MEASUREMENT OF THE EFFECTIVE MAGNETIC FIELDS ACTING ON Co^{60} *NUCLEI IN DILUTE SOLID SOLUTIONS OF* Co *IN* Pd

V. P. PARFENOVA, N. E. ALEKSEEVSKIĬ, A. L. ERZINKYAN, and V. S. SHPINEL'

Nuclear Physics Institute, Moscow State University

Submitted March 14, 1967

Zh. Eksp. Teor. Fiz. 53, 492–497 (August, 1967)

The effective magnetic fields acting on Co^{60} nuclei in Co–Pd alloys were measured by the oriented nuclei technique. Dilute solid solutions of Co in Pd were investigated for Co concentrations of 8.3, 2.0, 0.3, 0.1 and 0.03 at. %. The fields acting on Co^{60} nuclei in Co–Pd alloys were compared with the effective field acting on the Co nucleus in metallic Co. When the Co concentration was reduced from 8.3 to 0.1 at. %, the field acting on the Co^{60} nucleus increased but it decreased at a concentration of 0.03 at. %. The alloy retained its ferromagnetic properties even at the lowest concentration investigated (0.03 at. % of Co).

INTRODUCTION

ALLOYS of transition elements of the 3d-group based on Pd have recently been attracting attention because of the occurrence of impurity ferromagnetism, i.e., ferromagnetism of systems in which the magnetic centers are far from one another. It is assumed that the magnetic ordering in such systems is due to an indirect exchange interaction through the conduction electron band. Several experimental investigations have been published concerning the alloys in which transition metal atoms are dissolved in the fcc matrix of Pd. Alloys of elements of the 3d-group with Pd have a number of interesting features. Thus, solid solutions of Fe, Co, and Ni in Pd are ferromagnetic even when the concentrations of these elements are very low. It has been established that ferromagnetism is observed when the impurity content in Pd is at least 0.15 at. % of Fe,[1] 0.07 at. % of Co,[2] or 2.5 at. % of Ni.[1] These alloys have been investigated by magnetic methods and the results obtained have indicated that the magnetic moments per one impurity atom increase when the 3d-element dilution is increased. These moments reach values of $\approx 12\ \mu_B$ in the case of Fe–Pd alloys[1] and $\approx 10\ \mu_B$ in the case of Co–Pd alloys.[3]

In addition to magnetic investigations, which yield information on the macroscopic properties of a substance, microscopic investigations of the relevant systems have also been carried out. In particular, the effective magnetic fields acting on the impurity nuclei of the transition metal have been measured. Measurements of the effective magnetic fields acting on Fe^{57} nuclei have been carried out on Fe–Pd and Co–Pd alloys using the Mössbauer effect (in the latter case the Fe^{57} nuclei were impurities in the alloys). Measurements of the dependence of the effective magnetic field acting on the Fe^{57} nucleus on the concentration of Fe–Pd alloys[4] have shown that when the amount of Fe is reduced, the field decreases from a value of −335 kOe at 43 at. % Fe in Pd to −295 kOe for Fe in practically pure Pd (this value has been obtained by investigating a paramagnetic sample[5]). The results for Co–Pd alloys are different from those for Fe–Pd. The effective magnetic field acting on the Fe^{57} nuclei present as an impurity in Co–Pd alloys has been found to be independent of the concentration of Co. Mössbauer effect measurements in the range of concentrations 3–100 at. % Co[6] and 0.07–4.5 at. % Co,[2] have shown that the field acting on the Fe^{57} nucleus remains constant and approximately equal to 300 kOe.

Since the Mössbauer method can be used only to determine the field acting on an impurity Fe^{57} nucleus, it seemed interesting to carry out measurements of the effective magnetic fields acting directly on the Co nuclei in solid solutions of Co in Pd. In such measurements, it is convenient to employ the method of oriented nuclei, especially radioactive nuclei, because sensitive recording methods enable us to carry out investigations of alloys with very low concentrations of Co.

