Vacancy Ordering in Anion-deficient $LaNiO_3$

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(Z. Naturforsch. **30 a**, 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, $A^{3+}B^{3+}O_3$ (B = transition metal ion), possessing novel electrical and magnetic properties, are known to exhibit non-stoichiometry on one or more sub-lattices [1]. Oxidative non-stoichiometry in $LaMnO_3$ and $LaCrO_3$ has been recently examined [2], but little is known about anion-deficient non-stoichiometry in such systems. We find anion-deficient nono-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

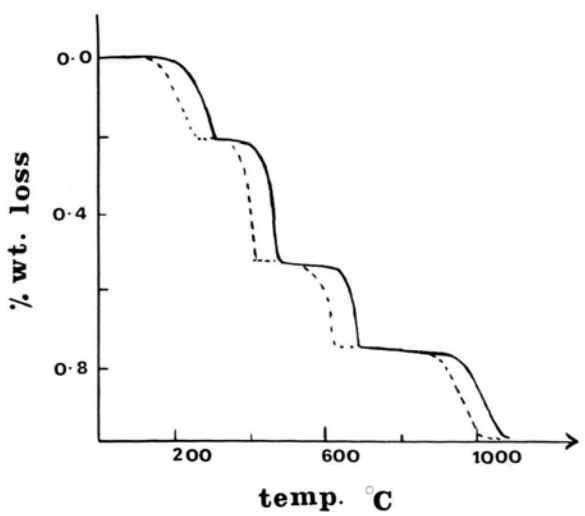

Fig. 1. Thermogravimetric curves of $LaNiO_3$ in air (broken curve) and in oxygen (full curve).

general formula $La_nNi_nO_{3n-1}$ with $n = 7$, 9, 13 and 30. X-ray diffraction measurements show that the rhombohedral unit cell [3] 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 $a_c \approx 3.85$ Å ($a_{rh} \approx 5.45$ Å) 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 $b \approx 2\, a_c$. 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 $SrFeO_{2.5}$-$SrFeO_3$ 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.

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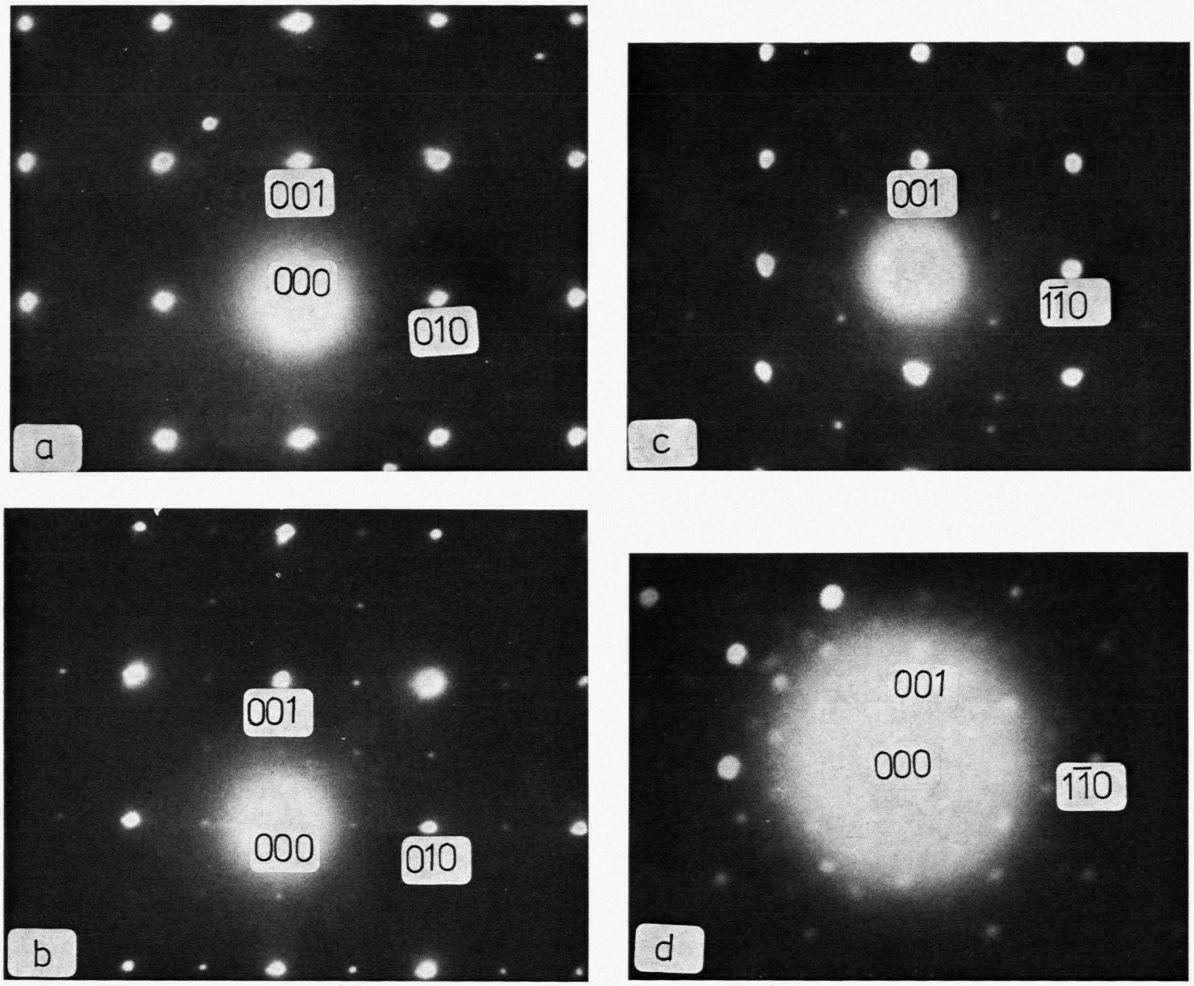

Fig. 2. Electron diffraction patterns of $LaNiO_3$ (a and c) and anion-deficient $LaNiO_3$ (b and d). The electron beam is along [100] in (a) and (b) and along [110] in (c) and (d).