Magnetic transitions in Pr_2NiO_4 single crystal

X. Obradors and B. Martinez
Institut de Ciència de Materials de Barcelona, CSIC Campus U. Autònoma, 08193 Bellaterra, Spain

X. Batlle
Departament Física Fonamental, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

J. Rodriguez-Carvajal, M. T. Fernandez-Diaz, and J. L. Martinez
Institut Laue Langevin, 156 X, 38042 Grenoble, France

P. Odier
Centre de Recherche sur la Physique des Hautes Temperatures, CNRS, 45071 Orléans, France

The magnetic properties of a stoichiometric Pr_2NiO_4 single crystal have been examined by means of the temperature dependence of the complex ac susceptibility and the isothermal magnetization in fields up to 200 kOe at $T = 4.2$ K. Three separate phases have been identified and their anisotropic character has been analyzed. A collinear antiferromagnetic phase appears first between $T_N = 325$ K and $T_{c1} = 115$ K, where the Pr ions are polarized by an internal magnetic field. At T_{c1} a first modification of the magnetic structure occurs in parallel with a structural phase transition (Bmab to $P4_2/ncm$). This magnetic transition has a first-order character and involves both the out-of-plane and the in-plane spin components (magnetic modes g_x and $g_xc_yf_z$, respectively). A second magnetic transition having also a first-order character is also clearly identified at $T_{c2} = 90$ K which corresponds to a spin reorientation process ($g_xc_yf_z$ to $c_xg_ya_z$ magnetic modes). It should be noted as well that the out-of-phase component of χ_{ac} shows a peak around 30 K which reflects the coexistence of both magnetic configurations in a wide temperature interval. Finally, two field-induced transitions have been observed at 4.2 K when the field is directed along the c axis. We propose that the high-field anomaly arises from a metamagnetic transition of the weak ferromagnetic component, similarly to La_2CuO_4.

In recent work a detailed neutron diffraction study of the structural and magnetic phase transitions in stoichiometric RE_2NiO_4 (La,Pr,Nd) oxides has been reported.[1–3] These works give evidence of a complex interplay between the orthorhombic-tetragonal phase transition occurring around 80–130 K, the weak ferromagnetism associated to the Ni ions and the internal magnetic field appearing in the rare earth ions. A careful analysis of the magnetic properties of these oxides,[4] particularly in single crystals, appears to be necessary in order to gain a full comprehension of the different magnetic phase transitions which are characteristic of these systems.

The magnetic structure of Pr_2NiO_4 polycrystalline samples was examined recently by means of neutron diffraction[3] and it was proposed that a collinear 3D antiferromagnetic ordering is established at $T_N = 325$ K (g_x mode). A weak ferromagnetic component is allowed below $T_{c1} = 115$ K, where a structural phase transition takes place. The averaged crystal structure is tetragonal ($P4_2/ncm$), but locally orthorhombic ($Pccn$).[1,3] The magnetic structure becomes $g_xc_yf_z$ (using the basic functions of $Pccn$). A new spin reorientation ($c_xg_ya_z$) occurs at a lower temperature showing important thermal hysteresis and phase coexistence.

We report here ac susceptibility and isothermal magnetization studies of a Pr_2NiO_4 stoichiometric single crystal for two mutually perpendicular directions which makes it possible to identify and characterize these magnetic transitions and to report a magnetic-field-induced transition akin to that observed in antiferromagnetic La_2CuO_4.

The single crystal used in this work was grown by the floating zone method at the CNRS Laboratory in Orleans. Details concerning the preparation procedure may be found in.[5] The stoichiometric sample was obtained by a reduction process in a mixture of $Ar\text{-}H_2$ at 625 K for 48 h. Single crystals from the same batch have been used in a recent elastic and inelastic neutron scattering experiment[6] which confirm the complete equivalence of this crystal with the polycrystalline samples previously investigated.[3]

The ac susceptibility, $\chi_{ac}(T) = \chi'(T) - i\chi''(T)$, was measured with the ac ripple field oriented parallel to the c axis or perpendicular to it, in any direction within the a-b plane. The magnetic field amplitude and frequency used in the experiment were $H = 5$ Oe and $\nu = 111$ Hz and the measurements were always performed on increasing temperature. The isothermal magnetization curves were measured in fields up to 20 T with an extraction inductive method available in the Service National des Champs Intenses, Grenoble.

