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MAGNETIC FIELDS ON Co^{60} AND Sn^{119} NUCLEI AND ELECTRON POLARIZATION IN CoPd AND FePd ALLOYS

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The magnetic fields on the nuclei of Co^{60} atoms were measured in CoPd alloys (by the oriented-nuclei technique) and on the nuclei of Sn^{119} impurity atoms in CoPd and FePd alloys (on the basis of the Mossbauer effect). A sharp dependence of the magnetic hyperfine interaction on the concentration of the 3d atoms was found. The measurements show that there exist two contributions of opposite sign to the field on the Co atomic nuclei. The positive contribution is dominant at small Co concentrations; the magnitude of the negative contribution increases with increase of Co concentration. At a Co concentration of 30 at.% these contributions approximately cancel each other and the magnetic hyperfine interaction is minimal for the Co nuclei. The field on the Sn^{119} nuclei is proportional to the mean magnetic moment $\overline{\mu}$ of the alloys, provided $\overline{\mu}$ is smaller than $0.8\,\mu_B$. At larger values of $\overline{\mu}$, a sharp deviation from proportionality is observed. The distribution of the conduction-electron polarization in the investigated alloys is discussed on the basis of the experimental results. It is suggested, in particular, that the large positive field on the Co nuclei is determined by the conduction-electron polarization induced by the proper magnetic moment of the Co.

INTRODUCTION

SOLID solutions of Fe and Co in Pd are ferromagnets with an unusual magnetic structure. In these alloys, the ferromagnetic ordering arises already at very low concentration of the 3d-metal (0.03 at.% of Co[2]), when direct exchange interaction between the magnetic moments of the 3d-atoms is certainly excluded. Measurements of the magnetic susceptibility[2,3] and neutron diffraction[4] in dilute solid solutions of Fe and Co in Pd have shown that a region of polarized Pd atoms (cluster), with effective radius on the order of 10 Å, is produced around each 3d atom; the polarization is maximal near the center of the cluster and decreases towards its periphery. Associated with the formation of the clusters is the occurrence of "giant localized moments," exceeding $10\,\mu_B$ in some cases. It is obvious that such localized moments are due to the polarization of a large number of Pd atoms, inasmuch as the proper magnetic moments of the 3d atoms in these alloys do not differ very strongly from their values in pure 3d metals[4,5].

To clarify the nature of the magnetic ordering of the systems under consideration, it is important to obtain information on the polarization of the conduction electrons, since these electrons should play an essential role in the formation of the ferromagnetic ordering at large distances between the magnetoactive centers. At the present time there is no method for directly measuring the polarization of the conduction electrons, but useful information concerning this polarization can be obtained by an indirect method, for example by analyzing the magnitudes and signs of the magnetic fields acting on the nuclei of the atoms in ferromagnetic metallic systems. It should be indicated in this case that the magnetic fields at the nuclei of atoms of different elements do not have equal sensitivity to polarization of the conduction electrons. Inasmuch as the question of the interaction between the observed magnetic field at the nucleus of the given atom with the magnetic characteristics of the surrounding is of great significance in the interpretation of the results, we shall consider it in greater detail in the Appendix.

In the present investigation we measured the magnetic field acting on the nuclei of Co^{60} atoms in CoPd alloys (by measuring the angular anisotropy of the γ radiation of the polarized nuclei), and the magnetic field acting on the nuclei of impurity Sn^{119} atoms in CoPd and FePd alloys (with the aid of the Mossbauer effect). The experimental data discussed in the Appendix show that the magnitude and sign of the magnetic field at the nuclei of the Co atoms depend strongly on the surrounding; the Sn atoms do not have a proper magnetic moment, and therefore the fields at the nuclei of these atoms are due entirely to the magnetic moments of the matrix atoms, and are connected with the polarization of the conduction electrons[6,7]. Measurements of the magnetic fields for the CoPd alloys were made in the entire concentration interval, while for the FePd alloys they were made in the range up to 20 at.% Fe, corresponding to the region of disordered solid solutions. The magnetic fields at the Co^{60} nuclei in CoPd alloys in the region of low Co concentrations (up to 8.38 at.%) were measured earlier in[1]. An interesting result was obtained recently by Cracknell et al.[8], namely, it was observed that in dilute alloys of Co with Pd the magnetic field at the Co-atom nuclei is positive (whereas in pure Co and in other "usual" ferromagnets it is negative). This result is very important for the interpretation of the experimental data obtained in the present paper.

