Anomalous structural phase transition in stoichiometric La$_2$NiO$_4$

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A detailed neutron-powder-diffraction experiment as a function of temperature has revealed the existence of a reversible structural transition at about 80 K in stoichiometric La$_2$NiO$_4$. This phase transition is characterized by the anomalous behavior of the orthorhombic strain with no apparent change of the space group (*Cmca*). Structure refinements demonstrate that the elastic anomaly arises from a sudden rotation of the equatorial plane of Ni octahedra [Ni-4O(1)] which becomes orthogonal to the elongation axis [O(2)-Ni-O(2)], thus increasing the effective local symmetry of Ni sites at temperatures below 80 K. This anomalous structural behavior is strongly dependent on the Ni^{+3} content and, up to now, has been observed only in the stoichiometric brown compound La$_2$NiO$_{4.00}$, which is three-dimensional-antiferromagnetically ordered below room temperature. These findings demonstrate that the similar transition observed in the parent copper oxides is a feature common to a number of layered perovskites and probably not directly related to superconductivity.

Layered perovskites La$_2$NiO$_{4+x}$ have been extensively studied in relation to their magnetic and transport properties.[1-10] However, most of these studies were performed on samples of unknown stoichiometries, and the spread of the results obtained by different authors is most likely explained by different content of Ni^{+3} in the samples.

Transport properties measured on La$_2$NiO$_{4+x}$ indicate an evolution from semiconductor-to-metallic behavior between 500–620 K.[1,2,4,7,9] The semiconducting properties have been explained[2,4] as resulting from the splitting of the $\sigma^*_{x^2-y^2}$ band due to the presence of short-range magnetic order. When the temperature is raised, the gap between $\sigma^{*1}_{x^2-y^2}$ and $\sigma^{*2}_{x^2-y^2}$ bands decreases to finally vanish when the local magnetic order is destroyed and the material becomes metallic.

Magnetic-susceptibility measurements on different samples[3,5,7,10] exhibit rather large variations due once again to poorly defined compositions. The most detailed and reliable susceptibility measurements were performed on single crystals by Buttrey, Honig, and Rao.[10] Their results show clear indication of magnetic ordering in nearly stoichiometric samples ($x \sim 0$).

Structural characterizations of La$_2$NiO$_{4+x}$ samples are, by far, less detailed than the physical properties measurements. Earlier works[4,11,12] describe the structure as isomorphous to K$_2$NiF$_4$-*I4/mmm*. Electron diffraction (7) has shown the existence of superlattice reflections corresponding to an orthorhombic $a\sqrt{2} \times a\sqrt{2} \times c$ distortion of the tetragonal cell. Recently, an orthorhombic form of La$_2$NiO$_{4+x}$ with space group *Pban* has also been reported;[13] we will show hereafter that the latter space group is erroneous.

All previous results point to a very strong dependence of both structural and physical properties on x. The interest of this material is now enhanced by the explosive experimental and theoretical work on related high-T_c supercon-

ductor cuprates: La$_2$NiO$_{4+x}$ is structurally very similar to La$_2$CuO$_4$ which belongs to the family of 40-K superconductors and better knowledge of its properties can give some insight into the mechanism of superconductivity. In particular, a number of recent papers on the parent cuprates[14-16] suggest a correlation between the low-temperature structural-elastic anomalies and the superconducting properties of these materials, which would support the theories based on phonon-mediated pairing mechanisms. As stoichiometric La$_2$NiO$_4$ is semiconducting and magnetically ordered below room temperature, the existence of similar structural anomalies in this material would clearly be independent of any electron ordering (and superconducting properties) and would point to a simpler mechanism for the transition. In the present Rapid Communication, we report the powder-diffraction study of stoichiometric La$_2$NiO$_4$ ($x = 0$) which shows an unusual and previously unobserved structural behavior at low temperature.

