Magnetic hyperfine interaction for Co^{60} in PdRhCo alloys

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The magnetic hyperfine fields on Co^{60} nuclei in the $(Pd_{1\,=\,x}Rh_x)_{0.99}Co_{0.01}$ system are measured by the oriented nucleus method for $0.005 \leq x \leq 0.23$. The dependence of the field on composition at low impurity concentrations is identical to the dependence previously measured [1] for the $Pd_{1-x}Co_x$ system. Variation of the hyperfine field strength for Co in the PdRhCo system can be explained (as in the case of the PdCo system) by variation of the positive contribution made to the field by polarization of the conduction electrons by the intrinsic magnetic moment of the Co atom. On the basis of the single concentration dependence of the fields in the PdRhCo and PdCo systems, it is concluded, that the Rh and Co atoms exert equal effects on the positive hyperfine field on their appearance in the first Co coordination sphere. The experimental results also show that the property of the Pd which leads to the appearance of strong positive magnetic fields for impurity 3d atoms is very sensitive to the nearest surroundings. A single impurity atom strongly interacting with the conduction electrons is sufficient to decrease the field strength sharply.

INTRODUCTION

An investigation of solid solutions of 3d transition metals in palladium has revealed a number of interesting features of the magnetic hyperfine interaction, which are characteristic of the indicated systems. These features become manifest primarily in the existence of large positive hyperfine fields at the impurity atoms Co and Ni in the Pd[1,2], this apparently being due to the unique properties of Pd, since no positive fields were observed at the nuclei of 3d elements in other matrices. Properties similar to those of 3d elements with Pd are exhibited by the corresponding alloys with Pt (for example, impurity ferromagnetism is observed in both types of alloy), but the field at Co in Pt is negative and is practically independent of the composition[3].

The oriented-nuclei procedure was used in[1] to measure the hyperfine magnetic fields H_{hf} at Co^{60} nuclei in PdCo alloys. The obtained dependence of H_{hf} on the Co concentration indicates that the field is positive at low Co concentrations (in accord with the results of Cracknell et al.[4]), decreases in absolute value when Co is added, and reverses sign at a Co concentration 25–35 at.%. A similar behavior of H_{hf} was also observed for Ni atoms in PdNi alloys[2].

Two explanations were offered for the large positive fields at the impurity atoms Co and Ni in Pd. Erich et al.[2] proposed that the positive field is due to the polarization of the matrix by the magnetic moment of the 3d atom, i.e., it is connected with the effect exerted on the magnetic hyperfine field on Co and Ni by the neighboring atoms. This assumption, however, contradicts modern notions concerning the effect of the environment on the magnetic hyperfine interaction. It is known that the magnetic moments of Pd atoms located near Co atoms are very small (less than 0.05 μ_B[5]). It must therefore be assumed that the environment can make only a very small contribution to the observed H_{hf} in dilute PdCl alloys.

The appearance of large positive fields is attributed in[1] to polarization of the conduction electrons by the intrinsic magnetic moment of the Co atom. It is known that the magnetic field at the nucleus of a magnetic 3d atom in a ferromagnetic matrix can be represented in the form

$$H = a\mu_i + b\mu_M, \tag{1}$$

where μ_i is the intrinsic magnetic moment of the atom, μ_M is the magnetic moment of the matrix atoms, and a and b are coefficients that are constant for a given impurity atom. The experimental data[1] and theoretical calculations[6] show that in first-order approximation the contribution made to the field by the intrinsic magnetic moment of a 3d atom can be represented in the form of a sum of two contributions of opposite sign (i.e., $a = -a_1 + a_2$). The negative contribution is due to the polarization of the internal s shells of the atom (polarization of the core); the positive contribution is due to the interaction of the magnetic moments with the electrons of the outer shells (the conduction electrons in the case of an atom in a metallic matrix). The negative contribution (according to theoretical calculations by Freeman and Watson[6]) is practically the same for all 3d atoms, and is approximately equal to 120 kOe/μ_B. The positive contribution cannot be calculated and is apparently very sensitive to singularities of the electron structure of the matrix, and also to the character of the wave functions of the magnetic 3d electrons. According to an analysis performed in[1], the positive contribution is large enough for Co and Ni atoms (but not for Fe) in ordinary ferromagnets (Fe, Co, Ni); in a Pd matrix it reaches values that are much larger than the negative contribution from the core polarization (i.e., the coefficient a_2 exceeds a_1 in absolute value). This is possible if the conduction-electron polarization by the magnetic moment of the impurity 3d atom (Co, Ni) is much stronger in the Pd matrix than in the ferromagnets Fe, Co, and Ni (this may be connected with the large density of the electronic states of Pd). The second term of the formula in[1], that due to the environment, also yields a negative contribution to the field at the nucleus of the 3d atom[1]. This contribution increases with increasing Co or Ni concentration in alloys with Pd, when the direct influence of these atoms on one another begins to come into play.