Preliminary results of the measurements of the effective magnetic fields acting on the Co^{60} nuclei in solid solutions of Co in Pd, determined by the method of oriented nuclei, have been reported by us in[7,8]. The present paper describes a continuation of the investigation of the effective magnetic fields acting on Co^{60} nuclei in Co–Pd alloys at various Co concentrations, right down to a minimum concentration of 0.03 at. %.

PREPARATION OF THE SAMPLES AND THE MEASUREMENT METHOD

Solid solutions of Co in Pd were prepared by melting together Co and Pd (of 99.9 and 99.999% nominal purity) in a high-frequency furnace filled with helium. Alloys with high concentrations of Co were prepared by melting together suitable amounts of the two components, while alloys with a low content were prepared by diluting high-concentration solid solutions in Pd. In this way, we prepared alloys with Co concentrations of 0.03, 0.1, 0.3, 2.0, and 8.3 at. %. An activation analysis was carried out on the alloys obtained in order to check their composition; we compared the induced Co^{60} activity in the samples under investigation and in pure Co. An additional check was provided by measuring the Curie temperatures of some samples, using a magnetic method. The activation analysis and the measurements of the Curie points confirmed the correctness of the determination of the Co concentrations in Pd. For example, the Curie point of the alloy with 0.1 at. % Co was $T_C = 6.7 \pm 1°K$, in agreement with the results of Bozorth et al.,[3] who reported $T_C = 7 \pm 1°K$ for an alloy of this composition.

The samples prepared by melting together the components were annealed for two to three days at ≈900°C, then they were rolled and disks, 2.5–4 mm in diameter and 0.2–0.3 mm thick, were cut from the rolled strips. Samples prepared in this way were irradiated with neutrons in a reactor to generate radioactive Co^{60} nuclei.

The nuclei were polarized by the standard method in which a very low temperature was reached by the method of adiabatic demagnetization of a paramagnetic salt (chromium-potassium alum) and the nuclei were polarized by the effective field in the ferromagnet. An investigated sample was soldered to the end of a copper cold duct, which was inserted in a chromium-potassium alum block. To improve the thermal contact between the cooling salt and the cold duct, copper foil tabs were silver-soldered to the duct. A magnetic field, produced in an electromagnet, was applied to the cooled sample. The value of the magnetic field employed in the present investigation was usually 5.7 kOe. Such a field was obviously sufficient to magnetize the Co–Pd samples to saturation but it did not affect the paramagnetic salt, which was separated by a distance of 20 cm (the length of the cold duct) from the sample and protected by a magnetic screen.

The temperature was determined from the value of the magnetic susceptibility of chromium-potassium alum. To convert the "magnetic" temperature to the "thermodynamic" scale, we used the results of Daniels and Kurti.[9] Thermal equilibrium between the chromium-potassium alum block and the sample was established after approximately 1 hour at $T \approx 0.03°K$, which was checked by special measurements of the effective magnetic field acting on the Co^{60} nucleus in metallic Co. The effective value of the magnetic field obtained in the present investigation, $(2.08 \pm 0.12) \times 10^5$ Oe, was in good agreement with the published value of H_{eff} for the Co nucleus in metallic Co, which confirmed that the temperature of the sample was determined correctly. Such measurements of temperature at the position of the sample under investigation were made before and after each series of measurements on the Co–Pd alloys, all of which were carried out under the same conditions (the same cooling salt block and the same cold duct were used). The measurements were carried out in 1.5–2 hours after the establishment of thermal equilibrium, during which period the temperature of the system increased to 0.06–0.07°K.

The 1.33 and 1.17 MeV γ rays of Co^{60} were recorded using four FÉU-13 photomultipliers with NaI(Tl) crystals, directed at 0° (180°) and 90° (270°) with respect to the direction of the magnetizing field H. Four, rather than two, detectors were used in order to increase the statistical accuracy.

