Investigation of the magnetic hyperfine interaction for impurity tin atoms in dilute Pd-Co solid solutions at low temperatures

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Magnetic hyperfine interaction for Sn^{119} impurity atoms in Pd-Co alloys is investigated by the γ-resonance technique for Co concentrations ranging from 0.3 to 5 at.% when direct exchange interaction between the 3d atoms should be absent. Magnetic measurements were performed to determine the Curie temperatures (T_C) and mean magnetic moments of the alloys. It is found that the dependence of T_C on Co content in Pd is in good agreement with the theoretical predictions. Mossbauer-effect investigations show that the effective magnetic field at the impurity tin nuclei increases monotonically on increase of the Co concentration in the alloys and reaches (9 ± 1) kOe for the sample with the highest CO concentration (5 at.%). The field is positive. The magnetic measurements show that in the Co and Pd concentration range investigated the effective field strength at Sn^{119} nuclei is proportional to the mean magnetic moment per alloy atom. On variation of the tin impurity from 0.2 to 6.0 at.% in a Pd-Co (2 at.%)-Sn (y) alloy, the field strength H_{eff} at the Sn nuclei remains constant within the limits of experimental error.

INTRODUCTION

The magnetic properties of solid solutions of Co in Pd reveal a number of interesting features. It has been established that ferromagnetic ordering in such alloys occurs at a very low concentration of the magnetic impurities when a direct exchange interaction between the 3d-atoms can be excluded[1-6].

An investigation of the magnetic susceptibility of Pd-Co alloys at low Co concentration[1] has shown that the magnetic moment per atom of the ferromagnetic impurity reaches the "giant" value ~10 μ_B. At the same time, experiments on magnetic scattering of slow neutrons by Pd-Co alloys[2] have made it possible to establish that at a 3d-metal concentration less than 1 at.% the intrinsic magnetic moments of the Co atoms differ little from their values in pure Co, and the moments induced by polarization by the Pd atoms closest to the impurity do not exceed 0.05 μ_B. It was also found that around each 3d atom there occurs a region of polarized Pd atoms (a cluster) with an effective radius on the order of 10 Å, in which up to 200 atoms of the matrix participate. With increasing 3d-atom concentration, the degree of polarization of the Pd decreases. These results confirm the conclusion that the giant moments connected with the 3d-metal impurity are due to the fact that each impurity atom perturbs a large number of Pd atoms.

In a study of the phenomenon of impurity ferromagnetism of Pd alloys with 3d metals, important information on their properties is obtained by investigations of the magnetic -hyperfine interaction for atoms that enter in the composition of these alloys. In this connection, an appreciable number of experimental papers has been devoted to a determination of the magnitudes and signs of the magnetic fields acting on the nuclei of the atoms in the Pd-Co alloys (and also Pd-Fe alloys).

The effective magnetic fields at the Co^{60} nuclei in Pd-Co solid solutions were investigated in[3] by measuring the angular anisotropy of the γ radiation of polarized Co nuclei. The measurements were performed at small Co concentrations (from 0.03 to 8.3 at.%). It was noted that the effective field at the Co^{60} nuclei increases with decreasing Co content in the solution, and reaches a maximum value 280 ± 20 kOe at a concentration 0.1 at.% (according to NMR data, the field in pure Co is H_{eff} = −215 kOe[7]). Since the magnetic moments of the 3d-shell of Co in Pd-Co alloys and in pure Co do not differ significantly[2], it follows, in the opinion of the authors, that the dependence of H_{eff} on the Co concentration should be attributed to polarization of the conduction electrons. In analogous measurements[8] it was shown that at low concentrations of the 3d-atoms in a Pd-Co alloy, the field at the nuclei of the Co atoms coincides with the direction of magnetization of the matrix, i.e., the sign of the field is positive (whereas in pure Co the field is negative).

NMR on the nuclei of Pd^{105} atoms were investigated in a number of Pd-Fe and Pd-Co atoms.[9,10]. A great similarity of the resonance with the Pd nuclei in these alloys was noted. It was found that with increasing 3d-atom concentration the average magnetic field at the nuclei of the Pd atoms increases monotonically. Thus, (see[9]), in the Pd-Fe system the field changed from 72 kOe in almost pure Pd to 89 kOe in an alloy containing 25% of 3d-atoms. It was emphasized in[10] that when the concentration of the magnetic impurity exceeds several percent, the polarization of the Pd matrix can be regarded as homogeneous.

