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# Influence of oxygen stoichiometry on the antiferromagnetic ordering of single crystals of $La_2NiO_{4+\delta}$

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We report here on magnetic measurements of well-characterized single crystals of $La_2NiO_{4+\delta}$, for H both parallel and perpendicular to the *c* axis, and for compositions in the range $0<\delta<0.067$. The antiferromagnetic ordering temperature is shown to be very sensitive to the oxygen stoichiometry parameter $\delta$. A discontinuity in the $\delta$ dependence of the Néel temperature has been observed and is attributed to a change in the structure. For $0.055\le\delta\le0.067$ we report a time dependence of the remanent magnetization in the basal plane, which suggests that an anisotropic spin-glass phase exists over a narrow composition range in this system.

## I. INTRODUCTION

The lanthanum nickelate system, $La_2NiO_{4+\delta}$, where $\delta$ expresses the degree of oxygen excess, has received considerable attention in the past few years. The striking similarities between $La_2CuO_4$ and $La_2NiO_4$ in the structure and lower dimensionality, coupled with the discovery of superconductivity in the cuprates, added a new impetus for research on the nickelates.[1-20] Although a number of studies have addressed the dependence of the antiferromagnetic ordering temperature on $\delta$, a systematic investigation of this variation with $\delta$ over a wide range of stoichiometry, temperature, and magnetic fields has not yet been undertaken. It is known that stoichiometric $La_2NiO_4$ orders with a Néel temperature ($T_N$) of 650 K, while for $\delta\ge0.04$ the ordering temperature falls below 200 K. The nature of the depression of the ordering temperature $T_N$ with increasing $\delta$, and whether this depression is continuous or discontinuous, has been an open question. From extensive magnetic measurements in the present work, we address the variation of $T_N$ with $\delta$ and report that a discontinuity is encountered. We correlate this discontinuous nature of the $T_N$ with $\delta$ as arising from a change in the crystallographic structure. We also report observations on a new spin-glass phase that exists over a narrow composition range.

Lanthanum nickelate exists over a broad range of oxygen stoichiometry, with the excess oxygen accommodated interstitially in the lattice.[1-3] Jorgensen *et al.*[1] showed that excess oxygen is incorporated as an interstital oxygen defect near the $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ site in the orthorhombic *Fmmm* structure. They observed a two-phase region in the intermediate composition range $(0.02\le\delta\le0.13)$, similar to that observed in $La_2CuO_{4+\delta}$. From density and thermogravimetric measurements on single crystals of $La_2NiO_{4+\delta}$, Schartman and Honig[2] determined the point defect equilibrium and the oxygen pressure dependence of $\delta$ in $La_2NiO_{4+\delta}$ in the range 1000–1200 °C. Based on these results it is now possible to regulate the oxygen stoichiometry by appropriate annealing of the samples.

Several reports[4-6] have dealt with the structural phase transitions in $La_2NiO_{4+\delta}$. For $\delta=0$, the material transforms from the high-temperature tetragonal (HTT) to a low-temperature orthorhombic (LTO) phase close to 680 K.[7,8] A second structural phase transition from the LTO phase to a low-temperature tetragonal (LTT) phase occurs near 70 K.[4,6] The transition at 70 K is accompanied by a change in the antiferromagnetic spin structure.[6,9]