DESCRIPTION OF THE EXPERIMENT AT MAIN MEASUREMENT RESULTS

The samples for the investigation were prepared by melting the corresponding amounts of the components (the purity of the initial metals was 99.98%) in vacuum. After melting, the samples were homogenized in vacuum at 1000°C for 8–12 hours. To measure the angular anisotropy of the γ radiation of the polarized Co^{60} nuclei, the prepared alloys were bombarded by neutrons in a reactor; the measurement procedure is described in[1,9].

For the measurements with the aid of the Mossbauer effect, metallic tin enriched with ~0.5 at.% Sn^{119} was introduced into the samples. The absorption spectra were measured on samples rolled into foils or prepared in the form of powders. A detailed study was made of the influence of annealing on the form of the spectra; it was established that at large concentrations of Co in the CoPd alloys, the solubility of the impurity Sn in the equilibrium state of the alloy is very low (about 0.1 at.% Sn at 60 at.% Co and approximately 0.6 at.% Sn at 45 at.% Co). At Sn concentrations exceeding the indicated limits of formation of solid solutions, annealing leads to the appearance in the spectrum of a narrow absorption line with an isomer shift 1.75 mm/sec, which greatly differs from the shift corresponding to the solid solution (1.54 ± 0.03 mm/sec). We assume that the appearance of such a line is connected with the formation of a nonmagnetic phase (intermetallide). In this connection, we shall discuss below only the results of Mossbauer measurements obtained with quenched alloys, in which the Sn distribution corresponds to a disordered solid solution. For some of these alloys, the measurements were made with different concentrations of the Sn impurity (from 0.1 to 1.0 at.%); it was shown that in the indicated limits the change of the tin concentration have no essential influence on the form of the absorption spectrum.

The absorption spectra were measured with sources in the form of the compound $BaSnO_3$, which contains the isotope Sn^{119m}, with the aid of an automatic spectrometer with a multichannel analyzer in the time-variation mode. All the measurements of the FePd alloys and of the CoPd alloys containing less than 25% Co were made at 78°K. For the CoPd alloys with larger Co content, most measurements were made at room temperature; for these alloys, the Curie temperatures are sufficiently high and cooling of the samples to 78°K did not lead to a noticeable change in the form of the absorption spectrum The sign of the field on the Sn^{119} nuclei was determined by measuring the absorption spectra in external magnetic fields of intensity up to 15 kOe.

In disordered solid solutions, the magnetic field at the nucleus of the given atom usually depends strongly on the local configuration of the neighboring atoms. Both measurement methods used by us give in this case information only concerning the average field for the atoms of the given sought. We see, for example, from Fig. 1 that individual components of the hyperfine structure cannot be resolved in the absorption spectrum. Both a theoretical analysis and experiment show that (at least in the magnetic field range from 2 to 80 kOe) the magnitude of the field H and the total width Γ of the absorption spectrum at half the height are linearly connected. In our case this relation is given by

$$\Gamma = 0.14\ H + 0.70, \tag{1}$$

(Γ is in mm/sec and H is in kOe); for the indicated interval of H, this relation is satisfied with accuracy not worse than 10%. We have assumed that this relation is retained also for the unresolved spectra observed in the CoPd and FePd alloys, if H is taken to mean the average field $\bar{H}$ at the Sn^{119} nuclei. The results discussed below, which were obtained by such a reduction of spectra, show that this assumption is apparently reasonable.

