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Neutron Diffraction Studies of the Crystal and Magnetic Structure of $Nd_{1.5}Sr_{0.5}NiO_4$

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The crystal structure and magnetic ordering of $Nd_{1.5}Sr_{0.5}NiO_4$ which shows a susceptibility maximum at 17 K have been investigated by neutron diffraction. A tetragonal K_2NiF_4-type structure is confirmed at room temperature with a = 3.7756(3) Å and c = 12.485(1) Å. A mean Ni–O distance of 1.986(5) Å reflects the presence of equal concentrations of Ni^{2+} and Ni^{3+}. Low temperature neutron diffraction data to 11 K reveal features not apparent in the bulk susceptibility. Below 50 K a broad, diffuse reflection at Q = 0.835 Å^{-1} is found which can be indexed as ($\frac{1}{2}$00) relative to the chemical cell. The intensity of this peak has an unusual temperature dependence with abrupt increases between 25 and 21 K and between 14 and 11 K. The correlation length derived from the peak width decreases from a constant value of 20(4) Å between 14 and 21 K to 12(2) Å at 11 K. Also at 11 K a resolution-limited reflection appears which can be indexed as (101) on a magnetic cell with $a_M = \sqrt{2}a_{CH}$ which is typical for long-range antiferromagnetic order in K_2NiF_4 structure compounds. The diffuse ($\frac{1}{2}$00) reflection is ascribed to short-range magnetic order on the Ni sublattice while the long-range order below 11 K involves most likely Nd–Ni intersublattice coupling. Both forms of order coexist at 11 K. © 1992 Academic Press, Inc.

Introduction

In a recent study the structural, electrical, and magnetic properties of the system $Nd_{2-x}Sr_xNiO_{4+y}$ have been reported (*1*). A structural transformation from orthorhombic to tetragonal symmetry at room temperature was observed at $0.1 < x < 0.2$. The tetragonal phase was assumed to have the K_2NiF_4 structure. The oxygen content also varied with y = 0.16(3) to 0.12(3) for $x <$ 0.1 while y = 0.00(3) for $x > 0.2$. For $x <$ 1.0 the materials are semiconductors.

The magnetic susceptibilities show only paramagnetic behavior for most of the solid solution phases except for the range $0.4 \leq x \leq 0.7$, where a susceptibility maximum is seen near 17 K which could signal the onset of long-range magnetic order (LRMO).

Materials related to the $Nd_{2-x}Sr_xNiO_4$ series include $La_2NiO_{4-\delta}$, La_2CuO_4, Nd_2NiO_4, and K_2NiF_4. K_2NiF_4 is the paradigm for layered AF materials and La_2CuO_4 is of course the parent of the family of copper oxide superconductors. The magnetic ions in K_2NiF_4 are arranged in two layers dis-

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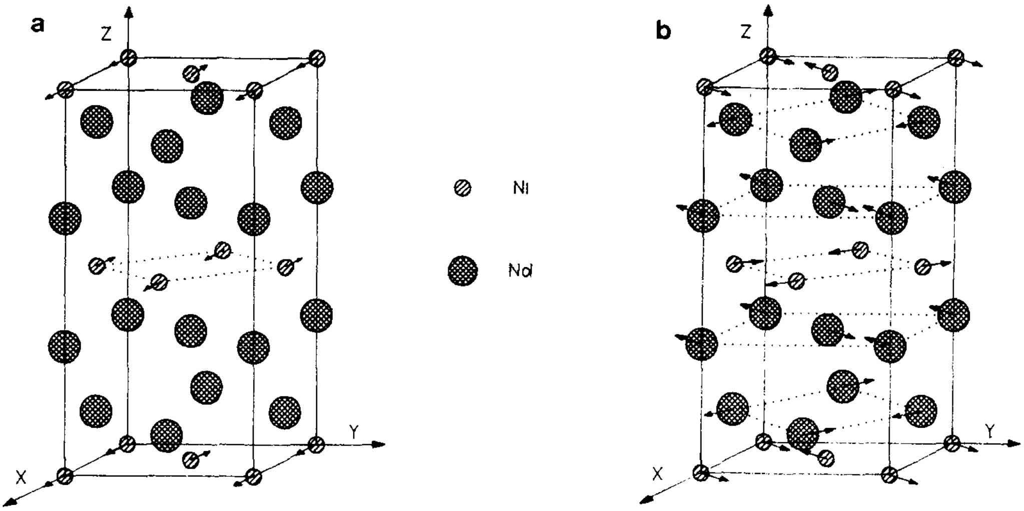

