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Kondo effect and spin-glass freezing of the magnetic impurities Cr, Mn, and Fe in superconducting palladium hydride

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Through low-field ac susceptibility measurements we have determined the depression of the superconducting transition temperature T_c in palladium hydride ($T_{c0}=9.3$ K) as a function of impurity concentration x for Cr, Mn, and Fe. For Cr and Fe similar values for the initial T_c depression were found, i.e., -150 K/at.% Cr and -145 K/at.% Fe. From resistivity experiments we are able to estimate the Kondo temperatures T_K, i.e., $T_K \simeq 10$ K for Cr and $T_K \simeq 5$ K for Fe. Since $T_K \simeq T_{c0}$, these systems exhibit an enhanced pair breaking as described by the theory of Müller-Hartmann and Zittartz. In contrast, for Mn the initial T_c depression is -21 K/at.% and $T_K << T_{c0}$, as can be concluded from our resistivity measurements. This means that Mn in PdH exhibits a temperature-independent pair breaking of the Abrikosov and Gor'kov type. However, at larger Mn x values a shoulder appears in $T_c(x)$. We interpret this enhanced superconductivity, according to the theory of Soukoulis and Grest, as being due to the onset of time correlations and short-range antiferromagnetic ordering between the Mn moments. These interaction effects are a precursor to the spin-glass freezing at a lower temperature T_f. Our results suggest a favorable coexistence of superconductivity with the spin-glass state.

I. INTRODUCTION

During the past nine years since its discovery,[1] the superconductivity in palladium hydride has remained a topic of considerable interest. Up until now, only three systems, PdH, Th_4H_{15}, and AlH, exhibit an increase in the superconducting transition temperature upon hydrogenation.[2] PdH is unique insofar as pure Pd is nonsuperconducting, at least down to 1.7 mK,[3] and instead is an exchange-enhanced, incipient ferromagnet. When Pd is alloyed with small amounts of the $3d$ magnetic impurities Mn, Fe, and Co, a "giant moment" ferromagnetic order is produced.[4] Cr and Ni in Pd are exceptions to this behavior, for they are spin-fluctuation systems which require a sufficiently strong "magnetic" local environment via a larger concentration of Cr or Ni before local moments appear and cause magnetic ordering.[4] Upon charging Pd with large quantities of H, superconductivity has been detected between 0.76 to 1.00 H-to-Pd ratios.[5] At the latter ratio a maximum $T_c=9$ K has been attained for H, with $T_c=12$ K for D. This inverse isotope effect has particular significance regarding the mechanisms (optical modes and anharmonicities) for superconductivity in PdH and PdD.[6]

The electronic properties of the β-phase PdH show a diamagnetic behavior[7] similar to the noble metals. By adding $3d$ magnetic impurities to superconducting PdH we would expect a strong pair breaking of the Abrikosov-Gor'kov type[8] which could be modified by the Kondo effect between the $3d$ impurities and the conduction electrons.[9] At higher concentrations a spin-glass frozen state should appear. Giant moment effects are not found in a diamagnetic host, so there are no complications with ferromagnetic ordering manifesting itself below the nearest-neighbor percolation concentration, $\approx$17 at.% in a fcc lattice. Thus the $(Pd_{1-x}M_x)H$ system with $M=$Cr, Mn, or Fe offers a unique possibility with which to study a noble-metal-like, Kondo, superconducting spin-glass. Here there should exist a dramatic interplay between the Kondo effect and the superconductivity, and in addition, at larger M concentrations, a coexistence of the spin-glass and superconducting states. The latter has recently been treated theoretically where either no significant influence of spin-glass freezing on superconductivity is predicted[10] or an enhanced superconductivity due to spin-glass ordering is expected.[11]

In this paper we present the results of low-field ac susceptibility, χ, investigations on $(Pd_{1-x}M_x)H$ with $M=$Cr, Mn, or Fe, and resistivity ρ measurements on $(Pd_{1-x}Mn_x)H$. We combine these results with previous studies of χ and ρ on $(Pd_{1-x}Fe_x)H$ (Refs. 12–14) and $(Pd_{1-x}Cr_x)H$ (Refs. 12, 15, and 16). Thereby an overall picture is obtained for the suppression of the superconductivity with and without the Kondo effect and with the onset of spin-glass freezing in $(Pd_{1-x}M_x)H$ systems. The next section gives the experimental details of our sample preparation techniques and the χ and ρ measurements. Section III contains and compares the experi-

mental results for all three (Cr, Mn, and Fe) impurities. In the final Sec. IV our results are discussed, contrasted with other magnetic superconductors, and related to the theory.

II. EXPERIMENTAL DESCRIPTION

Dilute *PdM* (M = Cr, Mn, or Fe) alloys were produced by melting together, in a high-frequency induction furnace under argon atmosphere, weighted amounts of pure Pd with an analyzed higher concentration alloy of *PdM*. In this way concentration errors caused by the weighing accuracy or small weight losses during melting become negligible. The ultrapure Pd was supplied by Johnson and Matthey, Co. (S82061) who analyzed the major impurities to be 2-ppm Fe and 1-ppm Si. After melting a number of times to ensure homogeneity, the various dilute magnetic alloys were rolled into 30-μm- or 0.1-mm-thick foils using thin Mylar sheets to prevent iron contamination during the rolling process. To diminish the amount of lattice dislocations and strains introduced by this rolling process the alloys were annealed for 4 h at 500 °C in vacuum. The samples with magnetic impurity concentrations less than 1500 ppm were analyzed by Johnson and Matthey through atomic absorption, while the higher magnetic impurity concentrations were determined by a spectrophotometric analysis. Good agreement was always found for the magnetic impurity concentrations with the nominal values.

