Journal of Magnetism and Magnetic Materials 110 (1992) 337–342
North-Holland

High field magnetization in $Pr(Ni_{1-x}Co_x)_5$ single crystals

A.R. Ball [a], D. Gignoux [a], F.E. Kayzel [b], D. Schmitt [a] and A. de Visser [b]

[a] *Laboratoire Louis Néel, CNRS, 166X, 38042 Grenoble Cedex, France*
[b] *Van der Waals–Zeeman Laboratorium, Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands*

Received 20 November 1991

Magnetization measurements in fields up to 38 T performed at low temperature on single crystals of the hexagonal $Pr(Ni_{1-x}Co_x)_5$ compounds for $x = 0$, 0.05, 0.10 and 0.20 are presented. In $PrNi_5$ we observe highly original behaviour predicted by the knowledge of the Crystalline Electric Field parameters and arising from the existence of a non-magnetic singlet ground state; namely transitions associated with the field induced "anticrossing" and "crossing" of the two lowest states along the [100] and [120] directions, respectively. The measurements performed on the other compounds have allowed us to study the dependence of this behaviour on Co substitutions.

1. Introduction

The rare-earth intermetallic compounds RNi_5 and RCo_5 (R = rare earth) crystallize in the hexagonal $CaCu_5$-type structure [1]. The Co based compounds are ferromagnets with a high Curie temperature and have been extensively studied because of technological applications. However, in these compounds, both R and Co ions are magnetic and it is therefore difficult to separate their individual contributions to the magnetic properties, particularly the anisotropy due to the rare earth. In contrast, in the Ni based compounds, the 3d shell of Ni is almost full, hence its contribution to magnetism is very small [2]. It is therefore possible to study more precisely the properties of rare earth alone.

Among the RNi_5 series, $PrNi_5$ is a fascinating compound because, although small ferromagnetic exchange interactions between Pr ions are present, it does not order down to a very low temperature because of the existence of a Crystalline Electric Field (CEF) singlet ground state [3]. Moreover, due to the large Van Vleck susceptibility associated with a relatively small separation between this singlet and the next excited states, this compound has been successfully used for cooling through the adiabatic demagnetization process [4].

The CEF parameters were first determined in $PrNi_5$ from susceptibility measurements neglecting the Ni contribution [5] and from inelastic neutron scattering experiments [6]. Since then a large number of other studies have been undertaken on this compound. Thus, thermal expansion measurements [7,8], magnetic and magnetoelastic measurements taking into account the Ni contributions [9] and finally point contact spectroscopy experiments [10] have been successively performed, each experiment leading to a slight adjustement of the CEF parameters, the different sets of which remain very similar (table 1).

Recently, point contact spectroscopy performed in magnetic fields up to 20 T has shown two different kinds of metamagnetic processes occuring at low temperature for a magnetic field applied along the two symmetry directions perpendicular to the *c*-axis namely the [100] and

Correspondence to: Dr. A.R. Ball, Laboratoire Louis Néel, CNRS, P.O. Box 166X, Grenoble Cedex 38042, France.

[120] directions [10]. From the field dependence of the energy position of the first excited CEF levels, an anticrossing of the lowest two levels has been observed along the [120] axis around 15 T, while a crossing was anticipated along the [100] direction for a magnetic field of about 25 T. This was predicted in part by a previous theoretical and experimental investigation of polycrystalline $PrNi_5$ [11]. This led us to undertake a complete study of the high field magnetization processes of a single crystal of $PrNi_5$ at low temperatures and along the main symmetry directions (section 2).

In parallel, we have investigated the effect of substituting Ni by Co in $PrNi_5$ on the Ni-rich side [12]. It turns out that single crystals are very difficult to obtain in the RCo_5 series, making it more delicate to interprete the anisotropic magnetic properties. On the other hand, large single crystals of good quality are available in the RNi_5 series, as well as in compounds where up to 60% of Ni has been replaced by Co [13]. Investigating such single crystals of $Pr(Ni_{1-x}Co_x)_5$ compounds may then lead to a better understanding of the appearance of magnetism on Co and the role of this latter in the magnetic properties of RCo_5 compounds (section 3).