In the study of Pd-Co alloys, extensive use has also been made of the Mossbauer procedure with addition of Fe^{57} or Sn^{119} atoms as impurities in the alloys. Measurements performed with the aid of the Mossbauer effect on nuclei of Fe^{57} impurity atoms in a Pd-Co alloy at concentrations from 0.07 to 4.5 at.% Co[4] and from 3 to 100 at.% Co[11] have shown that the effective field at the Fe^{57} nucleus remains constant at ~300 kOe.

Interesting studies were performed recently[12,13] with the object of determining the magnitude and sign of the field at Co^{57} nuclei in dilute alloys, Pd + 0.1 at.% Co^{57}, with the aid of the Mossbauer effect at infralow temperatures. It was shown that the sign of the field at the Co nucleus is positive, and the magnitude of the field is H_{eff} = 260 ± 20 kOe. This result agrees well with the data obtained with the aid of the oriented-nuclei procedure[3,8].

Important information on Pd-Co alloys is obtained by measurements of the magnetic fields at Sn impurity atoms. Sn impurity atoms are convenient because they have no magnetic moment of their own. It is usually assumed that the main source of the hyperfine field at nuclei of nonmagnetic atoms is the interaction of these atoms with the polarized conduction electrons[7,14-16].

In[5,17], the Mossbauer effect was used to investigate the effective magnetic fields acting on nuclei of impurity Sn^{119} atoms in Pd-Co alloys at relatively large Co concentrations (larger than 5.5 at.%). The average fields at the Sn^{119} nuclei turned out to be small, and the individual components of the hyperfine structure could not be resolved. It was assumed that the linear relation between the field H_{eff} and the total width Γ_e of the absorption spectrum at half height is preserved for the unresolved spectra. Thus, the value of the average field as a function of the composition of the alloy was determined from the width of the absorption line.

We were especially interested in investigating the magnetic hyperfine interaction for Sn impurity atoms in solid Pd-Co solid solutions in the region of low Co concentrations (less than 5 at.%), when there should be no direct exchange interaction for the magnetic atoms.

EXPERIMENT AND MEASUREMENT RESULTS

We prepared for the investigations Pd-Co solid solutions with the following Co contents (at.%): 0.3, 0.45, 0.9, 1.6, 2.0, 2.5, 3.0, 4.0, and 5.0. The initial materials were Pd with a resistance ratio $\rho(300°K)/\rho(4.2°K) = 3000$[5,18], and Co of purity 99.998. The prescribed amounts of the initial materials were melted in a high-frequency furnace. The prepared samples were annealed in a vacuum for 8—10 hours at t = 1000°C.

The Curie points of the alloys (T_C) were determined with apparatus described earlier[5]. The measured values of T_C were compared with the data of[5], where the compositions of the samples were monitored by quantitative chemical analysis. It was found from the comparison that the concentration of the Co in the given alloys differed from the calculated values by no more than 10%.

As shown earlier[5], when several percent of an Sn impurity are added to Pd-Co alloys, a considerable decrease of the Curie temperatures is observed. This circumstance was taken into account during the preparation of the sample intended for measurements with the aid of the Mossbauer effect. To minimize the influence of the Sn on the magnetic properties of the alloys, a very small amount of Sn (0.2 at.%) enriched with Sn^{119} (88.7 at.%) was introduced into the obtained Pd-Co solid solutions. The experiment showed that when 0.2 at.% Sn is added, the Curie points of the alloys remain unchanged within the limits of the measurement error.

To establish the dependence of the effective field at the Sn^{119} nuclei on the concentration of the tin, we also prepared Pd + Co (2.0) + Sn(y) alloys[1)] with the following Sn contents (y in at.% Sn):

Tin, enriched (Sn^{119} — 88.7 at.%): $y = 0.2$; 1.4

Tin, natural (Sn^{119} — 8.6 at.%): $y = 2.0$; 4.0; 6.0.

The absorption spectra were measured on samples rolled into foils. At room temperature, all the absorbers had the same effective thickness relative to Sn^{119}, namely $C_a = 0.67 + 0.07$ (for alloys with 0.2 at.% Sn, this corresponded to a geometrical thickness ~80 μ).

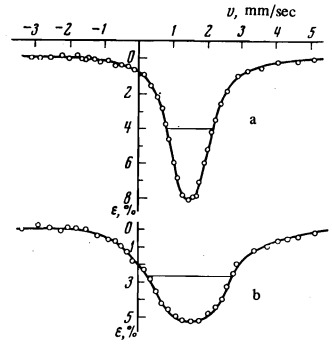

FIG. 1. Typical resonance-absorption spectra: a—Pd + Sn (0.2 at.%), b—Pd + Co (5 at.%) + Sn (0.2 at.%). T = 4.2°K.

