

determination of the value of $\chi(\Gamma_{14})$ from the magnetization isotherms is difficult because a transition to the Γ_4 phase occurs even at small fields. The theoretical $H_{th}^c(T)$ and $H_{th}^b(T)$ curves calculated from the values of λ_F and λ_G that we have found show good agreement between theory and experiment over the whole temperature interval $10K < T < T_M$ (Fig. 2). We note that at a fixed temperature, formula (27) actually determines two values of λ_F : $\lambda_F > 0$ and $\lambda_F < 0$. The sign of the parameter λ_F in (29) was chosen precisely from the consideration of best agreement of the temperature behavior of the $H_{th}^b(T)$ curve with the experimental points.

As is seen from (29), (30), and (10), in $DyFeO_3$ the relations $H_G \gg H_F$, H^{dip} are satisfied; this justifies all the approximations made in the derivation of formula (21) for the anisotropy K_R .

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- ¹A slight lack of compensation of it caused by weakly ferromagnetic cant of the d -ion sublattices.
- ²In $DyFeO_3$ there is still the dipole field exerted on the Dy^{3+} ions by the Fe^{3+} ions. It is calculated exactly (see below).
- ³Exceptions are $GdFeO_3$ and $GdCrO_3$, where the f - d exchange is practically isotropic, since the ground state of the Gd^{3+} ion is of S type.
- ⁴The plane parallel to the ab plane of the crystal and passing through the sites occupied by RI (Fig. 1).
- ⁵Analysis of the crystalline field in $DyFeO_3$ also leads to the same result.¹²
- ⁶The small terms $\frac{1}{2}a_1 F_x^2$ and $\frac{1}{2}a_3 F_z^2$ have already been discarded in the original TP (14) for the subsystem of Fe^{3+} ions.
- ⁷The interaction with F , $\mu_B \hat{S} A_2(\hat{L})F$, and also the R-Fe dipole

interaction may split the doublet when G departs from the ab plane; but the magnitude of these interactions is insufficient for a reorientation $\Gamma_4 \rightarrow \Gamma_2$ in $DyFeO_3$.

⁸We recall that in phase Γ_4 , $G \parallel a$; in phase Γ_1 , $G \parallel b$; and in phase Γ_2 , $G \parallel c$. The symbols Γ_i denote the corresponding irreducible representations of the symmetry group of the orthoferrites; Γ_{14} is a reducible representation consisting of Γ_1 and Γ_4 . In phase Γ_{14} , the vector G lies in the ab plane.

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Magnetic hyperfine interaction for Co impurity atoms in a PdAu matrix

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The oriented-nuclei procedure is used to measure the magnetic hyperfine fields for ^{60}Co in the ferromagnetic system $[Pd_{1-x}Au_x]_{0.99}Co_{0.01}$ with $0 \leq x \leq 0.15$. The data obtained indicate that the hyperfine field at Co remains practically unchanged when part of the Pd atoms is replaced by Au atoms, at least up to a concentration of 0.15 at. % Au. It can be concluded from these results that the Au atoms, just as the Pd atoms, produce a positive hyperfine field at the impurity Co atoms which have a localized magnetic moment. The concentration dependence of the hyperfine field can be described with an empirical formula consisting of a sum of contributions, viz., the polarization of the core and the partial contributions corresponding to the presence of the Pd or Au atoms in the first coordination sphere of the Co impurity atom in question. The possible mechanisms responsible for the positive hyperfine field at a $3d$ atom are briefly discussed.

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INTRODUCTION

The great interest in the investigations of magnetic hyperfine interaction for impurity $3d$ atoms in alloys with $4d$ and $5d$ metals is due to the fact that large pos-

itive hyperfine fields were observed for Co and Ni atoms in Pd matrices. This result turned out to be unexpected, since the only previously known values of the fields for $3d$ atoms were negative, a fact ascribed to the dominant contribution from the polarization of the

electron core by the intrinsic d -moment of the impurity atom. The mechanism responsible for the positive field at the impurity $3d$ atom is still not completely clear.

It is known that the hyperfine field of the magnetic ion is determined by the polarization by the spin d -moment of the internal field s shells and of the external s electrons and by the orbital angular momentum of the d electron. According to calculations by Watson and Freeman,¹ the polarization of the internal s electrons (core polarization) makes a negative contribution to the hyperfine field, while the polarization of the external s electrons (conduction electrons in the case of metals) and the orbital angular momentum make positive contribution to the field at the nucleus. It must be noted, however, that until recently it was regarded as established that the orbital angular momentum in $3d$ metals is quenched by the crystal field.

