_N because of the 20% uncertainty in v_F. Nonetheless, from this data we can say that NV is close to zero with an uncertainty of less than half the distance between the theoretical curves. ($NV = 0 \pm 0.05$.) This would give a transition temperature at a maximum of ~1 μK. The resistance of Pd has been measured down to 1.7 mK with no evidence for superconductivity.[15]

In order to proceed in evaluating the paramagnon contribution we need some information about the electron-phonon interaction. Calculated values of λ for Pd range from 0.1 to 0.8 with the most recent value being 0.4.[6] Previous studies of proximity sandwiches have shown that structure occurs in the second derivative tunneling characteristic at the van Hove singularities in the phonon density of states of the normal metal. The fractional deviation from BCS behavior in the first derivative is proportional to $\lambda^2\Omega_N^2/\omega_0^2$ and from this and our data on other metals we could use the tunneling data on Pd to extract its λ.[9] The paramagnons could only mask the phonon structure if they had a similar van Hove singularity at the same energy.

Figure 3 shows the second derivative characteristic of a 30-Å film of Pd backed by Pb. This was one of several junctions with low noise and little extraneous structure at high bias voltages. The position of the Pd longitudinal acoustic phonon peak is indicated by the arrow.[14] There is little if any structure at this frequency compared with what could be expected for a λ of 0.4. The induced gap was 0.44 mV. For comparison we also have shown the equivalent tunneling characteristic

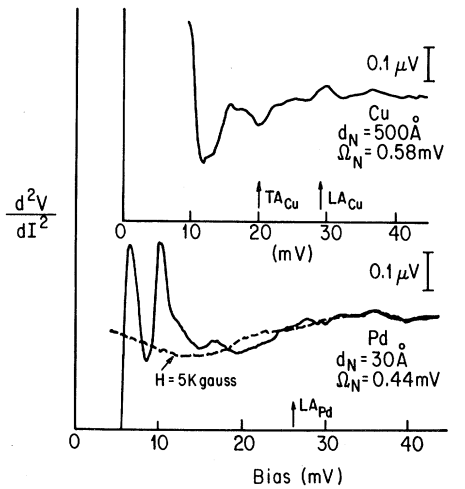

FIG. 3. Second derivative tunneling characteristic taken with a 1-mV ac modulation for Pd-Pb and Cu-Pb junctions in the bias voltage region corresponding to peaks in the phonon density of states.

for Cu backed by lead (with a purposefully lowered transmission coefficient) with an induced gap of 0.58 mV.[16] The Cu phonon at 28 mV is clearly seen. Cu has a λ of 0.13 ± 0.02.

The structure near ω_{LA} for Pd in Fig. 3 is one of the largest we have seen in searching for Pd phonons in many junctions. We have not been able to convincingly show to our own satisfaction that the structure is not extraneous. Therefore we cannot use this technique to evaluate λ for Pd, rather we can only set an upper limit to its value by analyzing our sensitivity and comparing with other materials studied. We find that λ for Pd is less than 0.2. If we assume that the value of the Coulomb term, μ^*, is 0.13 ($NV = \lambda_{ep} - \mu^* - \lambda_{para}$) then we find that the absence of superconductivity in Pd may be entirely explained without a repulsive interaction due to paramagnons (λ_{para}).

Recent measurements by Dye *et al.*[13] of the de Haas–van Alphen effect in Pd have demonstrated that the averaged *d*-band velocity is reduced from calculated band-structure values by a factor which corresponds to a mass enhancement of ~0.4. For mass enhancement and specific heat λ_{para} and λ_{ep} are *additive*. Thus their measurement also shows that the paramagnons do not have as large an effect as has been expected. The calculations presented in Ref. 4 indicate that both the electron-phonon interaction (as measured by tunneling) and the paramagnon repulsion are renormalized by $1+\lambda_{para}$. This effect may well explain why the electron-phonon interaction we have found is below the calculation of Ref. 6. However, the reduction of λ_{ep} by a factor of 2 requires $\lambda_{para} \sim 1$. This would produce a net repulsive interaction as $(\mu^* + \lambda_{para})/(1+\lambda_{para}) \sim 0.5$.

In conclusion, we have found that total electron-electron interaction in Pd is close to zero and that any singlet state superconductivity could only occur in the microkelvin region. Although we cannot evaluate the electron-phonon coupling constant λ_{ep} we have found that it is smaller than 0.2 from the absence of pronounced structure in the tunneling density of states in the energy range corresponding to the peaks in the phonon density of states. The reduction of the phonon structure may be due to renormalization effects caused by the paramagnons. However, this would require a larger repulsive interaction than is seen. Further calculations of the effects of paramagnons on superconductivity are needed to account for the properties of palladium.

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