Buttrey *et al.* were the first to perform magnetic susceptibility measurements on single crystals of $La_2NiO_{4+\delta}$ as a function of $\delta$.[10] In the absence of thermogravimetric data on this system at the time, their control over oxygen stoichiometry could not be known precisely. The weak ferromagnetic component detected at low temperatures led to the suggestion that $La_2NiO_{4+\delta}$ is a canted antiferromagnet. Their measurements were limited to three values of $\delta$ and to temperatures between 77 and 300 K. Their results demonstrated that stoichiometry considerations cannot be ignored in this system. Later, Schartman *et al.*[11] undertook the study of the high temperature magnetic susceptibility of well-characterized single crystals of $La_2NiO_{4+\delta}$, where it was demonstrated that stoichiometric $La_2NiO_4$ orders antiferromagnetically, with a Néel temperature $T_N = 650$ K. On combining the results of Buttrey *et al.*[10] and Schartman *et al.*,[11] it appears that the antiferromagnetic ordering temperature at 650 K for $\delta = 0$ decreases to below 200 K for $\delta \simeq 0.034$. The spectacular drop in the ordering temperature with a small variation in $\delta$ is thus evident, but the nature of this depression, and whether it is continuous or discontinuous, needs a more detailed and systematic study. More recently, Aeppli and Buttrey[9] have reported on the magnetic properties of samples with $\delta = 0$ and 0.05. In their work, the Néel temperature for $\delta = 0.05$ was found to be 70 K, while the $\delta = 0$ sample was found to be antiferromagnetically ordered at room temperature, consistent with the earlier findings of Schartman and Honig.[11] Other magnetic measurements for stoichiometric $La_2NiO_4$ have led to occasional observations of a minority superconducting phase.[12–15] Lastly, some compositions with $\delta \geq 0.06$ have recently been characterized using neutron-diffraction;[16] these indicate that the Néel temperature for samples with $\delta = 0.065$, 0.067 and 0.077 are 74, 68, and 49 K, respectively.

Thus, though many prior magnetic studies have already been performed on the $La_2NiO_{4+\delta}$ system, a complete systematic investigation of the magnetic properties and their dependence on oxygen stoichiometry is lacking. Also, very few investigations have probed the behavior of the system below 77 K. The objective of this paper is twofold: First, we report a systematic study on single crystals of $La_2NiO_{4+\delta}$ over the composition range $0 \leq \delta \leq 0.067$, to probe the dependence of the magnetic ordering on oxygen stoichiometry. Second, we report measurements extending the temperature range from 4 to 900 K. Besides discussing the discontinuity in the $\delta$ dependence of $T_N$, we also report observations on the time dependence of the remanent magnetic moment below 20 K, and suggest an interpretation for this behavior.

## II. EXPERIMENTAL WORK

Single crystals of $La_2NiO_{4+\delta}$ were grown using a radio-frequency skull-melting technique.[17] Tetragonal crystals thus obtained were oriented using the Laue technique, and cut to obtain faces parallel and perpendicular to the *c* axis. Following the thermogravimetric results of Schartman and Honig,[2] crystals usually measuring about $0.5 \times 0.3 \times 0.2$ cm$^3$ were annealed in a controlled $CO/CO_2$ atmosphere at 1273±5 K for 24 hours to fix the desired oxygen content. The oxygen fugacity was monitored using a zirconia-yttria oxygen-transfer cell. The estimated uncertainty in $\delta$ is $\pm 0.001$.[2] Samples were quenched after the anneal and the surface layers of the crystal were removed by polishing to ensure a uniform and homogeneous oxygen concentration. Samples were stored in sealed containers under argon atmosphere.

Magnetic measurements at low temperatures (4–300K) were performed on a vibrating sample magnetometer (VSM) or a SQUID magnetometer. A Faraday balance was used for the high-temperature (365–900 K) measurements. Room-temperature x-ray powder diffraction analyses were carried out on a Siemens Diffrac 500 diffractometer on all compositions for which magnetic measurements were undertaken.

## III. RESULTS

### A. Magnetic measurements

Figure 1(a) shows the temperature dependence of $\chi^* \equiv M/H$, where $M$ is the magnetization and $H$ is the applied field, for a sample with $\delta = 0$ and the applied field along the *c* axis. Above 650 K, the magnetization is temperature-independent, consistent with the fact that the system undergoes an insulator to metal transition with rising temperature at 650 K.[18] Below 650 K, the magnetization increases with decreasing temperature and exhibits a nonlinear field dependence. Note that $\chi^*$ decreases as $H$ is increased. Figure 1(b) exhibits the temperature dependence of $\chi^*$ with the applied field now in the basal (*a*-*b*) plane, showing that an anisotropy in magnetic behavior arises below 650 K. Recent neutron-