Recent papers²⁻⁴ indicate that the hyperfine field at impurity Co atoms in gold is also positive. The systems PdCo and AuCo differ substantially in their magnetic properties: whereas a small admixture of Co in Pd makes the system ferromagnetic and leads to formation of "giant" localized magnetic moments connected with the impurity atom, no giant magnetic moments are produced in AuCo and the system does not become ferromagnetic. In the investigation of the nuclear orientation of ^{60}Co in the paramagnetic system AuCo in an external magnetic field, the measured Knight shift turned out to be positive,³ $K = +29\%$. The same quality was obtained also in NMR experiments. In measurements of the specific thermal conductivity of AuCo alloys the estimate obtained for the hyperfine field at Co was $|H| \sim 190$ kOe.⁵ In investigations of the specific heat and of the magnetization^{5,6} it was established that an isolated Co atom and a pair of Co atoms that have no other Co atoms as nearest neighbors, do not have any magnetic moment. A magnetic moment appears at Co only when the Co atoms is in a group of three or more atoms.

Interesting results were obtained by Flouquet and Brewer,⁷ who measured the asymmetry of the β particles emitted by oriented nuclei of ^{60}Co in an AuCo alloy. It was observed that the hyperfine field, which is positive in the dilute alloy, reverses sign with increasing Co concentration and becomes negative at -11 at.% Co. The authors attribute the negative hyperfine field to the magnetic Co atoms, in contrast to the nonmagnetic isolated Co atoms, for which the field is positive.

The present paper was undertaken to assess the influence of Au atoms on the positive hyperfine field at the impurity atom Co in the ferromagnetic system $[\text{Pd}_{1-x}\text{Au}_x]_{0.99}\text{Co}_{0.01}$ when the Co atoms of a localized magnetic moment (the latter condition, naturally, imposed a limitation on the maximum Au concentration). An earlier investigation of the $[\text{Pd}_{1-x}\text{Pt}_x]_{0.99}\text{Co}_{0.01}$ system⁸ has established that replacement of the Pd atoms by Pt decreases the positive hyperfine field at the Co. In the limit of a dilute PtCo alloy, the hyperfine field at Co is negative and its magnitude corresponds to the polarization of the core.

DESCRIPTION OF EXPERIMENT AND MEASUREMENT RESULTS

The magnetic hyperfine field at the Co atoms was determined from the anisotropy of the angular distribution of the gamma rays of oriented ^{60}Co nuclei. The ^{60}Co nuclei were polarized at low temperatures in the ferromagnetic samples $[\text{Pd}_{1-x}\text{Au}_x]_{0.99}\text{Co}_{0.01}$ at $0 \leq x \leq 0.15$. The investigated samples were prepared by melting in vacuum the appropriate amounts of the initial components (of nominal purity 99.98%), followed by homogenization in vacuum at 1000°C for 40 hours. The samples in the form of disks of 3 mm diameter and 0.10–0.12 thickness were bombarded by neutrons to obtain radioactive ^{60}Co nuclei.

To obtain infralow temperatures we used the procedure of adiabatic demagnetization of a paramagnetic salt. The temperature was measured with the aid of a ^{54}Mn (Ni) nuclear thermometer soldered together with the investigated sample at the end of a cold finger made of oxygen-free copper, the other end of which was pressed into potassium-chrome-alum block.⁸ An external magnetic field up to 13 kOe, produced by an electromagnet, was applied to the sample.

The gamma radiation was registered by a volume Ge(Li) detector (with a 512-channel NTA-512 analyzer) in the direction of external orienting magnetic field.

The angular distribution of the gamma rays emitted by the polarized nuclei can be represented in the form

$$W(\theta) = 1 + \sum_{k=2,4,\dots} A_k G_k f_k Q_k P_k(\cos\theta),$$

where f_k is a parameter describing the degree of orientation of the parent nucleus, A_k is a parameter that describes the angular dependence of the considered gamma transition, G_k is a depolarization parameter governed by the preceding unobservable transitions (since the lifetimes of the excited levels from which we experimentally observable transitions of ^{60}Co and ^{54}Mn proceed do not exceed 10^{-12} sec, the depolarization due to relaxation effects in the intermediate state can be neglected), Q_k is the correction for the finite solid angle of the detector, and $P_k(\cos\theta)$ are Legendre polynomials.