The degree of polarization of the nuclei is described by the Brillouin function

$$f_1 = B_I(\beta) = \frac{2I+1}{2I} \coth\left(\frac{2I+1}{2}\beta\right) - \frac{1}{2I} \coth\left(\frac{\beta}{2}\right),$$
$$\beta = \frac{\mu H_{eff}}{IkT}. \qquad (1)$$

Here, μ is the magnetic moment of the nucleus, H_{eff} is the effective magnetic field acting on the nucleus, k is Boltzmann's constant, T is the temperature, and I is the nuclear spin.

The angular distribution of Co^{60} γ rays (both transitions are of the E2 type) can be described by the following formula:[10]

$$W(\vartheta) = 1 - {}^{15}/_{7} N_2 f_2 P_2(\cos\vartheta) - 5 N_4 f_4 P_4(\cos\vartheta), \qquad (2)$$

where $N_2 = I/(2I - 1)$, $N_4 = I^3/(I - 1)(2I - 1)(2I - 3)$; f_2 and f_4 are functions of the orientation, governed by the parameter β; $P_2(\cos\vartheta)$ and $P_4(\cos\vartheta)$ are the Legendre polynomials; the angle ϑ is measured from the nuclear orientation axis.

At not-too-low temperatures, when β is small, $f_4 \ll f_2$ and, therefore, the last term in Eq. (2) can be neglected. The orientation function

$$f_2 = \frac{2(I+1)}{3I} - \frac{f_1}{I} \coth\frac{\beta}{2} \qquad (3)$$

is found by measuring the anisotropy of the angular distribution of the γ rays emitted by the nuclei polarized or aligned at low temperatures. The decay scheme of the Co^{60} nucleus (I = 5) is known and, therefore, the coefficient N_2 as well as the explicit form of the dependence of f_2 on β [Eq. (3)] are known, so that we can determine the parameter β, having measured the value of the anisotropy $\epsilon = [W(\pi/2) - W(0)]/W(\pi/2)$. Since the magnetic moment of the Co^{60} nucleus is also known ($\mu = 3.800 \pm 0.007$ nuclear magnetons[11]), the value of the effective magnetic field acting on a nucleus, H_{eff}, can be found if we know the temperature of a sample.

RESULTS OF MEASUREMENTS AND DISCUSSION

The results of measurements of the effective magnetic fields acting on the Co^{60} nuclei in solid solutions of Co in Pd of several concentrations were as follows:

At. % Co :	8,3	2.0	0.3	0,1	0,03
H_{eff}, 10^5 Oe :	2,06±0.18	2,60±0.18	2,60±0.20	2.8±0,20	1.30±0,10

The errors indicated in the above table are random and do not include the inaccuracy in the determination of the temperature.

Examination of the values obtained shows that the effective field increases when the Co–Pd system is diluted with palladium and at low Co concentrations the field is even greater than the field acting on the nucleus in pure Co. For 8.3 at. % Co in Pd, the field acting on the Co^{60} nucleus is equal to the field in metallic Co, while at 0.1 at. % Co it reaches its maximum value representing $(2.8 \pm 0.20) \times 10^5$ Oe. The dependence of H_{eff} on the impurity concentration obtained in the present investigation is different from the previously determined (by means of the Mössbauer effect) dependence of the field acting on the Fe^{57} nucleus in the Fe–Pd system, for which the field decreases when the concentration of Fe is reduced.[4] The investigation of even more dilute solid solutions shows that the field acting on the Co^{60} nucleus decreases and we find that $H_{eff} = (1.30 \pm 0.10) \times 10^5$ Oe for 0.03 at. % Co.

