

## Calorimetric study of the structural and magnetic ordering in $R_2NiO_4$ ( $R = La, Pr$ and $Nd$ )

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**Abstract** - The structural and magnetic transitions of the series of rare-earth oxides  $R_2NiO_4$  ( $R = La, Pr$  and  $Nd$ ) have been studied in connexion with heat-capacity results. First-order structural transitions from the low-temperature tetragonal  $P4_2/nm$  phase to the higher temperature orthorhombic  $Bmab$  phase have been detected at 56, 121.2 and 138 K for the La, Pr and Nd compounds, respectively. All show thermal hysteresis and long thermal equilibration times. The three-dimensional magnetic ordering of the  $Ni^{2+}$  ions produces a small peak in the heat capacity at around 325 K for the three compounds, indicating the existence of a stronger two-dimensional interaction. No sign of three-dimensional ordering of the  $R^{3+}$  ions has been found. The lattice heat capacity has been estimated from the phonon dispersion relations of  $La_2NiO_4$ , and the low-temperature excess heat capacity has been interpreted as Schottky anomalies coming from the electronic energy levels of  $Pr^{3+}$  and  $Nd^{3+}$ . For  $Pr^{3+}$ , the two lowest energy states have equal degeneracy and are separated by an energy of 50 K. The results for  $Nd^{3+}$  have been correlated with inelastic neutron scattering data. A broad shoulder below 10 K for  $Nd_2NiO_4$  has been ascribed to an additional splitting of 17 K in the lowest crystal-field doublet due to the interaction with the internal magnetic field.

### INTRODUCTION

The study of Ni oxides of that type  $R_2NiO_4$  ( $R = La, Pr$  and  $Nd$ ) presents a great variety of structural and magnetic phenomena. That have attracted considerable attention in the last five years on account of their rich phenomenology and the relation between their structural, magnetic and transport properties. Their structural and magnetic connexion to the first family of high-temperature superconductors makes them suitable as model cases related to superconductivity.

Structurally they are layered perovskites with single layers of corner-sharing  $NiO_6$  octahedra. The ideal high-temperature tetragonal structure distorts through tilts of these octahedra at temperatures that depend on the size of the interspace rare-earth atoms. So, the compounds follow similar structural transitions at different temperatures.

Both the  $Ni^{2+}$  and  $R^{3+}$  ions can have magnetic moments that contribute to the magnetic properties. The  $Ni^{2+}$  ions form a planar lattice with strong covalent Ni-O bonds that transmit the superexchange interaction. The  $R^{3+}$  ions are kept at a long distance in this structure and can interact to each other with a weaker energy, being also influenced by the magnetic moments of the  $Ni^{2+}$  sublattice.

When the samples are doped with an excess of oxygen, new magnetic phases and a semiconducting behavior appear. No metal-insulator transitions are found as in the  $R_2CuO_4$  family. The insulating stoichiometric compounds have been studied in great detail with structural (1-4), magnetic (5-6) and spectroscopic (7-8) techniques. Nevertheless, some uncertain ordering transitions have been reported for the rare-earth ions (6).

Calorimetric measurements are very useful in determining the type and character of the ordering phenomena and the transition temperatures, and can also give important information about the low-energy electronic states.

This paper reports heat-capacity measurements of  $\text{La}_2\text{NiO}_4$ ,  $\text{Pr}_2\text{NiO}_4$  and  $\text{Nd}_2\text{NiO}_4$ . The calorimetric results are then analyzed to clarify the nature of the structural transitions, the magnetic ordering of the  $\text{Ni}^{2+}$  sublattices and the electronic energy levels of the rare-earth ions, together with the consequences with regard to the possible cooperative ordering of their magnetic moments.

### EXPERIMENTAL AND HEAT-CAPACITY RESULTS

Samples with an excess of oxygen content were prepared first by solid-state reaction from the rare-earth oxides  $\text{R}_2\text{O}_3$  ( $\text{R} = \text{La}, \text{Pr}$  and  $\text{Nd}$ ) and  $\text{NiO}$  at  $1350^\circ\text{C}$ . The samples were reground several times to secure a homogeneous product. The black samples obtained were reduced with a hydrogen flow for 12 hours at  $210^\circ\text{C}$  to obtain the stoichiometric brown final compounds. The absence of the original products or the intermediate black phase was checked by X-ray powder analysis.