By a method similar to that reported by Wiley and Fradin,[17] the alloy samples were charged electrolytically with hydrogen. In Fig. 1 a schematic diagram of the electrolytic cell is shown. The electrolytic solution consisted of one part 38% HCl in H_2O to nine parts CH_3OH. As a catalyst 0.2 g/l thiourea was added.[18] The electrolytic solution was renewed every few charging cycles to eliminate possible variations in the hydrogenation. In order to obtain a homogeneous hydrogen transport to the 5-mm-wide and 30-μm-thick sample strip, it was installed as a cathode between two plane-parallel Pt plates serving as the anode. The Pt strips, which are 0.1-mm thick and 10-mm wide, are spaced 10 mm from the sample foil. The electrolytical cell was driven with a current of 15 mA per cm^2 sample area by a constant current supply. For mechanical support the Pt strips are firmly attached to a polyvinylchloride holder. The sample foil is also fastened with the lower end to this same construction, while to the upper end of the sample a 0.1-mm-diameter Pt wire is spot welded. The sample is kept under a light tension by a weight attached to this Pt wire. This is used to maintain the sample in place as its volume expands during hydrogenation. Through the Pt wire spot welded to the sample foil and similar Pt wires spot welded to the Pt anodes, the

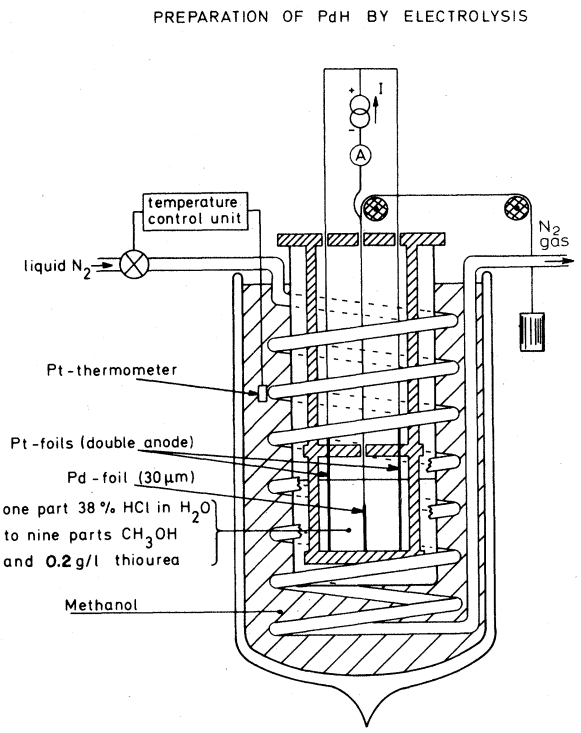

FIG. 1. Schematic diagram of the electrolytic charging cell.

electrolytical cell is thus supplied with current during the hydrogenation process. The electrolytical cell was immersed in a Dewar containing methanol which was cooled by cold nitrogen gas circulating through a coil wound from copper tubing and placed around the Pyrex charging cell. The temperature of the methanol was determined with a temperature calibrated Pt resistor. The copper tubing was attached to a liquid-nitrogen vessel via a solenoid valve. With the use of a temperature control unit, Cryson (TRL5), which was connected to the valve and the Pt resistor, the electrolytical cell could be cooled to any temperature between 0 and −100 °C and kept constant in temperature to within a few degrees. As can be seen from the pressure vs H-to-Pd isotherms[19] a high H-to-Pd (1:1) ratio can be reached only at low temperatures. Unfortunately also at low temperatures the diffusion rate of hydrogen in the Pd matrix decreases strongly,[19] which results in a very time consuming charging process. To optimize the hydrogenation procedure the cell was stepwise cooled, starting with a period of 3 h at −40 °C followed by 3 h at −70 °C and finally a period of 12 h at −90 °C. After completion of the hydrogen charging the sample was immediately stored under liquid nitrogen. From there the sample was brought into the measuring cryostat at liquid-helium temperatures within a few minutes without allowing the sample temperature to rise above liquid-nitrogen temperature. Identical

charging procedures were strictly followed and maintained for all the alloy samples reported in this paper. Concentrations of [H]/[Pd] = 0.99 were obtained. As described below, this concentration is believed to be reproducible.

The superconducting transition temperatures were determined using the standard low-field ac susceptibility technique. The driving field at a frequency of 140 Hz did not exceed 1 Oe. There was no compensation for the earth's magnetic field so a static field of about 0.5 Oe was present at the sample.

For the resistivity measurement the samples were charged under a hydrogen pressure of 10 atm for 4 h at a temperature of 500 °C. After that the sample was slowly cooled overnight to room temperature under the same 10-atm hydrogen pressure and then mounted with current and voltage leads and cooled within one hour in the measuring cryostat. The hydrogen content, usually [H]/[Pd] = 0.7, was determined and followed by weighing a dummy, control sample during the mounting procedure. The sample dimensions were $50 \times 2 \times 0.1$ mm^3. The resistivity was measured with a four-point-probe technique with a dc current of 20 mA, constant to a few ppm and a voltage determination accurate to about 2 parts in 10^5.