FIG. 1. (a) Magnetic structure on the transition metal sublattice of $K_2N_iF_4$, La_2CuO_4, and La_2NiO_4. (b) Magnetic structure of Nd_2NiO_4 below 8 K, where both sublattices exhibit LRMO (after Ref. (*10*)).

placed by a vector $\frac{1}{2}(a + b + c)$. Intralayer magnetic interactions are strongly AF due to nearest neighbor 180° Ni–F–Ni superexchange while interlayer pathways are much more convoluted, Ni–F–K–F–Ni, causing these interactions to be much weaker. Also, the interlayer correlations are weakened further by a symmetry cancellation or frustration effect due to the existing intraplanar AF order. As a result, two-dimensional, short-range (as long-range order is not usually possible in two dimensions) correlations dominate at high temperatures (up to 180 K for K_2NiF_4). This is usually manifested by the appearance of diffuse reflections in the neutron diffraction pattern with a characteristic asymmetric line shape around reciprocal lattice points $(10l)$ where the indices refer to the magnetic cell (*2*). LRMO can occur only when the frustrated interplanar correlations lock in at much lower temperatures (97 K for K_2NiF_4). The specific magnetic structure found for K_2NiF_4 in the LRMO state is shown in Fig. 1a (*2, 3*). It is clear that the magnetic unit cell has dimensions $a_M = \sqrt{2}a_{CH}$, $c_M = c_{CH}$, where the subscripts refer to the magnetic (M) and chemical (CH) cells. Thus, the magnetic unit cell contains four magnetic ions.

La_2CuO_4, La_2NiO_4, and Nd_2NiO_4 have crystal structures which are derived from the tetragonal K_2NiF_4 cell by an orthorhombic distortion such that $a_{OR} \approx b_{OR} \approx \sqrt{2}a_T$ and $c_{OR} \approx c_T$ (*4–7*). Thus each of these compounds have four magnetic ions per chemical unit cell, considering the small cation site only. Stoichiometric $La_2NiO_{4+\delta}$ and $La_2CuO_{4+\delta}$, i.e., $\delta = 0$, both exhibit LRMO (*8, 9*). For La_2NiO_4 the magnetic structure is essentially the same as that for K_2NiF_4 except that the moment direction is parallel to the a-axis rather than to the c-axis (*8*). In this case the chemical and magnetic unit cells are the same size. A similar magnetic structure exists for La_2CuO_4 with the moment direction along b (*9*). Nd_2NiO_4 represents a more complex case with two magnetic sublattices. A detailed study of Nd_2NiO_4 indicates that the Ni^{2+} sublattice orders below 320 K with a structure which is essentially identical to that for La_2NiO_4

(*10*). The signature for LRMO in all of the above cases is the appearance of new reflections in the neutron diffraction pattern of the sort ($h0l$) or ($0hl$), depending on the moment direction. In the case of tetragonal K_2NiF_4 these indices refer to the larger magnetic unit cell while for the others the chemical and magnetic cells are identical.

