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Possibility of Superconductivity in Pd_cAg_{1-c} Alloys

B. L. Gyorffy, A. Pindor,[a] and W. M. Temmerman
H. H. Wills Physics Laboratory, University of Bristol, Bristol BS81TL, United Kingdom
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On the basis of a Korringa-Kohn-Rostoker coherent-potential–approximation calculation of the band structure and the electron-phonon mass enhancement in a number of Pd-rich Pd_cAg_{1-c} alloys, it is argued that some of these could be superconducting at observable temperatures ($0.01\ K \leq T_c \leq 0.5\ K$). It is suggested that these systems provide a unique possibility for studying the effects of paramagnons on the superconducting state.

As is well known, pure crystalline palladium is almost a ferromagnet at low temperatures[1] and it is also a would-be superconductor.[2] In a careful theoretical study of the electron-phonon interaction, Pinski, Butler, and Allen[3] found that the mass enhancement factor is $\lambda_{ep}^{Pd} = 0.4$. This implies that pure palladium should become superconducting below $T_c = 0.3$ K. The nonexistence of ordinary, singlet, superconductivity in this system[4] is explained by reference to large paramagnetic fluctuations (paramagnons) which induce a repulsive force between electrons with antiparallel spins and therefore prevent Cooper pairing.[1] Consider now alloys of palladium with silver. As silver is added to the palladium host the density of states at the Fermi energy, $n(\epsilon_F)$, goes down.[5] This reduces the Stoner enhancement factor S and consequently the paramagnetic fluctuations drastically.[6] In this Letter we shall argue that the electron-phonon mass enhancement does not decrease quite so rapidly in the palladium-rich alloys. Thus we predict that for palladium concentrations $0.6 \leq c_{Pd} \leq 0.8$ the electron-phonon attraction can overcome the repulsion due to the exchange of paramagnons. We estimate that these alloys will be superconducting with $0.01 \leq T_c \leq 0.5$ K.

In what follows the basis of our discussion will be the result, due to Appel,[7] that for a concentrated random alloy the effective electron-phonon mass-enhancement factor $\bar{\lambda}_{ep}$ may be written as

$$\bar{\lambda}_{ep} = c\,\frac{\eta_A}{M_A\langle\omega^2\rangle_A} + (1-c)\frac{\eta_B}{M_B\langle\omega^2\rangle_B}, \qquad (1)$$

where 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 of the appropriate atoms, and η_A, η_B are partially averaged local electronic factors. Similar expressions have been used with success in the case of two-component ordered compounds.[8] The form of Eq. (1) also follows from a consideration of the Eliashberg equation within the coherent-potential approximation (CPA).[9]

To the accuracy of our theory $M_{Pd} \approx M_{Ag}$. Though the larger Ag atom strains the host lattice we shall also take $1/\langle\omega^2\rangle_{Pd} = 1/\langle\omega^2\rangle_{Ag}$. Within the Debye model, $1/\langle\omega^2\rangle$ may be estimated as $1/\sqrt{2}\theta_D^2$. The observed behavior of θ_D with increasing Ag concentration[10] is that, initially, θ_D decreases slowly. The lattice begins to soften more rapidly only at $c_{Pd} \approx 0.5$. This fact is surprising, since the lattice parameter is increasing linearly in this concentration range, and may have profound consequences. If we regard η_{Pd} and η_{Ag} as largely atomic parameters, independent of the density of states $n(\epsilon_F)$,[11] then we are forced to conclude that $\bar{\lambda}_{ep}$ decreases only as

$c(\eta_{Pd}-\eta_{Ag})$. On the other hand, the susceptibility drops dramatically.[6] Consequently, one might expect superconductivity in some of these alloys. We shall now attempt a quantitative theory of $\bar{\lambda}_{e\phi}$.

It is now well established that the electron-phonon interaction in transition metals is well described by the rigid muffin-tin approximation.[12] Within the scattering-theory approach to this problem, η_α (α = Pd or Ag) may be written as[13]