III. RESULTS

About one year ago we reported preliminary measurements on the susceptibility of $(Pd_{1-x}Cr_x)H$ and $(Pd_{1-x}Fe_x)H$.[12] In the meantime we improved the electrolytical preparation to obtain much more stoichiometric and homogeneous PdH. For pure PdH we observe a reproducible superconducting transition temperature T_c of 9.3 K with a width (10–90%) of less than 0.5 K. Using the results of Miller and Satterthwaite[20] for the dependence of T_c on the hydrogen concentration, we can estimate the hydrogen to Pd ratio to be slightly over 0.99 in the PdH sample. The alloying of a few hundred ppm of magnetic impurity with Pd is not expected to alter the [H]/[Pd] ratio of the sample significantly.[21] Nevertheless, for higher magnetic impurity concentrations (> 1 at.%) the hydrogen-to-metal ratio will probably be lowered as may be seen from the change in the pressure vs hydrogen-to-metal isotherms on alloying.[19]

In Fig. 2 some typical measurements of $\chi(T)$ are shown for hydrogenated $Pd_{1-x}Mn_x$: $x = 0$, 0.158, 0.320, and 1.40 at.%. The susceptibility χ, which was negative (diamagnetic) in the superconducting state was measured with increasing temperature beginning at 1.4 K. The broadness of the superconducting transitions T_c can be attributed to hydrogen gradients within the thickness of the sample foil. The susceptibility measurements were carried out with the sample

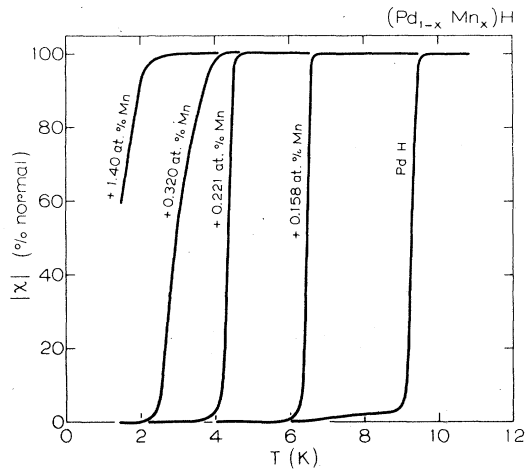

FIG. 2. Susceptibility vs temperature for $(Pd_{1-x}Mn_x)H$, $x = 0$, 0.158, 0.221, 0.320, and 1.40 at.% Mn.

foil oriented parallel to the driving ac magnetic field, however, this orientation was not better than about 10°. This gave rise to rather large demagnetization effects. Therefore for the incomplete superconducting transitions we could only roughly normalize the susceptibility signal to resolve the percentage of the transition. Nevertheless, the accuracy in the determination of T_c even in these cases is better than 0.5 K.

In Fig. 3 the superconducting transition temperatures T_c are plotted versus magnetic impurity concentration x for a number of hydrogenated $Pd_{1-x}Mn_x$ al-

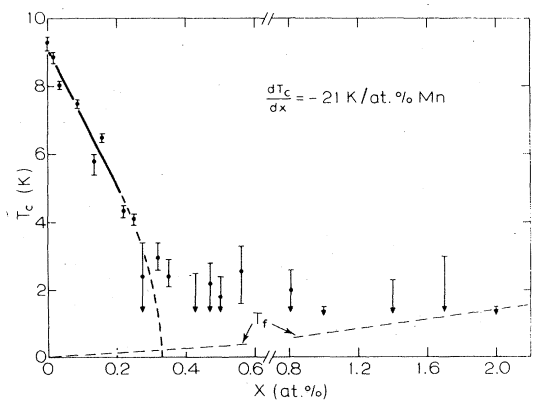

FIG. 3. Superconducting transition temperatures for $(Pd_{1-x}Mn_x)H$ determined from susceptibility measurements. The solid line represents the best linear fit to the data above $T_{c0}/2$ and the heavy dashed line is the extension according to the AG theory. The light dashed line (T_f) represents an extrapolation from high temperatures of the spin-glass freezing temperature (Ref. 22).

loys. The dots give the temperature where 50% of the sample has become superconducting, while the bars give the width of the transition from 10 to 90% of the transition. An arrow means an incomplete transition. Carefully following the identical charging procedure for all alloy samples, we carried out two $\chi(T)$ measurements per magnetic impurity concentration. The results were averaged and are plotted in Fig. 3 for Mn, in Fig. 4 for Cr, and in Fig. 5 for Fe.

By neglecting the Kondo effect and interactions between the magnetic impurities a linear initial depression of T_c in the low-concentration limit is predicted by the Abrikosov-Gor'kov (AG) theory of paramagnetic pair breaking.[8] This dependence is certainly consistent with our experimental results up to 350 ppm for both Fe and Cr and up to 0.25% for Mn. The initial slopes dT_c/dx were obtained by a least-squares fit to the data. The initial depression of the superconducting transition temperature by the magnetic impurities dT_c/dx is determined as -145 ± 15 K/at.% Fe, -150 ± 15 K/at.% Cr, and -21 ± 2 K/at.% Mn in the linear regimes. Using these initial slopes, we have calculated the complete AG $T_c(x)$ dependence and these are shown by the dotted lines in Figs. 3–5. For both Fe and Cr at magnetic impurity concentrations above 350 ppm the transitions become broader and are not complete. Within the experimental accuracy a slight deviation from AG theory to higher T_c at large x values is present for Fe and Cr. For Mn the situation is completely different. Also here at higher Mn concentrations, above 0.25 at.%, the transitions become broader and incomplete. This is probably owing to less homogeneous and less stoichiometric hydrogenated alloys, since the solubility of hydrogen decreases with increasing magnetic impurity concentration.[19] Despite the limited experimental accuracy we clearly observe a superconducting transition temperature T_c at about 2 K which is roughly independent of the Mn x for concentrations ranging from 0.4 up to 2 at.% Mn. The dotted line in Fig. 3 labeled with T_f is a linear extrapolation to low Mn concentration of the spin-glass freezing temperature $T_f = 2$ K as determined at 3 at.% Mn.[22]