Stoichiometric La$_2$NiO$_4$ is a brown material, clearly distinct from the black oxidized La$_2$NiO$_{4+x}$ (the black color results from the presence of small amounts of Ni^{+3}). The reduction of La$_2$NiO$_{4+x}$ at high temperature is rather difficult to control, and often yields small amounts of metallic Ni and lanthanum oxide. The sample preparation method is described elsewhere[17] and involves reduction of the oxidized precursor (obtained by standard ceramic procedures) at relatively low temperature (510 K) under a dry-hydrogen atmosphere and a careful monitoring of the reduction process by thermogravimetry. Chemical analysis could not detect the presence of Ni^{+3} in the freshly prepared material. We found that La$_2$NiO$_{4.00}$ is unstable under normal storage conditions and easily reacts with atmospheric moisture to give small amounts of lanthanum hydroxide La(OH)$_3$. Therefore, special care was taken to avoid degradation of the sample

used for this study. In contrast with the oxidized materials, which are tetragonal, x-ray diffraction shows that $La_2NiO_{4.00}$ is orthorhombic at room temperature. We observed the transition from the high-temperature tetragonal (assumed to be $I4/mmm$ K_2NiF_4) to the orthorhombic symmetry to occur at approximately 700 K. The neutron-diffraction experiment was carried out at the high-flux powder diffractometer D1B of the Institute Laue-Langevin, Grenoble. D1B is equipped with a 400-cell position-sensitive detector (PSD) spanning an angular range of 80° (2θ). The use of a fixed PSD enables us to obtain a very high relative accuracy in the evolution of cell parameters. The sample was held in a helium cryostate and its temperature was varied linearly from 3 to 275 K at a rate of 0.33 K/min. A diffraction pattern was extracted every 3 min, thus giving a difference of 1 K between two consecutive sets of data. The complete data consist in a set of 321 patterns, which were analyzed with the Young-Wiles option[18] of the STRAP package[19] designed for automatic Rietveld refinement of large sets of sequential powder-diffraction patterns.

All data, taken in 1-K steps, were refined in the space ground $Cmca$; the space group $Fmmm$ (Ref. 14) is precluded by the observation of nuclear reflections (122) and (221) forbidden by F centering. The space group $Pncb$ (standard setting $Pban$) was previously proposed for La_2NiO_4 by Odier, Leblanc, and Choisnet[13] to account for the reflection (011); both neutron polarization analysis and the temperature dependence of the integrated intensity of this line have shown[20] its magnetic origin which rules out the latter space group. $Pccn$ (Ref. 21) which is a subgroup of $Cmca$ would also be compatible with the observed nuclear reflections; however refinement in this group does not improve the fits in spite of the larger number of independent structural parameters. The final $R_{nuclear}$ factors for the 321 patterns range from 3.8% to 4.5%. The limited angular range (80° in 2θ) covered by the PSD and long wavelength (2.52 Å) precludes the refinement of individual temperature factors; therefore, only an overall temperature factor was refined. The number of positional parameters is only five whereas the number of nuclear Bragg peaks is twenty five, which is sufficient to determine the main geometrical features of the transition.

