

Vacancy Ordering in Anion-deficient LaNiO_3

P. L. Gai and C. N. R. Rao *

Inorganic Chemistry Laboratory, University of Oxford,
Oxford OX1 3QR, England

(Z. Naturforsch. **30a**, 1092–1093 [1975];
received June 7, 1975)

LaNiO_3 loses oxygen in well-defined equilibrium stages. Electron diffraction studies show the presence of superstructure due to vacancy ordering in an anion-deficient sample.

Transition metal oxide systems of perovskite structure, $\text{A}^{3+}\text{B}^{3+}\text{O}_3$ (B = transition metal ion), possessing novel electrical and magnetic properties, are known to exhibit non-stoichiometry on one or more sub-lattices¹. Oxidative non-stoichiometry in LaMnO_3 and LaCrO_3 has been recently examined², but little is known about anion-deficient non-stoichiometry in such systems. We find anion-deficient non-stoichiometry in LaCoO_3 and LaNiO_3 . Of these, LaNiO_3 is particularly unique in that it shows evidence for several well-defined equilibrium phases in the oxygen-loss curve (Figure 1). The stages in Fig. 1 approximately correspond to the

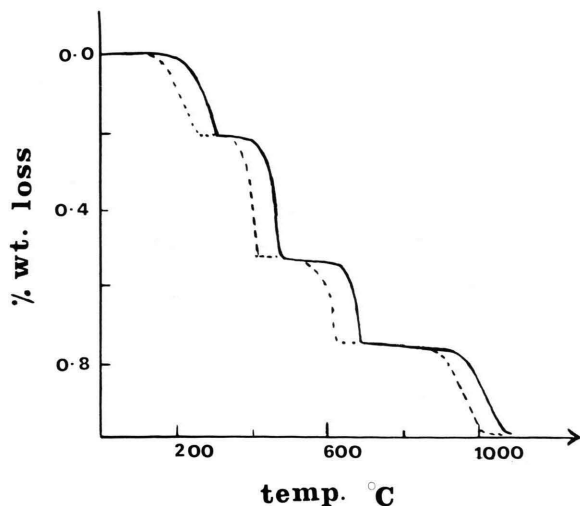


Fig. 1. Thermogravimetric curves of LaNiO_3 in air (broken curve) and in oxygen (full curve).

general formula $\text{La}_n\text{Ni}_n\text{O}_{3n-1}$ with $n = 7, 9, 13$ and 30. X-ray diffraction measurements show that the

* Commonwealth Visiting Professor (1974–75): Address after July 1975: Department of Chemistry, Indian Institute of Technology, Kanpur, India, for reprint requests.

¹ J. B. Goodenough and J. M. Longo, Landolt-Bornstein, New Series, Group III, Vol. 4a, Springer-Verlag, New York 1970.

² B. C. Tofield and W. R. Scott, J. Solid State Chem. **10**, 183 [1974].

³ A. Wold, R. J. Arnolt, and J. B. Goodenough, J. Appl. Phys. **29**, 387 [1958].

rhombohedral unit cell³ of LaNiO_3 is retained in all these compositions and that the cell-volume increases slightly with temperature (oxygen-loss). All the compositions (upto 1% weight-loss in Fig. 1) exhibit metallic resistivities and Pauli-paramagnetism^{4, 5}.

Since X-ray diffraction showed no evidence of superstructure due to vacancy ordering in the anion-deficient LaNiO_3 , we considered it worthwhile to examine the electron diffraction patterns. Freshly prepared LaNiO_3 by the flux method^{3, 6} was heated to 900 K corresponding to 0.75% weight-loss and quenched in liquid nitrogen. The quenched sample was immediately examined under a Siemens 102 electron microscope fitted with a double tilt goniometer state ($\pm 45^\circ$) at an accelerating voltage of 100 keV. A selection of reciprocal lattice sections with the electron beam parallel to [100], [110], and [111] was obtained. Electron diffraction patterns thus obtained with the anion-deficient sample are compared with the patterns of the parent LaNiO_3 (before heating) in Figure 2.

The anion-deficient sample clearly shows weak superlattice spots. The cell dimension of LaNiO_3 measured on the basis of the simple cubic cell is $a_c \approx 3.85 \text{ \AA}$ ($a_{rh} \approx 5.45 \text{ \AA}$) while the anion deficient sample seems to have orthorhombic or body-centred tetragonal symmetry with lattice parameters $a \approx c \approx 2\sqrt{2}a_c$ and $b \approx 2a_c$. Thus, we have established the presence of superstructure due to anion vacancy ordering in anion-deficient LaNiO_3 . Similar superstructures have been recently found in the $\text{SrFeO}_{2.5}\text{-SrFeO}_3$ system^{7, 8}. It appears that electron diffraction is particularly effective in the study of such superstructures caused by vacancy ordering. This may be because of the short wavelength of the electrons and the small size of the domains giving superstructure.