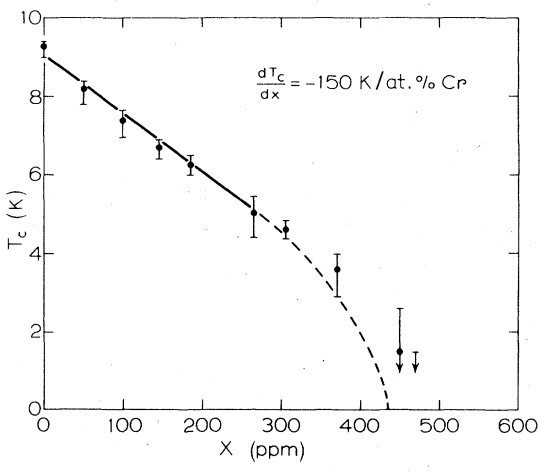

FIG. 4. Superconducting transition temperatures for $(Pd_{1-x}Cr_x)H$ determined from susceptibility measurements. The solid line represents the best linear fit to the data above $T_{c0}/2$ and the dashed line is the extension according to the AG theory.

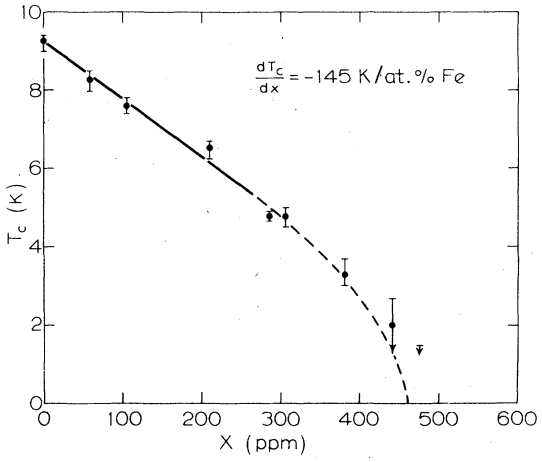

FIG. 5. Superconducting transition temperature for $(Pd_{1-x}Fe_x)H$ determined from susceptibility measurements. The solid line represents the best linear fit to the data above $T_{c0}/2$ and the dashed line is the extension according to the AG theory.

For $(Pd_{1-x}Cr_x)H_{0.7}$ the electrical resistivity ρ as a function of temperature has been investigated by Senoussi *et al.*[16] and Mydosh,[15] who also studied the $\rho(T)$ behavior of $(Pd_{1-x}Fe_x)H_{0.7}$.[13] These authors showed that PdH with both Fe and Cr impurities forms a Kondo system which exhibits a large negative temperature coefficient of resistivity at low temperatures. Furthermore, at larger impurity concentrations a spin-glass freezing is detected in $\rho(T)$ by a turnover to a positive $d\rho/dT$. This minimum-maximum behavior with decreasing temperature is typical for a noble-metal-host Kondo spin-glass.[23] The Kondo temperatures estimated from the resistivity data are $T_K \simeq 5$ K for $(Pd_{1-x}Fe_x)H_{0.7}$ and $T_K \simeq 10$ K for $(Pd_{1-x}Cr_x)H_{0.7}$. As a basis of comparison for *Ag*Fe, T_K is also about 5K while for *Ag* Cr T_K is of order 0.01 K.[4]

It should be noted that the hydrogen-to-metal ratio of the dilute magnetic alloys for the resistivity study was 0.7, so no superconductivity was present. The resistivity of $(Pd_{1-x}Mn_x)H$ was measured since these data are not available in the literature. In Fig. 6 we have plotted the measured $\rho(T)$ curves for four hydrogenated $Pd_{1-x}Mn_x$ alloys with $x = 0$, 0.1, 0.5, and 3 at.% Mn. The hydrogen-to-metal ratio was 0.72 for

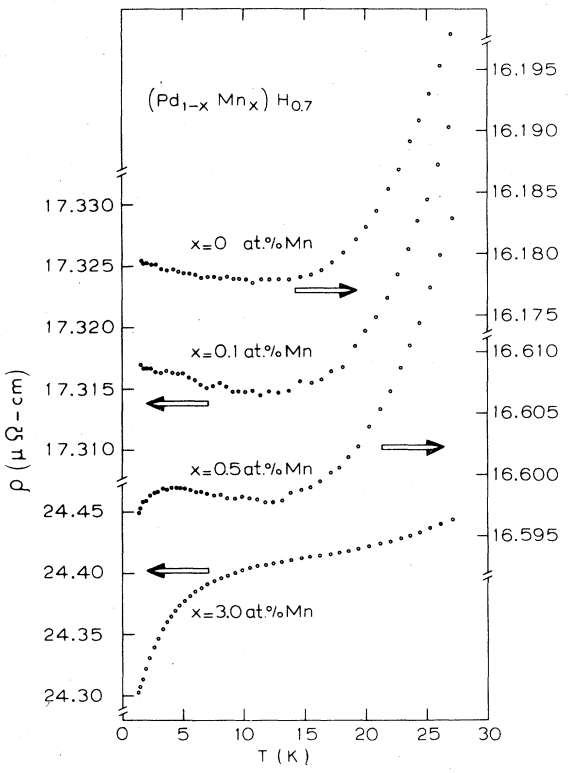

FIG. 6. Electrical resistivity vs temperature for $(Pd_{1-x}Mn_x)H_{0.7}$ with $x=0$, 0.1, 0.5, and 3 at.% Mn.