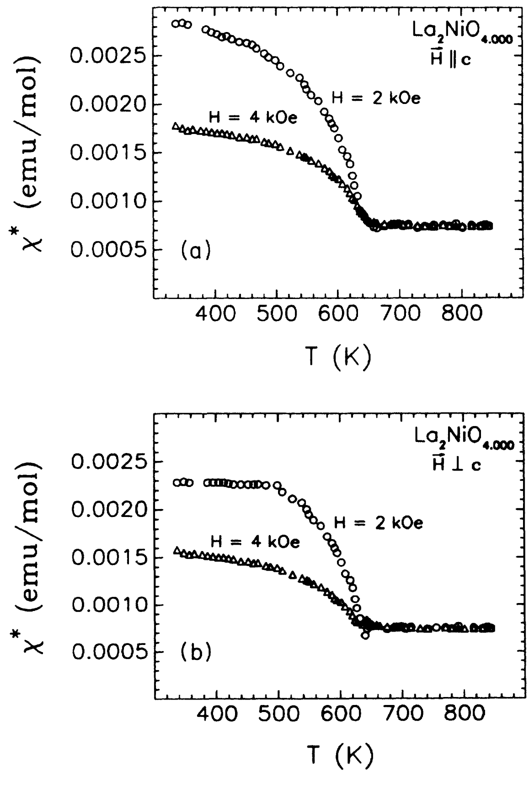


FIG. 1. (a) $\chi^* = M/H$ as a function of temperature for $La_2NiO_4$ ($\delta = 0$), with the applied magnetic field along the *c* axis. (b) $\chi^* = M/H$ as a function of temperature for $La_2NiO_4$ ($\delta = 0$) with the applied magnetic field perpendicular to the *c* axis.

diffraction results have indicated antiferromagnetic ordering at room temperature,[9] with our results suggesting the antiferromagnetic ordering temperature to be $T_N = 650$ K for $\delta = 0$, consistent with earlier findings.[11] The decrease in $\chi^*$ in Figs. 1(a) and 1(b) with increasing magnetic fields at $T < 650$ K can be understood on the basis of the room temperature $M(H)$ plot shown in Fig. 2. The high field linear portion extrapolates to a nonzero intercept; thus, the $M(H)$ curve is a superposition of a small parasitic ferromagnetic saturation component and a linear paramagnetic component. The data in Fig. 1 were obtained in low magnetic fields, where the magnitude of the saturating component is comparable to that of the linear component, thereby leading to a lowering of $\chi^*$ with increasing magnetic field. A small remanence and hysteresis in the $M(H)$ behavior at 300 K again is indicative of parasitic ferromagnetism which arises from the slight canting of the antiferromagnetically ordered spins. Our susceptibility data for $\delta = 0$ are in good agreement with earlier observations.[11] The data of Figs. 1 and 2 are typical of all compositions in the range $0 \leq \delta \leq 0.004$.

The results shown in Fig. 3 are typical of the temperature dependence of $\chi^*$ for $\delta \geq 0.005$. As seen from the inset, there is evidence for the onset of antiferromagnetic ordering near 210 K for a sample with $\delta = 0.005$.

As the oxygen stoichiometry is increased to a value of $\delta = 0.039$, the $M(T)$ appears as shown in Fig. 4. The cusp in the magnetic moment near 135 K marks the onset of antiferromagnetic order. We attribute the peak at 25 K in the basal plane to a weak ferromagnetic phase, as inferred from the $M(H)$ behavior below 25 K. The nature and the origin of this transition appears similar to that of the canting discussed later.

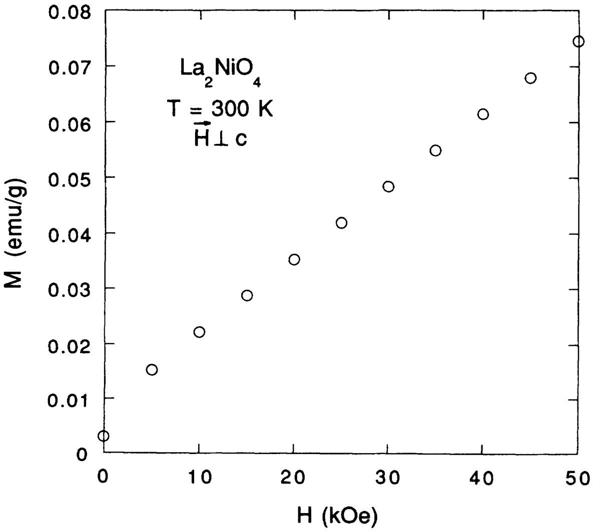


FIG. 2. Magnetization as a function of the magnetic field at 300 K for $\delta = 0$, with the applied field along the $c$ axis.