Adiabatic and ac heat capacity were measured on the three samples between 2 and 350 K and reported in (9-10). The molar values have been obtained after subtracting the sample vessel contribution measured on a separate run. Fig. 1 represents the experimental heat-capacity points for the three compounds. The lattice contribution has been deduced from the measured phonon dispersion relations on  $\text{La}_2\text{NiO}_4$  that permit an evaluation of the density of states (11) and, consequently, of their heat-capacity contribution by using the harmonic oscillator model. It has been plotted together with the experimental data.

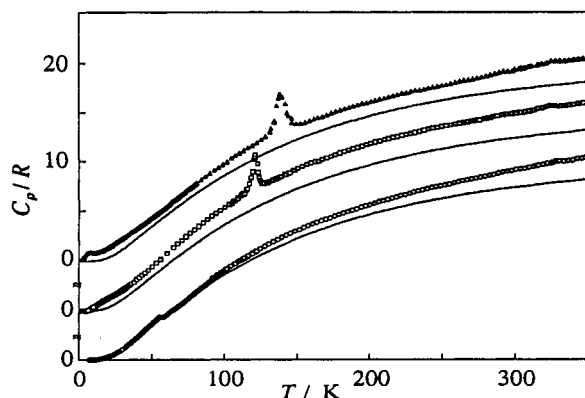


Fig. 1. Molar heat-capacity of:  $\circ$   $\text{La}_2\text{NiO}_4$ ,  $\square$   $\text{Pr}_2\text{NiO}_4$ ,  $\triangle$   $\text{Nd}_2\text{NiO}_4$ . Continuous lines represent the lattice contribution calculated from the density of states of  $\text{La}_2\text{NiO}_4$  (11). Note the vertical shift for each curve.

Very long equilibration times have been found at low temperatures that made adiabatic calorimetry impracticable. Ac calorimetry was used instead in some ranges. The consistency of the results obtained with both techniques was checked through smooth regions and rounded anomalies. Only the peak of  $\text{La}_2\text{NiO}_4$  at 56 K could be lower than the real one due to the absence of first-order contributions on the ac detection. The magnetic and structural transition temperatures,  $T_N$  and  $T_c$ , together with the anomalous heat-capacity maximum and entropy of the magnetic transition,  $\Delta C_m$  and  $\Delta S_m$ , are given in Table 1.

TABLE 1. Experimental thermodynamic parameters and tilt angle of the  $\text{Ni}^{2+}$  magnetic moments from the  $ab$  plane.

Compound	$T_N/K$	$\Delta C_m/R$	$\Delta S_m/R$	$T_c/K$	$\theta/^\circ(6)^*$
$\text{La}_2\text{NiO}_4$	328	0.13	$0.4 \times 10^{-3}$	56	0.14
$\text{Pr}_2\text{NiO}_4$	324	0.20	$0.6 \times 10^{-3}$	121.2	19.3
$\text{Nd}_2\text{NiO}_4$	325	0.17	$0.5 \times 10^{-3}$	138	14.6

\*  $1^\circ = (\pi/180)$  rad

## STRUCTURAL TRANSITIONS

The rare-earth nickelates  $R_2NiO_4$ , with  $R = La, Pr$  and  $Nd$ , have crystallographically the  $K_2NiF_4$ -type structure. The high-temperature archetype stable phase is the tetragonal  $I4/mmm$  shown in Fig. 2. It consists of square-planar layers formed by linked  $NiO_6$  octahedra arranged together with the rare-earth atoms in a layered perovskite structure.