For Nd_2NiO_4 the interaction between the Nd^{3+} and Ni^{2+} sublattices has been studied. Evidence for polarization of the Nd^{3+} ions by the ordered Ni^{2+} ions is found below 70 K in the form of a strong enhancement of the intensity of the (011) reflection as the temperature is lowered. This is accompanied by a decrease in the background near (011) as paramagnetic scattering from the Nd^{3+} sublattice is removed. The Nd^{3+} sublattice exhibits LRMO below 8 K which is shown in Fig. 1b (*10*).

What can be anticipated for $Nd_{1.5}Sr_{.5}N_iO_4$? On a formal basis the Ni sublattice is composed of equal concentrations of Ni^{2+} ($S = 1$) and Ni^{3+}, which is probably low spin ($S = \frac{1}{2}$). There is evidence from the paramagnetic susceptibilities that μ_{eff} for Ni^{3+} is anomalously small (*1*). Thus, the Ni^{2+} sublattice is diluted relative to Nd_2NiO_4. As a result both intra- and interplanar magnetic interactions will be weakened; the all-Ni^{3+} compound, $NdSrNiO_4$, shows no sign of magnetic order, although neutron diffraction studies are lacking. Intrasublattice interactions will also be frustrated due to the element of randomness which is introduced. It is thus likely that LRMO will be more difficult to achieve for $Nd_{1.5}Sr_{0.5}NiO_4$ than for Nd_2NiO_4. In addition the Nd^{3+} sublattice is also diluted by diamagnetic Sr^{2+} which will weaken and frustrate the Nd–Ni and Nd–Nd sublattice interactions. In order to provide more definitive information regarding the crystal and magnetic structure of this complex material, particularly concerning the existence of LRMO, neutron diffraction measurements were undertaken.

Experimental

The sample of $Nd_{1.5}Sr_{0.5}NiO_{4+\delta}$ with $\delta = 0.00(3)$ was prepared as described previously (*1*). About 10 g were loaded into a thin-walled aluminum can which was filled with helium exchange gas and sealed with an indium wire gasket. Neutron powder diffraction data were collected at the McMaster Nuclear Reactor using $\lambda = 1.3913$ Å neutrons and a position sensitive detector. This system has been described previously (*11*). Sample temperature was varied in the range 300 to 11 K with a closed-cycle refrigerator and temperatures were measured with a calibrated diode and controlled to 0.01 K. Measurements at room temperature were performed in a thin-walled vanadium can. Magnetic susceptibility data were obtained with a SQUID magnetometer as described previously (*1*).

Results and Discussion

The Room Temperature Crystal Structure

As mentioned, $Nd_2NiO_{4+\delta}$ crystallizes in an orthorhombically distorted version (*Abma*) of the K_2NiF_4 structure (*I4/mmm*) (*6*). For $Nd_{2-x}Sr_xNiO_4$ a composition-induced transition from the *Abma* structure to a tetragonal structure was observed to occur between $x = 0.1$ and $x = 0.2$ at room temperature. Powder neutron diffraction data confirm the K_2NiF_4-type structure for the $x = 0.5$ sample studied here, as shown in Fig. 2. The data were analyzed by the Rietveld or profile refinement method and the results are displayed in Table I. In Table II selected bond distances are shown.

For $Nd_{1.5}Sr_{0.5}NiO_{4.00}$ the average Ni valence is 2.50 which implies equal amounts of Ni^{2+} and Ni^{3+} on a formal basis. The observed Ni–O distances seem to reflect this. A recent study of $NdNiO_3$ (*12*) with all Ni^{3+} gives a mean Ni–O distance of 1.943(9) Å while in Nd_2NiO_4 (*6*) with all Ni^{2+} the corresponding distance is

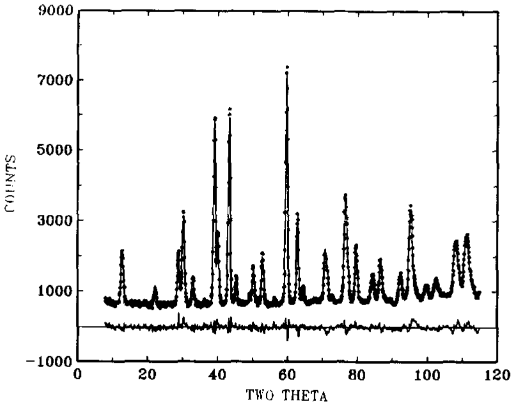

FIG. 2. Powder neutron diffraction data for $Nd_{1.5}Sr_{0.5}Ni_{4.00}$. The closed circles represent the data points, the solid line is the calculated profile, and the bottom curve is the difference plot.