To explain further the nature of the magnetic hyperfine interaction in Pd, we deemed it of interest to study the influence of a third component on the hyperfine field for a 3d atom. To this end we have measured in the present study the dependence of the field at Co^{60} on the composition in the system $(Pd_{1-x}Rh_x)_{0.99}Co_{0.01}$ at

$0.005 \leq x \leq 0.23$. The choice of rhodium was dictated by the fact that the magnetic properties of the PdRh alloy have been investigated quite adequately. This system becomes ferromagnetic in a wide range of Rh concentrations when small amounts of Co are added.

DESCRIPTION OF EXPERIMENT AND MEASUREMENT RESULTS

The magnetic hyperfine fields at the Co atoms in the system $(Pd_{1-x}Rh_x)_{0.99}Co_{0.01}$ were determined from the anisotropy of the angular distribution of the γ radiation from polarized Co^{60} nuclei. The investigated samples were prepared by fusing appropriate amounts of the components (the initial metals were 99.98% pure) in vacuum, followed by homogenization at 1000°C for 7–10 hours. Samples in the form of disks 3–4 mm in diameter and 0.2–0.3 mm thick were bombarded with neutrons to obtain the radioactive Co^{60}. The γ radiation was registered by two scintillation counters located along the orienting field (at angles 0 and 180°). A previously described[7] adiabatic demagnetization procedure was used to obtain infralow temperatures. The temperature was measured with a low-temperature $NiMn^{54}$ thermometer in Ni soldered together with the investigated sample to the end of a copper cold finger. The other end of the cold finger was pressed into a block of potassium chrome alum.

The $NiMn^{54}$ source was obtained by precipitating manganese chloride containing radioactive Mn^{54} onto a plate of metallic nickel, followed by annealing in a hydrogen atmosphere for 48 hours. After annealing, the surface of the plate was thoroughly cleaned and etched with hydrochloric acid.

The choice of the $NiMn^{54}$ system as the thermometer was dictated by the fact that the field at the Mn nucleus in Ni is known with good accuracy and, unlike the corresponding value for Mn in Fe, the scatter of the experimental values is small. In the temperature calculations we used the value $H_{hf} = -321.3$ kOe[8]. The 8-kOe orienting magnetic field applied to the sample was produced by an electromagnet. According to the available experimental data, this value is sufficient to magnetize NiMn to saturation[9]. Although there are no corresponding data for the PdRhCo system, it was assumed that the investigated samples were also magnetized to saturation in such a field.

From the simultaneously measured angular anisotropy of the γ quanta of Co^{60} and of Mn^{54}, taking into account the known value of H_{hf} for Mn^{54}, we calculated the hyperfine magnetic field at Co^{60} in the PdRh matrix. In the calculations we introduced corrections for the background, and also for the pedestal under the Mn^{54} photopeak due to the Compton effect from the Co^{60}; the contribution of the latter was included with allowance for the anisotropy of the angular distribution of the γ quanta. The sample temperature at the start of the measurements was 0.02°K.

