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Search for superconductivity in Pd-Ag alloys

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We have measured low-temperature properties of twelve Pd_cAg_{1-c} samples ($0.59 \lesssim c \lesssim 0.81$) and find no evidence of superconductivity.

The primary determinant of the superconducting transition temperature in a metal is the electron-phonon coupling constant $\lambda_{e\text{-ph}}$. First-principles theoretical calculations[1] predict that $\lambda_{e\text{-ph}}$ for Pd is large ($\lambda_{e\text{-ph}}^{Pd}=0.4$), which implies that pure Pd could become superconducting. Bardeen-Cooper-Schrieffer (BCS) (i.e., singlet pairing) superconductivity requires the pairing of antiparallel spins (Cooper pairs). On the other hand, Pd also exhibits large paramagnetic fluctuations (paramagnons) which favor parallel spin alignment.[2] Because of this, pure Pd is not expected to exhibit ordinary singlet pairing superconductivity. Theoretical predictions[2] favor the existance of triplet pairing in high purity Pd, in analogy to the superfluidity of ^{3}He. An experimental search for triplet pairing superconductivity has shown that pure Pd is not superconducting down to temperatures of 7.0 mK and for fields smaller than 1.7 μT.[3]

Recently Gyorffy, Pindor, and Temmerman[4] predicted that Pd_cAg_{1-c} *alloys* with $0.6 \lesssim c_{Pd} \lesssim 0.8$ will be superconducting with transition temperatures $0.01 \leq T_c \leq 0.5$ K. The magnetic susceptibility of Pd-Ag alloys decrease rapidly with increasing Ag concentration, which is interpreted as a quenching of the large paramagnetic fluctuations (the so-called Stoner susceptibility enhancement).[5] These authors calculated that $\lambda_{e\text{-ph}}$ should decrease more slowly (i.e., linearly) with increasing Ag concentration, and concluded that Pd-Ag alloys should be superconducting for the above range of Ag concentration.

Gyorffy *et al.*[4] support the qualitative idea presented above with a first-principles band-structure calculation within the KKR-CPA (Korringa-Kohn-Rostoker coherent-potential approximation). The results of this band-structure calculation are in good agreement with photoemission studies and agree well in the appropriate limits with band structures of pure Pd and pure Ag. The electron-phonon matrix elements are calculated within the rigid muffin-tin approximation with a similar method originally developed by Sinha[6] and formulated more simply by Gaspari and Gyorffy.[7] This calculation predicts transition temperatures $0.01 \leq T_c \leq 0.5$ K for concentrations $0.6 \lesssim c_{Pd} \lesssim 0.8$.

We have searched for superconductivity in twelve different Pd_cAg_{1-c} alloys having Pd concentrations within this range and have found no evidence for superconductivity down to a temperature of 10 mK. Our twelve samples were prepared in an Al_2O_3 crucible using 9.999 + % pure Ag and 9.999 + % pure Pd. Mass spectrographic analysis on the starting material showed the presence of less than 5 ppm of iron, less than 0.1 ppm of cobalt, and less than 0.6 ppm of nickel. The constituents were outgassed at 666 °C in vacuum 7×10^{-4} Pa, heated up rapidly to 1575 °C ($\sim$1 h) under 70 Pa of argon, and held at this temperature for half an hour. The samples were then rapidly cooled to room temperature. To assure homogeneity, nine of the samples were annealed at 1200 °C for $\sim$62 h. The samples were then spark cut and lightly etched using nitric acid. Neutron activation and wet chemical analysis were performed on the samples showing the final concentration to be within $\sim$2% of the starting concentration. Chemical analysis on several parts of one ingot shows that sample homogeneity is better than 1%.

The samples were inductively tested for superconductivity with experimental procedures similar

to those used at NBS in the production of fixed-point superconductive devices.[8,9] The external magnetic field at the site of the sample was shielded to less than $1-2\times10^{-6}$ T and the test ac field had a peak-to-peak value of 2.3×10^{-6} T in the primary coils. The minimum sensitivity of the apparatus implies that we could have observed perfect diamagnetism in 0.001 of the volume of each sample. Since this was not observed, we are forced therefore to conclude that none of the samples are superconducting to that level of detection.