From the simultaneously measured angular anisotropy of the 1173- and 1332-keV gamma ray of ^{60}Co and of the 835-keV gamma rays of ^{54}Mn , taking into account the known value of the hyperfine field for Mn in Ni, $H_{\text{hf}} = -321.3$ kOe,⁹ we calculated the hyperfine field for Co. The temperature and the hyperfine field were calculated with a BESM-6 computer using a specially developed program. The measurements were made in the temperature interval 16–30 mK at three values of the external oriented magnetic field, namely 8, 10, and 13 kOe. The anisotropy in the 10 and 13 kOe fields was the same within the limits of errors.

The results of the measurements of the hyperfine fields at the Co in the PdAu matrix are shown in the figure. The values of $H_{\text{hf}}(\text{PdAu})/H_{\text{hf}}(\text{Pd})$ are given as functions of the Au concentration. It is seen from the figure that in the investigated system the field at the Co is practically independent of the composition of the al-

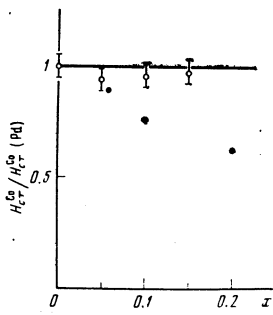


FIG. 1. Dependence of the hyperfine field at an impurity of 1 at. % Co in a $\text{Pd}_{1-x}\text{Au}_x$ matrix on the Au concentration (O). Solid curve—calculation by formula (2). For comparison, the figure shows the corresponding values for an impurity of 1 at. % Co in a $\text{Pd}_{1-x}\text{Pt}_x$ matrix (●).⁸

loy. Since it is known that $H_{\text{hf}} > 0$ for Co in Pd, it follows from the derived relation that the hyperfine field remains positive when gold is added, at least up to concentrations not exceeding 15 at. % Au. We can thus, conclude that replacement of part of the Pd atoms by Au atoms in the nearest environment of Co does not affect substantially the magnitude of the hyperfine field at the Co. The figure shows by comparison, besides our present results, data obtained earlier⁸ for the system $[\text{Pd}_{1-x}\text{Pt}_x]_{0.99}\text{Co}_{0.01}$. It is easily seen that these dependences are substantially different.

An analysis of the concentration dependence of the hyperfine field at the impurity Co atom and the $\text{Pd}_{1-x}\text{Pt}_x$ matrix⁸ has shown that the positive contribution to the hyperfine field decreases linearly with increasing Pt concentration. The dependence of the field at Co in the indicated system is described by the simple empirical formula

$$H_{\text{hf}} = a_1 \mu_i + a_2^{\text{Pd}} \frac{12 - \langle n \rangle}{12} \mu_i, \quad (1)$$

where μ_i is the intrinsic magnetic moment of the impurity atom, $a_1 = -120 \text{ kOe}/\mu_B$ (core polarization¹), $a_2^{\text{Pd}} = +227 \text{ kOe}/\mu_B$ determines the positive contribution to the hyperfine field caused by the palladium in the limit $x=0$, and $\langle n \rangle$ is the average number of the platinum atoms in the first coordination sphere of the impurity atom Co, which has 12 atoms in the case of a face-centered lattice.

It is possible to describe in a similar manner the dependence of the hyperfine field at the Co in the system $[\text{Pd}_{1-x}\text{Au}_x]_{0.99}\text{Co}_{0.01}$. Since it follows from the results that the positive contribution at the Co impurity atom, due to the Au atoms in the nearest surrounding of the given Co atom, is not equal to zero, the corresponding dependence can be represented in the form

$$H_{\text{hf}} = a_1 \mu_i + a_2^{\text{Pd}} \frac{12 - \langle n \rangle}{12} \mu_i + a_2^{\text{Au}} \frac{\langle n \rangle}{12} \mu_i, \quad (2)$$

where $\langle n \rangle$ is the average number of gold atoms in the first coordination sphere, and a_2^{Au} is the positive contribution made by the gold to the field at the Co. Unfortunately, there are no data on the value of the intrinsic magnetic moment of Co in the PdAu(Co) system; we made therefore the simplest assumption that the moment varies linearly from a value $2.1\mu_B$ (in the Pd matrix¹⁰) to $1.2\mu_B$ (in the Au matrix). The last quantity was obtained from measurements of the magnetization

of dilute AuCo alloys.⁶ If we use this value of the moment and the value of the hyperfine field $H_{\text{hf}} = 190 \text{ kOe}$ corresponding to the case of "magnetic" Co atoms in the Au matrix, then we obtain for the coefficient a_2^{Au} the value $a_2^{\text{Au}} = +278 \text{ kOe}/\mu_B$. We can now estimate the course of the hyperfine field in the considered system as a function of the gold concentration. Calculation by formula (2) yields an almost constant H_{hf} up to $x=0.5$. The figure shows the calculated curve. It can be noted that, despite the different behavior of the resultant hyperfine field at the impurity Co atoms in the matrices $\text{Pd}_{1-x}\text{Pt}_x$ and $\text{Pd}_{1-x}\text{Au}_x$, it is possible to describe the concentration dependences of the hyperfine fields in both cases with the aid of a single formalism.

