

## Co Impurity in Palladium: Giant Moment and Kondo-like Coupling

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We describe nuclear orientation experiments performed on dilute alloys of *PdCo*. Assuming the proportionality between the hyperfine field and the magnetization, we show that the Co impurity is in a Kondo-like state at low temperatures ( $T < 100$  mK). We discuss the link between the Co positive hyperfine field and its weak Kondo coupling.

In the palladium lattice, Mn, Fe, and Co impurities polarize strongly the palladium atoms. Usually, these giant moments are described by a ferromagnetic exchange coupling between the spin  $S$  of the impurity and the spin  $s$  of the conduction electron.<sup>1</sup> This type of Hamiltonian neglects completely the possible existence of a Kondo-like singlet state at low temperatures since this state would involve an antiferromagnetic coupling.

The existence of a Kondo-like state in the case of a giant moment is established for the *PtCo* alloy which has a giant moment of  $3.6\mu_B$  and a Kondo temperature near 1 K.<sup>2,3</sup> In order to check the possibility that such a behavior can occur for a stronger giant moment, we have performed nuclear orientation experiments (NO) on dilute alloys of *PdCo* where the Co atoms have a giant moment of  $10\mu_B$ .<sup>4</sup>

In the special case of *PdCo* alloys, the observation of the strength of any Kondo coupling is particularly important if we try to understand the origin and the reason of a positive hyperfine field on the Co nuclei. Ordinarily, it is admitted that for strongly magnetic  $3d$  impurities ( $T_K < 100$  K) only the spin magnetism is satisfied and that consequently the corresponding hyperfine field must be negative.

In *PdMn* alloys, for the NO experiment, the enhanced magnetization of the impurity appears as a simple enhancement of the electronic Zeeman term  $g\mu_B HS_z$ . The manganese effective field  $H_{\text{eff}}$  follows the free spin Hamiltonian value  $H_g^S$  with  $S = \frac{5}{2}$  and  $g = 3$ .<sup>5</sup> That corresponds to a giant mo-

ment of  $7.5\mu_B$ , in agreement with higher-temperature susceptibility results.<sup>6</sup>

In the experiments performed on the *PdCo* alloys, we compare the measured effective field  $H_{\text{eff}}$  with the theoretical function  $H_g^S$  calculated for a giant moment of  $10\mu_B$ . An experimental curve lying below this function will be interpreted as being due to a Kondo-like state if we are sure that the experimental data represent the intrinsic one-impurity magnetization.

Commercial radioactive solution of  $^{60}\text{CoCl}_2$  was purified by ion exchange or by ether extraction in order to eliminate as much iron as possible. The cleaned activity was electroplated or directly painted on a Pd wire which has a nominal purity better than 99.999%. (The Pd wire was manufactured by the Johnson Matthey Company.) The Pd sample was then melted under a secondary vacuum on a water-cooled copper hearth using a high-frequency furnace. The weight of the melted sample was typically 0.5 g. No difference has been observed between the two type of radioactive depositions.

Because the samples were made of bulk materials, we have performed magnetization experiments and neutron analysis on the same samples. The magnetization measurements define the macroscopic polarization of the probe. They were performed in the range 0.05–4 K in an applied field up to 3000 Oe. Neutron activation analysis indicates that the magnetic impurities detected by the magnetization measurements are iron atoms which are present despite the precautions taken in the preparation of the samples.

The NO experiments have been made between 3 and 25 mK in an applied field up to 40 000 Oe. The temperature is measured in high fields by a ferromagnetic NO thermometer of  $Ni^{54}Mn$  and in low fields by a paramagnetic thermometer of  $Pd^{54}Mn$  which is calibrated in a preliminary experiment with a primary  $Co^{60}Co$  thermometer. The experimental anisotropy are measured with an uncertainty  $\Delta E$  better than 0.5%; the relative accuracy on  $H_{eff}$  is better than 5%.