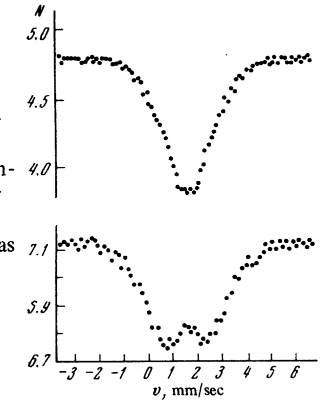

FIG. 1. Spectra of resonance absorption of γ quanta by nuclei of impurity Fn^{119} atoms in CoPd alloys (5.5 at.% Co), measured at 78°K without an external magnetic field (upper figure) and in an external magnetic field of 8 kOe (lower figure). Abscissas —velocity of the γ-quanta source, ordinates—intensity of the quantum flux in arbitrary units.

The main results of the measurements are shown in Figs. 2 and 3. The sign of the field for the Co^{60} nuclei was not determined. For the Sn^{119} nuclei it was shown that the average fields are positive in a wide range of concentrations of the CoPd alloys (from 5.5 to 75 at.% Co) and in all the investigated FePd alloys (the widths of the absorption lines increased with increasing intensity of the external magnetic field).

DISCUSSION OF RESULTS

A. Magnetic Fields at the Nuclei of the Cobalt Atoms

As seen from Fig. 2, the magnetic field at the nuclei of the Co atoms in the CoPd alloys changes strongly when the composition of the alloy changes. The field

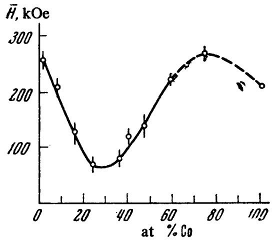

FIG. 2

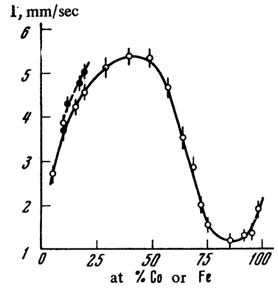

FIG. 3

FIG. 2. Mean value of the absolute magnitude of the field H at the Co^{60} nuclei in CoPd alloys as a function of the Co concentration.

FIG. 3. Line width Γ in the absorption spectra for the impurity atoms Sn^{119} in the alloys CoPd (○) and FePd (●) as a function of the 3d-atom concentration.

is maximal at low Co concentrations (H = 280 ± 20 kOe and 0.1 at.% Co[1]). The mean value $\overline{H}$ of the absolute magnitude of the field, determined in our experiment, decreases with increasing Co concentration, reaching a maximum at 25–35 at.% Co; with further increase of the Co concentration, $\overline{H}$ again increases, reaching a value close to that of the field in pure Co at approximately 60 at.%. The observed dependence of the field on the concentration can be understood by taking into consideration the result of[8], where it was shown that at small concentrations of Co in the CoPd alloy the field at the Co-atom nuclei is positive. Inasmuch as in pure Co the field, as is well known, is negative, it is obvious that there exist in the CoPd alloys at least two contributions to the field at the Co nuclei, with opposite signs, one of which prevails at small Co concentrations and the other at large concentrations. The observed maximum of H (Fig. 2) corresponds to that region of concentrations in which the two contributions approximately cancel each other.

In the region of small Co concentration, it is possible to neglect the influence of the Co atoms on one another and to consider the isolated Co atom in the Pd matrix. Taking into account the high sensitivity of the field for Co to the environment, one might assume that the observed large positive field is due to the polarization of the conduction electrons by the magnetic moments of the matrix atoms (the second term of formula (A.1)). Then, however, we must also assume that the magnetic moments of the Pd atoms are large, and the polarization of the conduction electrons in the CoPd alloys has a sign opposite that of the polarization in ordinary ferromagnets (Fe, Co, Ni). The two last assumptions contradict the available experimental data. The results of neutron-diffraction investigations[4] show that (at least at small Co concentrations) the magnetic moments of the Pd atoms are very small (not larger than $\mu_B/20$); the assumption that the sign of the polarization of the conduction electron is reversed does likewise not agree with the experimental data, for in this case one would observe large positive fields at the Pd atoms. (Budnick et al.[10] indicate that the field at the Pd nuclei are negative in the FePd alloys, and the data discussed below for the Sn impurity atoms show that the sign of the polarization of the conduction electrons is the same in the CoPd and FePd alloys.) We thus reach the conclusion that the observed large positive field at the Co nuclei is due to electron polarization connected with the magnetic moment of the Co itself.