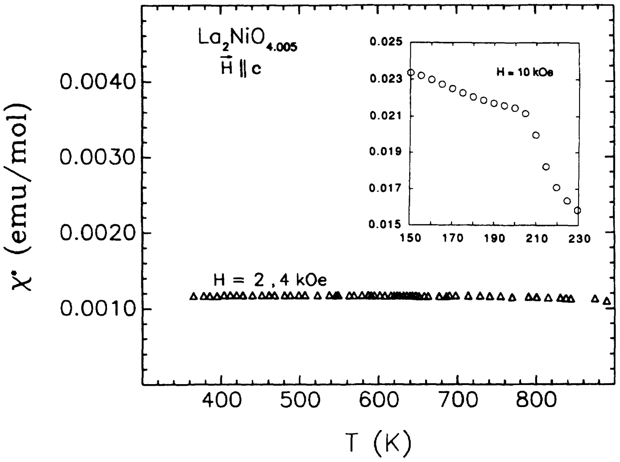


FIG. 3. $\chi^*$ as a function of temperature for La$_2$NiO$_{4+\delta}$; $\delta = 0.005$, with magnetic field along the $c$ axis. The inset shows the antiferromagnetic ordering transition near 210 K.

The $M(T)$ behavior and the temperature dependence of $\chi$ and $1/\chi$ (inset) for $\delta = 0.058$ are shown in Fig. 5. While we infer a Néel temperature of $T_N = 55$ K, we again observe the additional low-temperature peak when the applied field is along the basal plane. For compositions with a large value of $\delta$, a Curie-Weiss behavior begins to appear, as shown in the inset. A numerical fit to the Curie-Weiss law of the form $\chi = C/(T - \Theta)$ yields $\mu_{\text{eff}} = 0.64\mu_B$, $\Theta_{ab} = -154$ K, and $\Theta_c = -205$ K, where $\mu_{\text{eff}}$ is the effective moment, and $\Theta$ is the Curie temperature.

Upon increasing $\delta$ to the composition range $0.055 \leq \delta \leq 0.067$, a relaxation effect of the remanent magnetic moment was encountered below 20 K. In these measurements, the temperature was first stabilized; next, a magnetic field was applied, and the field was then rapidly lowered to zero. The initial time ($t = 0$) is defined to be the instant when the magnetic field drops to zero. The remanent moment decayed with time $t$ in the manner

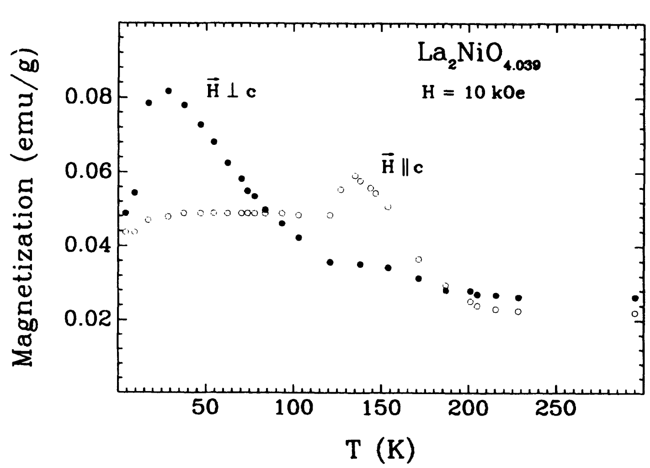


FIG. 4. Temperature dependence of the magnetization for $\delta = 0.039$, with applied field both parallel and perpendicular to the $c$ axis.