The complex ac susceptibility was measured to identify the different phase transitions in Pr_2NiO_4. In Fig. 1 the in-phase component χ' is displayed for both orientations of the magnetic field, parallel to the c axis and perpendicular to it. Three different regimes may be clearly identified. At $T_N = 325$ K a 3D long-range antiferromagnetic ordering of Ni ions was identified by means of neutron diffraction and down to $T_{c1} = 115$ K the magnetic structure remains collinear as in La_2NiO_4 (g_x mode).[1,7] In this temperature range the magnetic susceptibility follows closely a Curie–Weiss law with an effective magnetic moment sightly

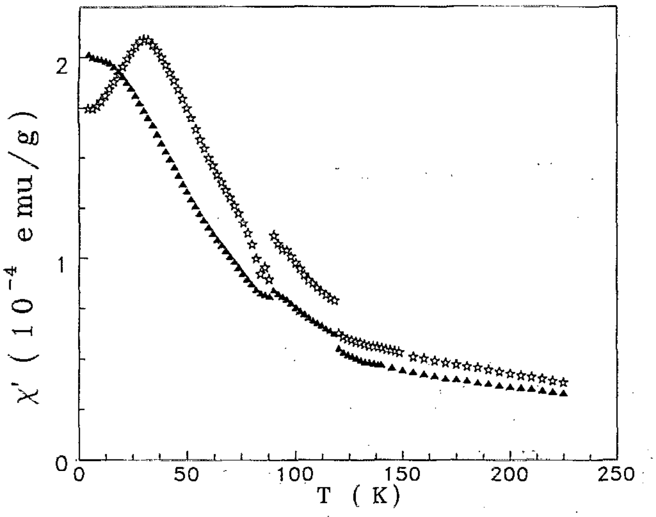

FIG. 1. In-phase component of the complex ac susceptibility of Pr_2NiO_4 single crystal measured with the magnetic field ($H=5$ Oe) parallel to the c axis (Δ) and perpendicular to it ($*$).

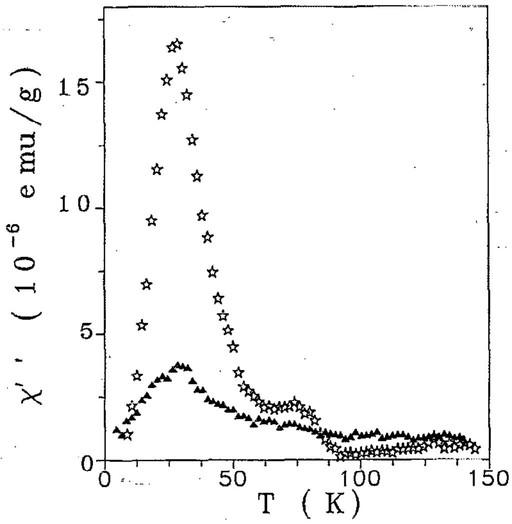

FIG. 2. Out-of-phase component of the complex ac susceptibility measured at $H=5$ Oe parallel (Δ) and perpendicular ($*$) to the c axis.

higher than the theoretical one of Pr^{3+} ions ($\mu_{\text{eff}} = 4.0$ vs $3.58\mu_B$/ion). This enhancement has also been observed previously by other authors[8] in Pr_2NiO_4 and in Nd_2NiO_4.[4] This discrepancy may be easily explained by considering the exchange interaction effects between Ni and Pr ions. The application of an external magnetic field induces a net magnetization in the Ni sublattice and hence the Pr ions sense an internal field in addition to the staggered exchange magnetic field.[9] This results in a modified Curie constant $C^* = C_{\text{Pr}}(1 + H_i/H_a)$, and assuming the validity of the mean-field approximation the Ni-Pr exchange integral is evaluated $J_{\text{Pr-Nd}} = 0.8$ meV. This value is very similar to that observed in Nd_2NiO_4,[4] and definitely higher than that calculated in T' cuprates such as Gd_2CuO_4.[10] The structural phase transition occurring at $T_{c1} = 115$ K is detected very clearly in both $\chi'(T)$ curves (Fig. 1). This structural phase transition involves a modification of the crystal symmetry (Bmab to $P4_2/ncm$) associated with a change of the octahedron tilting axis (see Refs. 1–3 for a detailed description). The magnetic mode associated with the new low-temperature phase is Γ_{3g} with basis functions $g_xc_yf_z$,[3] thus allowing an in-plane spin reorientation and the formation of a ferromagnetic component along the c axis. The discontinuity observed in $\chi'(T)$ clearly points to a first-order character of the transition and the existence of anomalies in both directions suggest that a spin reorientation exist towards the c axis and within the a-b plane. These reorientations are probably small and may not be detected by means of neutron diffraction.