It is shown in the Appendix that the field resulting from the polarization of the electrons by the proper magnetic moment of the impurity 3d atom can be represented by a sum of two contributions of opposite signs, and for Co in the usual ferromagnetic matrices both these contributions are nearly equal in absolute magnitude. To explain the experimental data it is necessary to assume that for an isolated Co atom in Pd the positive contribution due to the polarization of the conduction electrons by the moment of the Co atom itself increases sharply. Such an increase of the positive contribution implies a high density of the polarized conduction electrons near the Co atom, which in turn can be connected with the high density of the electronic states of Pd. Such an assumption concerning the nature of the positive field at the cobalt nuclei makes it possible to explain in natural fashion the observed dependence of the field on the composition of the alloy (Fig. 2). Inasmuch as the proper magnetic moment of the Co atom changes insignificantly when the composition of the alloy changes[4,5], it is necessary to take into consideration, in the analysis of the dependence of $\overline{H}$ on the composition of the alloy, only those factors which are connected with the environment of the given Co atom.

According to the data of[1], the field changes little in the concentration interval from 0.1 to 2 at.% Co. When the concentration increases, it is necessary to take into account the direct influence of the Co atoms on one another. At a concentration of 10 at.% Co, the relative weight of the configurations corresponding to one, two, and three Co atoms in the first coordination sphere of the given atom already amounts to about 60% of the total number of configurations. The appearance of Co atoms among the nearest neighbors of the given atom leads, on the one hand, to a negative contribution to the field from the nearest surrounding (the second term of the formula (A.1)) and, on the other hand, to a decrease of the aforementioned positive contribution due to the high density of the electronic states of Pd. As a result, the average field $\overline{H}$ decreases with increasing Co content in the alloy; the observed minimum of $\overline{H}$ near 30 at.% Co denotes that the field at the nucleus of an atom having three (or four) and more Co atoms among its nearest neighbors becomes negative. With further increase of the cobalt concentration, the relative weight of the configurations producing the negative field increases, corresponding to an increase of $\overline{H}$ in the range from 35 to 60 at.% Co. Allowance for the interaction with the more remote neighbors obviously can be significant only in an exact quantitative analysis of the experimental data.

At a Co concentration 75 at.%, an increase is observed in the magnetic field compared with its value in pure Co; the cause of this increase is not clear.

B. Magnetic Field at Nuclei of Tin Impurity Atoms

The magnetic fields at the nuclei of the impurity Sn atoms in CoPd alloys and FePd alloys are due to the polarization of the conduction electrons by the magnetic moments of the matrix atoms. At a given alloy composition, the field varies as a function of the local configuration of the atoms, and therefore the absorption spectra represent broad lines with an unresolved hyperfine structure. Let us see how the composition of the alloys affects the average effective field $\overline{H}$ determined from the absorption line width in accordance with formula (1). This field is connected with the average polarization of the conduction electrons of the alloy which, in turn, is determined by the average magnetic moment $\overline{\mu}$ per alloy atom.