pure PdH as determined by weighing. This ratio decreases with increasing Mn concentration to [H]/[Pd] = 0.68 for the 3 at.% Mn alloy. Since these hydrogen-to-metal ratios are all well within the diamagnetic β-phase we do not expect a significant influence of this variation in H-to-Pd ratio on the Kondo contribution to $\rho(T)$. Note that on the contrary the residual resistivity, caused by lattice imperfections (nonstoichiometry), is quite strongly dependent on the exact hydrogen concentration.[14] Because of this and uncertainties in the sample dimensions the absolute value of the measured resistivity can only be determined to within 10%. The $\rho(T)$ behavior of pure PdH shows a shallow minimum at about 10–12 K, where the phonon contribution to the resistivity is usually T independent. Below 10 K, down to the lowest temperatures measured, there is a small upturn in the measured resistivity of 1.6 nΩ cm. The experimental accuracy is ± 0.2 nΩ cm. For the hydrogenated alloy with 0.1 at% Mn a similar behavior is observed with an upturn of 2.0 nΩ cm. However, for 0.5 at.% Mn an additional downward curvature in $\rho(T)$ is observed below 4 K. This is probably due to the growth of short-range magnetic order well above the spin-glass freezing temperature $T_f \simeq 0.4$ K as obtained by linear extrapolation of the T_f's for 3 or more at.% Mn.[22] The effect of this short-range order (the precursor of the spin-glass state) well above T_f in $\rho(T)$ is very clearly present in the $\rho(T)$ behavior of the hydrogenated 3 at.% Mn alloy. Here $T_f \simeq 1.5$ K.[22] Finally we emphasize that, within the experimental accuracy, we can hardly detect an additional contribution in $\rho(T)$ due to the Kondo effect in the hydrogenated 0.1 at.% Mn alloy.

IV. DISCUSSION AND COMPARISON WITH THEORY

The depression of superconductivity by magnetic impurities has been reviewed by Maple.[24,25] A useful starting point for a phenomenological understanding is the Abrikosov-Gor'kov (AG) theory.[8] This theory describes the depression of the superconducting transition temperature T_c by "good" magnetic moments, which are randomly distributed in the superconducting host and in the paramagnetic state, i.e., do not interact with each other. A universal approach[8] to the problem is made by introducing a pair breaking parameter α, given by the following relation[24]

$$\alpha = \hbar^{-1} x N(E_F) J_{sd}^2 S(S+1) \ , \tag{1}$$

where x is the magnetic impurity concentration and $N(E_F)$ is the density of states at the Fermi energy for one spin direction. J_{sd} is the conduction-electron–local-moment exchange-interaction parameter and S is the spin of the magnetic impurity for which the orbital angular momentum is assumed to be quenched. The critical pair breaking parameter α_{cr} for complete destruction of superconductivity is given by

$$\alpha_{cr} = 0.14 k_B T_{c0}/\hbar \ , \tag{2}$$

where T_{c0} is the transition temperature of the superconducting host. The depression of T_c with α is given by the universal relation

$$\ln(T_c/T_{c0}) = \psi(\tfrac{1}{2}) - \psi(\tfrac{1}{2} + 0.14\alpha T_{c0}/\alpha_{cr} T_c) \ , \tag{3}$$

where ψ is the digamma function. For the shape of the AG depression of T_c vs x we refer to the preceding Sec. III. In the low magnetic impurity concentration limit, Eq. (3) has the linear asymptotic form

$$T_c/T_{c0} = 1 - 0.691(\alpha/\alpha_{cr}) \ . \tag{4}$$

Substituting Eqs. (1) and (2) we find the initial T_c depression with x for temperature independent (AG) pair breaking

$$\frac{dT_c}{dx} = -4.93 k_B^{-1} N(E_F) J_{sd}^2 S(S+1) \ . \tag{5}$$

For magnetic impurities exhibiting the Kondo effect when dissolved in a superconducting host, the pair breaking parameter α is no longer temperature

independent. The theory of superconducting Kondo systems has been developed by Müller-Hartmann and Zittartz (MH-Z).[9] In this theory the universal relation Eq. (3) for the T_c depression with x is still valid, but α/α_{cr} must be replaced by the relation

$$\frac{\alpha}{\alpha_{cr}} = xA\frac{\pi^2 S(S+1)}{\ln^2 T/T_K + \pi^2 S(S+1)} , \quad (6)$$

where $A=[0.14(2\pi)^2 k_B N(E_F) T_{c0}]^{-1}$. This expression directly shows that α has a maximum at temperatures near the Kondo temperature T_K and goes to small values for both the limits $T \ll T_K$ and $T \gg T_K$. This means that in Kondo superconductors a strong depression of T_c with magnetic impurity concentration is to be expected when $T_{c0} \simeq T_K$. An interesting feature of temperature-dependent pair breaking is the possible occurrence of reentrant superconductivity.[9,24]

Since the Kondo temperature T_K plays a very important role in superconducting pair breaking by magnetic impurities we focus now on the Kondo, negative-temperature coefficient in the resistivity in order to ascertain the Kondo temperature T_K. From such $\rho(T)$ measurements Mydosh has estimated $T_K \simeq 5$ K for $(Pd_{1-x}Fe_x)H_{0.7}$ (Ref. 13) and $T_K \simeq 10$ K for $(Pd_{1-x}Cr_x)H_{0.7}$ (Ref. 15). Thus for both Fe and Cr $T_K \approx T_{c0}$. However, as can be seen from Fig. 6 for $(Pd_{1-x}Mn_x)H_{0.7}$, only a very small Kondo contribution to the measured resistivity can be found within the measuring accuracy of 0.2 nΩ cm. From this we may conclude that T_K is at least a few orders of magnitude smaller for $(Pd_{1-x}Mn_x)H$ compared to $(Pd_{1-x}Fe_x)H$ and $(Pd_{1-x}Cr_x)H$. A "good" local moment is present at low temperatures on the Mn sites since the spin-glass freezing occurs as exemplified by the decrease in the spin disorder resistivity as T is reduced. Therefore the opposite limit of a very large $T_K > 100$ K can be excluded.