For that purpose, large single crystals with $x = 0$, 0.05, 0.10 and 0.20 were grown from 99.9% pure Pr and 99.999% pure Ni and Co by the Czochralski technique in a cold crucible induction furnace at the Laboratoire Louis Néel at Grenoble. From the ingots two parallelepipeds (three for $x = 0$) of about $2 \times 2 \times 6$ mm^3 of each compounds were spark cut with their long dimension along [100] and [120] (and also along [001] for $x = 0$). Magnetization measurements, at 1.4 and 4.2 K, were performed in fields up to 38 T in the High-Field Installation of the University of Amsterdam. Measurements were carried out by pulse in which the field increases or decreases linearly in time. For a more accurate determination of the magnetization below 21 T, step-wise pulses with field intervals that can be programmed were also employed. Isothermal variations were measured along the [100] and [120] (and also along [001] for $x = 0$) directions of the four compounds, the long dimension being parallel to the applied field.

2. High field magnetic properties of $PrNi_5$

2.1. Theoretical aspects

The magnetic properties of the $PrNi_5$ compound can be understood in the frame of the CEF model. The various sets of parameters found in literature (table 1) all lead to the same relative disposition for the 6 CEF states issued from the $J = 4$ multiplet:

$$D_4 = \Gamma_1 + \Gamma_3 + \Gamma_4 + 2\Gamma_5 + \Gamma_6,$$

where the Γ_i's are irreducible representations of the hexagonal point group D_{6h} under consideration [14]. Among them, the ground state is the Γ_3 singlet, the Γ_1 singlet and the $\Gamma_5^{(1)}$ and Γ_6 doublets lying between 30 and 50 K above. Under the

Table 1
Various sets of parameters for $PrNi_5$ found in the literature; B_l^m are the CEF parameters, n the bilinear exchange coefficient, α and χ_{Ni} the Ni parameters (see ref. [9]); the energies of the lowest CEF levels are also reported

Ref.	7	6	15	9	10
B_2^0 [K]	5.57	5.82	5.68	5.84	5.80
B_4^0 [10^{-2} K]	4.20	4.94	4.43	4.53	5.20
B_6^0 [10^{-4} K]	9.40	8.77	6.51	8.86	8.00
B_6^6 [10^{-2} K]	3.02	3.10	3.61	3.14	3.10
n [kOe/μ_B]	0	28	32	21	35
α			0.06	0.06	0.06
χ_{Ni} [$10^{-4}\mu_B$/kOe]			3.7	3.7	3.7
Γ_6 [K]	39	39.4	49.2	39.8	42.2
$\Gamma_5^{(1)}$ [K]	54	48.2	47.9	48.7	41.6
Γ_1 [K]	17.6	23	38.9	23.1	38.3

application of a magnetic field along the [100] and [120] directions, these lowest CEF levels transform, according to the new symmetry of the system (C_2 point group) as [14]:

$H \| [100]$ $\Gamma_6 \rightarrow \Gamma_1 + \Gamma_2$,
$\Gamma_5 \rightarrow \Gamma_1 + \Gamma_2$,
$\Gamma_1 \rightarrow \Gamma_1$
$\Gamma_3 \rightarrow \Gamma_2$,

$H \| [120]$ $\Gamma_6 \rightarrow \Gamma_1 + \Gamma_2$,
$\Gamma_5 \rightarrow \Gamma_1 + \Gamma_2$,
$\Gamma_1 \rightarrow \Gamma_1$,
$\Gamma_3 \rightarrow \Gamma_1$.

It immediately follows that the first two CEF levels may cross each other in the first case, because they belong to the different representations Γ_1 and Γ_2, and indeed they do cross (see below). In the second case this, however, is impossible because they both belong to the same representation Γ_1, leading to an anticrossing.