$$\eta_\alpha=\frac{\epsilon_F^{\,2}}{\bar{n}(\epsilon_F)\pi^2}\left\{2\,\frac{\sin^2(\delta_0^{\,\alpha}-\delta_1^{\,\alpha})}{\sin^2\delta_0^{\,\alpha}\sin^2\delta_1^{\,\alpha}}\,\mathrm{Im}\,\bar{\tau}_{00}^{\alpha;00}(\epsilon_F)\,\mathrm{Im}\,\tau_{1,1}^{\alpha;00}(\epsilon_F)+4\,\frac{\sin^2(\delta_1^{\,\alpha}-\delta_0^{\,\alpha})}{\sin^2\delta_1^{\,\alpha}\sin^2\delta_2^{\,\alpha}}\,\mathrm{Im}\,\bar{\tau}_{11}^{\alpha;00}(\epsilon_F)\,\mathrm{Im}\,\bar{\tau}_{22}^{\alpha;00}(\epsilon_F)\right.$$
$$\left.+6\,\frac{\sin^2(\delta_2^{\,\alpha}-\delta_3^{\,\alpha})}{\sin^2\delta_2^{\,\alpha}\sin^2\delta_3^{\,\alpha}}\,\mathrm{Im}\,\bar{\tau}_{22}^{\alpha;00}(\epsilon_F)\,\mathrm{Im}\,\bar{\tau}_{33}^{\alpha;00}(\epsilon_F)\right\}, \quad (2)$$

where $\bar{n}(\epsilon_F)$ is the averaged density of state, $\delta_l(\epsilon_F)$ is the phase shift which describes the scattering at $\vec{R}_0$, the position of a selected site occupied by the α-type atom, and $\tau_{L,L'}^{\alpha;00}(\epsilon_F)$ is the "on the energy shell" component of the site-diagonal scattering-path operator[14] averaged over all configurations which leave an α-type atom at the site $\vec{R}_0$. The symbols L,L' which appear as suffixes of this quantity describe the angular momentum of the incoming and outgoing partial waves and they stand for both l and m. The bar over $\bar{\tau}_{l,l'}^{\alpha;00}(\epsilon_F)$ means that the corresponding quantity has been averaged over the m quantum number. We note that in Eq. (2) we have neglected the nonspherical contributions since these were found to be small in pure Pd.[3] The attractive feature of writing η_α as in Eq. (2) is that $\tau_{l,l'}^{\alpha;00}$ is readily available at the end of a Korringa-Kohn-Rostoker (KKR) CPA calculation[15] for the band structure of a random alloy.

We have investigated a series of Pd_cAg_{1-c} alloys within the KKR-CPA scheme. The broad features of the band structure are in good agreement with the available photoemission experiments,[16] indicating that the underlying potential functions define a sensible one-electron theory. Being a first-principles approach, the KKR CPA makes no use of the band structure of the pure constituent elements. However, in the limit $c=1$ and $c=0$ it is the same as a conventional KKR calculation. In these limits our calculation agrees with previous work on pure Pd and Ag. The details of this work will be published elsewhere.

Our calculated densities of states at the Fermi energy of the various alloys considered are listed in Table I. The corresponding values for the linear temperature coefficient of the specific heat, γ^0, are plotted in Fig. 1 together with the experimental data. Because our calculated $\bar{n}(\epsilon_F)$ agrees well with experiments in the Ag-rich alloys and appears to extrapolate to the accepted calculated value of $n(\epsilon_F)$ for pure palladium, we assume that our calculated densities of states are correct and attribute the difference[17] $\gamma^{exp}-\gamma^0$ to mass enhancement due to electron-phonon interaction and paramagnetic fluctuations. We measure this deviation by the total enhancement factor λ^{tot} defined by the relation $\gamma^{exp}=\gamma^0(1+\lambda^{tot})$. The values of λ^{tot} are listed in Table I and plotted in Fig. 2. Evidently, after an initial drop it stays roughly constant until at least 40% Ag is added and then drops precipitously.

We now assume that $\lambda^{tot}=\lambda^{e\phi}+\lambda^{SF}$ where $\lambda^{e\phi}$ is the contribution from the electron-phonon interaction and λ^{SF} is a consequence of spin fluctuations. From the sharp decrease of χ we expect that λ^{SF} decreases rapidly with increasing Ag con-

TABLE I. Calculated and empirical quantities relevant to the determination of T_c.

Percentage Pd	$n(\epsilon_F)$, states of one spin per eV	Θ_D (K)	$\langle\omega^2\rangle^{1/2}$ scaled with Θ_D	η_{Pd} (eV Å^{-2})	η_{Ag} (eV Å^{-2})	$\lambda_{e\phi}$ calc.	λ_{tot}	λ_{SF}
100	1.176	290	166			0.41	0.72	5.4
90	1.105	286	163	2.67	0.104	0.45	0.49	3.4
80	0.826	281	160	2.49	0.108	0.43	0.51	−0.31
70	0.644	277	159	2.26	0.106	0.34	0.44	
60	0.489	277	158	2.04	0.096	0.23	0.23	
50	0.251	274	156	2.76	0.079	0.14	0.23	