The results are described in terms of an effective field  $H_{eff}$ .  $H_{eff}$  is that magnetic field acting on the nuclei which would give the same  $\gamma$  anisotropy as the experimental anisotropy. This method of representing the data is very sensitive to any local misalignment of the local hyperfine field axes when the temperature is low enough for the nuclei to be highly oriented with respect to these local fields. When magnetic interactions like those for the spin-glass occur, the resulting misalignment means that  $H_{eff}$  strongly decreases with increasing  $T^{-1}$ .<sup>7</sup>

Figure 1 shows, for the more dilute alloys ( $C_{Fe} \leq 22$  ppm), the variation of  $H_{hf}$  vs  $1/T$  for different applied fields. As the hyperfine field is positive,<sup>8</sup>  $H_{hf}$  is defined by the relation

$$H_{hf} = H_{eff} - H,$$

where  $H_{eff}$  is the effective field deduced from the experimental  $\gamma$  anisotropy. When the electronic magnetization is completely polarized along  $H$ , the saturation value of the hyperfine field is +195

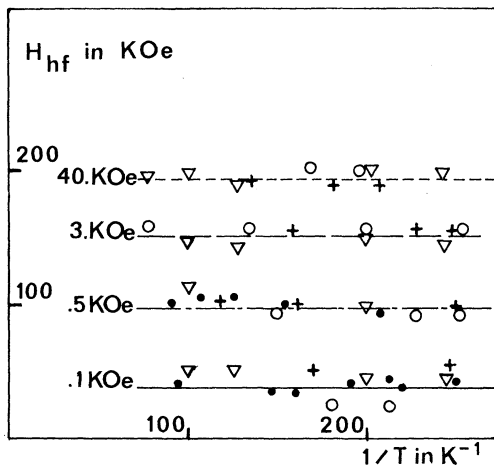


FIG. 1. Variation of the hyperfine field,  $H_{hf}$ , of  $^{60}Co$  vs  $T^{-1}$  for four different applied fields (40 000, 3 000, 500, and 100 Oe). The lines represent the corresponding mean values. The symbols describe the following iron parasitic concentration in parts per million: ●, undetermined; ▽, 7.8; +, 6.4; and ○, 21.6.

$\pm 6$  kOe. This value is in excellent agreement with that obtained by Gallop,  $210 \pm 10$  kOe.

For  $H > 500$  Oe, a single value of  $H_{eff}$  independent of  $T^{-1}$  can be attributed to the Co nuclei, so this behavior can be taken to characterize a single-impurity effect. In order to avoid any discussions about the effects of the iron impurities, we referred to the magnetization results obtained for a sample containing 7.8 ppm of iron (Fig. 2). Even at 55 mK, the iron impurities are easily polarized for  $H \geq 700$  Oe. As the magnetic saturation follows almost a Brillouin function  $B_g^S$  for  $S = 5$  and  $g = 2$  down to 55 mK, there is no doubt that at 5 mK, the iron atoms are fully saturated for  $H \geq 500$  Oe. Therefore, the lack of a saturation for the Co effective field at 5 mK in this sample is a single-impurity effect.

The field dependence of  $H_{hf}$  at 5 mK (Fig. 3) shows that  $H_{eff}$  strongly decreases from any theoretical function calculated for a giant moment of  $10\mu_B$ : The Co impurity is submitted to a strong Kondo coupling.

We emphasize here that an NO experiment is a purely static measurement which, like an ordinary magnetization experiment, is not affected directly by the dynamic fluctuation of the electronic spin  $S$  if this fluctuation is not correlated with a modification of the electronic energy level.

Whatever the electronic relaxation time of the local moment in the absence of any Kondo coupling, the experimental data must fit a free spin function  $H_g^S$  (weak coupling limit defined by Flouquet<sup>9</sup> and Flouquet and Brewer<sup>10</sup>). As the Kondo coupling increases, the electronic moment becomes more coupled to the conduction electron.