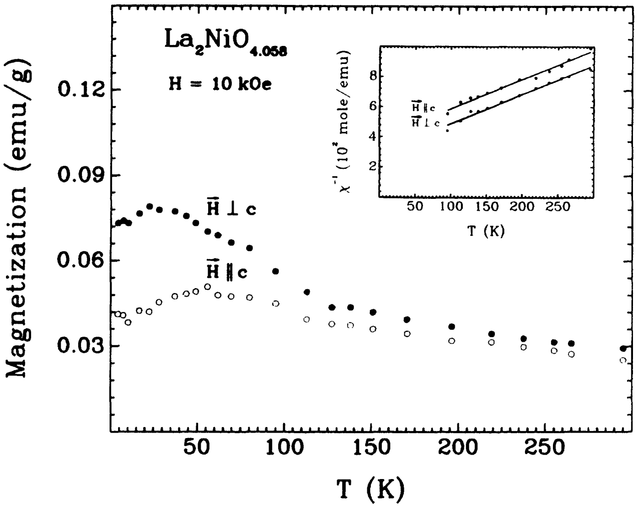


FIG. 5. Temperature dependence of the magnetization for $\delta=0.058$. The inset shows the $\chi^{-1}(T)$ variation above $T_N$.

shown in Fig. 6 for $\delta=0.06$. The decay in remanent moment was found to be linear in $\log t$ (see inset). It should be carefully noted that this phenomenon was observed only when the field was applied perpendicular to the $c$ axis. A similar phenomenon has also been encountered in our earlier studies on the $La_{2-x}Sr_xNiO_4$ system.[19] A possible interpretation of this behavior in terms of the properties of an anisotropic spin-glass phase is discussed in the next section.

### B. Structural characterization

The variation of the lattice parameter with $\delta$ in Fig. 7, obtained using x-ray diffraction,[20] shows that as $\delta$ is reduced, the difference between the $a$ and $b$ cell parameters grows. Since the $c$ parameter increases systematically with $\delta$, the oxygen interstitials are believed to be accommodated at the lattice sites between the LaO layers, in agreement with the point defect equilibrium hypothesis and the density measurements.[1,2] Interstitial accommodation between the LaO layers is facilitated by the positive charge of the $La_2O_3$ layers; the introduction of a negatively charged defect species between the layers obviously helps stabilize the lattice. In such a situation, any deviation from stoichiometry should increase the $c$ parameter, in agreement with our observations. Consistent with these observations, we also observe that as $\delta$ is reduced from 0.07 to 0 (for the stoichiometric sample), the (200) peak in the tetragonal phase of the large $\delta$ sample begins to broaden and shows signs of splitting into the (200) and (020) peaks. Definitive splitting begins to emerge at or below $\delta=0.01$.

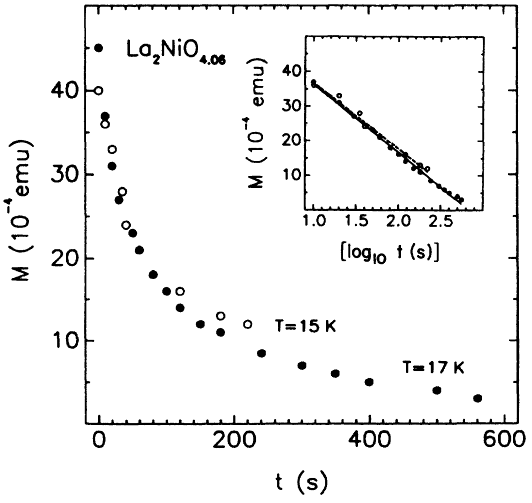


FIG. 6. Time dependence of the remanent magnetization for $\delta=0.06$. The inset shows the dependence of remanent magnetization with $\log t$.

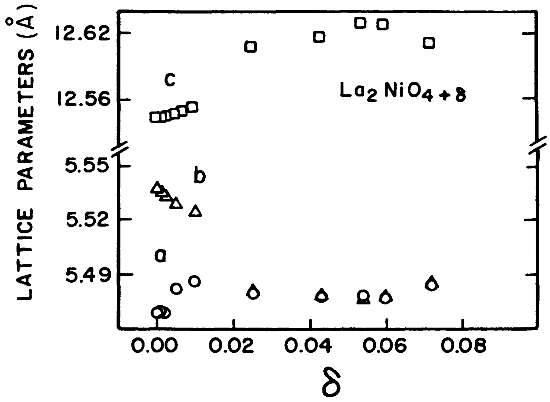
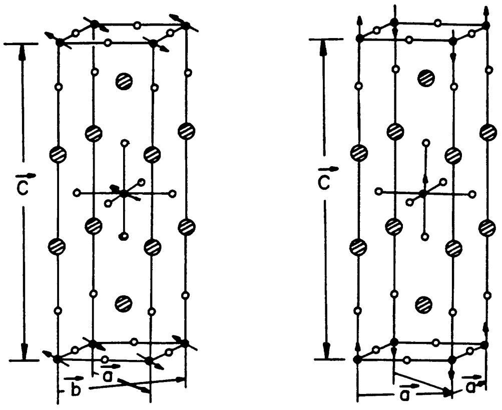


FIG. 7. Variation of the lattice parameters with $\delta$ at room temperature for $La_2NiO_{4+\delta}$.

