

Influence of Nonstoichiometry on the Magnetic Properties of Pr_2NiO_4 and Nd_2NiO_4 *

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Received February 19, 1987

Magnetic susceptibility measurements are reported on single-crystal specimens of $\text{Pr}_2\text{NiO}_{4+\delta}$ and $\text{Nd}_2\text{NiO}_{4+\delta}$ as a function of oxygen nonstoichiometry, δ . Although only minor deviations from the Curie-Weiss law are observed for severely nonstoichiometric samples, both $\text{Pr}_2\text{NiO}_{4+\delta}$ and $\text{Nd}_2\text{NiO}_{4+\delta}$ exhibit evidence of long-range magnetic order as δ becomes small. $\text{Nd}_2\text{NiO}_{4+\delta}$ decomposes to form Nd_2O_3 and NiO under sufficiently reducing conditions. © 1988 Academic Press, Inc.

Introduction

Since the first report of the effect of oxygen nonstoichiometry on the structure and physical properties of La_2NiO_4 (1), considerable effort has been devoted to the study of stoichiometry-dependent properties (2-6). In spite of this growth of interest in La_2NiO_4 , no comparable studies have been reported for the analogous phases Pr_2NiO_4 and Nd_2NiO_4 .

The lanthanide nickelates all exhibit layered structures closely related to the tetragonal K_2NiF_4 structure. Geometric constraints relating the Ln -O and Ni-O bond distances relating parallel to the layers result in stretching of the Ln -O distance and compression of the Ni-O distance relative to values encountered in the parent oxides; this feature results in a canting of the NiO_6 octahedra. Structural distortions, present in all lanthanide nickelates below ~ 700 K,

are likely to influence transport and magnetic properties of these phases. Whereas the distortion in $\text{La}_2\text{NiO}_{4+\delta}$ results in a structure of orthorhombic symmetry, based on a $\sqrt{2} \times \sqrt{2} \times 1$ supercell (2, 4, 6, 7), the distorted K_2NiF_4 -type structures of $\text{Pr}_2\text{NiO}_{4+\delta}$ and $\text{Nd}_2\text{NiO}_{4+\delta}$ are of lower symmetry (2, 8, 9). In addition, the magnitude of these distortions is a function of both oxygen nonstoichiometry and temperature (2, 10). As a consequence, the transport and magnetic properties of these phases may be expected to be a sensitive function of T and δ .

Recently, we reported the existence of long-range magnetic order in $\text{La}_2\text{NiO}_{4+\delta}$ for specimens with small deviations from ideal oxygen stoichiometry, δ , (3); this effect changes extensively with δ . As was the case for severely nonstoichiometric $\text{La}_2\text{NiO}_{4+\delta}$ (11), both $\text{Pr}_2\text{NiO}_{4+\delta}$ and $\text{Nd}_2\text{NiO}_{4+\delta}$ previously have been reported to show no evidence of long-range order down to 4 K (11, 12). In the present study we investigate the dependence of the magnetic susceptibil-

* Dedicated to John B. Goodenough.

ity of $\text{Pr}_2\text{NiO}_{4+\delta}$ and $\text{Nd}_2\text{NiO}_{4+\delta}$ on δ and T , using oriented single crystals.

Experimental

Polycrystalline 99.99% pure Pr_2NiO_4 and Nd_2NiO_4 were prepared by solid-solid reaction of NiO with Pr_6O_{11} and Nd_2O_3 , respectively, at 1200°C in air, using nickel crucibles. The sintered product in each case was used as starting material for growth of single crystals from the melt under the appropriate atmosphere using radio frequency skull melting. The details of the crystal growth procedure and subsequent phase characterization are described elsewhere (13).

Analysis of the extent of oxygen nonstoichiometry was carried out by iodometric titration under a nitrogen atmosphere.

Single-crystal specimens were oriented by X-ray Laue backreflection to within $\pm 1^\circ$ of the desired direction before being cut.

Magnetic susceptibility measurements were carried out from 65 to 300 K using the Faraday method. The specimen orientation

was verified visually within the balance assembly.