This can be easily seen by diagonalizing the full Hamiltonian including the CEF term plus the Zeeman and bilinear exchange coupling. Adding magnetoelastic and quadrupolar terms and taking into account the Ni contribution as in ref. [9] does not fundamentally change the results. The theoretical magnetization curves along the 3 main symmetry directions are shown in fig. 1 for several temperatures. In these calculations, we have used the set of parameters of ref. [9] which gives the best overall agreement with our high field measurements (see below). Using the other sets of parameters leads to similar results, the main

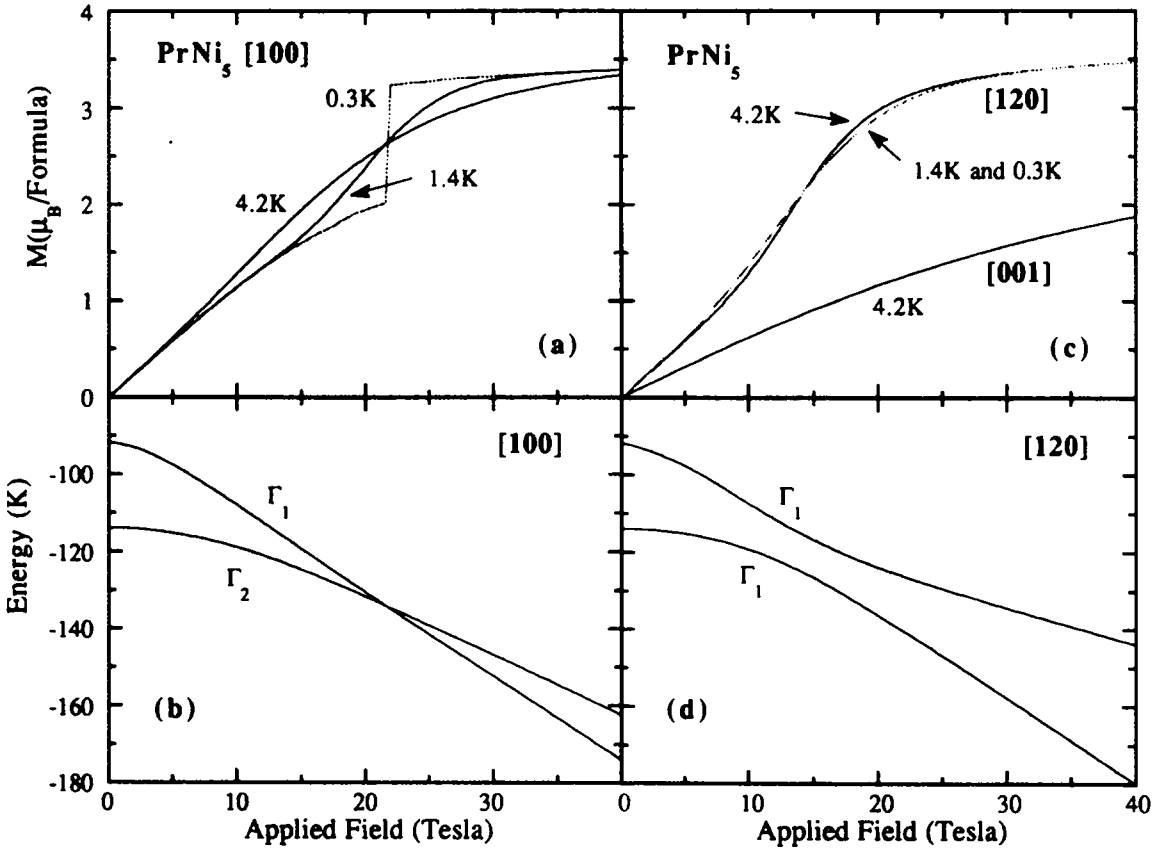

Fig. 1. Calculated variations of M versus H in $PrNi_5$ with parameters of ref. [9] at different temperatures along the [100] (a), [120] and [001] directions (c). The field dependence of the 2 lowest energy levels along [100] (b) and [120] (d) are also reported.

difference being the exact value of the critical field along the [100] direction, this value ranging from 17 to 29 T according to the parameters. It is worth noting that the critical field along the [120] axis is less affected by the different sets of parameters.