We therefore conclude that at room temperature, for the range of $\delta$ between 0.06 and 0.01, a tetragonal phase persists, but as $\delta$ is lowered further towards the stoichiometric limit, the orthorhombic phase is observed. Thus, at room temperature, there appears to be a critical composition around $\delta=0.01$ where the structure undergoes a transformation from the tetragonal high $\delta$ limit to an orthorhombic low $\delta$ limit. Our systematic studies are in agreement with prior observations on samples with large $\delta$ which are believed to be tetragonal,[18] while those with $\delta$ approaching zero are orthorhombic.[21]

## IV. DISCUSSION

The $La_2NiO_4$ structure is an orthorhombic distortion of the $K_2NiF_4$ structure. These compounds differ in the antiferromagnetic alignment of their magnetic moments, as shown in Fig. 8. Using neutron-diffraction techniques, Birgeneau *et al.*[22] demonstrated that, as the temperature was lowered to 97 K, the spin correlations within the $NiF_2$ layers in $K_2NiF_4$ increased, with an onset of three-dimensional ordering at $T_N=97.2$ K. The magnetic structures of $La_2NiO_4$ and $K_2NiF_4$ are similar with ordering in the former involving alignment of the Ni moments along the $a$ axis in the basal plane, while in the latter the



(a) (b)

$La_2NiO_{4+\delta}$ (Bmab) $K_2NiF_4$ type (I4/mmm)

$\vec{S} \parallel [100]$ $\vec{S} \parallel [001]$

FIG. 8. The magnetic structure of (a) $La_2NiO_{4+\delta}$ and $K_2NiF_4$. The large shaded circles represent La in (a) and K in (b), while the small open circles represent O in (a) and F in (b). The closed circles represent Ni in both (a) and (b).

moments align along the $c$ axis. In both cases, there is no net coupling between nearest-neighboring Ni planes; instead, coupling occurs between next-nearest neighbor planes. While $K_2NiF_4$ and $La_2NiO_{4+\delta}$ have obvious similarities, the electrons in $K_2NiF_4$ are localized, and this compound is well described by the Heisenberg model. In contrast, the electrons in $La_2NiO_4$ ($\delta=0$) are itinerant above $T_N$, making it inappropriate to apply the Heisenberg model.

Our findings are in agreement with earlier work which showed that large correlations within the NiO layers are responsible for the high ordering temperature ($T_N=650$ K) of stoichiometric $La_2NiO_{4+\delta}$.[11] The temperature dependence of $\chi^*$ for $T<T_N$, shown in Fig. 1, is anomalous. Similar results have, however, been observed for the $BiPbSr_2MnO_6$ and $BiPbCa_2MnO_6$ systems,[23] and also in $LaTiO_3$.[23] The sudden decrease in $\chi^*$ with rising $T$ near $T_N$ may signal the disappearance of the canting associated with the antiferromagnetic order at about 650 K. Such canting can occur as a result of the Dzialoshinskii-Moriya antisymmetric superchange interaction.[24,25] A necessary condition for this interaction to have a nonzero contribution is the absence of the inversion center of symmetry. The tetragonal $K_2NiF_4$ does possess an inversion center of symmetry; however, the tilting of the nearest-neighbor $NiO_6$ octahedra in opposite directions away from the $c$ axis in the (001) plane of the distorted structure[18] removes the inversion symmetry that would otherwise be present in the undistorted structure, thereby enabling an antisymmetric superexchange interaction that can give rise to the canting. Since an insulator-metal transition occurs close to 650 K for stoichiometric $La_2NiO_4$,[7,18] the decrease in the $\chi^*$ may also be connected with the closing of the gap that accompanies this transition near $T_N$. The metallic nature of $La_2NiO_4$ and the temperature dependence of $\chi^*$ suggest a Pauli-like paramagnetic behavior above 650 K.