A second first-order spin reorientation transition is also clearly detected in the $\chi'(T)$ curves (Fig. 1) at $T_{c2} = 90$ K. This second transition matches that observed in neutron diffraction patterns and low-field magnetization measurements.[3] A strong thermal hysteresis is associated with this transition and hence the observation of the susceptibility discontinuity precisely at this temperature is probably fortuitous. This transition was identified as a spin reorientation with new low-temperature basis functions [$c_xg_ya_z$ (Ref. 3)] which implies an in-plane spin reorientation and the development of an antiferromagnetic stacking of the c-axis weak ferromagnetic component. Again, the observation of the χ'_{ac} discontinuity in both directions points to a reorientational process involving all the spin components.

These spin reorientation processes may be further characterized by looking at the out-of-phase component of the complex susceptibility (Fig. 2). As it may be clearly seen in the figure, a strong dissipation exists in both orientations when the second transition occurs at $T_{c2} \cong 90$ K. Above this temperature, where the weak ferromagnetic component exists, the dissipation is only sightly different from zero, thus implying a small canting of the magnetic moments.

From the neutron diffraction investigation[3] it was concluded that the low-temperature spin reorientation transition was sluggish, with a wide temperature interval where both magnetic modes coexist. Our ac susceptibility measurements should reflect this character of the transition. This is probably the origin of the dissipative terms displayed in Fig. 2. The fact that the peak is more prominent for the in-plane configuration means that the reorientation process is more important in this direction, as we should expect for a nearly 90° rotation of the in-plane spin components ($g_xc_yf_z$ to $c_xg_ya_z$ magnetic modes transition). When going down in temperature, the reorientation process is finally completed and so $\chi''(T)$ goes to zero.

The low-temperature appearance of χ' is, in some sense, anomalous. The saturation of the susceptibility in the c-axis parallel configuration is consistent with a singlet ground state for the Pr^{3+} ions, but the perpendicular orientation curve shows a prominent peak at $T \cong 30$ K, very near to the maxima observed in the $\chi''(T)$ curves. It is not very clear what the origin of this anomaly is but the coincidence of both maxima suggests that the anomaly could

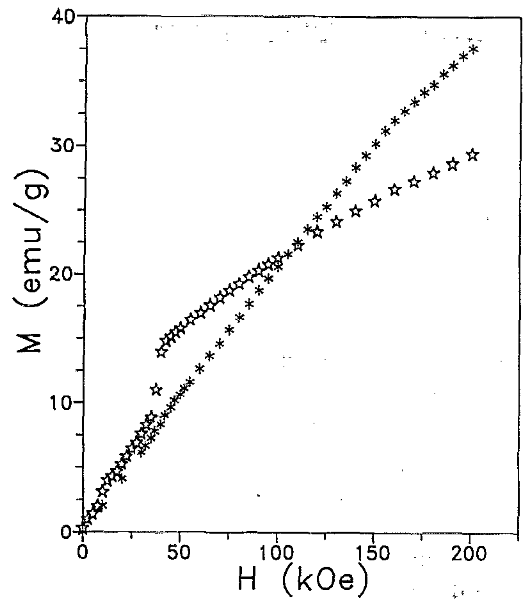

FIG. 3. Isothermal magnetization curves measured in decreasing magnetic field with H parallel (⋆) and perpendicular (*) to the c axis.

mostly reflect the progress in the reorientation process, rather than an intrinsic effect of the magnetic susceptibility of the Pr ions. This is, however, an open question.

We have finally undertaken an investigation of the magnetic properties under magnetic fields. We report here some preliminary results of this investigation. In Fig. 3 we show the isothermal magnetization curves at $T = 4.2$ K in fields up to 200 kOe, for both magnetic field orientations. As it becomes immediately apparent two field-induced transitions occur in the c-axis configuration, while in the other direction only a slight curvature is observed above $H \simeq 150$ kOe.

The field-induced transitions occur, at this temperature, at $H_{c1} = 9$ kOe and $H_{c2} = 39$ kOe, the total field-induced magnetization corresponds to $M_0 = 1.1\mu_B$/f.u. and the magnetization discontinuity occurring at H_{c1} amounts $\Delta M \simeq 0.13\mu_B$/f.u. It should also be noted that while the differential susceptibility has hardly changed at H_{c1}, it shows a strong decrease above H_{c2}, and actually only around 11 T the magnetization reaches saturation.