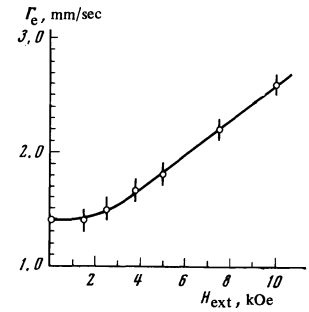

FIG. 2. Experimental absorption line width in alloy Pd + Sn (0.2 at.%) as a function of the external field at T = 4.2°K.

In order for the geometrical thicknesses of the Pd + Co (2.0) + Sn(y) samples not to differ too strongly in this case, we used both enriched and natural tin in these alloys. The effective thickness was monitored by measuring the Mossbauer effect at T = 300°K, when all the alloys were paramagnetic.

The absorption spectra were measured at constant velocities, with a source in the form of the compound SnO_2, using the setup described in[19]. To study the influence of the external field on the absorption spectrum, we used a superconducting solenoid. The mobile source and the photomultiplier were carefully shielded against the stray magnetic field. Detailed investigations for all alloys were carried out 77 and 4.2°K. At T = 4.2°K, all the alloys were ferromagnetic, and at T = 77°K some of the samples were in the paramagnetic state.

As seen from Fig. 1, the absorption spectra of the considered solid solutions Pd-Co had an unresolved hyperfine structure. The line shape turned out to be close to the Lorentz shape. The effective field at the nuclei of the Sn^{119} atoms was determined as a function of alloy composition from the absorption line width.

According to the data of Bozorth et al.[1], when the Co concentration in the Pd is less than 5 at.%, the lattice of the alloy remains face-centered cubic. The lattice parameter changes in this case from a value 3.89 Å in pure Pd to 3.87 Å in a solid solution with Co concentration 5 at.%. As noted above, it follows from the foregoing magnetic measurements that a small Sn impurity does not change the Curie temperature of the alloys. This makes it possible to compare the absorption-line broadening connected with the magnetic ordering in the Pd + Co (x) + Sn (0.2) alloy with the equal broadening of the line in the paramagnetic alloy Pd + Sn (0.2), due to superposition of an external field at T = 4.2°K.

The results of the measurements are shown in Figs. 2—4. The effective field at the nuclei of the Sn atoms in Pd-Co solid solutions increases smoothly with increasing concentration of the 3d metal, and amounts to $H_{eff} = 9 \pm 1$ kOe at 5 at.% Co. The sign of the field is

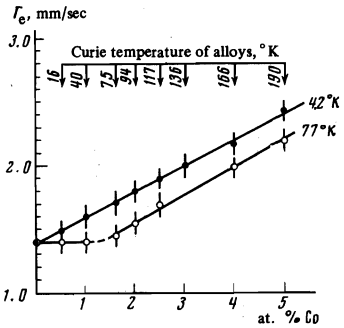

FIG. 3. Dependence of Γ_e in the alloys Pd + Co (x) + Sn (0.2 at. %) on the cobalt magnetic-impurity content x. At T = 77°K, some of the alloys were in the paramagnetic state.

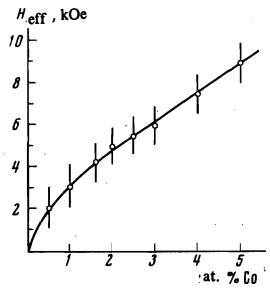

FIG. 4. Effective magnetic field at the nuclei of the Sn impurity atoms as a function of the Co content in the alloys Pd + Co (x) + Sn (0.2 at. %) at T = 4.2°K.

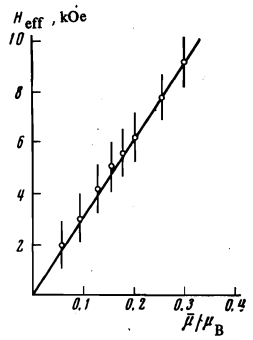

FIG. 5. Effective magnetic field at the nuclei of impurity Sn atoms vs. the average magnetic moment of the alloys.

positive. (The line widths of the absorption spectra increased with increasing external field; see also[20].)

The magnetic measurements of the system Pd + Co (x) + Sn (0.2) show that the average magnetic moment $\bar{\mu}$ per atom of the alloy increases monotonically with increasing Co concentration. It follows from the experimental data that the dependence of H_{eff} at the Sn nuclei on the average magnetic moment $\bar{\mu}$ per alloy atom is close to linear (Fig. 5).

Figure 6 shows the results of investigations of the effective field on the Sn content (y) in Pd + Co (2.0) + Sn (y) alloys. We see that within the limits of the measurement errors the effective field at the Sn nuclei remains unchanged, whereas the values of T_C of the alloys "drop" from 94 to 20°K.