The stability of this structure is determined by the dynamics of these almost rigid octahedra. Structural phase transitions are driven by lattice instabilities that mainly depend on the ionic radii. The structure distorts through tilts of the  $NiO_6$  octahedra and some bond contractions. On lowering the temperature, there is a tilt of the octahedra around the  $[110]$  axis through a second-order phase transition to the orthorhombic  $Bmab$  phase. This transition occurs at 700 K for  $La_2NiO_4$  (2), the tilt angle being  $5.8^\circ$  at 120 K (1), and would be reached at 1500 K for  $Pr_2NiO_4$  and 1900 K for  $Nd_2NiO_4$ , calculated by extrapolation of the orthorhombic strains.

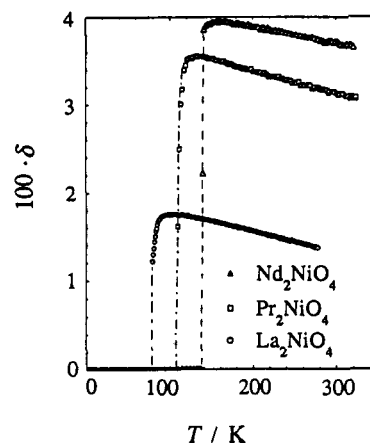
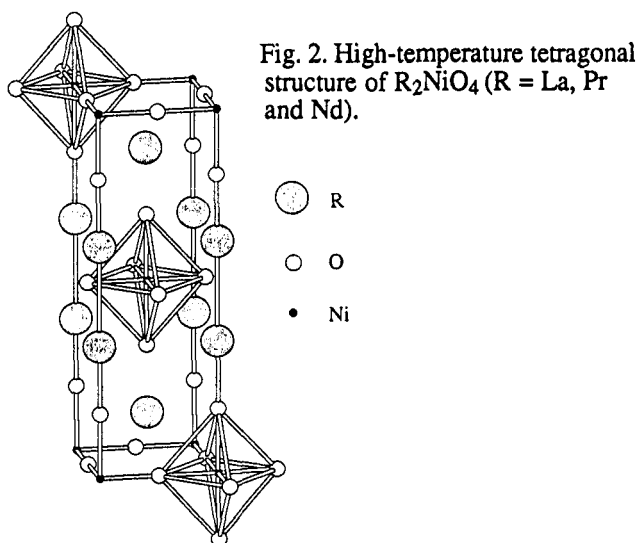


Fig. 3. Orthorhombic distortion in the  $Bmab$  phase and first-order transition to  $P4_2/nm$ .

At lower temperatures, a new tilt around the original tetragonal  $[100]$  axis for  $z=0$  and around  $[010]$  for  $z=1/2$  produces a first-order transition to the low-temperature tetragonal  $P4_2/nm$  structure. This tilt is  $6^\circ$  for  $La_2NiO_4$  (1). The first-order character is required for this transition due to the absence of a group-subgroup relationship between the  $Bmab$  and  $P4_2/nm$  structures. The orthorhombic distortion,  $\delta = 2(b-a)/(b+a)$ , is represented in Fig. 3 for these compounds. The transition is sharp, as expected for the first-order nature. Recent more detailed X-ray diffraction studies (2) have found a second orthorhombic  $Pccn$  phase for  $La_2NiO_4$  at low temperatures instead of the low-temperature tetragonal  $P4_2/nm$ . The transition is found to be first-order in spite of  $Pccn$  being a subgroup of  $Bmab$ . A coexistence temperature region has been found for both structures.

Sharp peaks appeared in the calorimetric measurements corresponding to these first-order structural transitions at 121.2 and 138 K for  $Pr_2NiO_4$  and  $Nd_2NiO_4$ , respectively. The smoother peak of  $La_2NiO_4$  at 56 K corresponds to ac calorimetric measurements that cannot measure the first-order component of the peaks. Similar rounded peaks were also obtained for the other two compounds with the ac technique. Strong hysteresis has been found in all the three samples, with disappearance of the peaks on ac cooling measurements.