From the present available data it seems difficult to get a full account of all this complex behavior, but it seems possible to propose a reasonable model for the transition occurring at H_{c2}. From the neutron diffraction data[2,3] and previous magnetization investigation[4] we know that the Ni ions and the rare earths have an antiferromagnetic ordering and in Pr_2NiO_4 the magnetic moments and their orientation with respect to the c axis, at $T = 1.5$ K, amount to: $\mu(Ni^{2+}) = 1.57(6)\mu_B$, $\vartheta = 71°$ and $\mu(Pr^{3+}) = 1.28(5)\mu_B$, $\vartheta = 42°$. The magnetization discontinuity corresponding to a metamagnetic-like transition of the out-of-plane spin components matches very well the observed value $M_0 = 1.1\mu_B$/f.u. We suggest then that this transition follows closely that observed in La_2CuO_4,[11] i.e., the resultant magnetization is forced to become parallel with the external magnetic field above H_{c2} (Pr magnetic moments parallel and Ni moments antiparallel). It is out of our scope, in the present stage, to account for the field-induced transition observed at H_{c1}. We can only note that in the c-axis parallel configuration after the decrease of the magnetization a small remanence is observed ($M_r = 0.5$ emu/g $= 0.04\mu_B$/f.u.) while in the perpendicular orientation no remanence at all is observed. This may be indicative of some magnetic defects in the antiferromagnetic stacking of the weak ferromagnetic out-of-plane component. We might consider the possibility that the low-field transition is associated to some of these defects (for instance stacking faults in the antiferromagnetic ordering).

In summary, this work gives full support to the conclusions reported from a previous neutron diffraction investigation, concerning the structural and magnetic transitions in Pr_2NiO_4. The strong anisotropy of the magnetic susceptibility is more a reflection of the spin reorientation processes than an intrinsic crystal-field effect of the Pr^{3+} ions. Two field-induced transitions have been found and one of them has been interpreted as a metamagnetic-like transition of the weak ferromagnetic component, similarly to La_2CuO_4.

This work has been partially supported by the Dirección General de Investigación Científica y Técnica (PB89-71), the Spanish Comisión Interministerial de Ciencia y Tecnología (MAT89-425), the MIDAS program and the EECCODEST (Sc1-0036-F). We are very grateful to the Service National des Champs Intenses, CNRS-MPI, Grenoble for allowing us to use their experimental facilities.

[1] J. Rodriguez-Carvajal, J. L. Martinez, J. Pannetier, and R. Saez-Puche, Phys. Rev. B 38, 7148 (1988); J. Rodriguez-Carvajal, M. T. Fernandez-Diaz, and J. L. Martinez, J. Phys. Condens. Matter 3 (in press).
[2] M. T. Fernandez-Diaz, J. Rodriguez-Carvajal, J. L. Martinez, F. Fernandez, and R. Saez-Puche, Europhys. Lett. 11, 261 (1990).
[3] M. T. Fernandez-Diaz, J. Rogriguez, J. L. Martinez, G. Fillion, F. Fernandez, and R. Saez-Puche, Z. Phys. B. Condens. Matter. 82, 275 (1991); D. J. Buttrey, J. D. Sullivan, G. Shirane, and K. Yamada, Phys. Rev. B 42, 3944 (1990).
[4] X. Obradors, X. Batlle, J. Rodriguez, J. L. Martinez, M. Vallet, J. Gonzalez-Calbet, and J. Alonso, Phys. Rev. B 43, 10451 (1991); X. Batlle, X. Obradors, M. J. Sayagues, M. Vallet, and J. Gonzalez-Calbet (unpublished).
[5] K. Dembinski, J. M. Bassat, J. P. Coutures, and P. Odier, J. Mater. Sci. Lett. 6, 1365 (1987).
[6] J. L. Martinez, M. T. Fernandez-Diaz, J. Rodriguez, and P. Odier, Phys. Rev. B. (in press).
[7] G. Aeppli and D. J. Buttrey, Phys. Rev. Lett. 61, 203 (1988); G. H. Lander, P. J. Brown, J. M. Honig, and J. Spalek, Phys. Rev. B 40, 4463 (1989).
[8] R. Seaz-Puchez, F. Fernandez, J. Rogriguez, and J. L. Martinez, Solid State Commun. 72, 273 (1989).
[9] M. Matsuda, K. Yameda, K. Kakurai, H. Kadowaki, T. R. Thurston, Y. Endoh, Y. Hidoka, R. J. Birgeneau, R. A. Kastner, P. M. Gehring, A. H. Moudden, and G. Shirane, Phys. Rev. B 42, 10098 (1990).
[10] M. Tovar, X. Obradors, F. Perez, S. B. Oseroff, R. J. Duro, J. Rivas, D. Chateigner, D. Bordet, and J. Chenavas (to be published).
[11] T. Thio, T. R. Thurston, N. W. Preyer, P. J. Preone, M. A. Kstuer, H. P. Jenssen, D. R. Gabbe, C. Y. Chen, R. J. Birgeneau, and A. Aharony, Phys. Rev. B 38, 905 (1988).