Magnetic transitions in Nd_2NiO_4

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Five different magnetic phase transitions have been identified and characterized in stoichiometric Nd_2NiO_4 by means of magnetic-susceptibility and isothermal-magnetization measurements. A collinear antiferromagnetic ordering of Ni^{2+} magnetic moments exists between $T_{N1} \approx 320$ K and $T_{c1} \approx 130$ K where an orthorhombic-to-tetragonal structural phase transition occurs. In this temperature range, Nd^{3+} ions follow a simple paramagnetic Curie-Weiss-like behavior, while a weak ferromagnetic component appears below 130 K. An internal magnetic field on the Nd^{3+} ions develops with this structural phase transition. Two additional transitions are observed at $T_{c2} \approx 68$ K and $T_{c3} \approx 45$ K which are characterized by a sudden increase of the weak ferromagnetic component. Finally, a peak of the differential susceptibility at $T_{N2} \approx 11$ K marks a long-range antiferromagnetic ordering of the Nd^{3+} ions. The internal magnetic field acting on the Nd ions was evaluated to be 5.2 T in the 20 K$-T_{c2}$ temperature range.

The study of the magnetic properties of R_2NiO_4 (R =La, Pr, Nd) has raised an undeniable interest since the discovery of p-type superconductivity in hole-doped antiferromagnetic La_2CuO_4 and n-type superconductivity in electron-doped Nd_2CuO_4.[1] More recently, some authors have pointed out that high-T_c superconductivity also exists in these Ni oxides below about 70K.[2]

The crystal structures of the La and Nd cuprates differ, while that of the corresponding Ni oxides remains isomorphous to the La_2CuO_4-type structure. This asymmetry among the Cu and Ni oxides reveals fundamental differences in the crystal chemistry of both elements. From a magnetic point of view, however, the Cu and Ni sublattices behave quite similarly: In both cases, a long-range three-dimensional (3D) antiferromagnetic order develops below about 320 K, while strong (2D) antiferromagnetic fluctuations persist above the Néel temperature.[3] The magnetic behavior of the cuprates isomorphous to Nd_2CuO_4 appears much more complex because of the existence of the R-Cu and R-R magnetic interactions, which lead, in some cases, to a long-range magnetic ordering of the rare-earth elements, which may even coexist with the superconducting state.[4]

In recent works,[5–7] it has been shown by means of neutron diffraction that stoichiometric R_2NiO_4 (R =La, Pr, Nd) oxides have a room-temperature orthorhombic structure ($Bmab$) while at a lower temperature T_{c1}, which depends on the size of the rare-earth element (from 80 to 130 K), a first-order structural phase transition appears in all these compounds. This structural phase transition involves a sudden reorientation of the NiO_6 octahedra, and the crystal symmetry increases to tetragonal ($P4_2/ncm$). The antiferromagnetic order of stoichiometric La_2NiO_4 has been clearly identified by means of polarized neutron diffraction,[6] and the Néel temperature appears to be very near to that of stoichiometric La_2CuO_4 (T_N =320 K).

In the case of Nd_2NiO_4, a complex magnetic behavior has been anticipated from the previous neutron-diffraction experiment.[7] For instance, a low-temperature (T_{N2}= 11 K) long-range antiferromagnetic ordering of the Nd^{3+} ions was identified, similarly to Nd_2CuO_4.[8] Other magnetic anomalies were also detected at some intermediate temperatures signaling the existence of spin reorientations probably related to those observed in Nd_2CuO_4 by means of neutron diffraction.[9]

In this work we report macroscopic magnetization measurements on stoichiometric Nd_2NiO_4 allowing us to identify up to five different magnetic phase transitions being either related to cooperative long-range magnetic ordering (Ni and Nd ions), to spin reorientations associated with the orthorhombic-to-tetragonal structural phase transition, or to other unexplained mechanisms. It is very straighforward to note that the results presented here are strictly in coincidence with those reported in the neutron-diffraction study, even if a new sample has been used in this new investigation. This gives further confidence to the reliability of the experimental procedures.