DISCUSSION OF RESULTS

The investigations of the alloys Pd + Co (x) and Pd + Co (x) + Sn (0.2) have shown that the dependence of the Curie temperatures on the Co concentration in Pd agree well with results of other measurements[4-6] performed by different methods. It should be noted, however, that in the region of very small Co concentrations in Pd, the Curie temperatures obtained from the kink of the resistivity plot $\rho(T)$[6] are smaller than the values of T_C obtained from magnetic measurements[5] and from measurements with the aid of the Mossbauer effect[4] (see the table).

Recently Korenblit and Shender[21] examined the in-

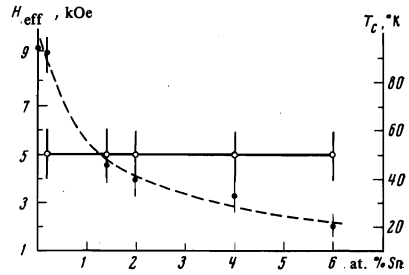

FIG. 6. Value of H_{eff} at the Sn^{119} nuclei at T = 4.2°K and at the Curie temperature of the alloys, as a function of the concentration of the Sn concentration in the system Pd + Co (2.0 at. %) + Sn (y): ○–H_{eff}, ●–T_0;

Curie temperatures of Pd + Co (x) alloys at different Co concentrations

x, at. %	T_c, °K	x, at. %	T_c, °K
Present data and data of[5]		Data of[4]	
0.1	2.1 ± 0.5	0.07	1.55 ± 0.1
0.3	8.5 ± 2	0.19	6.5 ± 0.5
0.45	16 ± 3	0.49	18.8 ± 3
0.9	40 ± 5	1.91	90 ± 1
1.6	75 ± 5	4.5	186 ± 1
2.0	94 ± 5		
2.5	117 ± 8	Data of[6]	
2.7	126 ± 8		
3.0	136 ± 8	0.1	0.78 ± 0.01
4.0	166 ± 8	0.2	2.95 ± 0.05
5.0	190 ± 10	0.29	6.45 ± 0.05
6.0	212 ± 10	0.51	16.2 ± 0.2
7.5	240 ± 10	0.73	27.5 ± 0.3
8.3	250±10	1.05	44.0 ± 0.5
9.4	268 ± 10		
10.4	290 ± 10		

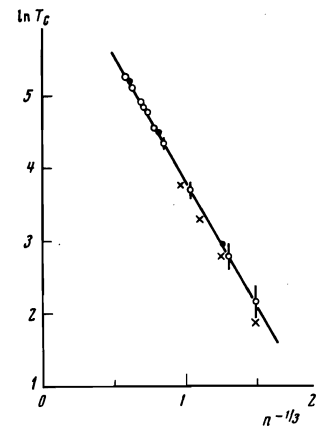

FIG. 7. Dependence of T_C on the Co impurity concentration (in at. %): ○–present data, ●–after[4], X–after[6].

fluence of fluctuations in the arrangement of the impurities on the thermodynamic and kinetic properties of dilute ferromagnetic alloys of the Pd-Co type. They have shown that the transition temperature should be of the order of the interaction energy of the magnetic impurities situated at an average distance from one another. They obtained the following dependence of the Curie temperatures on the impurity concentration:

$$T_c \sim \exp(-1/an^{1/3}), \quad (1)$$

where n is the concentration of the magnetic impurity, $a \approx R$, and R is the impurity-interaction radius.

Figure 7 shows the dependence of ln T_C on $n^{-1/3}$, plotted from the results of the present paper and those of others[4,6]. It is seen that the agreement between the theory and the experimental data is good in a wide range of impurity concentrations. This confirms the correctness of the model assumed by Korenblit and Shender[21] to describe the interaction of impurities in impurity ferromagnets.

As is well known, the interpretation of the data on

magnetic hyperfine fields in ferromagnets encounters considerable difficulties, since these fields contain, as a rule several contributions of equal order of magnitude. The theoretical models explain qualitatively the observed regularities for the hyperfine interaction of impurity atoms in ferromagnetic matrices but unfortunately do not permit a quantitative calculation.

The dependence of H_{eff} at the Sn nuclei on the concentration of the Co in Pd, observed in the present study, can be understood by starting from the generally accepted premise that the main contribution to the field at the nucleus of a diamagnetic atom is made by contact interaction with polarized conduction electrons[7,14-16]. At low Co concentrations one can apparently neglect the influence of the Co atoms on Sn and consider an isolated impurity Sn atom in a Pd matrix. The magnetic field at the Sn nucleus is due to the polarization of the conduction electrons by the magnetic moments of the matrix atoms. In this case an important role is played by the average polarization of the conduction electrons, which is determined by the average magnetic moment $\bar{\mu}$ per atom of the alloy.