Along the [120] direction (fig. 1c), a metamagnetic process is observed at about 12 T, its character remaining smooth even at very low temperature. This is characteristic of an anticrossing (see fig. 1d) because, at the critical field, there is no discontinuity in the CEF ground state but only a quicker modification of its composition in the $|J,M_J\rangle$ basis. On the opposite, along the [100] direction (fig. 1a), another kind of metamagnetic process is observed, this latter becoming sharper and sharper as the temperature is lowered, until a step-like behaviour is reached at 0 K. Note that this transition is strongly temperature dependent and vanishes at 4.2 K. This is now associated with the crossing of the lowest two CEF levels (see fig. 1b), because at 0 K, there is a discontinuity in the nature of the ground state at the critical field. At last, and for sake of completeness, the calculation for a magnetic field along the *c*-axis also is reported (fig. 1c). The variation is roughly linear up to 40 T and noticeably smaller than in the basal plane. This anisotropic feature is a direct consequence of the sign of the second order CEF parameter which favours the basal plane.

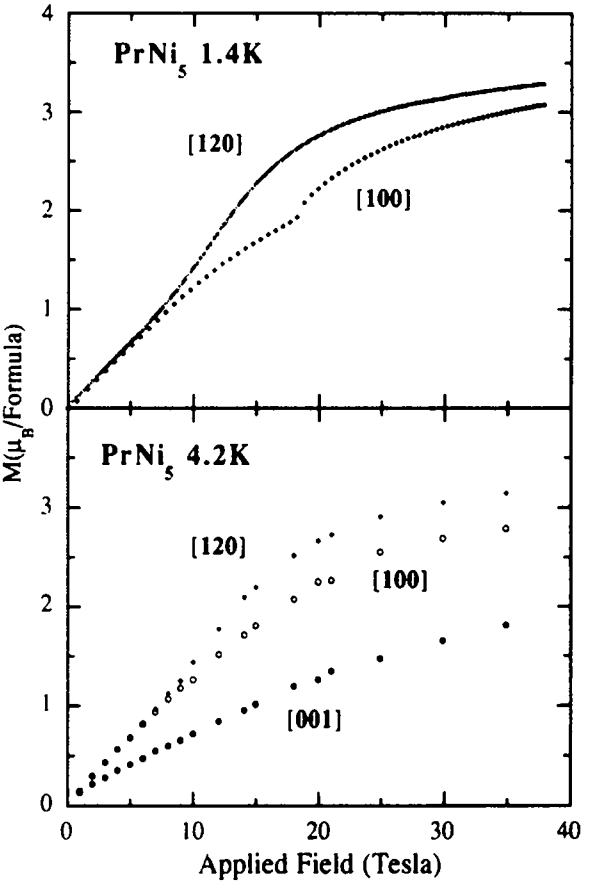

Fig. 2. Experimental variations of M versus H in $PrNi_5$ along the different symmetry directions.

2.2. *Experimental results*

Fig. 2 shows M versus H measured on $PrNi_5$ along the [100] and [120] directions at 1.4 and 4.2 K as well as along the [001] direction at 4.2 K. These variations are quite similar to the theoretical ones shown in fig. 1a regarding to their shape as well as their thermal evolution. Indeed: (i) along [120] isothermal variations are almost the same at 1.4 and 4.2 K, and exhibit the positive curvature associated with the anticrossing; (ii) along [100], at 1.4 K a sharp transition is observed at 18.5 T whereas it has disappeared at 4.2 K; (iii) along [001] the monotoneous variation can be quite well superposed with that of fig. 1. The curves shown in fig. 1 were calculated with the set of parameters which give the best agreement with the observed ones. Note that this set of parameters, which includes quadrupolar interactions, is that which accounts simultaneously for the largest number of experiments. The value of the transition field along [100] is directly related with the energy $E(\Gamma_1)$ of the first excited singlet state in zero applied field. The set of parameters used in fig. 1 leads to a transition field close to the observed one and to $E(\Gamma_1) = 23$ K. Besides, point contact spectroscopy measurements, performed on a different sample from that used in the present study, led to a direct measurement of $E(\Gamma_1)$ of 38 K and accordingly to a transition field of around 31 T. We can then conclude that the CEF parameters, especially B_4^0, are sample dependent. This can explain the scattering of the

set of CEF parameters determined so far. Some experimental features of the magnetization curves are, however, not explained: (i) the calculated amplitude of the transition along [100] at 1.4 K is larger than the observed one; (ii) in high field the calculated magnetizations in the basal plane are larger than the observed ones; and finally (iii) the observed anisotropy of the magnetization at 38 T between [120] and [100] is larger than the calculated one. This shows the limit of the model used which is already rather sophisticated. Other terms unknown up to now must play a non-negligible role in high field.

