Magnetic hyperfine interaction for ^{60}Co in alloys containing palladium and platinum

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The magnetic hyperfine fields at ^{60}Co nuclei in ferromagnetic $Co_{0.01}(Pd_{1-x}Pt_x)_{0.99}$ alloys are measured over the entire composition range $0 \leqslant x \leqslant 1$ by the method of oriented nuclei. The results show that as Pt atoms are substituted for Pd atoms, the hyperfine field at Co decreases from a maximum positive value for the dilute alloy of Co in Pd, changes sign at a Pt concentration of about 50 at.%, and then increases in absolute magnitude to a maximum negative value for the dilute alloy of Co in Pt. This behavior of the hyperfine field as a function of the platinum concentration can be attributed primarily to a decrease of the positive contribution to the field, which is due to polarization of the conduction electrons by the intrinsic magnetic moment of the Co atoms. In the limiting case of an impurity Co atom in a Pt matrix, the positive contribution is nearly zero, and the hyperfine field is almost entirely determined by the contribution from core polarization. The concentration dependence of the hyperfine field for the $Co_{0.01}(Pd_{1-x}Pt_x)_{0.99}$ system, as well as the previously measured dependence for the $Co_{1-x}Pt_x$ system, are satisfactorily described by simple empirical formulas. The results are compared with the positive contribution to the hyperfine field at Co, Ni, and Fe in binary alloys of these metals with palladium.

1. INTRODUCTION

Recent studies of alloys of 3d elements with palladium have revealed certain interesting features , characteristic of these systems, of the magnetic hyperfine interaction of 3d atoms. The large positive hyperfine fields found at impurity Co and Ni atoms in Pd[1-5] have not yet been found for 3d elements in other matrices. In these alloys the hyperfine field decreases in absolute value with increasing CO or Ni concentration and changes sign at a concentration of ~30 at.% Co[2] or ~50 at.% Ni[4, 5]. In interpreting the experimental results on the fields at CO and Ni nuclei in Pd matrices, the authors of[2, 5] gave what appear at first glance to be similar explanations for the origin of the positive contribution to the hyperfine field. However, while Tansil et al.[5] assume that the positive hyperfine field at the 3d atom is due only to the properties of the palladium matrix, Balabanov et al.[2] emphasize that the positive contribution is present even in pure 3d matrices, even though the resultant hyperfine field in these matrices is negative. It will become clear from what follows that this last assertion is essential for an understanding of the behavior of the hyperfine field in the systems considered here.

The hyperfine fields at 3d atoms in ferromagnetic Fe, Co, and Ni matrices are well represented by the following empirical formula[2, 6]:

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

in which μ_i is the intrinsic magnetic moment of the impurity atom, μ_M is the mean magnetic moment of the matrix atoms, and the coefficients a and b are constant for a given impurity atom. The first term in (1) represents the contribution to the hyperfine field due to the intrinsic magnetic moment of the impurity 3d atom, and the second term represents the contribution due to the surroundings and is proportional to the mean atomic magnetic moment of the matrix. An analysis of the available experimental data[2] supports the conclusion that the contribution to the field from the intrinsic magnetic moment of the 3d atom can be expressed as the sum of two terms of opposite sign. The first term, which is negative, is associated with the polarization of the inner atomic s shells (core polarization), and the second term, which is positive, is due to the interaction of the magnetic moment with electrons of the outer shells (with the conduction electrons in the case of an atom in a metallic matrix). According to the theoretical calculations of Freeman and Watson[7], the negative contribution is virtually the same for all 3d atoms and is approximately equal to -120 kOe/μ_B. The positive contribution cannot be directly calculated and is apparently very sensitive to the electronic structure of the matrix. In accordance with these ideas we may rewrite Eq. (1) as follows:

$$H_{HF}=a_1\mu_i+a_2\mu_i+b\mu_M, \tag{2}$$

where $a_1 < 0$, $a_2 > 0$, and $b < 0$. The first term in (2) represents the core polarization contribution to the field, and the second term, the contribution due to polarization of the conduction electrons by the intrinsic magnetic moment of the 3d atom.