## MAGNETIC ORDERING OF THE $Ni^{2+}$ SUBLATTICE

These compounds are paramagnetic above 330 K. The magnetic moment of the Ni ions has been found to be close to the saturation value for  $Ni^{2+}$ . They interact antiferromagnetically through the basal oxygen ions with a magnetic exchange constant  $J \approx -170$  K. A much weaker interplane exchange produces three-dimensional ordering at around 325 K with small differences in temperatures for the three compounds. The rare-earth ions do not affect these transitions and behave paramagnetically in this crystallographic phase.

The heat-capacity measurements show tiny peaks at 328, 324 and 325 K for  $\text{La}_2\text{NiO}_4$ ,  $\text{Pr}_2\text{NiO}_4$  and  $\text{Nd}_2\text{NiO}_4$  respectively, corresponding to the long-range ordering temperatures of the  $\text{Ni}^{2+}$  ions. The small anomalies give only a residual entropy gain because most of the total entropy associated with magnetic spins has been acquired already with lower-dimensional interactions, two-dimensional in these cases.

The theoretical magnetic entropy for  $\text{Ni}^{2+}$  is  $\Delta S = 1.1 R$  and the heat-capacity jump for a purely three-dimensional ordering would be  $\Delta C_m = 2 R$  in a molecular-field approximation. Nevertheless, for a two-dimensional system, previous calculations (10) give  $\Delta C_m = 0.16 R$  at the three-dimensional ordering temperature, which compares well with the experimental values in Table 1.

The magnetic structures have been determined with elastic neutron scattering (1,3,4,12). The  $\text{Ni}^{2+}$  magnetic moments order antiferromagnetically at around 325 K for all three compounds with the spins parallel to the [110] axis (Fig. 4a).

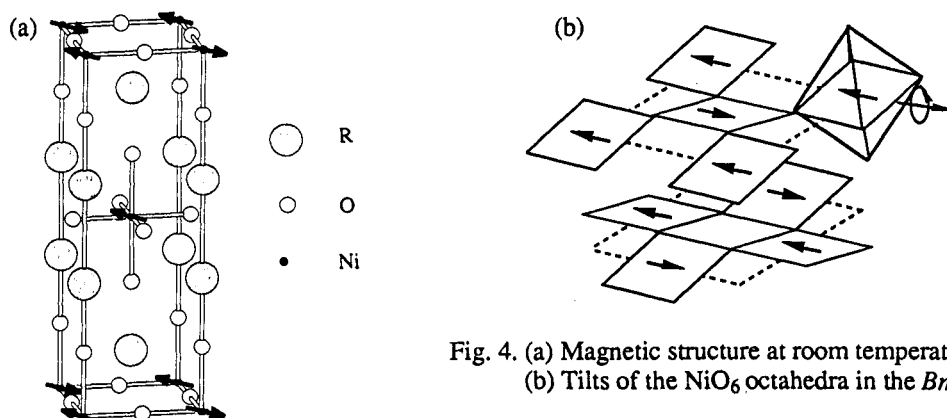


Fig. 4. (a) Magnetic structure at room temperature. (b) Tilts of the  $\text{NiO}_6$  octahedra in the  $Bmab$  phase.

The structural transition to the orthorhombic phase produces a tilt of the  $\text{NiO}_6$  octahedra around an axis parallel to the spins that does not affect their orientation and maintains the same type of magnetic ordering, as shown in Fig. 4b. Contrary to that, the magnetic moments in  $\text{La}_2\text{CuO}_4$  are in the [110] direction (13), perpendicular to the structural tilt axis, which induces spin canting in the  $c$  axis.

The transition to the low-temperature tetragonal structure allows the existence of canting in the  $\text{Ni}^{2+}$  moments, producing weak ferromagnetism. The canting angle has been reported to increase on lowering the temperature, being very small for  $\text{La}_2\text{NiO}_4$  (6). The values at 1.5 K are given in Table 1. A reorientation of the magnetic moments of  $\text{Ni}^{2+}$  has been reported for  $\text{Pr}_2\text{NiO}_4$  which change their direction below 117 K, reaching a non-collinear structure at 1.5 K (5).

Our magnetic susceptibility measurements for  $\text{Pr}_2\text{NiO}_4$  (Fig. 5) show a very small change in the in-phase signal at 120 K, coinciding with the structural transition. Below 90 K, different signals appear on warming and cooling, with a simultaneous out-of-phase component indicating the existence of hysteresis.