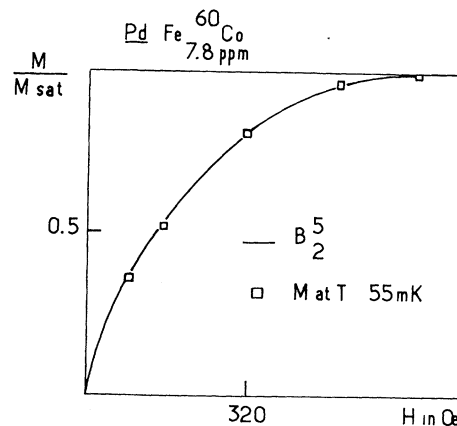


FIG. 2. At 55 mK, field dependence of the magnetization of the sample containing 7.8 ppm of iron. The solid line represents the Brillouin function  $B_2^5$ .

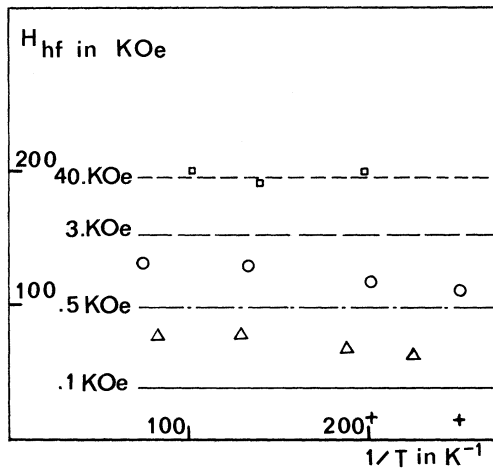


FIG. 3. At 5 mK, field dependence of the hyperfine field of  $^{60}\text{Co}$ . The dashed and solid curves represent the free enhanced spin value  $H_{10}^1, H_5^2$ . The symbols are those of Fig. 1.

In the limit of the strong coupling (defined by  $k_B T_K A$ ,  $A$  being the hyperfine coupling energy), the nuclear and electronic spins of the impurity are well decoupled. One can really describe the experiments with an effective hyperfine field proportional to the local magnetization and independent of the nuclear spin of the probe.

In order to estimate the strength of the Kondo-like coupling, we assume proportionality between  $H_{\text{hf}}$  and the impurity magnetization  $m$ . If we interpret the positive sign of  $H_{\text{hf}}$  as due to an orbital contribution,<sup>11</sup> this hypothesis supposes that the orbital and spin magnetizations are characterized by the same Kondo temperature  $T_K$ . With this assumption,  $T_K$  can be evaluated simply from the initial slope of  $H_{\text{eff}}$  vs  $H$  using the relation

$$\frac{H_{\text{hf}}}{H_{\text{hf}}^{\text{sat}}} \sim \frac{\chi H}{m_{\text{sat}}} \sim \frac{\mu_{\text{eff}}^2}{3k_B T_K} H,$$

where  $\chi$  and  $m_{\text{sat}}$  represent, respectively, the susceptibility and magnetization of the Co impurity. The value  $T_K = 120 \pm 40$  mK is in agreement with the hypothesis of a strong coupling limit.

For an NO experiment, the magnetic interactions can simply be summarized (i) by a change in the magnitude of the average magnetization, (ii) by the degree of misalignment between the local symmetry axis  $\vec{Z}$  seen by the nuclei and the macroscopic symmetry axis defined by the polarized magnetic field ( $\vec{Z}$  is defined by the vector sum of the molecular field and  $\vec{H}$ ). As is report-

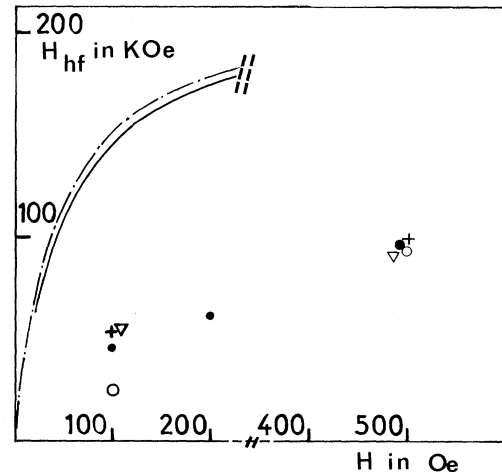


FIG. 4. The temperature dependence of the hyperfine field of the  $^{60}\text{Co}$  diluted in a 72-ppm iron sample shows a characteristic spin-glass behavior. The horizontal lines are the mean values obtained on more dilute samples (Fig. 1); the symbols describe the different field variations of  $H_{\text{hf}}$ .