It was pointed out in[2] that the coefficient a_2 is fairly large for Co and Ni atoms in ordinary ferromagnetic (Co, Fe, Ni) matrices, even though it is still smaller than a_1. This conclusion follows immediately from the fact that the coefficient a in Eq. (1) for Co and Ni is considerably smaller than 120 kOe/μ_B. The positive contribution reaches much larger values in the palladium matrix, with the result that at low Co and Ni concentrations the resultant hyperfine field is positive.

The discovery of positive hyperfine fields at magnetic 3d atoms in Pd stimulated the study of the hyperfine interaction for Co in Pt, for Pt has been usually regarded as in many respects analogous to Pd. Alloys of 3d elements with Pt, like such alloys with Pd, are ferromagnetic even at low concentrations of the 3d elements; moreover, giant magnetic moments also arise in these alloys, even though they are smaller than the corresponding magnetic moments in the alloys with Pd. Measurements of the hyperfine field at Co in Pt showed, however, that there is no analogy with the CoPd and

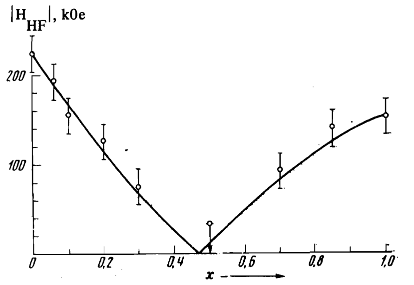

FIG. 1. Hyperfine magnetic fields at Co impurity atoms in $Pd_{1-x}Pt_x$ matrices containing 1 at.% Co. The curve was calculated from Eq.(3)

NiPd systems. The hyperfine field at Co was found to be negative[8] and only slightly concentration dependent[9]. This result shows that there is an obvious difference between the formation of the hyperfine field at 3d atoms in systems of these two types. The fact that the field at Co in Pt is negative indicates that in this system the positive contribution, which is proportional to the intrinsic magnetic moment, is small.

In order to reach a more detailed explanation of the peculiarities of the hyperfine field and of the effect of platinum on the positive contribution to that field we undertook a study of the magnetic fields at Co nuclei in ferromagnetic alloys of the composition $Co_{0.01}(Pd_{1-x}Pt_x)_{0.99}$. This system is convenient because in analyzing the hyperfine field on can neglect the contribution from the matrix (the last term in Eq. (2)) in the first approximation and assume that the resultant field is determined entirely by core polarization and the interaction of the intrinsic magnetic moment of Co with the conduction electrons (the first two terms in Eq. (2)). This is due to the fact that the magnetic moments of Pd and Pt are small and that the Co concentration in the alloy is also small. The effect of platinum on the positive field should appear even more clearly since the positive contribution to the hyperfine field at impurity Co atoms in Pd is large as compared with the corresponding contribution in pure Co.

2. EXPERIMENTAL PROCEDURE AND RESULTS

The magnetic hyperfine field at the Co atoms was determined from the anisotropy in the angular distribution of the γ rays emitted by oriented ^{60}Co nuclei. The ^{60}Co nuclei were polarized at low temperatures in ferromagnetic specimens of composition $Co_{0.01}(Pd_{1-x}Pt_x)_{0.99}$ with $0 \le x \le 1$. The specimens for study were prepared by fusing together appropriate quantities of the initial components (nominal purity, 99.98%) and subsequently homogenizing at 1000°C for ~20 hr. The disk shaped specimens 3–4 mm in diameter and 0.2–0.3 mm thick were irradiated with neutrons to produce the radioactive ^{60}Co nuclei. The γ rays were recorded with a solid Ge(Li) detector working into a 512 channel type NTA-512 analyzer and a scintillation γ-ray spectrometer using an NaI(Tl) crystal, mounted at angles of 0 and 180° to the direction of the external orienting field.

The required ultralow temperatures were obtained by adiabatic demagnetization of potassium chrome alum. The temperature was measured with a nuclear thermometer consisting of ^{54}Mn in Ni and whic, together with the specimen, was soldered to the end of a copper heat pipe[10]. An 8 kOe external magnetic field produced by an electromagnet was applied to the specimen.