The results of measurements of the hyperfine field for 1 at.% Co in a PdRh matrix are shown in Fig. 1 as a function of the Rh concentration. The sign of the hyperfine field at the Co nucleus was determined¹⁾ in a separate experiment from the asymmetry of the Mössbauer hyperfine spectrum of Fe^{57}, measured at infralow temperatures. The Co^{57} source introduced into the $(Pd_{99.98}Rh_{0.02})_{0.99}Co_{0.01}$ was cooled by adiabatic demagnetization of iron-ammonium alum to a temperature 0.2° K. The stainless-steel absorber was kept at room temperature. Owing to the unequal populations of the sublevels of the hyperfine structure of the parent nucleus Co^{57}, which is proportional to the Boltzmann factor, the hyperfine-structure components in the Mössbauer spectrum of Fe^{57} exhibit an intensity asymmetry whose sign depends on the direction of the magnetic field at the Co nucleus[10]. The field at Co determined in this manner turned out to be positive, and from the monotonic dependence of the field on the Rh concentration we could conclude that the field at the Co nucleus is positive in the entire investigated range of Rh concentrations in PdRhCo alloys, just as in PdCo alloys (at not very large Co concentrations).

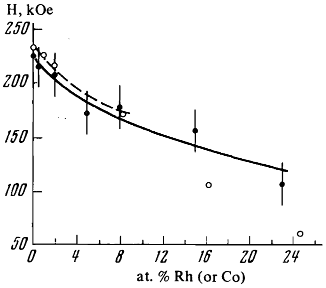

FIG. 1. Hyperfine magnetic fields for an impurity of 1 at. % Co in a $Pd_{1-x}Rh_x$ matrix (dark circles) and fields at Co in $Pd_{1-x}Co_x$ alloys from [1] (light circles).

DISCUSSION

It is seen from Fig. 1 that the hyperfine field at Co in the PdRhCo alloy decreases monotonically with increasing Rh concentration. Turning to formula (1), we see that the lowering of the field at Co can be due either to a decrease in the intrinsic magnetic moment of Co or to a decrease in the coefficient a (the second term of formula (1), which is due to the contribution of the environment, is small, as indicated above, and the field is determined mainly by the first term). As follows from the results of Jaccarino and Walker[11], the magnetic self-moment of Co remains constant in the entire range of investigated concentrations. It must therefore be concluded that the change of the field is due to the change of the coefficient $a = -a_1 + a_2$. Since the coefficient a_1, which determines the contribution from the core polarization, is constant with sufficient accuracy, the entire change of the field is obviously connected with the coefficient a_2, i.e., with the decrease of the positive contribution from the conduction-electron polarization by the intrinsic magnetic moment of Co. It should be noted that the observed concentration dependence of the hyperfine field at the Co does not correlate with the course of the magnetic susceptibility of the matrix: the susceptibility of the PdRh system has a clearly pronounced maximum at a concentration ~5 at.% Rh, and in the region of small Rh concentrations it is, on the average, larger than the susceptibility of pure palladium[12].

Figure 1 also shows the dependence of the hyperfine field on composition for Co^{60} in the PdCo system[1]; we see that at low Co concentration (so long as the contribution from the environment can be neglected), the behavior of the hyperfine field is in this case identical with that considered above²⁾. It follows somewhat unexpectedly from this result that replacement of the Pd atoms by Rh or Co atoms in the nearest neighborhood of Co produces the same effect on the positive contribution to the field at the Co atoms in both alloy systems.

In this connection, however, we point out the available

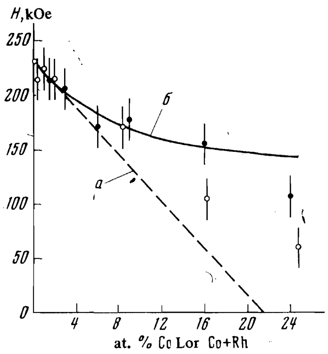

FIG. 2. Dependence of the field at the Co^{60} nucleus on the total impurity concentration: ●—for the PdRhCo system, ○—for the PdCo sytem. The curves are calculated with allowance for the additive (a) and non-additive (b) contributions made to the field by the nearest impurity neighbors.

data on the Knight shift of Rh^{103} in the PdRh system[13]. From a comparison of the measured Knight shift of Rh (at low Rh concentrations) with the Knight shift of Pd^{105} in metallic Pd, it was concluded that the local susceptibility of Rh in PdRh is approximately 3 times larger than the susceptibility of the palladium matrix. Only ~12% of the impurity susceptibility is concentrated at the Rh site, and the remaining 80% is distributed over the sites of the nearest Pd neighbors. Since it is known that an isolated Co impurity in Pd gives rise to an appreciable polarization of the surrounding atoms, it can be assumed that the local susceptibility of the Co in the PdCo system, just as that of Rh in the PdRh system, is also high. Then there is physical justification for the similar influence exerted on the hyperfine field by the isoelectronic Co and Rh when they appear among the nearest neighbors of Co, i.e., the decrease of the field when the "competing" Co atoms and Rh atoms are added to the systems PdCo and PdRhCo, respectively.