The results obtained in the present paper can be briefly formulated as follows.

1. The appearance of Au atoms as the nearest neighbors of the Co impurity atom (the system PdAuCo) does not lead to a noticeable change of the positive hyperfine fields at Co. A partial contribution to the positive field, due to the Au atoms when they appear in the first coordination sphere, is at any rate not less than the corresponding contribution due to the palladium atoms.

2. The localized magnetic moment at the Co atom in palladium does not decrease noticeably with increasing gold concentration (at least at concentrations up to 15 at. %); this differs from the case of other diamagnetic impurities, for example silver and copper.¹¹ At a gold concentration of 15 at. %, some 85.8% of the Co atoms have in the first coordination sphere one or more gold atoms, while 55.6% have two and more gold atoms.

3. The gold atoms ensure conditions for the existence of a positive contribution to the hyperfine field not only in a paramagnetic system, as was established by measurement of the Knight shift,²⁻⁴ but also in a ferromagnetic system.

DISCUSSION

As already noted in the Introduction, the sources of positive contribution to the hyperfine field can be the unquenched orbital angular momentum of Co or polarization of the conduction electrons by the intrinsic magnetic moment of the Co. Evidence exists for and against the existence of unquenched orbital angular momentum in systems of 3d metals. Hirst¹² considered theoretically the possibility of partial unquenching of the orbital angular momentum of the 3d atom for cases similar to PdCo and AuCo, as a result of the spin-orbit interaction, but there are still no direct experimental facts confirm this hypothesis.

NMR investigations were made on ⁵⁹Co and ⁶¹Ni in the alloys PdCo (Ref. 13), and PdFeCo, and PdFeNi (Ref. 14). The obtained values of the hyperfine fields agree with the already known data.^{15,16} The observed residual broadening of the NMR line for C, ~50 MHz, was the reason why the authors of the cited papers considered, an alternate mechanism of orbital interaction as the source of the positive hyperfine field, besides the mechanism of polarization of the conduction electrons by the intrinsic magnetic moments of the impurity atom. However, the splitting of the NMR line as a result of

the quadrupole interaction due to the orbital angular momentum was not observed in experiment. The concept of partial unquenching of the orbital angular momentum cannot explain why this behavior of the impurity is not observed in all cases: for a Co impurity in Pt, for example, the hyperfine field is negative, although in other respects the systems PdCo and PtCo have similar properties. Recent measurements of ferromagnetic resonance in dilute Fe and Co alloys in Pd and Pt¹⁷ have shown that the values of the g factors for PdCo and PtCo are close, 2.33 and 2.29 respectively. At the same time all the available data on the hyperfine field can be explained as being due to polarization of the conduction electrons by the intrinsic magnetic moment μ_i , if it is recognized that the degree of polarization depends on the nearest environment of the impurity atom Co.

In Refs. 15 and 16, in which the fields at Co and Ni and Pd were measured respectively with the aid of the procedures of oriented nuclei and the Mössbauer effect, this approach made it possible to explain not only the positive field at Co and Ni in dilute alloys with palladium, but also the concentration dependences of H_{hf} in Pd_{1-x}Co_x and Pd_{1-x}Ni_x. It is similarly possible to interpret the concentration dependence of H_{hf} for Co in the system [Pd_{1-x}Au_x]_{0.99}Co_{0.01}. In the empirical formula (2), the second and third terms, which describe the positive contributions to the hyperfine field, can be regarded as partial contributions due to the polarization of the conducting electrons by the intrinsic moment of the Co atom, which has palladium and gold atoms, respectively, as the nearest neighbors. It is seen thus that although the presence of a localized magnetic moment in Co is in this system obviously due to the predominant palladium environment, the gold atoms also create conditions for the existence of a positive contribution to the hyperfine field at Co.

The models considered in Refs. 6, 15, and 16 do not explain, of course, why it is precisely the palladium and gold atoms which ensure the positive hyperfine field at Co (or Ni) whereas the platinum atoms, for example, do not have this property. It is important, how-

ever, that it becomes possible to connect in a natural and simple manner the positive contribution with the singularities of the magnetic moment of Co and with the local configuration of the atoms (without introducing additional parameters). Obviously, the positive field depends on just which of the atoms are located near the given Co atom.

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