Results and Discussion

Magnetic susceptibility data for $\text{Pr}_2\text{NiO}_{4+\delta}$ samples with various values of δ are presented in Fig. 1. In each case crystals were oriented with $H \parallel c$ (i.e., \perp to the layers). No evidence of long-range magnetic order was observed down to 65 K for unannealed specimens ($\delta \approx 0.09$); however, significant deviations from the Curie-Weiss law are apparent at low temperatures. As δ becomes small, the onset of long-range magnetic order with a substantial net ferromagnetic component is observed near 100 K; the net moment increases as δ decreases. This likely is attributable to the increase in structural distortions which arise with decreasing δ . Attempts to measure the susceptibility with $H \perp c$ were not successful due to the sizable torque favoring alignment with $H \parallel c$, the easy axis.

Data for annealed ($\delta \approx 0.04$) and unan-

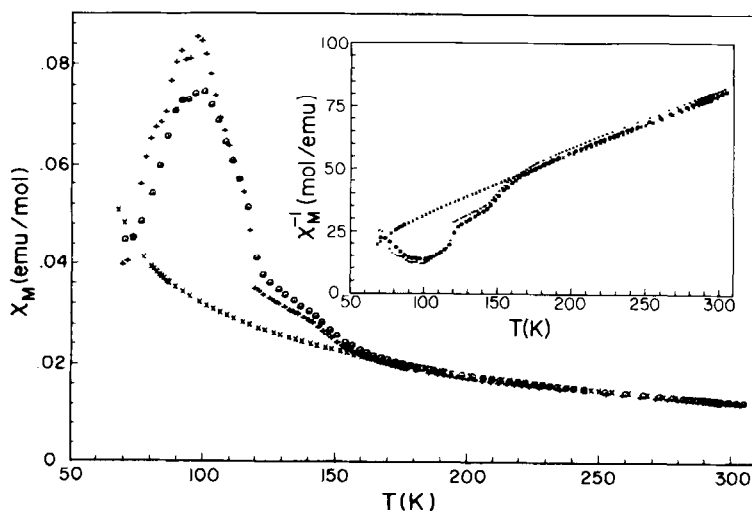


FIG. 1. Magnetic susceptibility as a function of temperature, with Curie-Weiss law plot inset for $\text{Pr}_2\text{NiO}_{4+\delta}$. \times , as grown; $\delta = 0.090$; \odot , annealed in CO_2 at 1200°C , $\delta \approx 0.003$; $+$, annealed in 99.25% $\text{CO}_2/0.75\%$ CO at 1200°C ($\log f_{\text{O}_2} = -6.75$), $\delta \approx 0.003$.

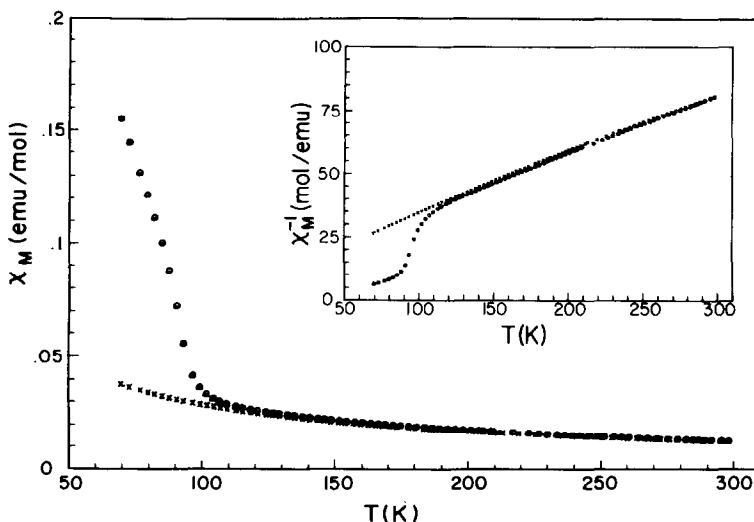


FIG. 2. Magnetic susceptibility as a function of temperature, with Curie-Weiss law plot inset for $\text{Nd}_2\text{NiO}_{4+\delta}$. \times , as grown, $\delta = 0.090$; \circ , annealed in 99.0% CO_2 /1.0% O_2 at 1200°C , $\delta = 0.055$.