Another important parameter here is the spin value S of the magnetic impurity atom. Burger[26] has derived from high-temperature susceptibility measurements on hydrogenated Pd, alloyed with $3d$-transition-metal spin values $S=\frac{5}{2}$ for both Fe and Mn, while for Cr, S is concluded to be close to 2.

For $(Pd_{1-x}Fe_x)H$ and $(Pd_{1-x}Cr_x)H$ the experimentally determined initial slopes dT_c/dx are -145 K/at.% Fe and -150 K/at.% Cr. At low magnetic impurity concentrations, $T_c(x)$ is directly proportional to the MH-Z pair breaking parameter α/α_{cr} given by Eq. (6) setting $T=T_{c0}$. Substituting the Kondo temperatures T_K as estimated by Mydosh[13,15] and the spin values S as derived by Burger[26] very similar and large pair breaking parameters are expected for $(Pd_{1-x}Fe_x)H$ and $(Pd_{1-x}Cr_x)H$. This is in qualitative agreement with experiment. The *maximum* initial depression of T_c in the MH-Z theory is given by Eq. (6) with $T=T_{c0}=T_K$ or simply $\alpha/\alpha_{cr}=xA$. Therefore from Eq. (4) we have $|(dT_c/dx)_{max}|=0.125/k_B N(E_F)$ which is independent of J_{sd} and S. Using the density of states at the Fermi level calculated by Papaconstantopoulous *et al.*[27] for PdH, $N(E_F)=3.14$ states/Ry spin unit cell, we obtain $|(dT_c/dx)_{max}|=63$ K/at.%. Thus, the maximum theoretical depression of $T_c(x)$ is a factor of 2.4 smaller than our measured values $\simeq 150$ K/at.% for $(Pd_{1-x}Fe_x)H$ and $(Pd_{1-x}Cr_x)H$. This, we believe, represents a shortcoming in the theory of MH-Z[9] and prevents a quantitative comparison of our results with the theory. There are other Kondo superconductors which also have experimental $|dT_c/dx| > 0.125/k_B N(E_F)$, see Table I and the associated references for Zn $[N(E_F)=2.14$ states/Ry spin unit cell] and for Cd $[N(E_F)=2.48$ states/Ry spin unit cell]. Nevertheless we can proceed with a qualitative comparison. From Eq. (6) a slight decrease in α/α_{cr} is expected for temperatures somewhat below T_K, which in turn causes a small tail or upturn to appear in the $T_c(x)$ dependence at large x values. Such a deviation (see Figs. 4 and 5) has been observed in both the $T_c(x)$ dependences of $(Pd_{1-x}Cr_x)H$ and $(Pd_{1-x}Fe_x)H$ being somewhat the stronger for $(Pd_{1-x}Cr_x)H$, which is also in accord with the estimated Kondo temperatures given above. An estimate of the magnetic ordering temperature, i.e., the spin-glass freezing temperature, T_f, may be obtained by extrapolating the susceptibility peak temperatures to zero Cr or Fe concentration. At 500 ppm for both Cr and Fe, a $T_f \simeq 0.1$ K is indicated.[14] This means that a study of the coexistance of superconductivity and spin-glass magnetism in $(Pd_{1-x}Cr_x)H$ and $(Pd_{1-x}Fe_x)H$ is impossible because Kondo weakening of the magnetic moments will dominate over the interaction between good moments due to $T_K \gg T_f$.

For $(Pd_{1-x}Mn_x)H$ a much smaller initial slope $dT_c/dx=-21$ K/at.% Mn is observed compared to $(Pd_{1-x}Fe_x)H$ and $(Pd_{1-x}Cr_x)H$. From the resistivity data a $T_K \ll 1$ K has been estimated for Mn in PdH. In the limit of $T_K/T_{c0} \to 0$, MH-Z have shown[9] that their theory reduces to the simple AG case. This is essentially Eq. (6) in the limit $\ln^2 T_{c0}/T_K \gg \pi^2 S \times (S+1)$ and setting

$$T_K \approx T_F \exp\{-1/[N(E_F)2|J_{sd}|]\} .$$

In order to gain some estimate of T_K we assume that the "good" moment AG limit is a reasonable approximation for $(Pd_{1-x}Mn_x)H$. From Eq. (5) we obtain a J_{sd} value of 0.13 eV. Using the above equation for T_K with T_F (the Fermi temperature) equal to 10^5 K for PdH,[27] $T_K \approx 10^{-2}$ K. Such a Kondo temperature is consistent with the resistivity data. However, for spin values larger than $\frac{1}{2}$ ($S=\frac{5}{2}$ for Mn impurities), the condition $\ln^2 T_{c0}/T_K \gg \pi^2 S(S+1)$ requires a $T_K < 10^{-5}$,[9] so that the full Ag limit has not yet been reached in $(Pd_{1-x}Mn_x)H$ and Kondo fluc-

TABLE I. Classification of some Kondo superconductors containing $3d$ impurities: (i) $T_K << T_{c0}$, (ii) $T_K \simeq T_{c0}$, and (iii) $T_K >> T_{c0}$.