The average polarization of the conduction electrons in CoPd and FePd increases monotonically with increasing concentration of the 3d atoms, a fact manifest, for example, in the monotonic increase of the average magnetic field at the nuclei of the Pd atoms[10,11]. If the magnetic field at the Sn nuclei were to depend linearly on $\bar{\mu}$, then we should expect in this case an analogous growth of the average field with increasing concentration of the 3d-atoms. For Sn, however, an anomalous dependence of the field on the magnetic moment of the matrix atom is observed (as is well known, the field is positive for Sn in an Ni matrix, and negative in Fe and Co matrices). We shall show that the observed dependence of the average field at the Sn^{119} nuclei in the alloys CoPd and FePd agrees well with other data on fields for Sn in metallic ferromagnets. The results obtained for the alloys CoPd and FePd, together with other known data, are presented in Fig. 4, in the form of a plot of $\bar{H}$ vs. $\bar{\mu}$. We see that at small $\bar{\mu}$ (up to $\bar{\mu} \approx 0.8\ \mu_B$) the magnetic field is positive and is approximately linear in $\bar{\mu}$. It is important that the previously obtained data for CuNi alloys[12] and the data for the CoPd and FePd alloys lie well on a single straight line.

The proportionality of the field to $\bar{\mu}$ is violated when $\bar{\mu}$ exceeds one Bohr magneton. The negative contribution to the field increases sharply with $\bar{\mu}$, leading to a sharp decrease of the field; at $\bar{\mu} \approx 1.6\ \mu_B$, the field should be close to zero (this can be verified experimentally). Inasmuch as the nature of the observed anomalous dependence on the field on $\bar{\mu}$ was not investigated in practice, it is difficult at present to offer a nonambiguous well founded interpretation for this dependence. We propose, however, that the observed anomaly is connected with the redistribution of the conduction electrons near the impurity atom with increasing magnetic moment of the matrix atoms. Apparently the "compensation effect" observed in[12] for magnetic fields at Sn in alloys has the same nature. In this connection, interest attaches to a detailed investigation of the fields at the nuclei of the atoms V and Zr, for which similar anomalies can become just as clearly pronounced as for Sn[7].

The results of the present investigation show that investigations of the magnetic fields at nuclei in alloys can yield, in principle, useful information not only concerning the origin of these fields, but also concerning the electronic structure of the alloys. It is difficult to explain the observed dependences of the magnetic hyperfine interaction in the investigated alloys on the basis of the conventional representations; the interpretation requires the use of certain premises, which apparently call for additional experimental verification. For a more reliable interpretation of the data, it is important to investigate the magnetic hyperfine interaction in other alloys of 3d and 4d metals, using a larger group of impurity atoms. We note that the isotope Fe^{57}, which is widely used in Mossbauer-effect experiments, is unfortunately not very suitable for this purpose, since in Fe the magnetic hyperfine interaction is relatively insensitive to the polarization of the conduction electrons.

APPENDIX

MAGNETIC FIELDS AT THE NUCLEI OF 3d ATOMS IN METALLIC FERROMAGNETS AND POLARIZATION OF THE CONDUCTION ELECTRONS

The magnetic fields at the nuclei of atoms in metallic ferromagnets are determined in the general case both by the electronic structure of the given atoms and by the magnetic characteristics of the surroundings. For atoms which have no magnetic moment of their own, the field at the nucleus is proportional in first approximation to the magnitude of the magnetic moment of the atoms of the matrix[6,7]; in the remaining cases, an appreciable contribution can be made to the field by the electron polarization due to the proper magnetic moment.

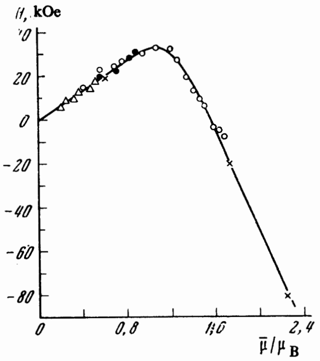

FIG. 4. Dependence of the average field $\bar{H}$ at the nuclei of impurity Sn^{119} atoms in metallic ferromagnets on the magnitude of the average magnetic moment $\bar{\mu}$ per atom of the alloy: ○ – CoPd, ● – FePd, Δ – CuNi, × – Fe, Co, Ni.