The lattice image of LaNiO_3 showed 3.85 Å fringes where as the anion-deficient sample seemed to show presence of faults. A systematic study of the lattice images of LaNiO_{3-x} for different values of x would be most interesting, although it may be difficult to examine them under equilibrium conditions. Such a study could indeed reveal the presence of well-defined phases similar to the crystallographic shear structures or Magneli phases.

⁴ J. B. Goodenough, J. Appl. Phys. **39**, 403 [1968].

⁵ P. Ganuly and C. N. R. Rao, Mat. Res. Bull. **8**, 405 [1973].

⁶ A. Wold, B. Post, and E. Banks, J. Amer. Chem. Soc. **70**, 4911 [1957].

⁷ C. Greaves, A. J. Jacobson, B. C. Tofield, and B. E. F. Fender, Acta. Cryst. B **31**, 641 [1975].

⁸ B. C. Tofield, C. Greaves, and B. E. F. Fender, Mat. Res. Bull. (1975), in print.



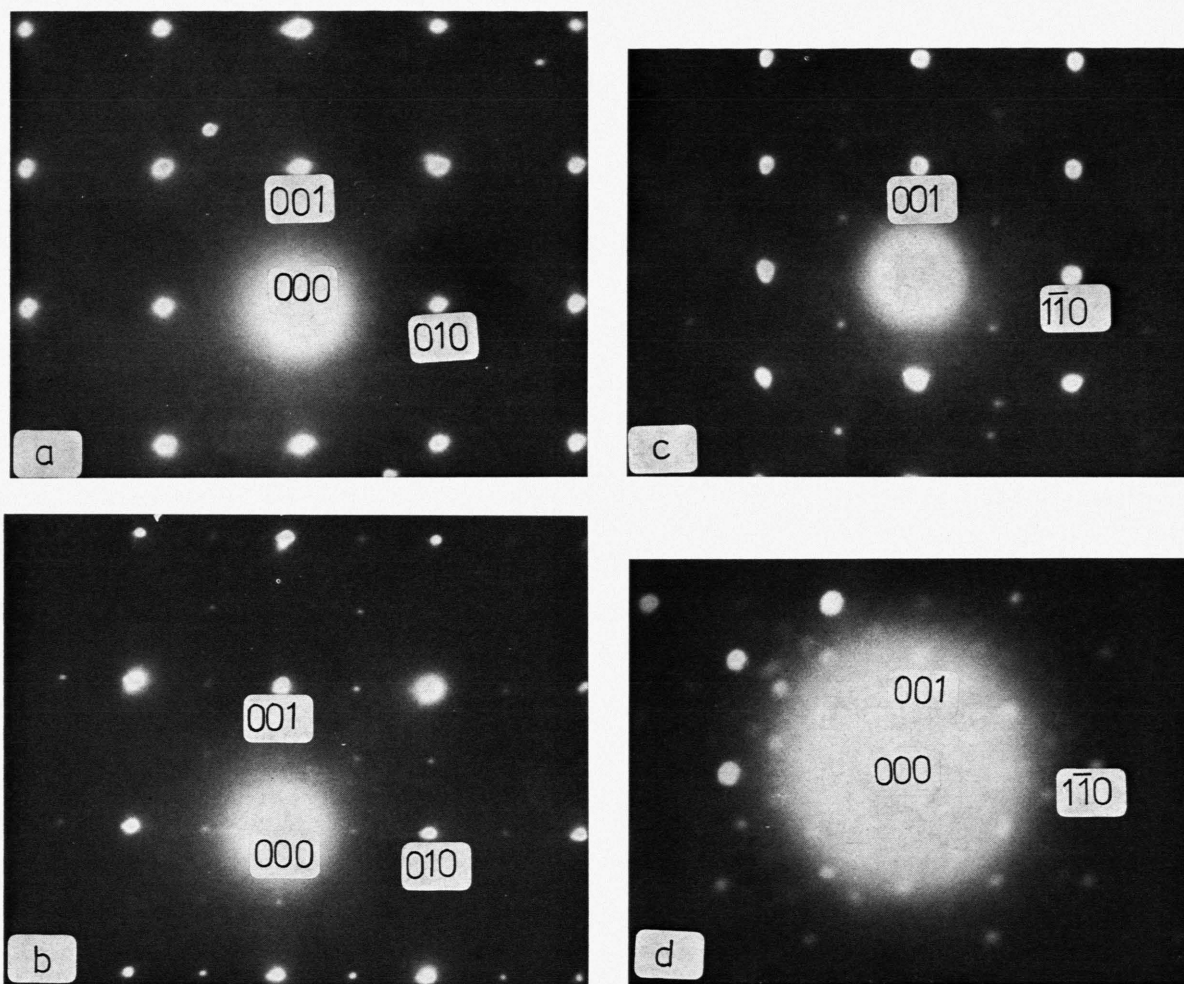


Fig. 2. Electron diffraction patterns of LaNiO_3 (a and c) and anion-deficient LaNiO_3 (b and d). The electron beam is along [100] in (a) and (b) and along [110] in (c) and (d).