Figure 4 shows that for samples with $\delta \geq 0.005$, a prominent cusp develops in $\chi^*$ at a temperature near 135 K which we interpret to be the Néel temperature. The maximum in $\chi^*$ is observed only for fields applied along the $c$ axis. On the basis of neutron scattering data, Aeppli and Buttrey[9] have shown that for $\delta=0.05$ the system orders antiferromagnetically at $T_N \simeq 70$ K. Our measurements on a similar composition yields a maximum in susceptibility along the $c$ axis ($\chi_{\parallel}^*$) at $T_N \simeq 73$ K. We have used this correspondence to interpret the maximum in $\chi_{\parallel}^*$ as an indication of the Néel temperature $T_N$ for the range $0.005 \leq \delta \leq 0.058$. The observation of the maximum in $\chi^*$ along only one crystallographic direction is a consequence of the strong anisotropy in $La_2NiO_{4+\delta}$.

The variation of $T_N$ with $\delta$ for $La_2NiO_{4+\delta}$ has been plotted in Fig. 9. The ordering temperature is nearly composition-independent in the regime $0 \leq \delta \leq 0.004$, with $T_N \simeq 650$ K. It is possible to correlate the sudden discontinuity in $T_N$ near $\delta=0.005$ with structural changes. As our results indicate, room-temperature x-ray diffraction experiments reveal a decreasing degree of orthorhombicity with increasing $\delta$. For $\delta \geq 0.01$, we find the material to be tetragonal at room temperature, while compositions with $\delta \leq 0.01$ are orthorhombic. The association of the discontinuity in $T_N$ at $\delta=0.005$ with a structural change is thus supported by the change in the structure from a tetragonal to an orthorhombic phase shown in Fig. 7 to occur around $\delta \simeq 0.01$. The existence of a biphasic region in the composition range $0.005 \leq \delta \leq 0.01$ cannot be ruled out, though prior structural studies indicate that the biphasic region extends over the range $0.02 \leq \delta \leq 0.13$.[1] Unlike the cuprates, where a small amount of oxygen excess destroys magnetic ordering,[26] we observe that the ordering in $La_2NiO_{4+\delta}$ persists over a broader range of oxygen stoichiometry. A similar discontinuity in the Néel temperature has also been observed[27] in the $YBa_2Cu_3O_{6+x}$ system, where the $T_N$ changes slowly until the

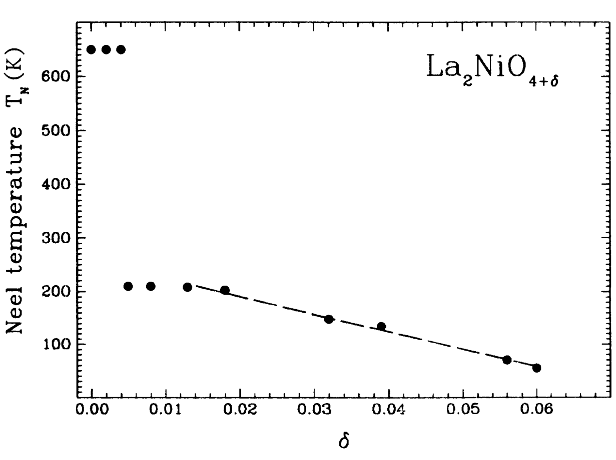


FIG. 9. Variation of the Néel temperature $T_N$ with $\delta$ for $La_2NiO_{4+\delta}$.

tetragonal-to-orthorhombic transition is approached, at which point it quickly falls to zero, followed by the onset of superconductivity as $x$ is increased further. In $La_2NiO_{4+\delta}$, the tetragonal phase appears at the point of discontinuity; the dependence of the Néel temperature in the tetragonal phase on $\delta$ is discussed below.