According to calculations by Watson and Freeman[13], the main contribution to the magnetic field at the nuclei of 3d metals is due to polarization of s-electrons of the internal shell, resulting from exchange interaction with the magnetic 3d-electrons. In this approximation, the field at the nucleus should be proportional to the magnetic moment of the given atom and should be negative. Experimental data show, however, that the magnetic fields at the nuclei of 3d-elements in different ferromagnetic matrices are not proportional to the proper magnetic moment of the atom, and depend also strongly on the magnetic moments of the neighboring atoms. An analysis of the experimental data for the impurity atoms Fe, Co, and Ni in metallic ferromagnetic matrices shows that these fields can be represented by the formula (see, for example,[14])

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

where μ_i is the magnetic moment of the atom itself, μ_M is the magnetic moment of the atoms of the matrix, and a and b are coefficients that are constants for the given impurity atom. It is important to emphasize that the first term in this formula corresponds to polarization by means of the proper magnetic moment μ_i not only of the internal shells of the atom, but also of the external electrons (electrons of the conduction band). The contribution made to the field by the polarization of the internal shells is unconditionally negative. There are no direct experimental data concerning the magni-

Coefficients a and b in formula (A.1) for atoms of Mn, Fe, Co, and Ni [kOe/μ_B]

	Mn	Fe	Co	Ni
a	—100	—84	—30	—25
b	—108	—66	—104	—100
b/a	1.08	0.79	3.47	4.0

0

tude and sign of the contribution connected with the polarization of the external electrons by the proper moment of the atom. However, general theoretical considerations[6,13,15] show that this contribution should be positive. The coefficient a in formula (A.1) is actually the sum of two coefficients of opposite signs. The second term of (A.1) is due to the contribution connected with the polarization of the conduction electrons by the magnetic moments of the matrix atoms. This contribution to the field was considered in detail in[7].

If we take into consideration the experimental data obtained in[14,16], then we can show that formula (A.1) is valid not only for Fe, Co, and Ni but also for Mn (both for Mn impurity atoms and for the intermetallic compounds in the Mn-Ni system; in the latter case μ_M in the formula (A.1) should be taken to mean the average magnetic moment of atoms that are the neighbors of the given atom Mn). Using the available data, we have calculated by least squares the coefficients a and b of formula (A.1) for the atoms Mn, Fe, Co, and Ni (see the table). With these values of the coefficients, formula (A.1) describes very well the experimental data: the deviations of the experimental values from those given by formula (A.1) do not exceed several percent. The quantities b/a given in the table characterize the relative rule of the contribution made to the field by the magnetic moments of the matrix atoms. These quantities are not small for any of the considered atoms; we see that the fields at the nuclei of the Co and Ni atoms are specially sensitive to the polarization of the conduction electrons by the magnetic moments of the matrix atoms.

As was noted above, the coefficient a of formula (A.1) can be written in the form of a sum $a_1 + a_2$, where $a_1 < 0$ and characterizes the polarization of the s-electrons of the internal shells of the atom, whereas a_2, which characterizes the contribution made to the field by the polarization by the moment μ_i of the external electrons should be positive. It can be assumed that the coefficient a_1 does not depend (or depends little) on the properties of the matrix. The coefficient a_2, on the other hand, can, generally speaking, depend strongly on the electronic structure of the matrix (for example, on the density of the electronic state in the conduction band). It must therefore be borne in mind that formula (A.1) with the coefficients obtained from the data for the matrices Fe, Co, and Ni (see the table) may turn out to be not applicable for a larger group of matrices. Unfortunately, there are no experimental data from which to determine directly the values of the coefficients a_1 and a_2. It can be assumed qualitatively that for the atoms Co and Ni (in the three matrices under consideration) the small value of the coefficient a of formula (A.1) is due to the fact that the absolute magnitude of a_1 exceeds the absolute magnitude of a_2 only slightly.

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