Figure 1 shows the temperature variation of the powder-diffraction patterns of $La_2NiO_{4.00}$. The most striking effect is the merging of the reflections (002)-(200) and (022)-(220) upon cooling, at a temperature near 80 K. The transition is reversible, but we have not yet studied a possible hysteresis under cycling the temperature around T_c. The thermal evolution of the most important geometric parameters is represented in Fig. 2(a) and 2(b). The phase transition is first characterized by a reduction of the orthorhombic splitting (or spontaneous strain) $s_0 = 2(c-a)/(a+c)$. Upon cooling from room temperature (RT), the strain parameter increases monotonically, reaches a maximum value at about 100 K, which is the onset temperature of the transition, then falls off. The volume expansion (Fig. 3) also changes sharply at the transition temperature. The structural parameters involved in the transition are essentially related with the
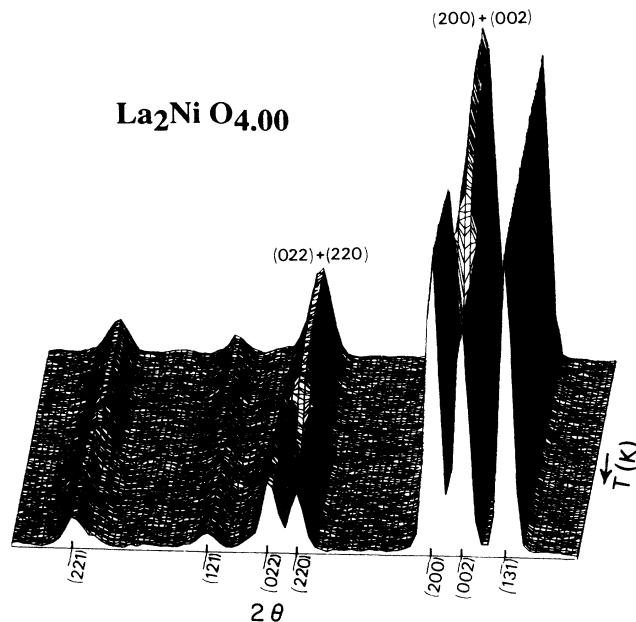

FIG. 1. Thermal evolution of the neutron-powder-diffraction pattern of $La_2NiO_{4.00}$ in the temperature range 3 to 275 K ($\lambda = 2.52$ Å, sampling: 1 K/pattern).

geometry of the $(Ni-O_6)$ octahedra. As shown in Fig. 4(a), the Ni^{+2} octahedron is tilted around the a axis, in such a way that the basal plane of the octahedron makes an angle α_1 with the basal plane (a,c) of the unit cell; this angle is smaller than the angle α_2 defined by the long axis of the octahedron O(2)-Ni-O(2) and the b axis of the unit cell. The local symmetry of the Ni cations is monoclinic $2/m$ as required by the Wyckoff position [Fig. 4(a)] of $Cmca$. A temperature decrease below room temperature first induces a rotation of the (rigid) octahedra thus increasing the orthorhombic distortion while preserving the difference of about 1.5 degrees between α_1 and α_2. At the transition temperature $T_c = 80$ K, the angle α_1 unexpectedly increases and becomes equal to α_2 [Fig. 4 (b)]. This experimental result implies that, within the limits of experimental errors, the effective local symmetry of Ni *increases* below 80 K and becomes close to orthorhombic mmm. The change of the tilt angles is accompanied by a sharp increase (by about 0.003 Å) of the distances Ni-O(1) in the basal plane. The distance Ni-O(2) decreases monotonically from room temperature and does not exhibit any sharp change at the transition temperature.