2.015(5) Å. These values should be compared with the weighted mean Ni–O distance found here of 1.986(5) Å.

TABLE I

UNIT CELL CONSTANTS, ATOMIC POSITIONS, AND THERMAL PARAMETERS FOR $Nd_{1.5}Sr_{0.5}NiO_4$ FROM PROFILE REFINEMENT OF NEUTRON POWDER DATA AT 295 K

Space group	*I4/mmm*
a (Å)	3.7756(3)
c (Å)	12.485(1)
Volume ($Å^3$)	177.97(3)
R_{WP}	6.12
R_P	4.68
R_N	4.80
R_E	2.30
No. of profile points	1000
Independent reflections	71
No. of parameters	23
d-space range (Å)	0.825–13.29

Atom	Position	*B* ($Å^2$)
Nd/Sr	0 0 0.3607(3)	0.29(5)
Ni	0 0 0	0.44(6)
O1	0 0 0.1747(4)	1.39(6)
O2	0 $\frac{1}{2}$ 0	0.61(7)

Magnetic Susceptibility

The temperature dependence of the inverse susceptibility for $Nd_{1.5}Sr_{0.5}NiO_4$ is shown in Fig. 3. Note the Curie–Weiss region over the range from 380 to about 200 K followed by a gradual deviation from linearity. This is typical behavior for Nd^{3+} compounds which can be ascribed to the depopulation of crystal field split doublet states as the temperature is lowered. Near 17 K a somewhat broad susceptibility maximum is observed, Fig. 4a, which seems to indicate the onset of some form of magnetic ordering in which the Nd^{3+} sublattice participates. From the results of Ref. (*1*) it is clear that the bulk susceptibility of all of the $Nd_{2-x}Sr_xNiO_4$ phases is dominated by the Nd^{3+} ions. Any unusual behavior associated with the *Ni* sublattice alone will be masked and difficult to separate from the total measured susceptibility. An attempt was made to account semiquantitatively for the Nd^{3+} contribution using the susceptibility for the isostructural material $NdSrGaO_4$ (*16*). For this compound only Nd^{3+} is magnetic, the lattice constants are similar, a = 3.8173(4) Å and c = 12.531(1) Å, and the Nd^{3+} environment should also be similar. In Fig. 4b is plotted the quantity χ ($Nd_{1.5}Sr_{0.5}NiO_4$) − 1.5χ ($NdSrGaO_4$). Note the small but positive difference susceptibility which increases with decreasing temperature down to about 50 K and then plummets. If it is assumed that this difference susceptibility represents an approximation to the Ni sublattice contri-

TABLE II

SELECTED BOND DISTANCES (Å) FOR $Nd_{1.5}Sr_{0.5}NiO_4$

Nd/Sr–O1	2.323(6) × 1
Nd/Sr–O1	2.706(1) × 4
Nd/Sr–O2	2.566(2) × 4
Ni–O1	2.181(5) × 2
Ni–O2	1.888(1) × 4
O1–O2	2.884(4) × 4
O1–O2	2.669(2) × 4