In the tetragonal phase, one anticipates some sensitivity of the magnetic ordering temperature to lattice distortions. Aeppli and Buttrey[9] report that the tetragonal configuration of the lattice is frustrated in the sense that there is no unique manner of stacking consecutive antiferromagnetic layers. Therefore, even a small concentration of defects in the slightly orthorhombic version of the lattice is likely to alter $T_N$ substantially. Furthermore, holes introduced by excess oxygen in $La_2NiO_{4+\delta}$ influence $T_N$ strongly for $0.005 \leq \delta \leq 0.06$. The hole wave functions are rather localized since the system is likely a semiconductor with a hopping-type conductivity;[18] there is no indication of an energy gap corresponding to the conductivity activation energy in the infrared spectrum. However, these hole wave functions may have a large radius since the conductivity activation energy is very small ($\varepsilon_a \simeq 30$ meV). Thus, the holes influence the exchange interactions in the plane, thereby reducing the correlation length between the spins in the same plane, and hence, $T_N$. While proposing the magnetic phase diagram of $La_2CuO_{4-y}$, Aharony *et al.* argued that the excess oxygen introduces holes that provide an effective ferromagnetic interaction between the Cu ions, thus frustrating the antiferromagnetic ordering.[26]

It has also been argued, on the basis of neutron scattering studies,[16] that the magnetic correlation length varies inversely with $\delta$. Our findings of a composition-independent regime between $\delta=0$ and 0.004 is in conflict with this prediction, since the identical $T_N$ for this range implies that the in-plane correlation length for those compositions should be similar. It was also inferred from neutron-diffraction experiments[16] that the oxygen interstitial defects resulting from $\delta>0$ would reduce the correlation length and hence, $T_N$. Our observations in Fig. 8 are in agreement with this observation for $\delta \geq 0.005$.

The interstitial accommodation of oxygen requires a local lattice distortion. There is general agreement that incorporation of excess oxygen in $La_2NiO_{4+\delta}$ is accompanied by a distortion of the $NiO_6$ units.[1,18] This significantly alters the Ni-O-Ni superexchange interactions, and appears to lower $T_N$. This provides another rationale for the suppression of magnetic ordering with increasing deviations from ideal oxygen stoichiometry.

Finally, as seen in Fig. 6, for $\delta$ between 0.055 and 0.067 a time dependence of the remanent magnetic moment has been encountered. In addition, below $T_N$, a cusp was observed in the $M(T)$ behavior near 18 K. This time dependence of the remanence, together with the maximum observed in $M(T)$, is interpreted as indicating a transition to a spin-glass phase. The suggestion of possible spin frustration in the tetragonal phase of $La_2NiO_{4+\delta}$ from neutron scattering studies[9] is confirmed in our experiments. The time dependence in Fig. 6 is observed only when the field is applied in the basal plane; thus only the in-plane component of the remanence exhibits this behavior. This suggests that the spin-glass state is highly anisotropic. The magnetic anisotropy and the spin-glass anisotropy reflects the quasi-two-dimensional structure of the material. The spin-glass transition temperature is estimated in our studies to be near 17 K.[19,28]

## V. CONCLUSIONS

We have demonstrated that even a small amount of oxygen excess alters the magnetic ordering in $La_2NiO_{4+\delta}$. This is reflected in the sudden drop of $T_N$ with $\delta$ above 0.005. We believe that the origin of this discontinuity is a structural transition. In the tetragonal phase, the Néel temperature decreases with increasing $\delta$ in a linear fashion. This we believe to be due to magnetic frustration caused by the holes that are generated by excess oxygen. In the cuprates, a small amount of oxygen excess destroys magnetic ordering.[26] However, the ordering in $La_2NiO_{4+\delta}$ persists over a broader range of oxygen stoichiometry. This may be due to the near-localization of the holes, which differs from $La_2CuO_{4-\delta}$, where the holes are believed to be itinerant.

A time dependence of the in-plane component of the remanent magnetization has been encountered. The variation of the remanent moment with $\log t$ is characteristic of a spin-glass state. The time dependence is observed only when the field is applied in the basal plane; thus, the spin-glass state is highly anisotropic.

We tentatively attribute the variation of $T_N$ with $\delta$ as arising from the structural distortion brought about by changes in oxygen stoichiometry. In particular, the changes in the nature of the variation of the $\delta$ dependence of $T_N$ reflects the change in the magnetic structure induced by structural instabilities in the material. In order to compare the role of Sr doping with that of oxygen excess on the magnetic ordering, since in both cases one introduces holes in the system, studies on the $La_{2-x}Sr_xNiO_4$ system have been undertaken and are currently in progress.

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