Stoichiometric Nd_2NiO_4 polycrystalline samples were synthesized by standard ceramic methods with a firing temperature of 1450 °C and an accumulated firing time of about 300 h. This long annealing was performed in order to get very good crystallinity. This is an important point in this system because, after the low-temperature structural phase transition, very stringent strains appear in the crystallites and these seem to be enhanced by the preexisting defects. A final reduction step was carried out by annealing the samples at 350 °C under a dry H_2 current. The quality of the sample was, indeed, verified by high-resolution neutron diffraction, which evidenced Bragg lines much narrower than those previously observed.[7]

Magnetic-susceptibility and isothermal-magnetization measurements were performed either with a Faraday balance or a Quantum Design SQUID magnetometer in magnetic fields up to 5 T. The temperature range investigated spanned from 4 to 300 K.

We have first studied the temperature dependence of the low-field magnetic susceptibility in order to identify the different transitions observed in the neutron-diffraction patterns. In Fig. 1, a typical curve is displayed. As it may be observed, a strong low-temperature magnetic polarization is observed, which needs a thorough analysis. In the inset of Fig. 1, a clear susceptibility upturn becomes prominent at $T_{c1}=130$ K. This temperature corresponds just to that where the orthorhombic-to-tetragonal phase transition occurs and thus implies that the change of the octahedra tilting axis associated with this structural phase transition carries also a reorientation of the Ni magnetic moments.

Two more transitions are observed in Fig. 1 which match the anomalies observed in the intensity of some magnetic Bragg reflections.[7] These anomalies are superposed to a strong low-temperature magnetic polarization of the Nd^{3+} ions.

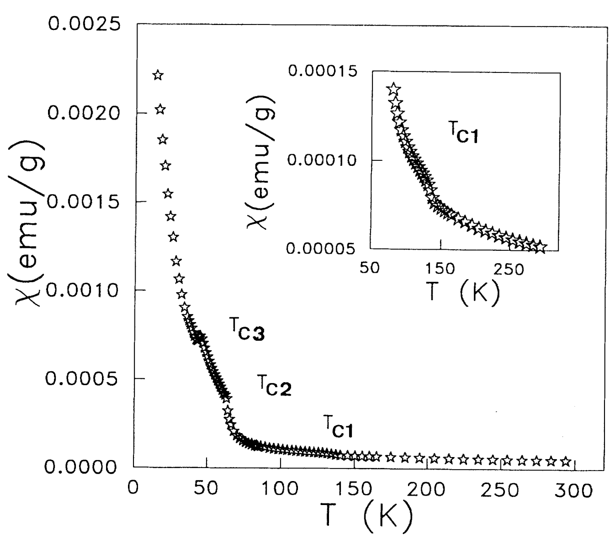

FIG. 1. Low-field magnetic susceptibility ($H=1.56$ kOe) of stoichiometric Nd_2NiO_4 in the temperature range 14–300 K. Inset: Detail of the curve showing the structural phase transition at $T_{c1}=130$ K.

A much deeper insight into the microscopic mechanisms of the complex magnetic behavior of Nd_2NiO_4 may be gained from the isothermal-magnetization curves. The high-field $M(H)$ curves may be represented in a wide temperature range by the equation

$$M(H,T)=M_0(T)+\chi_d H_a , \qquad (1)$$

where χ_d is a high-field differential susceptibility, H_a is the applied magnetic field, and $M_0(T)$ is the magnetization extrapolated at zero magnetic field from the linear high-field regime. This $M_0(T)$ is strongly temperature dependent, and it is very near to the remanence because of the nearly linear character of the isothermal-magnetization curves. The temperature dependence of the differential susceptibility χ_d and the zero-field extrapolated magnetization $M_0(T)$ are displayed in Figs. 2(a) and 2(b), respectively.

It should be noted first that the observed magnetization values are strongly dependent on the maximum previously applied magnetic field. This is an indication of the existence of ferromagnetic domains which cannot be reversed, even with the application of a magnetic field of 5 T, thus implying that the magnetic anisotropy of Nd_2NiO_4 should be quite important.