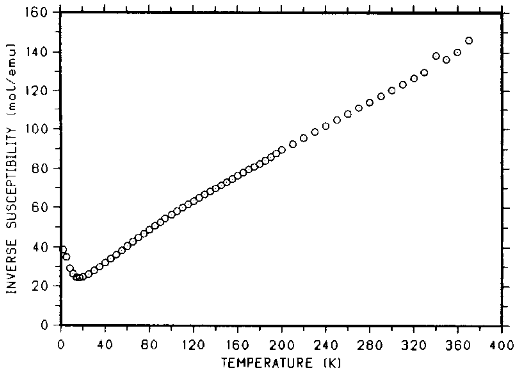

FIG. 3. Inverse susceptibility versus temperature for $Nd_{1.5}Sr_{0.5}NiO_4$. The applied field is 0.10 T.

bution, then the above behavior signals some form of AF magnetic order setting in well above 17 K. Only neutron scattering can confirm this hypothesis.

Low Temperature Magnetic Structure

Data sets were obtained at 11, 14, 17, 21, 25, 27, 30, 35, 40, and 50 K in the 2θ range 6°–30° which corresponds to a reciprocal space scattering vector or momentum transfer range of 0.47 to 2.33 Å^{-1}. The results can be summarized by considering the data at four temperatures, as shown in Figs. 5a–5d. First (Fig. 5a) at 50 K only the (002) and (101) reflections belonging to the chemical unit cell are seen. At 11 K (Fig. 5b), however, two new features appear, a rather broad, diffuse reflection at 2θ of 10.60(5)° [Q = 0.835(5) Å^{-1}] and a weak but narrow resolution-limited reflection at 16.40° (Q = 1.288 Å^{-1}). The diffuse peak can be indexed roughly as $(\frac{1}{2}00)$ in terms of the chemical unit cell.Given the rather large error in Q, this assignment is tentative and the reflection could well be slightly incommensurate. For convenience, however, it will be labeled $(\frac{1}{2}00)$ in the following discussion. The resolution-limited Bragg peak can be indexed on a different magnetic cell, $a_M = \sqrt{2}a_{CH}$, $c_M = c_{CH}$, as (101). As mentioned this is the typical cell and typical class of magnetic reflections reported for K_2NiF_4 structure compounds.

At 14 K (Fig. 5c) which is also below the susceptibility maximum (Fig. 4a) the Bragg peak is no longer seen but the diffuse peak persists. In fact the diffuse peak is still quite prominent at 27 K (Fig. 5d), well above the susceptibility maximum. The temperature dependence of the integrated intensity of the $(\frac{1}{2}00)$ reflection is plotted in Fig. 6 and is seen to be rather complicated. Note the sharp increase between 25 and 21 K followed by a plateau to 14 K and another sharp increase to 11 K. The observed FWHM for $(\frac{1}{2}00)$ is

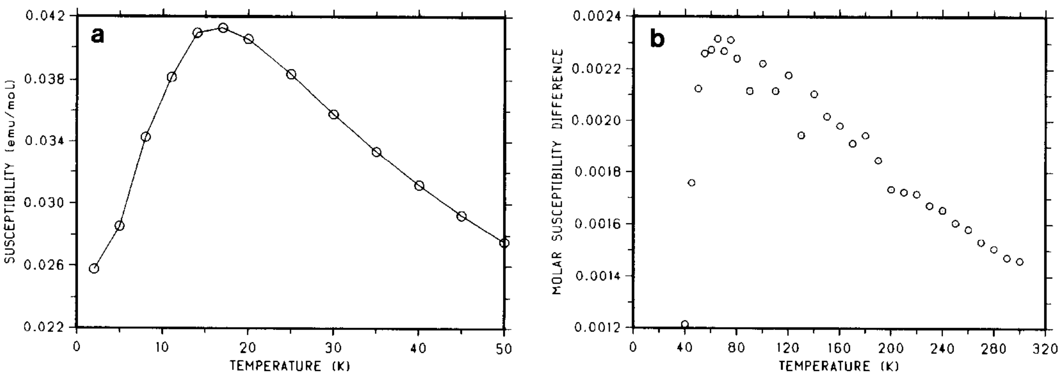

FIG. 4. (a) The susceptibility maximum for $Nd_{1.5}Sr_{0.5}NiO_4$ at an applied field of 0.10 T. (b) The difference susceptibility, χ ($Nd_{1.5}Sr_{0.5}NiO_4$) − 1.5χ ($NdSrGaO_4$), as a function of temperature.