Host	T_{c0} (K)	Imp.	$-dT_c/dx$ (K/at.%)	T_K (K)	Class.	Ref.
PdH	9.3	Cr	150	10	ii	This work
		Mn	21	$<<1$	i	This work
		Fe	145	5	ii	This work
Zn	0.875	Cr	200	1	ii	30,33
		Mn	300	1	ii	30,33
		Fe	13	180	iii	34,32
Al	1.196	Cr	8.1	1200	iii	34,32
		Mn	14	530	iii	34,32
		Fe	8.0	>1000	iii	34,32
Cd	0.55	Cr	140	≈ 0.5[a]	ii	28
		Mn	220	0.1	ii	29,31
PdSb	1.66	Cr	140	≈ 2[a]	ii	35
		Mn	11	$<<2$[a]	i	35
		Fe	8	$>>2$[a]	iii	35

[a]Predicted values.

tuations are still affecting the superconducting pair breaking.

For comparison we collect in Table I the properties of a number of Kondo superconductors containing $3d$ impurities. Three classes of Kondo superconductors can be distinguished: (i) $T_K << T_{c0}$ with weak T_c depression, (ii) $T_K \simeq T_{c0}$ with strong T_c depression, and finally (iii) $T_K >> T_{c0}$ with weak T_c depression. We can further use the superconducting and magnetic moment data on PdSb (Ref. 35) to predict the Kondo temperatures for Cr impurities ($T_K \approx T_{c0} \approx 2$ K), Mn impurities ($T_K << 2$ K) and Fe impurities ($T_K >> 2$ K).

For $(Pd_{1-x}Mn_x)H$ the near AG $T_c(x)$ dependence is followed up to 0.25 at.% Mn, see Fig. 3. However for higher Mn concentrations we observe an enhanced superconductivity up to at least 2 at.% Mn. Due to the experimental limitations as described above, we have to be conservative about the exact form of $T_c(x)$ above 0.25 at.% Mn, but obviously the pair breaking strength of the Mn impurities is greatly decreased at these higher Mn concentrations. This is most probably related to the short-range magnetic ordering of the Mn magnetic moments already present above the spin-glass freezing temperature. Such an effect is clearly seen in the $\rho(T)$ behavior, Fig. 6, as a smeared out decrease of the resistivity with decreasing temperature. The magnetic correlations between the Mn magnetic moments are mainly antiferromagnetic in origin as can be deduced from the negative paramagnetic Curie temperatures observed in $(Pd_{1-x}Mn_x)H_{0.7}$ via high-field susceptibility measurements by Burger.[26] We suggest that the antiferromagnetic nature of these short-range correlations for $T > T_f$ is very important in contributing to the pronounced decrease of the pair breaking strength in $(Pd_{1-x}Mn_x)H$ for $x > 0.25$ at.% Mn.

This suggestion is supported by experimental evidence on superconducting ternary and pseudoternary rare earth (RE) compounds as recently described by Maple.[36] Here very small values (0.01 eV) of the exchange interaction parameter J between the conduction-electron spins and the RE magnetic moments offers the possibility to study the interaction between superconductivity and long-range magnetic order. Definite experimental evidence has been obtained for the coexistence of superconductivity and long-range antiferromagnetic order, e.g., $Er_{1.2}Mo_6Se_8$, while long-range ferromagnetic order always destroys superconductivity, e.g., $ErRh_4B_4$. This supports our proposal that antiferromagnetic correlations tend to reduce the pair breaking effect, while ferromagnetic correlations tend to enhance the pair breaking effect.

Already for many years there have been observations of tails and other deviations from the AG theory in the depression of T_c at high magnetic impurity concentrations.[37] Such effects have been treated theoretically as due to the onset of short-range magnetic ordering.[38] This type of random magnetic "freezing" is now known as the spin-glass state and is the subject of considerable interest to determine its exact nature. Using the spin-glass concept, a few years ago Roth[39] reviewed the problem of the coexistence of superconductivity and magnetic order in pseudobinary Laves phase compounds, for example $Gd_xCe_{1-x}Ru_2$.[40] At high Gd concentrations a freez-

ing temperature $T_f(x)$ was observed, while at low Gd concentrations superconductivity with a $T_c(x)$ was found. The $T_c(x)$ and $T_f(x)$ curves cross at 2 K for $x \simeq 0.11$. At this Gd concentration a relatively strong T_c depression is observed compared to lower Gd concentrations. Here again ferromagnetic correlations between the Gd moments are probably causing this behavior. For Gd impurities there is no Kondo effect.

The coexistence of superconductivity and spin-glass freezing is presently of theoretical interest. Sadovskii and Skryabin[10] have analyzed the effect of spin-glass ordering upon the superconductivity and concluded that there is no mutual influence. Soukoulis and Grest[11] have introduced a model with a pair breaking parameter which includes both spatial and time correlation effects. From their model they calculate that spatial correlations which are ferromagnetic have a tendency to enhance the pair breaking, while spatial correlations for an antiferromagnet or spin-glass reduce the pair breaking. In addition time or dynamical correlations always reduce the pair breaking for all types of magnetic ordering. Thus in spin-glasses which typically exhibit dynamical correlations for $T > T_f$, it is possible to have an enhanced superconductivity above the freezing temperature. Our experimental results for Mn which show a shoulder in $T_c(x)$ are offered as support for this interpretation.

In conclusion we remark that $(Pd_{1-x}Fe_x)H$ and $(Pd_{1-x}Cr_x)H$ can be classified as enhanced pair breaking systems due to the Kondo effect ($T_K \approx T_{c0}$). On the other hand $(Pd_{1-x}Mn_x)H$ with $T_K << T_{c0}$ shows a near AG pair breaking, and additionally at larger Mn concentrations, there is an enhancement of the superconductivity due to the onset of time correlations and short-range antiferromagnetic spatial correlations which lead to the spin-glass freezing at a lower temperature. Thus here the evolution of the spin-glass state is most favorable for the coexistence with superconductivity.