The transition at 80 K is accompanied by a jump in magnetic susceptibility; below room temperature $\chi(T)$ is temperature independent down to ~ 100 K, but shows a sharp increase close to ~ 80 K and stays nearly constant at lower temperatures. The thermal evolution of the intensity of the strongest magnetic reflection (011) does not exhibit any anomaly at the transition temperature. This fact does not preclude, however, a small canting of the spins not detected by neutron-powder diffraction. Indeed, the structural transition is driven by the elastic properties of the La_2NiO_4 lattice and particular features of the interatomic potentials; small variations of the angles of su-
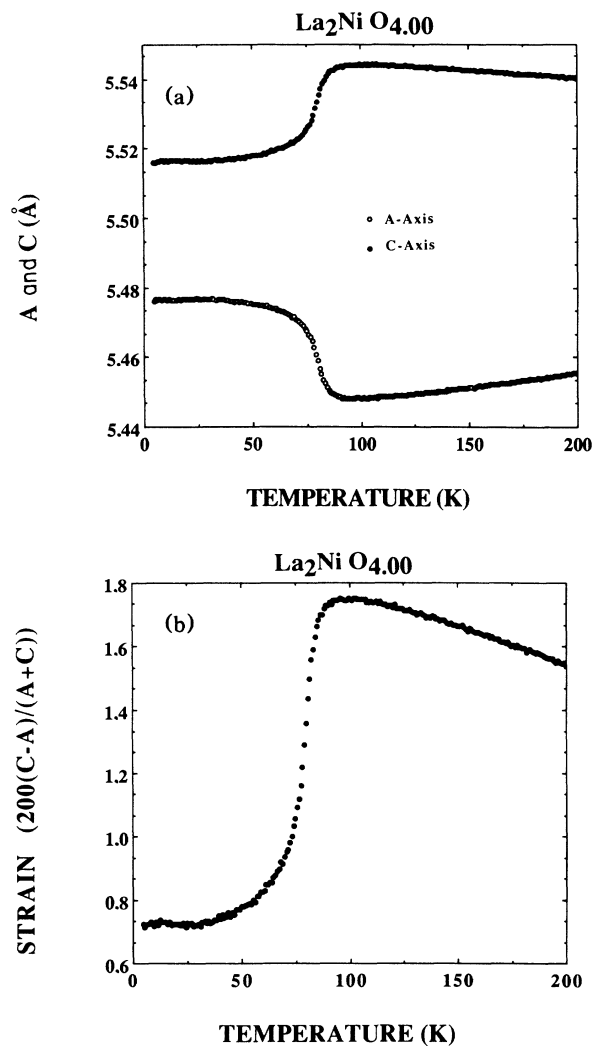
La$_2$Ni O$_{4.00}$

La$_2$Ni O$_{4.00}$

FIG. 2. Temperature dependence of (a) the in-plane unit-cell constants (a,c) and (b) the strain parameter s_0 of La$_2$NiO$_{4.00}$.

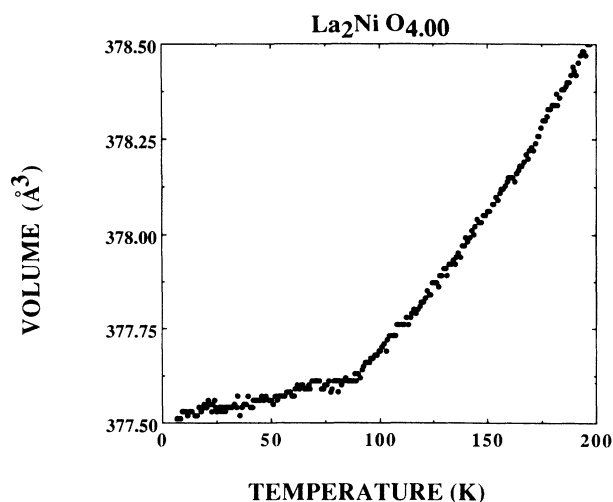## La$_2$Ni O$_{4.00}$

FIG. 3. Temperature dependence of the unit-cell volume of La$_2$NiO$_{4.00}$.

La$_2$Ni O$_{4.00}$

(a)