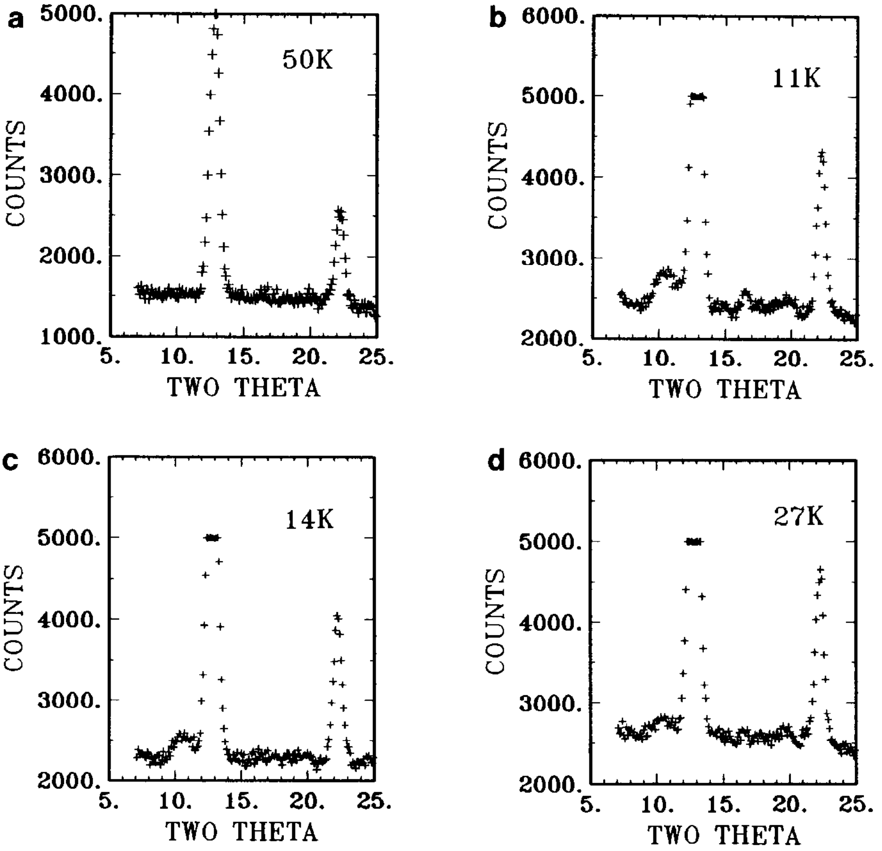

FIG. 5. Neutron diffraction data at the following temperatures: (a) 50 K, (b) 11 K, (c) 14 K, (d) 27 K. The two strong reflections are (002) and (101) of the chemical unit cell.

about twice that for a resolution-limited Bragg peak. An attempt was made to extract a correlation length by fitting the lineshape of the (½00) reflection as a convolution of a resolution-limited Gaussian and a Lorentzian. The details of the procedure have been described previously (*13*). This analysis yields a correlation length or magnetic domain dimension of 20(4) Å within the temperature interval 14 to 21 K. At 11 K the correlation length decreases sharply to 12(2) Å.