It should also be mentioned that in spite of a close examination of these isothermal-magnetization curves, we could not identify, within our experimental magnetic-field range, any magnetically induced phase transition, as observed in La_2CuO_4.[10] This fact is consistent with the magnetic structures proposed from a neutron-diffraction study of Nd_2NiO_4 (Ref. 7) ($g_x c_y f_z$ or $g_x + c_y f_z$ modes), which indicate the existence of a ferromagnetic component along the c axis rather than an antiferromagnetic one, as in La_2CuO_4. This ferromagnetic component develops at $T_{c1}=130$ K, i.e., at the structural phase transition. The first-order character of this phase transition may be indeed evidenced by some magnetization hysteresis when cycling the temperature. We should mention that only a very small magnetic hysteresis remained above this temperature, which we attribute to a tiny amount of metallic Ni formed during the high-temperature hydrogen reduction step. Nevertheless, there is no doubt about the rise of the weak ferromagnetic component at T_{c1}, thus giving full support to the group-theoretical arguments which show that no weak ferromagnetic component is possible within the space group *Bmab* in connection with the g mode.[11]

We should also take into account that this weak ferromagnetic component of the Ni magnetic moments lies at the origin of the magnetic anomaly observed in stoichiometric La_2NiO_4,[12] where the structural phase transition occurs at 80K.[5] This is also the temperature where it was claimed that minor phase high-temperature superconductivity develops in La_2NiO_4,[2] and so we would like to stress that extreme care should be taken when observing magnetic anomalies around this temperature.

The existence of further spin reorientations at $T_{c2} \approx 68$ K, and $T_{c3} \approx 45$ K, may be clearly stated from the anomalies observed in either the susceptibility or the saturation magnetization (Figs. 1 and 2). The observation of these anomalies in the region where the Nd ions are becoming progressively polarized by an internal magnetic field points to the existence of sudden increases of the z component of the internal magnetic field.

High-resolution neutron-diffraction patterns and high-field isothermal-magnetization measurements are presently being performed to explore further whether these additional spin reorientations are associated with any structural rearrangement. It is very likely, however, that these anomalies involve some kind of spin reorientations similar to those observed in Nd_2CuO_4,[9] where there is probably competition between magnetocrystalline anisotropy and magnetic exchange effects.

A long-range magnetic ordering of the Nd ions is finally clearly observed at $T_N = 11$ K through a peak in the $\chi_d(T)$ curve [Fig. 2(a)]. It is straighforward to note that this transition is hardly seen in the $M_0(T)$ curve, thus implying that the c-axis component of the internal magnetic field acting on the Nd ions is not modified by the long-range order of the Nd ions. This observation is in sharp contrast to the behavior of T' cuprates, such as Gd_2CuO_4,[13] where the internal magnetic field goes to zero when the Gd ions order magnetically, and thus implies that the rare-earth ions magnetic order competes with that of the Cu ions in the T' cuprates. It is also important to note that the long-range order transition identified here occurs at much higher temperatures than those observed in Nd_2CuO_4 ($T_N = 1.5$ K).[8] It is not clear at which point this may be simply associated with the different crystal structure of both compounds or with the enhanced magnetic interaction.

Below T_{c2}, and down to 20 K, the high-field differential susceptibility χ_d follows quite nicely a Curie-Weiss-like law, thus suggesting that the internal magnetic field could be temperature independent in this range. If we assume that the ferromagnetic component of Ni^{2+} ions remains temperature independent in this interval, Eq. (1) may be rewritten as