The angular anisotropies of the 117 and 1332 keV ^{60}Co and 835 keV ^{54}Mn γ rays were measured simultaneously, and the hyperfine field at the ^{60}Co nuclei was calculated from these results and the known value[11] $H = -321.3$ kOe of the hyperfine field for $Ni(^{54}Mn)$. In these calculations, corrections were made for the background and for the pedestal under the ^{54}Mn photopeak due to the Compton effect from ^{60}Co. The temperature of the specimen the measurements varied between 0.02 and 0.03°K.

Figure 1 shows the observed strength of the hyperfine magnetic field for 1 at.% Co in a $Pd_{1-x}Pt_x$ matrix as a function of the Pt concentration x. The measured fields are average absolute values, since the method used to determine the fields from the angular anisotropy of the γ rays does not determine the sign of the field. Since it is known, however, that the field at Co in Pd is negative[8], the experimental data (Fig. 1) show that as platinum replaces palladium in the matrix, the hyperfine field at first decreases, changes sign, and then increases in absolute value to a maximum negative value in $Co_{0.01}Pt_{0.99}$. The hyperfine field reaches its minimum absolute value at a concentration of about 50 at.%. In this concentration region the anisotropy is zero within the limits of the measurement errors. An estimate based on the magnitude of the statistical errors gives the strength of the hyperfine field as $\lesssim 35$ kOe.

3. DISCUSSION

It is evident from Fig. 1 that the field at a ^{60}Co nucleus depends strongly on the composition of the alloy. As was mentioned in the introduction, the hyperfine field in the $Co_{0.01}(Pd_{1-x}Pt_x)_{0.99}$ system is determined mainly by two contributions that are proportional to the intrinsic magnetic moment (see Eq. (2))– core polarization and polarization of the conduction electrons. In the absence of platinum (x = 0) the positive contribution to the field at Co is roughly twice the contribution from core polarization ($H_{HF} = +225 \pm 20$ kOe). In the $x \approx 0.5$ concentration region, these contributions virtually cancel one another so that $H_{HF} \approx 0$. At higher platinum concentrations ($x > 0.5$) the hyperfine field becomes negative and, as will be shown, at x = 1 it reaches a value corresponding to the contribution from core polarization.

Now let us consider the experimental dependence of the hyperfine field on the composition of the alloy in more detail. From the value of the hyperfine field for Co in the $Co_{0.01}Pt_{0.99}$ system ($H_{HF} = -155 \pm 20$ kOe) we can evaluate the coefficient a in formula (1): $a = H_{HF}/\mu_i$ (since the second term in this formula is close to zero). For the intrinsic magnetic moment of Co in the $Co_{0.01}Pt_{0.99}$ system we adopted the value $\mu_i = 1.3 \pm 0.1\ \mu_B$ obtained by linear extrapolation of data obtained from experiments on scattering of neutrons by CoPt alloys with high Co concentrations[11, 12]. From the value $a \approx -119$ kOe/μ_B obtained in this way it follows that the hyperfine field at a Co impurity atom in a Pt matrix is indeed equal to the contribution from core polarization, i.e., in this case the positive contribution is close to zero.

The composition dependence of the hyperfine field for the system under consideration is well represented by Eq. (2), provided it be assumed that the positive contribution varies linearly with the platinum concentration x (we recall that in this case we may neglect the contribution from the surroundings):

$$H_{HF}=a_1\mu_i+a_2^{Pd}(1-x)\mu_i. \qquad (3)$$

Here $a_1 = -120$ kOe/μ_B and $a_2^{Pd} = +227$ kOe/μ_B. The coefficient a_2^{Pd} determines the positive contribution to the hyperfine field in the limiting case x = 0. The numerical value given here was obtained from the value of H_{HF} for Co in $Co_{0.01}Pd_{0.99}$, using the relation $a_2^{Pd} = H_{HF}/\mu_i) + 120$ kOe/μ_B. Since the intrinsic magnetic moments μ_i of cobalt in $Co_{0.01}(Pd_{1-x}Pt_x)_{0.99}$ alloys are not known, in calculating the graph of Eq. (3) we assumed that the moments vary linearly from 2.1 μ_B in $Co_{0.01}Pd_{0.99}$[13] to 1.3 μ_B in $Co_{0.01}Pt_{0.99}$. As is evident from Fig. 1, Eq. (3) represents the experimental data quite well. Thus, we may conclude that the platinum atoms do not take part in forming the positive contribution to the hyperfine field.