Conclusions

Clearly, the neutron scattering results disclose a much more complicated magnetic behavior for $Nd_{1.5}Sr_{0.5}NiO_4$ than that suggested by the bulk susceptibility data alone. The following discussion is qualitative, necessarily, but is consistent with both the susceptibility and the neutron diffraction observations. First the appearance of the diffuse (½00) reflection near 45 K correlates well with the anomaly seen in the difference susceptibility data (Fig. 4b). As there is no anomaly in this temperature range in the bulk susceptibility (Fig. 3) which is Nd^{3+} dominated, this short-range magnetic order (SRMO) can be ascribed to the Ni sublattice. That this is SRMO in $Nd_{1.5}Sr_{0.5}NiO_4$ rather than LRMO as in Nd_2NiO_4 is not inconsistent with the element of randomness and frustration in the former rela-

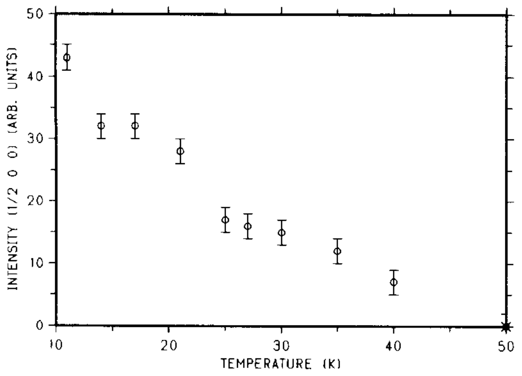

FIG. 6. Temperature dependence of the integrated intensity of the diffuse reflection $(\frac{1}{2}00)$.

tive to the latter. The periodicity implied by a $(\frac{1}{2}00)$ reflection is atypical for K_2NiF_4 structure compounds. Only a few materials are known which require a magnetic cell with $a_M = 2a_{CH}$, for example, $LaSrFeO_4$ and β-Sr_2MnO_4 (*14, 15*). In both cases the only reflections seen are of the $(h/2\ k/2\ l)$ type but $(\frac{1}{2}00)$ is not present, indicating a different magnetic structure for $Nd_{1.5}Sr_{0.5}NiO_4$, presumably with a moment direction parallel to the *c*-axis. The SRMO may be two dimensional or three dimensional in nature. As mentioned earlier, two-dimensional SRMO in K_2NiF_4 structure compounds is usually signaled by diffuse scattering with a distinctive asymmetry associated with a different location in reciprocal space, namely (100), where the indices refer to an $a_M = \sqrt{2}a_{CH}$ cell (*2, 3*). The observed lineshape for $(\frac{1}{2}00)$ seems to be well described by a convolution of a Lorentzian and a Gaussian. A definitive investigation of the dimensionality implied by the $(\frac{1}{2}00)$ reflection would require single crystal data.

The temperature dependence of the SRMO shows two anomalies, between 25 and 21 K and between 14 and 11 K. The first sharp increase below 25 K is not reflected in the bulk susceptibility (Fig. 4a) and is, thus again, likely associated with the Ni sublattice. This may be due to a spin-reorientation. There is no sharp anomaly in the neutron diffuse intensity at 17 K, the χ_{MAX} temperature (Fig. 4a). The susceptibility maximum is rather broad and is not typical of LRMO. The ordering reflected here certainly involves the Nd sublattice and in this temperature range must involve Nd–Ni intersublattice coupling. In Nd_2NiO_4 this effect begins at 70 K and it is reasonable to expect a lower onset temperature for the random sublattice system studied here. That evidence for LRMO in the neutron data does not develop until between 14 and 11 K is consistent with the necessary reorientation of the Ni moments from one periodicity to another. This is also consistent with the significant decrease in domain size of the SRMO from 20 to 12 Å over the same temperature interval. The detailed magnetic structure at 11 K cannot be determined from one weak reflection but is likely similar to that for Nd_2NiO_4. It is remarkable that both LRMO and SRMO exist with different periodicities on the Ni sublattice at 11 K. Clearly, $Nd_{1.5}Sr_{0.5}NiO_4$ represents a very complex situation which cannot be understood fully from the results presented here. Extension of these measurements to lower temperatures would be valuable as would the study of systems such as $R_{1.5}Sr_{0.5}NiO_4$ where R represents other rare earths, including diamagnetic ions such as La. The investigation of single crystal samples will be necessary to provide definitive results.

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