3. Influence of Co substitution

Fig. 3 shows the magnetizations measured at 1.4 K along the [100] and [120] directions of the samples with $x = 0.05$, 0.10 and 0.20. Besides the onset of ferromagnetism which has been previously reported [12], the main features of the observed behaviours are the following:

(i) The transition along [100], associated with the crossing, disappears as soon as 5% of Ni is substituted by Co.

(ii) The anticrossing along [120] is retained for rather large Co concentrations. This can be seen from the field dependence of the differential susceptibilities shown in fig. 4. The well pronounced maximum around 12 T in $PrNi_5$ is reduced when the Co amount increases and becomes a bump around the same field which is still visible for $x = 0.10$ but has disappeared for $x = 0.20$.

(iii) The high field anisotropy decreases when x increases.

As mentioned above the position of the transition field is much more dependent on the crystal field parameters along [100] than along [120]. Then, in addition to a possible variation of CEF parameters from sample to sample, inhomogeneities due to the substitution can lead to a distribution of the crossing field along [100] which can explain why the transition along this axis is no more visible for $x = 0.05$, whereas the transition along [120] still exists for $x = 0.10$. We can, however, conclude that, at least for this latter

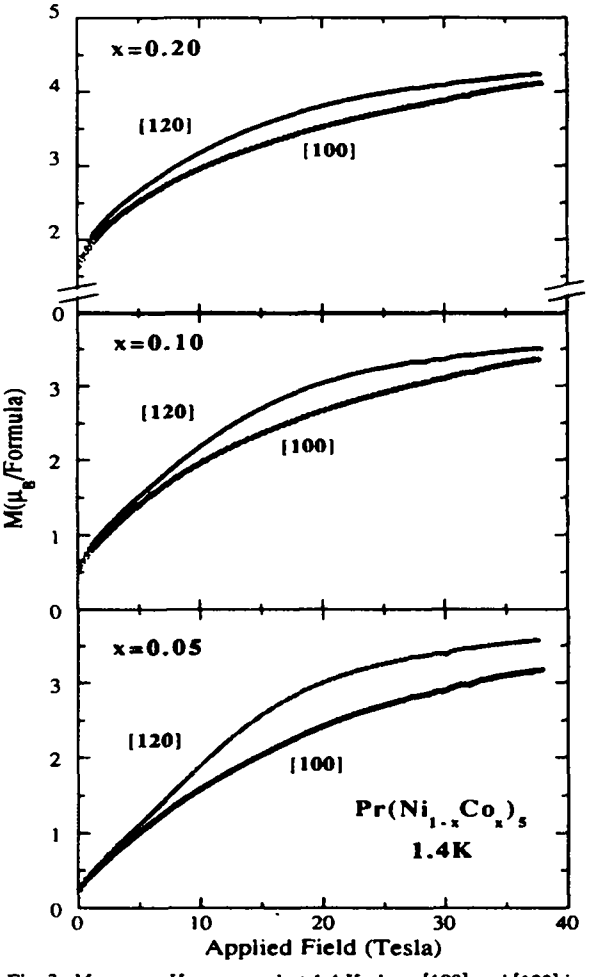

Fig. 3. M versus H measured at 1.4 K along [100] and [120] in the $Pr(Ni_{1-x}Co_x)_5$ compounds with $x = 0.05$, 0.10 and 0.20.

concentration, the Co–Pr interaction is not large enough to induce the high magnetization state of Pr, i.e. the exchange field due to Co on Pr is smaller than the metamagnetic field. The Co–Co interaction, which is responsible for the onset of magnetization in these pseudobinary compounds, is one order of magnitude larger as is generally observed in rare earth 3d transition metal intermetallics [16,17].