In view of these peculiarities of the behavior of platinum, we can give a less ambiguous interpretation of the previously found concentration dependence of H_{HF} for the $Co_{1-x}Pt_x$ system[9]. Again using Eq. (2) and noting that in this case we cannot neglect the contribution from the magnetic moments of the matrix, we obtain

$$H_{HF}=a_1\mu_i+a_2^{Co}(1-x)\mu_i+b\mu_M, \qquad (4)$$

in which the coefficient a_2^{Co} determines the positive contribution to the hyperfine field in the limiting case x = 0 (pure cobalt), while the coefficient b represents the contribution from the magnetic moments of the surroundings (μ_M is the mean magnetic moment for the alloy). The values of the coefficients in Eq. (1) are known from the systematics of hyperfine fields at Co nuclei in ferromagnetic matrices (see, e.g.,[2]): $a = a_1 + a_2 = -39$ kOe/μ_B and $b = -88$ kOe/μ_B, from which it follows that $a_2^{Co} = a + 120$ kOe/μ_B = 81 kOe.

Figure 2 gives experimental values of H_{HF} together with a curve calculated from Eq. (4) using the values given above for the coefficients. The magnetic moments μ_i and μ_M are known from[11, 12, 14]. From the adopted form of the concentration dependence of H_{HF} we may conclude that the fact that the hyperfine field at Co in $Co_{1-x}Pt_x$ is relatively constant is associated with the fact that the positive contribution due to the intrinsic magnetic moment of Co and the negative contribution from the magnetic surroundings roughly cancel one another.

On analyzing the experimental regularities presented above we may conclude that the positive contribution to the hyperfine field at Co is greatest in a dilute alloy of Co in Pd, is also present in pure Co, and is quite absent from a dilute alloy of Co in Pt.

As has already been pointed out, we associate the positive contribution to the field with the polarization of the conduction electrons by the intrinsic magnetic moment of the 3d atom. In this connection we must recall the work of Campbell[15], who, considering the mechanism responsible for the hyperfine field for a magnetic impurity atom, called attention to the existence of an additional contribution due to the admixture of s wave functions to the localized d state. Campbell illustrated the increase in the positive contribution with increasing s-d coupling by comparing the behavior of the hyperfine field with the Kondo temperature for 3d impurity atoms in noble metal matrices. The observed correlation indicates that the positive contribution to the hyperfine field will be greater for systems having higher Kondo temperatures (stronger s-d coupling). On the basis of these ideas we can conclude that the decrease in the positive contribution to the hyperfine field at Co in $Co_{1-x}Pt_x$ and $Co_{0.01}(Pd_{1-x}Pt_x)_{0.99}$ indicates weakening of the s-d coupling with increasing platinum content.

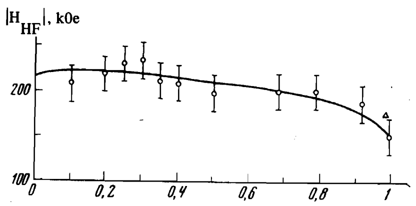

FIG. 2. Hyperfine magnetic fields at $Co_{1-x}Pt_x$ system[9]. The point marked with a triangle was taken from [8], and the value of H_{HF} for x = 0.99 was obtained in the present study. The full curve was calculated from Eq. (4).

For comparison let us consider the composition dependence of the positive contribution to the fields at Co, Ni, and Fe in binary alloys of these elements with palladium, using the available experimental data on hyperfine fields in these systems[2, 4, 5, 16]. Since we shall be interested only in the positive contribution, let us rewrite Eqs. (2) as follows: $H^+ = H_{HF} - a_1\mu_i - b\mu_M$, where H^+ is the positive contribution to the hyperfine field, proportional to the intrinsic magnetic moment of the 3d atom. As was mentioned in the introduction, the hyperfine fields at Co and Ni in Co_xPd_{1-x} and Ni_xPd_{1-x} exhibit similar behavior as functions of composition. Figure 3 gives values of the ratio H^+/μ_i of the positive contribution to the intrinsic magnetic moment calculated from this formula. The experimental values of H_{HF} were obtained from experiments on oriented nuclei[2] and from Mössbauer effect measurements[4, 5], and the values of μ_i and μ_M are known from neutron data[13, 17, 18] and from magnetic measurements[14, 17, 19]. The calculated values of H^+/μ_i are not very accurate, owing to the incompleteness of the data on the magnetic moments μ_i and μ_M, and also to the fact that the coefficients a_1 and b have been determined only approximately; nevertheless, it is obvious that in both systems the positive contribution increases with increasing palladium content and at low Co and Ni concentrations exceeds the corresponding contribution (per unit magnetic moment) in pure cobalt or nickel by a factor of about three. The observed strong composition dependence of the positive contribution to the field at Co and Ni at low concentrations of the 3d atoms shows that this contribution is very sensitive to the immediate surroundings of the impurity atom, as was already mentioned in[10], and confirms Campbell's conclusion[15] that the interaction responsible for this contribution is of short range type.