nealed ($\delta \approx 0.15$) $\text{Nd}_2\text{NiO}_{4+\delta}$ are presented in Fig. 2. As with unannealed $\text{Pr}_2\text{NiO}_{4+\delta}$, no long-range order was detected down to 65 K, but deviations from the Curie-Weiss law are observed. Attempts to reduce the magnitude of δ to values comparable to those obtained under reducing conditions for $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{Pr}_2\text{NiO}_{4+\delta}$ resulted in decomposition of the specimen into Nd_2O_3 and NiO . Decomposed crystals maintained an intact morphology, suggesting that the process is topochemical. Annealing under mildly reducing conditions with $\log f_{\text{O}_2} = -2.0$ at 1200°C did not result in decomposition; a long-range weak ferromagnetic net moment very similar to that of reduced $\text{Pr}_2\text{NiO}_{4+\delta}$ was then observed.

Magnetic measurements on both $\text{Pr}_2\text{NiO}_{4+\delta}$ and $\text{Nd}_2\text{NiO}_{4+\delta}$ display large field dependences below T_c . In previous studies (11, 12), no magnetic anomaly or long-range order and no field-dependent susceptibility was reported. This is probably a consequence of the large δ values attained by preparation of the compounds in air.

The nature of the magnetic ordering in

the lanthanide nickelates is not clear at this point. From structural considerations and from high-temperature susceptibility measurements (11, 12, 14, 15) the principal magnetic interactions are expected to be antiferromagnetic in nature. Weak ferromagnetic moments probably arise from the canting of the NiO_6 octahedra and from canting of the lanthanide $4f$ electron moments in Pr_2NiO_4 and Nd_2NiO_4 . Weak ferromagnetism is expected to be mediated by ordering of electron spins in the nearly itinerant $\sigma_{x^2-y^2}$ states within the basal plane. It seems unlikely that the moments as such are localized; however, ordering may result from the onset of a spin-density wave state. As expected from consideration of the tolerance factors (16) the structural distortions become increasingly significant as δ and the lanthanide radius are decreased.

A full understanding of the influence of nonstoichiometry on the magnetic properties, apart from the effect of changing the magnitude of structural distortions, requires a characterization of the defect structure. Although it is frequently

assumed that oxygen excess stoichiometry is achieved either by intergrowth of Ruddlesden–Popper type phases (17) or by metal atom deficiency, neither is clearly in evidence: Extensive studies of single-crystal specimens of La_2NiO_4 , Pr_2NiO_4 , and Nd_2NiO_4 by electron microscopy (7) has revealed no evidence of intergrowths, nor have deviations from the ideal Ln/Ni ratio been detected by chemical analysis, regardless of the δ value. The presence of metal atom vacancies would require either that $\text{Ln}/\text{Ni} \neq 2.00$ or that stoichiometric proportions of vacant Ln and Ni sites exist. Alternatively, excess oxygen may be present; however, the large size of the O^{2-} ion would seem to preclude its inclusion as an interstitial. However, the possible existence of a peroxide species as proposed by Ganguly (18) may provide a reasonable explanation of how excess oxygen may be incorporated. Careful density measurements are in progress to resolve this question. Except for the peroxide model, all other defect schemes involve the concomitant presence of Ni^{3+} . Conformation concerning the presence or absence of Ni^{3+} is essential for interpreting the strong influence of nonstoichiometry on the magnetic and transport properties in these materials.

In general the nature of the defect structures in K_2NiF_4 -type oxides is of critical importance for an understanding of their unusual physical properties. This is of particular relevance to the current enormous effort involving the superconducting properties of substituted lanthanum cuprates (19–22).

Acknowledgments

This research was supported on the ACS-PRF Grant 16579-AC3. The authors are greatly indebted to Pro-

fessor C. N. R. Rao and Dr. P. Ganguly for illuminating discussions. The skull melter was operated with the support of NSF-MRL Grant DMR 84-18453.

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