We can now consider jointly the concentration dependence of the hyperfine field for Co in the PdCo and PdRhCo systems. To this end, Fig. 2 shows the fields as functions of the Co concentration (PdCo system) or of the Rh + Co concentration (PdRhCo system). As seen from the figure, the field values for both systems of alloys satisfy the same relation with sufficient accuracy, at least at low impurity concentrations. One can attempt to connect the concentration dependence of the field with the probability for the appearance of Co or Rh impurity atoms in the nearest environment of the Co. For the face-centered Pd lattice, the number of nearest neighbors determining the first coordination sphere is 12. We represent the dependence of the field on the concentration in the form

$$H_{\mathrm{hf}}(x)=H_0-h\sum_{n=1}^{12}kP_n(x)=H_0-h\sum_{n=1}^{12}k\binom{12}{n}x^n(1-x)^{12-n}. \qquad (2)$$

Here H_0 is the value of the field in the limiting case of an isolated Co atom, $P_n(x)$ is the probability of appearance of n impurity-atom neighbors, x is the atomic concentration, and h is the amount by which the field at the Co is decreased when one of the nearest Pd atoms is replaced by a Co or Rh atom. This quantity, equal to ~90 kOe, was calculated from the experimental values of the field at low impurity concentrations, when only configurations with 0 or 1 impurity neighbors exist in practice. The meaning of the coefficient k will be made clear in the subsequent exposition.

We considered two extreme cases: a) the change of the field depends additively on all the nearest neighbors, k = n; b) the change of the field does not depend on the concrete number of impurity neighbors, provided that, of course, n ≥ 1, and in this case k = 1. The curves calculated under these assumptions are shown in Fig. 2. We see that the experimental points fit curve b well, i.e., the entire change of the field is actually due to one impurity neighbor in the nearest environment of Co, and the contribution of the remaining impurity neighbors is negligible. The noticeable deviation from the calculated curve observed for the PdCo system at large Co concentrations ($\gtrsim$ 10 at.%), is due to the fact that the environment begins to play a substantial role at these concentrations.

Before we proceed to the conclusions of the present work, we must note that the behavior of the impurity Fe atoms in Pd differs noticeably from that of Co and Ni, namely, the hyperfine magnetic fields at the Fe in PdFe are negative in the entire range of concentrations, and are close in magnitude to the field in metallic iron[14]. It follows from the systematics of the fields that this behavior is also characteristic of the Fe impurity in other ferromagnetic matrices. The field at the Fe is thus due mainly to the polarization of the inner s-shells and to a much lesser degree to the polarization of the conduction electrons; this is apparently connected with singularities of the wave functions of the d electrons of the Fe atom.

In conclusion, our results can be formulated in the following manner.

1. The change of the hyperfine field at the Co in the PdRhCo system is due (as in the PdCo system), to a change in the positive contribution, which we attribute to the polarization of the conduction electrons by the magnetic self-moment of the CO.

2. The Co and Rh atoms behave similarly with respect to their influence on the positive hyperfine field when they appear among the nearest neighbors of Co.

3. That property of Pd which determines the appearance of large positive fields at 3d-atom nuclei is very sensitive to the nearest environment, and even a single impurity atom that interacts strongly with the conduction electrons suffices to decrease this property sharply.

For a more detailed explanation of the nature of the considered phenomena, it is of interest to perform similar research with other impurities.

In conclusion, the authors consider it their pleasant duty to thank V. S. Shpinel' and N. N. Delyagin for a discussion of the results and S. I. Semenov for preparing the $NiMn^{54}$ source.

[1)] This result was obtained by A. S. Kuchna in our laboratory.

[2)] The values of the fields given in Fig. 1 for the PdCo system differ somewhat from the corresponding values of [1]. The reason is that the use of the Mn^{54} thermometer resulted in a more reliable determination of the temperature, so that the earlier results could be corrected.

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