La$_2$Ni O$_{4.00}$

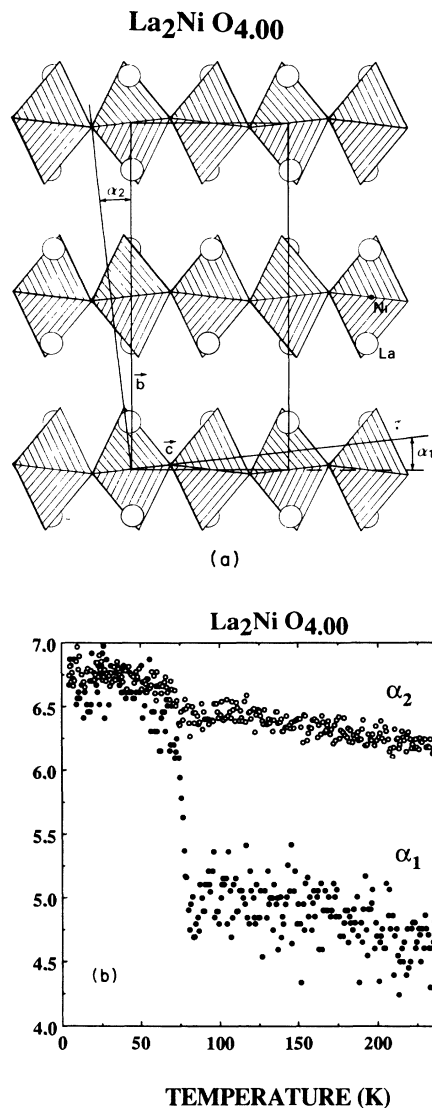FIG. 4. (a) View of the structure of La$_2$NiO$_{4.00}$ along [100], showing the tilt angles of Ni octahedra. (b) Temperature dependence of tilt angles α_1 and α_2.

perexchange $\theta(O(1)$-Ni-$O(1))$ could be the responsible (through the $\cos^2\theta$ dependence of the exchange integrals) of the appearance of a weak ferromagnetic component giving rise to the jump in susceptibility.

Oxidized samples La$_2$NiO$_{4+x}$ display both semiconductor to metallic electrical resistivity at high temperature and lack of three-dimensional (3D) long-range antiferromagnetic (AF) ordering[1-5] at low temperature. A sample of nominal composition La$_2$NiO$_{4.04}$ was found to be tetragonal, and in contrast with the findings of Aeppli and Buttrey[22] on a more oxidized single crystal, we have not detected any structural nor magnetic ordering transition between 4 K and room temperature.

A structural anomaly similar to that of La$_2$NiO$_{4.00}$, although less pronounced, has been reported previously for (La,Ba)$_2$CuO$_4$, and tentatively correlated with changes in

electrical resistivity.[14] Moreover, lattice distortions in La_2CuO_4-based superconductors have been analyzed from a theoretical point of view in relation with the coexistence of a Peierl distortion and conventional BCS state for superconductivity.[15] Recently, some authors[16] suggested that, between the superconducting state in $(La,Ba, Sr)_2CuO_{4-y}$ and the room-temperature state, exists an intermediate state which is probably the result of a subtle orthorhombic-orthorhombic transition and constitutes the "normal" state before the appearance of the superconducting ordering.

At the present stage of our investigation, we are able to confirm in a layered perovskite the existence of a orthorhombic-orthorhombic structural transition whose order parameter is related to the tilting of the $(Ni-O_6)$ octahedra. Since La_2NiO_4 is 3D AF ordered and semiconducting, our observation rules out that the rotations or the magnetic structure are unique in the high-T_c superconductors and sufficient conditions for the high-T_c superconductivity.

The most striking characteristic of La_2NiO_4 is that small changes in stoichiometry lead to drastic changes in their magnetic and structural properties. This feature is the main handicap in preparing homogeneous single crystals of controlled stoichiometry with a size suitable to study the phonon and magnon dispersion relations at low temperature, which is important information in understanding the nature of the described anomaly and getting a deeper insight into the role played by phonons or magnons in the related superconductor cuprates.

[1]P. Ganguly and C. N. R. Rao, Mater. Res. Bull. **8**, 405 (1973).

[2]J. B. Goodenough, Mater. Res. Bull. **8**, 423 (1973).

[3]P. Ganguly, S. Kollali, C. N. R. Rao, and S. Kern, Magn. Lett. **1**, 107 (1980).

[4]J. B. Goodenough and S. Ramasesha, Mater. Res. Bull. **17**, 383 (1982).

[5]K. K. Singh, P. Ganguly, and J. B. Goodenough, J. Solid State Chem. **52**, 254 (1984).

[6]P. Ganguly and C. N. R. Rao, J. Solid State Chem. **53**, 193 (1984).