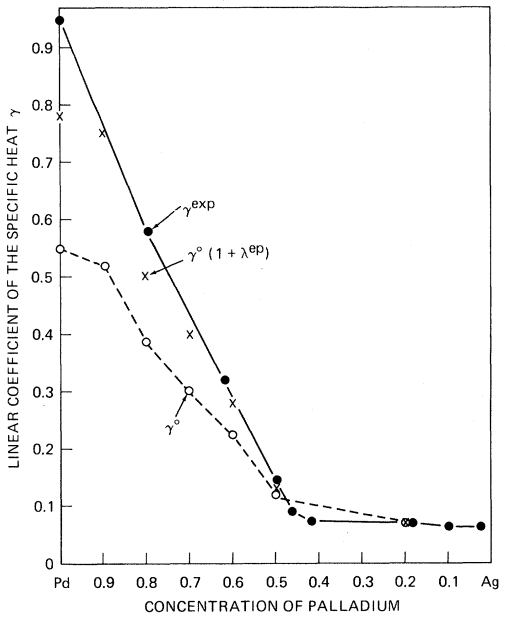

FIG. 1. The linear coefficient of the specific heat vs palladium concentration as calculated from the density of states (open circles), enhanced by the calculated electron-phonon interactions (crosses), and experiments (filled circles).

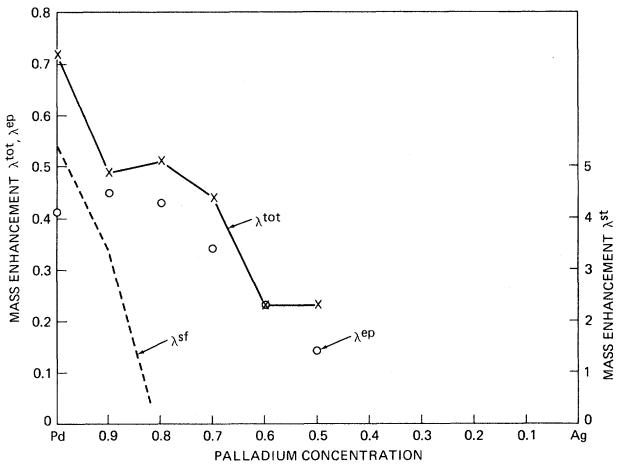

FIG. 2. The total mass enhancement factor λ^{tot} (crosses), the electron-phonon contribution λ^{ep} (circles), and the paramagnon contribution of λ^{SF} (dashed curve) vs palladium concentration.

centration. The fact that λ^{tot} does not decrease very much until 40% Ag implies that λ^{ep} is getting large relative to λ^{SF}. Since the strength of the pairing force $\lambda_{\mathrm{eff}}=\lambda^{ep}-\lambda^{\mathrm{SF}}$, this suggests that some of these alloys may become superconducting.

In order to test the correctness of the above picture we have calculated λ^{ep} using Eq. (2) and the results of our KKR-CPA calculation. Since we have solved the KKR-CPA equations only for $l\leq 2$, $\bar{\tau}_{33}^{\alpha;00}(\epsilon_{\mathrm{F}})$ was not directly available to us. On the other hand, this term was found to be significant in pure Pd by Butler.[2] Therefore, using matrix partitioning we derived an expression for

$$\lim_{\delta_3{}^{\mathrm{Pd}}\to\delta_3{}^{\mathrm{Ag}}\to 0} \sin^{-2}\delta_3{}^{\alpha}\,\mathrm{Im}\bar{\tau}_{33}^{\alpha;00}$$

in terms of $\bar{\tau}_{L,L'}^{\alpha;00}$, with $l,l'<2$ and $G_{lm;3m'}(q\epsilon)$. Evaluating this formula we found that the $l=3$ contribution in Eq. (2) on the Pd sites was only slightly less than the corresponding term in Butler's calculation.[2] The final values obtained for η^{Pd} and η^{Ag} are listed in Table I. To find λ^{ep} we had to estimate $1/\langle\omega^2\rangle$. Since our η^{Pd} appeared to converge satisfactorily toward the value of Butler for pure palladium and the measured values for Θ_{D} suggest that the phonon spectra are not changing rapidly in the concentration range of our interest, we used the very accurate values of $1/\langle\omega^2\rangle$ in Ref. 3 scaled according to the changes in Θ_{D} on alloying. These estimates are shown in Table I. From the η's and $1/\langle\omega^2\rangle$'s in Table I we have calculated λ^{ep} for the various alloys studied. The results are listed in Table I and plotted in Fig. 2. For clarity we also plotted $\gamma^{\mathrm{theor}}=\gamma^{0}(1+\lambda^{ep})$ in Fig. 1.