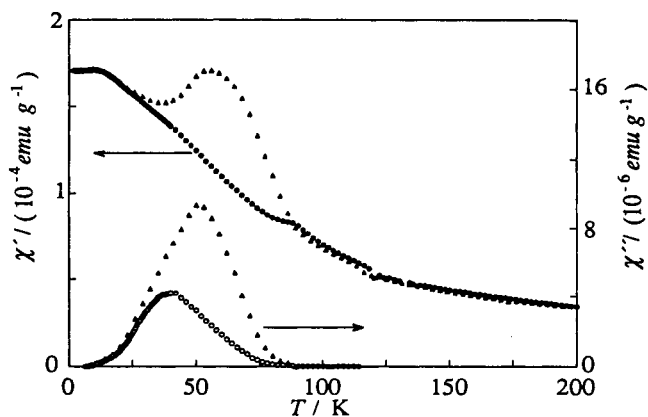


Fig. 5. Ac magnetic susceptibility of  $\text{Pr}_2\text{NiO}_4$  measured at 20 Hz: ●, ○ heating measurements; ▲, △ cooling measurements.

## ENERGY LEVELS OF THE MAGNETIC RARE EARTHS

Rare-earth ions can also contribute to the magnetic properties of the compounds. The ground-state multiplet of unfilled 4f shells splits due to the influence of electrostatic and magnetic fields.

In the low-temperature tetragonal phase, the  $R^{3+}$  ions are on a site of  $D_{4h}$  symmetry. Consequently, the ground-multiplet of  $\text{Pr}^{3+}$  splits into five singlets and two doublets due to the electric field created by the crystal, and the ground-multiplet of  $\text{Nd}^{3+}$  splits into five doublets. The energies of the resulting levels are in the thermal range, and substantial heat-capacity contributions can be expected due to their thermal population. The energy splitting of the ground-multiplet can be measured by inelastic neutron scattering.

The application of a magnetic field produces a further shift of some levels and a splitting of the doublets. In addition to external fields, an effective magnetic field can be induced on the  $R^{3+}$  sites by the ordered  $\text{Ni}^{2+}$  magnetic moments. The effective field acting on the  $\text{Nd}^{3+}$  sites has been estimated to be  $H = 5.2$  T on  $\text{Nd}_2\text{NiO}_4$  at 4.2 K (6).

For  $\text{Pr}^{3+}$ , a shoulder on the heat-capacity curve appears at around 20 K as shown in Fig. 6 after subtraction of the lattice heat capacity. A preliminary inelastic neutron scattering experiment (14) has shown a crystal-field transition at 4.4 meV with additional levels at higher energies. This level splitting would account for the experimental shoulder. Additional higher energy levels would contribute to the anomalous heat capacity at higher temperatures. The height of the anomaly indicates that the ground and first-excited levels have the same degeneracy. Moreover, the shape of the low-temperature magnetic susceptibility (Fig. 5) and the absence of any heat-capacity peak down to 2 K are consistent with a singlet ground-state for  $\text{Pr}^{3+}$ .

Measurements on  $\text{Nd}_2\text{NiO}_4$  showed excited levels at 8, 23, 38 and 49 meV (7) with an energy resolution of 1 meV. A large broadening of the absorption lines was observed and attributed to doubling of the lines due to the additional interaction of the internal magnetic field. The Schottky anomaly calculated with excited doublets at the energies given by the neutron scattering experiment is illustrated in Fig. 7. The experimental heat-capacity points have been drawn after subtracting the lattice contribution as estimated above. They show two bumps with maxima at 8 and 27 K, and differ from the Schottky calculation.

In view of the additional Zeeman splitting of the  $\text{Nd}^{3+}$  energy doublets induced by the internal magnetic field, our heat-capacity results predict  $\Delta = 17$  K for the energy splitting of the ground-doublet. The previously reported levels, together with this splitting and minor adjustments of  $\pm 1$  meV in the next two levels lead to excellent agreement with the experimental data as shown by the dashed line in Fig. 7. The doubling of the excited doublets would not appreciably affect the shape of the curve.