According to the performed measurements and the data of Bozorth et al.[1], when the Co concentration in Pd-Co alloys is increased, the average magnetic moment per atom of the alloy increases monotonically. This leads to the increase in the average polarization of the conduction electrons, a fact that manifests itself in a monotonic increase of the average field at the Sn nuclei. An analogous increase of the magnetic field is also observed at the Pd nuclei[10].

Campbell[15] analyzed the experimental data on the hyperfine fields for a large number of nonmagnetic impurities (from Ag to Te) in ferromagnetic metals on the basis of the model of Daniel and Friedel[14], with allowance for s-d hybridization. It was found that a suitable expression for the fields at the nuclei of nonmagnetic impurities in different ferromagnetic matrices is

$$H_i = \alpha\mu_h + \beta\mu_h^2, \qquad (2)$$

where μ_h is the magnetic moment of the matrix atoms and α and β are empirical coefficients that depend on the impurity and do not depend on the matrix. In particular, the following values of the coefficients are cited for Sn:

$$\alpha = 56.5 / \mu_B, \text{ kOe}; \ \beta = -42.5 / \mu_B^2, \text{ kOe}.$$

The measured values of H_{eff} at nuclei of Sn in a Pd-Co matrix indicate that the relation (2) is apparently not satisfied in this matrix. As follows from Fig. 5, the value of H_{eff} is directly proportional to the average magnetic moment $\bar{\mu}$ per atom of the alloy. The proportionality coefficient is equal to $30 \pm 3/\mu_B$, kOe, which is just over half the value of α cited above. The result, however, agrees well with the data of Balabanov et al.[17], who have shown that in Pd-Co alloys that contain many 3d atoms the magnetic field at the Sn is approximately proportional to $\bar{\mu}$ up to $\bar{\mu} \approx 10\ \mu_B$ and that the proportionality coefficient amounts to $\sim 33/\mu_B$, kOe.

Let us examine the behavior of H_{eff} at the nuclei of Sn atoms in Pd + Co (2.0) + Sn (y) alloys and the dependence of the Curie temperatures of these alloys on the concentration of the tin impurity, as shown in Fig. 6. If the ferromagnetic ordering in Pd-Co alloys is due to indirect exchange interaction via the conduction electrons (as is customarily assumed in many papers), then the sharp increase of the Curie temperature following the introduction of Sn apparently indicates scattering of the polarized carriers by the Sn impurities. Then, it would seem, a noticeable change in the polarization of the conduction electrons can take place near the impurity, with a corresponding change of H_{eff} at the Sn nuclei. In addition, it is known from magnetic measurements that when a nonmagnetic impurity is introduced into a ferromagnetic matrix, the saturation magnetization changes, as does the average magnetic moment per atom of the alloy. In this case this should also lead to a change in H_{eff} at the nuclei of the Sn atoms.

Experiments have shown, however, that the Sn impurity, while greatly lowering the Curie temperature, does not significantly change the average polarization of the conduction electrons in the considered alloys at $T = 4.2°K$. The result can be interpreted in accordance with the results of theoretical papers[21,22], where it is shown that the interaction of the impurity atoms in Pd is effected via indirect exchange of d-band holes, and that the contribution of the conduction s-electrons to the ferromagnetic interaction is negligibly small. In this case the tin impurity, by changing the density of states in the d-band of Pd, leads to a sharp change of the T_C of the alloys without significantly affecting the field at the Sn nuclei (at low temperatures), since this field is determined mainly by the polarized conduction s-electrons.

We also call attention to the fact that the chemical isomer shift has remained constant in the entire range of the Sn impurity concentrations, at 1.53 ± 0.03 mm/sec. In other words, the electron density at the nucleus of the Mossbauer atom apparently remains constant in a sufficiently wide range of concentrations. This is confirmed by the results of Chekin et al.[23], who have shown experimentally that for impurity Sn in many metallic matrices the isomeric chemical shift remains constant in the region of solid solutions.

In conclusion, the authors consider it their pleasant duty to thank V. I. Gorenburg, O. A. Nazin, and B. G. Antipov for help with the work, Yu. S. Karimov for performing some of the magnetic measurements, and A. P. Kir'yanov, V. D. Gorobchenko, and I. I. Lukashevich for a discussion of the results.

[1)] The parentheses indicate throughout the impurity contents in at. %.

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