Evidently, λ^{tot} and γ^{exp} agree well with λ^{ep} and γ^{theor}, respectively, up to 80% Pd. Beyond that the experiments and theory begin to depart, indicating the presence of paramagnons. In fact our calculation of $\bar{n}(\epsilon)$ is rather uncertain for $\mathrm{Pd}_{0.9}\mathrm{Ag}_{0.10}$ because our Brillouin-zone integration scheme was not sufficiently accurate to pick up all the complicated and well-defined structure associated with the Fermi-surface sheet about the X point in this alloy. At higher concentrations of Ag the bands were more smeared and consequently our integration routines more accurate. Our somewhat subjective estimate of these errors imply that for $\mathrm{Pd}_{0.9}\mathrm{Ag}_{0.10}$, λ^{tot} should be higher in line with a linear approach to λ^{tot} in pure Pd. The same errors would tend to lower λ^{ep} somewhat. With these adjustments the evidence for the disappearance of paramagnons for $c_{\mathrm{Pd}}\approx 0.8$ is particularly striking.

It must be emphasized that neither in our calculation of $\bar{n}(\epsilon_{\mathrm{F}})$, which together with γ^{exp} determined λ^{tot}, nor in our evaluation of $\eta^{\mathrm{Pd}},\eta^{\mathrm{Ag}}$ did we use any adjustable parameters. The only fitting concerned the scaling of $1/\langle\omega^2\rangle$. Thus, the

theory was nowhere adjusted to agree with the specific-heat data. Consequently, from the small and fluctuating $\lambda^{SF} = \lambda^{tot} - \lambda^{ep}$ for $0.8 \geq c_{Pd}$, we conclude that there are no paramagnons in these alloys. Since the electron-phonon interaction is still quite large for $c_{Pd} = 0.8$ and 0.7 we can thus expect superconductivity. For orientation we note that for $\lambda_{eff} = \lambda^{tot} = 0.43$, $\omega_{log} = 130$ K, and $\mu^* = 0.13$, we obtain[12] $T_c = 0.49$ K. Even if we take $\lambda^{tot} - \lambda^{ep} = \lambda^{SF}$ and therefore $\lambda_{eff} = \lambda^{ep} - \lambda^{SF}$ we get $T_c = 50$ mK.

Up till now we made no use of any model for the paramagnetic fluctuations. In order to ascertain whether the above picture is consistent with such models we calculated λ^{SF} from a simple one-parameter theory[18] which give $\lambda^{SF} = \frac{9}{2} \ln(S/3)$ where S is the Stoner enhancement factor $S = [1 - In(\epsilon_F)]^{-1}$. For $I = 0.787$ which gives $S = 10$ for pure Pd, the values of λ^{SF} for the first three of our alloys is shown in Fig. 2 and Table I. As is well known, such a simple model cannot fit both the specific heat data and the susceptibility. Nevertheless, λ^{SF} calculated above clearly indicates that one should not expect much λ^{SF} beyond $c_{Pd} = 0.8$. Note that the steep fall of S in the above calculation is consistent with the observed decrease of the susceptibility[6] χ.

In conclusion we note that if the alloys Pd_cAg_{1-c} with $0.8 \geq c_{Pd} \geq 0.6$ do indeed turn out to be superconductors they will be a most interesting class of systems in which one can study the interaction between magnetic fluctuations and superconductivity. Moreover, such an observation would be a strong hint that the superconductivity in amorphous Pd is merely a sign of the absence of paramagnons due to reduction in $n(\epsilon_F)$ by disorder.

[a]Permanent address: Institute of Physics PAN., Warszawa, Poland.

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Why Muons and Protons are Deep Donors in Si and Ge

Massimo Altarelli and William Y. Hsu[a]
Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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The deep impurity character of interstitial positive muons or protons in Si and Ge is shown to result from the valley-orbit interaction of the six conduction-band minima along Δ. This interaction, much stronger for interstitial than for substitutional point charges, leads to a breakdown of the effective-mass approximation and to the formation of a deep state. This is particularly striking in Ge, where the Δ minima are not the absolute ones.

Positive muons, injected into Si or Ge crystals, can capture an electron and form an impurity state analogous to muonium, after they come to rest in an interstitial position.[1] Although the binding energy is not measured directly, hyperfine frequency measurements show that the electron probability density at the muon is reduced, with respect to a free muonium, by a factor of