4. Conclusion

As a conclusion high field magnetization measurements on a single crystal of $PrNi_5$ give clear

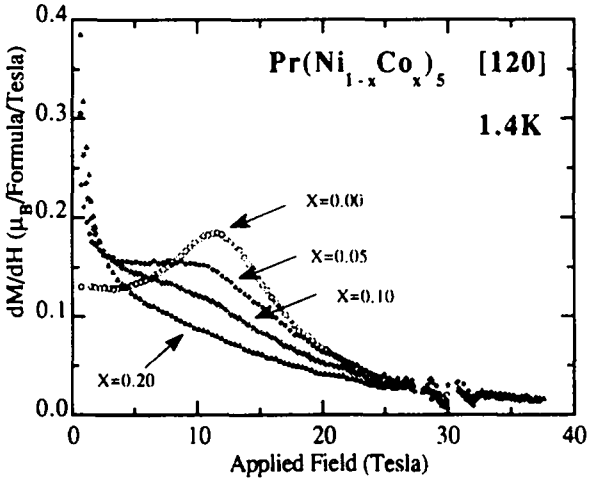

Fig. 4. Field dependence of the differential susceptibilities at 1.4 K along [120] in the $Pr(Ni_{1-x}Co_x)_5$ with $x = 0.05$, 0.10 and 0.20.

evidence of a quite original behaviour which was predicted from the knowledge of the CEF previously determined, i.e. a crossing and an anticrossing of the lowest singlet state when the field is applied along each of the symmetry directions perpendicular to the 6 fold axis of the hexagonal symmetry. As predicted thermal effects are much more sensitive on the transition associated with the crossing than that associated with the anticrossing. Finally, Co substitution at least up to $x = 0.10$ does not drastically modify the Pr behaviour.

Acknowledgements

This work has been partly supported by the European Commission with its Research and Development Programme BIREM-BREU-0068. We thank B. Gorges for his contribution in preparing the single crystals.

References

[1] J.H. Wernick and S. Geller, Acta Crystallogr. 12 (1959) 662.
[2] B. Bleaney, Proc. Phys. Soc. 82 (1963) 469.
[3] R.S. Craig, S.G. Sankar, N. Marzouk, V.U.S. Rao, W.E. Wallace and E. Segal, J. Phys. Chem. Solids 33 (1972) 2267.
[4] K. Andres and S. Darack, Physica 86 (1977) 1071.
[5] K. Andres, S. Darack and H.R. Ott, Phys. Rev. B 19 (1979) 5475.
[6] P.A. Alekseev, A. Andreeff, H. Griessmann, L.P. Kaun, B. Lippold, W. Matz, I.P. Sadikov, O.D. Chistyakov, I.A. Markova and E.M. Savitskii, Phys. Stat. Sol. (b) 97 (1980) 87.
[7] H.R. Ott, K. Andres, E. Bucher and J.P. Maita, Solid State Commun. 18 (1976) 1303.
[8] B. Luthi and H.R. Ott, Solid State Commun. 33 (1980) 717.
[9] V.M.T.S. Barthem, D. Gignoux, A. Nait-Saada, D. Schmitt and G. Creuzet, Phys. Rev. B 37 (1988) 1733.
[10] M. Reiffers, Y.G. Naidyuk, A.G.M. Jansen, P. Wyder, I.K. Yanson, D. Gignoux and D. Schmitt, Phys. Rev. Lett. 62 (1989) 1560.
[11] E. Leyarovski, J. Mrachkov, A. Gilewski and T. Mydlarz, Phys. Rev. B 35 (1987) 8668.
[12] A. Ball, D. Gignoux, B. Gorges, D. Schmitt and A. Tari submitted to J. Magn. Magn. Mater. 109 (1992) 185.
[13] R. Ballou, B. Michellutti and J. Voiron, J. Appl. Phys. 69 (1991) 5705.
[14] G.F. Koster, J.O. Dimmock, R.G. Wheeler and H. Statz, in: Properties of the Thirty-two Point Groups (M.I.T. Press, Cambridge, 1963).
[15] A. Nait-Saada, thesis, University of Grenoble (1980).
[16] D. Bloch and R. Lemaire, Phys. Rev. B 2 (1970) 2648.
[17] K.H.J. Buschow, Rep. Prog. Phys. 40 (1977) 1179.