The Fe_xPd_{1-x} system differs from the Co_xPd_{1-x} and Ni_xPd_{1-x} systems in that the hyperfine field at Fe in the Fe-Pd system is negative over the entire concentration range, varying from −295 kOe in a dilute alloy of Fe in Pd to −335 kOe for Fe concentrations of 20 at.% or higher[16]. The concentration dependence of H_{HF} is satisfactorily reproduced by Eq. (1) with $a = -84$ kOe/μ_B and $b = -66$ kOe/μ_B, and published values[3, 14, 17] of μ_i and μ_M. These values of a and b were simply taken from data on ferromagnetic 3d matrices. The somewhat unexpected result that H_{HF}

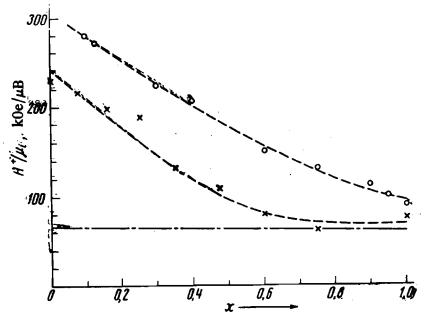

FIG. 3. Composition dependence of the positive contribution to the hyperfine field at 3d atoms in Ni_xPd_{1-x} (circles), Co_xPd_{1-x} (crosses), and Fe_xPd_{1-x} (dash-dot line) alloys.

for Fe in binary alloys with palladium is described in the same way as for Fe in 3d matrices can be interpreted (see Eq. (2)) as follows: The ratio H^+/μ_i of the positive contribution to the intrinsic magnetic moment for the Fe_xPd_{1-x} system remains constant over the entire concentration range and is equal to the positive contribution in metallic iron. This is indicated schematically in Fig. 3.

In summarizing the discussion of the principal experimental regularities observed for the magnetic hyperfine interactions in alloys of 3d elements with palladium and platinum, we can draw the following conclusions:

1. On the basis of the behavior of the hyperfine field at ^{60}Co in the $Co_{0.01}(Pd_{1-x}Pt_x)_{0.99}$ system, we can conclude that the positive contribution to the field decreases as Pd atoms are replaced by Pt atoms, and that the field at an impurity Co atom in a Pt matrix is almost entirely determined by core polarization. The observed composition dependence of the hyperfine field is well described by the simple formula (3).

2. Analysis of the previously measured[9] composition dependence of the hyperfine field at Co in the $Co_{1-x}Pt_x$ system, taking the newly discovered effect of Pt on the formation of the hyperfine field into account, confirms the conclusion that there is a positive contribution to the hyperfine field at Co atoms in metallic cobalt.

3. The composition dependences of the positive contribution to the hyperfine field obtained for Co, Ni, and Fe in binary alloys of these elements with Pd show that for the Co_xPd_{1-x} and Ni_xPd_{1-x} systems this contribution increases as the Co or Ni atoms are replaced by Pd atoms, whereas for the Fe_xPd_{1-x} system the positive contribution remains constant and equal to its value for pure iron.

4. If it be assumed that the positive contribution to the hyperfine field at magnetic 3d atoms is due to polarization of the conduction electrons by the intrinsic local d-shell magnetic moment via s-d interaction, the fact that there is no positive contribution for a dilute alloy of Co in Pt must be taken as indicating that the s-d interaction is much weaker in this system than for Co in Pd or for Co in metallic Co.

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