Magnetic investigations of the Co–Pd alloy containing 0.03 at. % Co have shown that this alloy goes over to

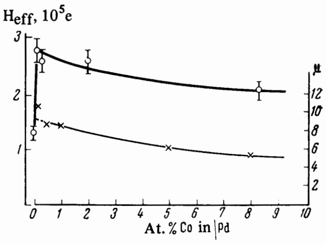

FIG. 1. Results of the measurements of the effective magnetic fields H_{eff} acting on Co^{60} nuclei in Co–Pd alloys containing various concentration of cobalt (upper curve). The figure includes the concentration dependence of the magnetic moment μ (expressed in Bohr magnetons) per one impurity atom (lower curve). [3]

the ferromagnetic state at $T_C = 1.2 \pm 0.3^\circ K$.[1)] Thus, in the working range of temperatures (0.03–0.07°K), all the investigated samples were in the ferromagnetic state. The lower value of the effective magnetic field acting on the Co^{60} nucleus in the alloy with 0.03 at. % Co may be due to a weakening of the ferromagnetic interaction due to the very strong dilution of the 3d impurity element.

The dependence of H_{eff} on the impurity concentration, presented in Fig. 1, resembles very closely the concentration dependence of the magnetic moment per one impurity atom of a 3d element in the case of solutions of Co in Pd[3] and Fe or Ni in Pd[1] (for comparison, Fig. 1 includes the magnetic moment curve for the Co–Pd system). The curve corresponding to the Fe–Pd system has a magnetic moment maximum at a concentration of 0.28 at. % Fe. At the minimum investigated concentration of 0.15 at. % Fe, the magnetic moment is less than the maximum value of the magnetic moment, equal to ≈12 μ_B.

In the case of the Co–Pd system, the ferromagnetism was retained at the minimum investigated Co concentration, but the value of the magnetic moment per one impurity atom was not determined for this concentration. The magnetic moment had its largest value of 10 μ_B for the solid solution with 0.1 at. % Co in Pd and it showed no tendency to decrease. The available data on the magnetic properties of the Fe–Pd and Co–Pd systems indicate that the Co ion behaves a little more "actively" in Pd alloys than the Fe ion. Thus, at a concentration of 0.15 at. % Fe in Pd the magnetic moment per one impurity atom is less than its maximum value, while in the Co–Pd system there is no such decrease even at 0.1 at. % Co. The same conclusion follows from the results on the Curie points: the Curie points of the Co–Pd alloys are higher, for the same impurity concentration, than the corresponding points of the Fe–Pd alloys. This may explain the different concentration dependences of H_{eff} of the Fe–Pd and Co–Pd systems; clearly, the determination of the causes of this difference in the behavior of the two systems requires further studies.

Taking the value of H_{eff} for the Co–Pd alloy with 0.03 at. % Co, we can compare the behavior of the effective field with the dependence of the localized magnetic moments acting on Fe and Ni atoms on the concentration of these atoms in Fe–Pd and Ni–Pd systems, whose magnetic moment passes through a maximum and then decreases in the case of high dilutions.[1] We may assume that the Co–Pd system behaves similarly but the decrease in the magnetic moment takes place at lower concentrations of Co than those observed for Fe.

The similarity of the dependences of the effective magnetic field acting on a nucleus and of the magnetic moment per one impurity atom indicates that the increase in H_{eff} is associated with the increase in the magnetic moment of a cluster formed by an impurity atom and the Pd atoms surrounding it.

Recent investigations of Low and Holden,[12] who have studied the magnetic scattering of slow neutrons in ferromagnetic Co–Pd and Fe–Pd alloys, have made it possible to determine the distribution of magnetic moments around an impurity center. It has been established that in alloys with low ferromagnetic impurity concentrations (≤1%), a large number of Pd atoms situated near the impurity become polarized; the degree of polarization becomes less when the concentration of the impurity is increased, which is obviously due to the overlap of the interactions of other impurity centers. The interaction, resulting in the polarization of Pd atoms, affects up to 200 atoms of the matrix and extends to distances of the order of 10 Å. At such distances between impurity atoms, the ferromagnetism of the alloy is still retained, as indicated by an estimate of the value of the minimum transition-metal impurity concentration necessary to obtain a ferromagnetic alloy.[1]