ed in the thesis of Taurian,<sup>7</sup> NO is mostly sensitive to the second effect. In order to give an order of magnitude, we mention that from 20 to 5 mK for an average misalignment of  $10^\circ$  and an average magnetization reduction of 1.6%,  $H_{\text{eff}}$  is multiplied by a factor 0.8. As has been mentioned before, NO experiments are thus very sensitive to spin-glass behavior.

Figures 1 and 3 show at low fields the presence of magnetic interactions. Different types of coupling between impurities may occur: for example, spin-glass interactions or an increase or decrease of the Kondo temperature. The first type of effect clearly occurs for an alloy with 72-ppm iron as is shown in Fig. 4 by the characteristic decrease of  $H_{\text{hf}}$  with increasing  $T^{-1}$ .

The situation of the  $\text{PdCo}$  alloys is quite different from that of the  $\text{PtCo}$  alloys. In  $\text{PtCo}$ , the Kondo temperature ( $T_K \sim 1$  K) is rather high, so the magnetic interaction between impurities becomes important only when an impurity interacts with another impurity inside the ferromagnetic polarization range. The local symmetry axis coincides always with  $H$  until the concentration is high enough ( $> 3000$  ppm) for the ferromagnetic coupling to dominate when the domain orientation plays a role. For  $\text{PdCo}$  alloys, since the Kondo temperature is lower, the interactions are not restricted to the ferromagnetic range and spin-glass behavior occurs at very low concentrations. Then, when the concentration increases, pre-

dominant ferromagnetic pair interactions appear.

Previous NO experiments on dilute alloys of *PdCo* have been performed by Gallop<sup>8</sup> down to 10 mK. If in low field our results are in rather good agreement with the Gallop's data, we have no interpretation about the difference between the results which are obtained in intermediate fields. Our results are checked on different samples; the hyperfine fields are detected using different types of NO thermometers in a large range of magnetic fields (50–40 000 Oe).

We have interpreted the NO experiments assuming the proportionality between the hyperfine field and the total magnetization of the impurity. This proportionality has been accurately verified in the case of the *PtCo* alloy by a direct experimental comparison.<sup>3</sup> Since the hyperfine field of Co in palladium has an unusual sign, magnetization experiments are actually performed on dilute alloys of *PdCo* in order to test the validity of such a hypothesis and eventually to compare the  $T_K$  value obtained by both methods.

If it is accepted that the positive sign of  $H_{hf}$  is associated with an unquenched local moment,<sup>11</sup> we must explain the origin of such unusual orbital contribution. The simple explanation is to correlate the low value of  $T_K$  with the positive sign. As  $T_K$  is low, the Co impurity inside its atomic cell is not too far from the usual picture found in insulators where the  $Co^{2+}$  ions may carry an orbital moment. The orbital magnitude is then related to the crystal field and to the spin orbit coupling. When the Kondo temperature increases, the ionic description is surely not true for *3d* impurities which have important *3d* phase shifts at the Fermi level; the impurity is better described by the Anderson hamiltonian.<sup>12</sup>

In agreement with this analysis, the variation of the hyperfine coupling for the *MoCo*, *WCo* cases<sup>13</sup> and for the *PtCo*, *PdCo* alloys shows that the orbital contribution is stronger in both pairs of

cases when the  $T_K$  value is lower. For a Co impurity we can recall the striking results that, at the opposite limit of a high Kondo temperature ( $T_K > 100$  K), the orbital Van Vleck Knight shift  $K$  becomes predominant: For example in *AuCo* alloys  $K_{Co} = 30\%$ .<sup>14,15</sup>

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