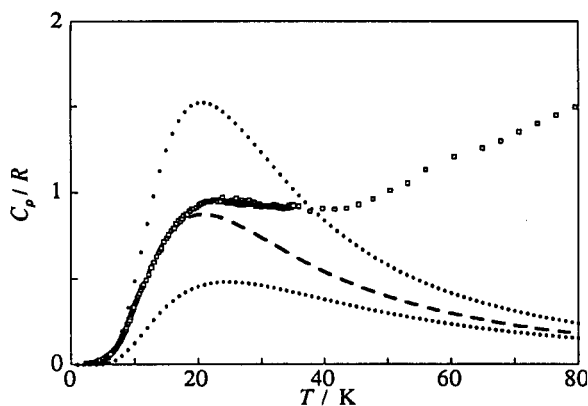


Fig. 6. Anomalous heat capacity of  $\text{Pr}_2\text{NiO}_4$ . The dashed line represents a Schottky anomaly for two levels with equal degeneracy and separated by  $\Delta = 50$  K. Combinations of one doublet and one singlet would give the dotted lines.

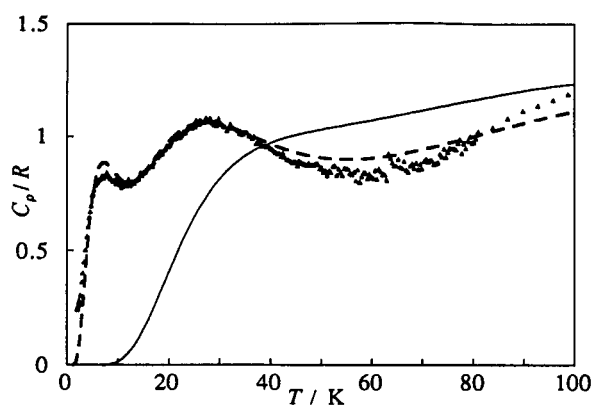


Fig. 7. Anomalous heat capacity of  $\text{Nd}_2\text{NiO}_4$ . The full curve represents the Schottky anomaly from the inelastic neutron scattering levels (7). The dashed curve includes a splitting of the ground-doublet,  $\Delta = 17$  K.

## CONCLUSIONS

The variety of structural and magnetic phenomena of the  $R_2NiO_4$  series of compounds have been studied with calorimetric techniques. The structural transitions between the orthorhombic  $Bmab$  and the low-temperature tetragonal  $P4_2/nm$  structure have been detected at 56, 121.2 and 138 K for the La, Pr and Nd compounds, respectively. A first-order character has been determined for this transition in the three compounds, and the coexistence of phases manifests with pronounced hysteresis and long thermal equilibration times.

There is a close magneto-structural correlation in which the type of structural distortion affects the spin orientation. The lattice promotes short-range magnetic interactions, and the long-range order of the  $Ni^{2+}$  sublattice is detected with small peaks at the ordering temperatures of 328, 324 and 325 K for the La, Pr and Nd compounds, respectively.

The crystalline-electric-field splits the ground-multiplet of the rare-earth ions at energies comparable to the thermal energies producing Schottky anomalies. An additional splitting has been detected due to the internal magnetic field induced by the ordered  $Ni^{2+}$  magnetic moments. The symmetry of the low-temperature structure allows the existence of a weak ferromagnetic component that influences the magnetic state of the rare-earth ions.

The lowest excited level of  $Pr^{3+}$  has been found to be 50 K. It has the same degeneracy than the ground-state. No further splitting is shown down to 2 K, suggesting a singlet ground-state. The magnetic splitting of the ground-doublet of  $Nd^{3+}$ , evaluated as 17 K, precludes its magnetic ordering. When considered in association with the higher levels reported for this compound, it gives a good account of the low-temperature anomalous heat capacity. There is no sign of any ordering transition for the magnetic rare-earth ions in the temperatures examined in the present experiment.

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