$$M(H_a, T) = M^0_{Ni} + \chi_d(H_i + H_a), \qquad (2)$$

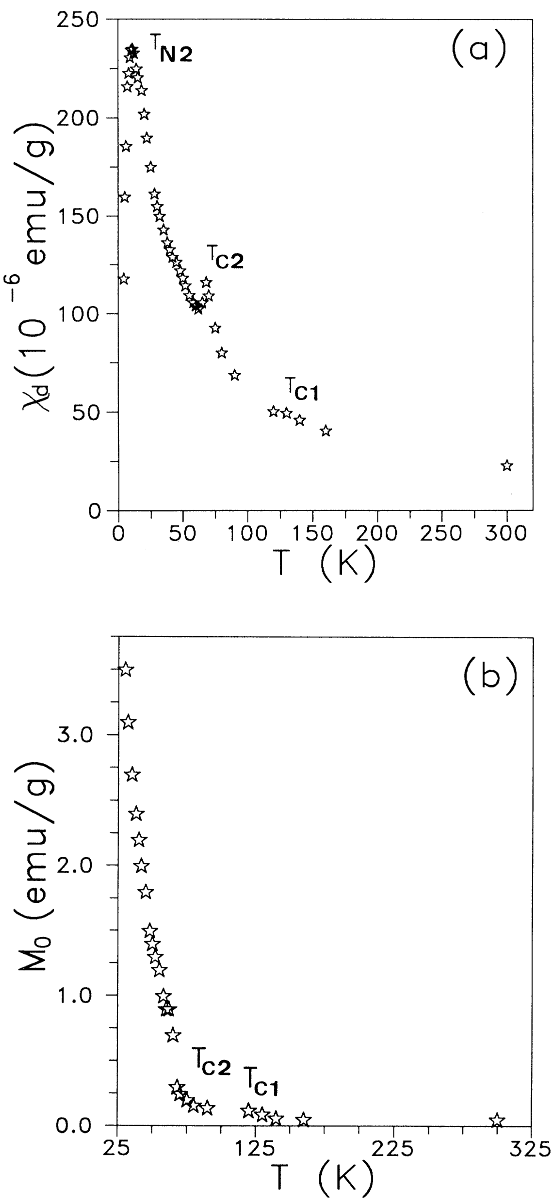

FIG. 2. (a) High-field differential susceptibility χ_d and (b) saturation magnetization M_0, as a function of temperature (maximum applied field $H_{max} = 1$ T).

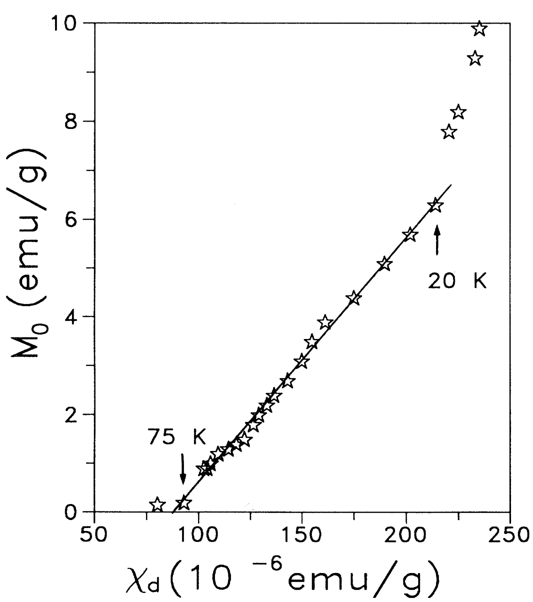

FIG. 3. Saturation magnetization $M_0(T)$ vs high-field differential susceptibilty $\chi_d(T)$, showing their linearity in the temperature range 20 K$-T_{c2}$.

where only χ_d has an explicit dependence on temperature. The observed linearity among $M_0(T)$ and $\chi_d(T)$ in this temperature range (Fig. 3) gives full support to our assumption and thus allows us to evaluate the internal magnetic field. The fitted values were $M_{Ni}^0=-0.36(7)$ μ_B/f.u., i.e., $\theta=13.1°$, and $H_i=5.2(6)$ T.

It is certain that this internal magnetic field acting on Nd ions is much higher than that observed in Nd_2CuO_4 or other rare-earth perovskites, such as $GdCrO_3$ (Ref. 14). This may be a reflection of the important growth of the weak ferromagnetic component in Nd_2NiO_4 but an increase of the exchange interaction could also be invoked. We note also that the negative sign of M_{Ni} means that the Nd-Ni superexchange interaction has an antiferromagnetic character. Also, the value of the Ni canting angle ϑ is not far from that deduced for the Nd ions from neutron diffraction ($\vartheta=18.2°$).[7] This slightly reduced value should not be taken as a proof of a noncollinear magnetic structure among Nd and Ni ions. Actually, within the magnetic-field range investigated here, M_0 is still increasing, thus indicating that the magnetic domains have not completely disappeared, and so our ϑ value is only a lower limit.

In summary, our work shows that even if the magnetic behavior of both Nd_2CuO_4 and Nd_2NiO_4 is highly complex, some severe differences on the rare-earth transition-metal interaction seem to exist. For instance, the T' cuprates seem to have, in some cases, a weak ferromagnetic component which appears within the *ab* plane while the ferromagnetic component in Nd_2NiO_4 is along the *c* axis. The origin of these ferromagnetic components and how they interact with the rare-earth ions is still not clear. This is a problem which now bears a strong interest in the context of the understanding of the relationship between high-temperature superconductivity and magnetism.[15] A full account of the magnetic properties of Nd_2NiO_4 and other isomorphous systems will be reported later on to contribute in the clarification of this problem.

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