[7]C. N. R. Rao, D. J. Buttrey, N. Otsuka, P. Ganguly, H. R. Harrison, C. J. Sandberg, and J. M. Honig, J. Solid State Chem. **51**, 266 (1984).

[8]J. Fontcuberta, G. Longworth, and J. B. Goodenough, Phys. Rev. B **30**, 6320 (1984).

[9]H. P. Tavares, Mater. Res. Bull. **20**, 979 (1985).

[10]D. J. Buttrey, J. M. Honig, and C. N. R. Rao, J. Solid State Chem. **64**, 287 (1986).

[11]A. Rabenau and P. Eckerlin, Acta Crystallogr. **11**, 304 (1958).

[12]H. Müller-Buschbaum and U. Lehman, Z. Anorg. Chem. **447**, 47 (1978).

[13]P. Odier, M. Leblanc, and J. Choisnet, Mater. Res. Bull. **21**, 787 (1986).

[14]D. McK Paul, G. Balakrishnan, N. R. Bernhoeft, W. I. F. David, and W. T. A. Harrison, Phys. Rev. Lett. **58**, 1976 (1987).

[15]T. C. Choy and Hong-Xing He, Phys. Rev. B **36**, 8807 (1987).

[16]S. Bhattacharya, M. J. Higgins, D. C. Johnston, A. J. Jacobson, J. P. Stokes, J. T. Lewandowski, and D. P. Goshorn, Phys. B **37**, 5901 (1988); S. Bhattacharya, M. J. Higgins, D. C. Johnston, A. J. Jacobson, J. P. Stokes, D. P. Goshorn, and J. T. Lewandowski, Phys. Rev. Lett. **60**, 1181 (1988).

[17]R. Saez-Puche, J. L. Rodríguez, and F. Fernández, Inorg. Chim. Acta **140**, 151 (1987).

[18]D. B. Wiles and R. Young, J. Appl. Crystallogr. **14**, 149 (1981).

[19]J. Rodríguez, M. Anne, and J. Pannetier, Institut Laue Langevin Report No. 87Ro14T, 1987 (unpublished).

[20]J. Rodríguez-Carvajal, J. L. Martínez, J. Pannetier, and R. Saez-Puche (unpublished).

[21]M. Onoda, S. Shamoto, M. Sato, and S. Hosoya, Jpn. J. Appl. Phys. **26**, L380 (1987).

[22]G. Aeppli and D. J. Buttrey, Phys. Rev. Lett. **61**, 203 (1988).
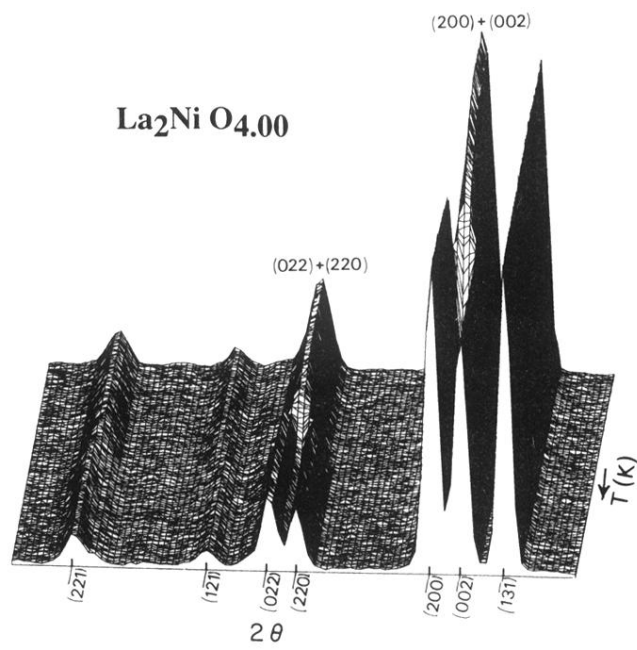
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