Since we did not observe superconductivity in these Ag-Pd alloys, we reexamine the basis for the theoretical prediction, which rely on the following:

(1) A large electron-phonon coupling constant ($\lambda_{e\text{-ph}}=0.4$) for Pd found from theoretical studies.

(2) The fast quenching of paramagnons by alloying Pd with Ag.

(3) The assumption that the electron-phonon coupling coefficients for an alloy can be written as

$$\bar{\lambda}_{e\text{-ph}}=c\frac{\eta_A}{M_A\langle\omega^2\rangle_A}+(1-c)\frac{\eta_B}{M_B\langle\omega^2\rangle_B}\ . \tag{1}$$

Here M_A and M_B are the atomic masses of the constituents, $1/\langle\omega^2\rangle_A$ and $1/\langle\omega^2\rangle_B$ are local averages of the mean square displacements, and η_A and η_B are averaged local electronic factors.

Since different first-principles calculations give large values for $\lambda_{e\text{-ph}}$ in Pd, this seems to be well established theoretically. However, recent proximity effect tunneling measurements[10] claimed that $\lambda_{e\text{-ph}}^{\text{Pd}}\leq 0.2$, contrary to these calculations.

The decrease of the magnetic susceptibility with increasing concentration of Ag is an experimental fact that strongly supports the claims that the Stoner enhancement factor does decrease rapidly with alloying.

The third assumption as expressed in Eq. (1) is based on the argument that the time an electron spends near each constituent (and hence be affected by that constituent) is proportional to the concentration of each constituent. Using a microscopic model, Appel[11] has shown this to be correct for a concentrated alloy only if the normal modes of the lattice can be decoupled. This assumption seems to be somewhat suspicious, although it has been used for ordered compounds with some success.

In summary, we have measured the ac susceptibility of Pd_cAg_{1-c} alloys in the range $0.59\lesssim c\lesssim 0.81$ and found them not to be superconducting above 10 mk—contrary to theoretical predictions. We have pointed out a few possible areas where the theoretical estimates may have been too optimistic. To balance the criticism, we also admit that the presence of even minute amounts of magnetic impurities in the samples could unexpectedly suppress the superconductivity to below 0.01 K.

Note added. After the completion of this manuscript one of us (R.J.S.) received a copy of an article before its publication[12] that reports similar results.

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[1]F. J. Pinski, P. B. Allen, and W. H. Butler, Phys. Rev. Lett. 41, 431 (1978).

[2]D. Fay and J. Appel, Phys. Rev. B 16, 2325 (1977); K. Levin and O. Vals, *ibid.* 17, 191 (1978); 20, 105 (1979).

[3]R. A. Webb *et al.*, J. Low Temp. Phys. 32, 659 (1978); F. J. Pinski, P. B. Allen, and W. H. Butler, in *Superconductivity in d and f Band Metals,* edited by H. Suhl and M. B. Maple (Academic, New York, 1980).

[4]B. L. Gyorffy, A. Pindor, and W. M. Temmerman, Phys. Rev. Lett. 43, 1343 (1979).

[5]F. E. Hoare, J. C. Matthewson, and J. C. Willing, Proc. R. Soc. London Ser. A 216, 502 (1953).

[6]S. K. Sinha, Phys. Rev. 169, 477 (1968).

[7]G. D. Gaspari and B. L. Gyorffy, Phys. Rev. Lett. 28, 801 (1972).

[8]R. J. Soulen and R. B. Dove, NBS Special Publication 260-62, US GPO, Washington, D. C. 20402, Stock No. 003-003-0204708-8.

[9]R. J. Soulen, Jr., J. F. Schooley, and G. A. Evans, Jr., Rev. Sci. Instrum. 44, 1537 (1973).

[10]L. Dumoulin, P. Nedellec, and P. M. Chaikin, Phys. Rev. Lett. 47, 208 (1981).

[11]J. Appel, Solid State Commun. 15, 1043 (1974).

[12]Ch. Buchal, B. Stritzker, M. Kubota, R. M. Mueller, and F. Pobell, Solid State Commun. 39, 771 (1981).