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[1]T. Skoskiewicz, Phys. Status Solidi (a) 11, K123 (1972); and B. Stritzker and W. Buckel, Z. Phys. 257, 1 (1972).
[2]B. Stritzker and H. Wühl, in *Topics in Applied Physics, Hydrogen in Metals II,* edited by G. Alefeld and J. Völkl (Springer, Berlin, 1978).
[3]R. A. Webb, J. B. Ketterson, W. P. Halperin, J. J. Vuillemin, and N. B. Sandesara, J. Low Temp. Phys. 32, 659 (1978).
[4]J. A. Mydosh and G. J. Nieuwenhuys, in *Handbook of Ferromagnetic Materials,* edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1980), Vol. I, Chap. 2.
[5]R. W. Standley, M. Steinback, and C. B. Satterthwaite, Solid State Commun. 31, 801 (1979).
[6]B. M. Klein, E. N. Economou, and D. A. Papaconstantopoulos, Phys. Rev. Lett. 39, 574 (1977); and B. N. Ganguly, Phys. Rev. B 14, 3848 (1976).
[7]R. J. Miller, T. O. Brun, and C. B. Satterthwaite, Phys. Rev. B 18, 5054 (1978).
[8]A. A. Abrikosov and L. P. Gor'kov, Sov. Phys. JETP 12, 1243 (1961) [Zh. Eksp. Teor. Fiz. 39, 1781 (1960)].
[9]E. Müller-Hartmann and J. Zittartz, Phys. Rev. Lett. 26, 428 (1971); Z. Phys. 234, 58 (1970); Phys. Rev. Lett. 26, 428 (1971). See also E. Müller-Hartmann, in *Magnetism V,* edited by H. Suhl (Academic, New York, 1973), Vol. V, Chap. 12.
[10]M. V. Sadovskii and Yu. N. Skryabin, Phys. Status Solidi (b) 95, 59 (1979).
[11]C. M. Soukoulis and G. S. Grest, Phys. Rev. B 21, 5119 (1980).
[12]J. C. M. van Dongen and J. A. Mydosh, Z. Phys. Chem (Frankfurt am Main) 116, 149 (1979).
[13]J. A. Mydosh, Phys. Rev. Lett. 33, 1562 (1974).
[14]J. P. Burger, S. Senoussi, and B. Soufaché, J. Less-Common Met. 49, 213 (1976).
[15]J. A. Mydosh, in *Magnetism and Magnetic Materials—1975 (Philadelphia),* edited by J. J. Becker, G. H. Lander, and J. J. Rhyne, AIP Conf. Proc. No. 29 (AIP, New York, 1975).
[16]S. Senoussi, J. P. Burger, and B. Souffaché, J. Phys. (Paris) 37, L-89 (1976).
[17]C. L. Wiley and F. Y. Fradin, Phys. Rev. B 17, 3462 (1978).
[18]J. P. Burger, D. S. MacLachlan, R. Mailfert, and B. Souffaché, Solid State Commun. 17, 277 (1975).
[19]F. A. Lewis, *The Palladium-Hydrogen System* (Academic, New York, 1967).
[20]R. J. Miller and C. B. Satterthwaite, Phys. Rev. Lett. 34, 144 (1975).
[21]J. S. Carlow and R. E. Meads, J. Phys. F 2, 982 (1972).
[22]G. Alquie, A. Kreisler, J. P. Burger, and B. Souffaché, J. Magn. Magn. Mater. 15, 735 (1980).
[23]J. S. Schilling, Adv. Phys. 28, 657 (1979).
[24]M. B. Maple, Appl. Phys. 9, 179 (1976).
[25]M. B. Maple, in *Magnetism-V,* edited by H. Suhl (Academic, New York, 1973), Vol. V, Chap. 10.
[26]J. P. Burger, Ann. Phys. (Paris) 9, 345 (1964).
[27]D. A. Papaconstantopoulous, B. M. Klein, J. S. Faulkner, and L. L. Boyer, Phys. Rev. B 18, 2784 (1978).
[28]T. Cleason, M. Hanson, and J. Ivarsson, Solid State Commun. 25, 655 (1978).
[29]T. Cleason, M. Hanson, and J. Ivarsson, Solid State Commun. 20, 233 (1976).

[30]R. Vaccarone, A. Morozzo della Rocca, A. Pilot, F. Vivaldi, and C. Rizzuto, Solid State Commun. 12, 885 (1973).
[31]H. Alloul, D. Deltour, and R. Clad, J. Phys. Soc. Jpn. 28, 661 (1970).
[32]A. E. Bell and A. D. Caplin, J. Phys. F 5, 143 (1975).
[33]C. Rizzuto, Rep. Prog. Phys. 37, 147 (1974).
[34]G. Boato, G. Gallinaro, and C. Rizzuto, Phys. Rev. 148, 353 (1966).
[35]T. H. Geballe, B. T. Matthias, B. Caroli, E. Corenzwit, J. P. Maita, and G. W. Hull, Phys. Rev. 169, 457 (1968).
[36]M. B. Maple, J. Phys. (Paris) 39, C6-1374 (1978).
[37]See R. D. Parks, in *Superconductivity,* edited by P. R. Wallace (Gordon and Breach, New York, 1969), Vol. 2, p. 625.
[38]See K. H. Bennemann, in *Superconductivity,* edited by P. R. Wallace (Gordon and Breach, New York, 1969), Vol. 1, p. 3.
[39]S. Roth, Appl. Phys. 15, 1 (1978).
[40]D. Davidov, K. Baberschke, J. A. Mydosh, and G. J. Nieuwenhuys, J. Phys. F 7, L47 (1977).