The magnetic moments of the 3d-shells of Fe and Co atoms have been determined[12] for dilute alloys of these elements with Pd: these moments are, respectively, (3.5 ± 0.4) μ_B and (2.1 ± 0.3) μ_B. The moments induced by the polarization of Pd atoms nearest to an impurity do not exceed (1/20) μ_B, confirming that the giant moments associated with impurities are due to the large number of Pd atoms perturbed by each Fe and Co impurity. Since the magnetic moments of the 3d-shells of the impurities are approximately constant, we may conclude that the magnetic field acting on the Co nuclei is not only due to the magnetism of the 3d-shell of the dissolved atom but also to the polarized environment of Pd atoms.

According to the model of Freeman and Watson,[13] we must consider two main contributions to H_{eff}: that of the polarization of the electron shells of the core and that of the polarization of electrons in the conduction band. If the magnetic moments of the 3d-shell of Co in Co–Pd alloys and in pure Co are not very different, the dependence of H_{eff} on the concentration should be ascribed to the polarization of the conduction electrons. Assuming (in agreement with[13]) that the contribution of the conduction electron polarization to H_{eff} is opposite in sign to the contribution of the polarization of the atomic core, we find that when the concentration of Co is reduced the degree of polarization of the conduction electrons decreases or the density of these electrons near the Co nucleus becomes less. The latter possibility seems more likely because a reduction in the degree of polarization of the conduction electrons would have reduced the average magnetic moment per one Co atom.

In conclusion, the authors regard it as their pleasant duty to thank their colleagues of the Low Temperature Physics Chair in the Physics Department of the Moscow State University, directed by Corresponding Member of the U.S.S.R. Academy of Sciences A. I. Shal'nikov, for the supply of liquid helium, N. A. Delyagin for discuss-

---

[1)] The magnetic measurements were carried out by G.E. Karstens, to whom the authors are indebted.

ing the results obtained, and V. N. Anishchenko for his help in this investigation.

---

[1] J. Crangle and W. R. Scott, J. Appl. Phys. **36**, 921 (1965).

[2] B. D. Dunlap and J. G. Dash, Preprint, 1966.

[3] R. M. Bozorth, P. A. Wolff, D. D. Davis, V. B. Compton, and J. H. Wernick, Phys. Rev. **122**, 1157 (1961).

[4] P. P. Craig, B. Mozer, and R. Segnan, Phys. Rev. Letters **14**, 895 (1965).

[5] P. P. Craig, D. E. Nagle, W. A. Steyert, and R. D. Taylor, Phys. Rev. Letters **9**, 12 (1962).

[6] D. E. Nagle, P. Craig, P. Barrett, D. R. F. Cochran, C. E. Olsen, and R. D. Taylor, Phys. Rev. **125**, 490 (1962).

[7] N. E. Alekseevskiĭ, V. N. Anishchenko, A. L. Erzinkyan, V. P. Parfenova, and V. S. Shpinel', ZhETF Pis. Red. **3**, 318 (1966) [JETP Lett. **3**, 206 (1966)].

[8] V. P. Parfenova, N. E. Alekseevskiĭ, A. L. Erzinkyan, and V. S. Shpinel', Tezisy dokladov 10-oĭ Mezhdunarodnoĭ konferentsii po fizike nizkikh temperatur (Abstracts of Papers presented at the Tenth International Conference on Low-Temperature Physics), Moscow, 1966, p. 359.

[9] J. M. Daniels and N. Kurti, Proc. Roy. Soc. (London), **A221**, 243 (1954).

[10] N. A. Tolhoek and J. A. M. Cox, Physica **19**, 101 (1953).

[11] W. Dobrowolski, R. V. Jones, and C. D. Jeffries, Phys. Rev. **101**, 1001 (1956).

[12] G. G. Low and T. M. Holden, Proc. Phys. Soc. (London) **89**, 119 (1966).

[13] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

Translated by A. Tybulewicz
56