JOURNAL OF SOLID STATE CHEMISTRY 71, 418–425 (1987)

The Crystallographic and Magnetic Structure of Ni_2O_3H

A. M. MALSBURY AND C. GREAVES

Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT, England

Received December 16, 1986; in revised form April 6, 1987

A nickel oxide hydroxide, nominally Ni_2O_3H, has been synthesized using hydrothermal techniques. The crystallographic and magnetic structures of the material have been determined at 4.5 K from powder neutron diffraction data. The material, which is nonstoichiometric with respect to Ni and H, contains Ni^{2+} and Ni^{4+} rather than Ni^{3+} and is orthorhombic (space group *Pnmn*; $a = 5.084(1)$ Å, $b = 2.9103(6)$ Å, $c = 13.954(3)$ Å). Magnetic moments are aligned along the c axis with antiferromagnetic order. Powder neutron diffraction data collected above the Néel temperature, at 298 and 473 K, revealed no significant changes to the structure or localized electron model.

Introduction

A preliminary report of the structure and conductivity of a mixed valent nickel oxide hydroxide of nominal composition Ni_2O_3H has previously been published (*1*). In the present report, the crystallographic structure at 4.5 K is described in detail together with previously unpublished results on the magnetic structure at this temperature; structural data obtained above the Néel temperature at 298 and 473 K are also described.

Sample Preparation and Characterization

A black oxidized nickel oxide hydroxide prepared by methods outlined previously (*1*) was hydrothermally treated (10 mole dm^{-3} NaOH solution, PTFE lined stainless-steel autoclave, 150°C, 200 bar, 16 hr) to increase the crystallinity of the sample. Use of an indexing program (*2*) showed the material to have an orthorhombic unit cell ($a = 5.084(1)$ Å, $b = 2.9103(6)$ Å, $c = 13.954(3)$ Å) and systematic absences suggested the space groups *Pn2n* or *Pnmn*. Nonstandard space group settings have been used to facilitate comparison of this unit cell with that of $Ni(OH)_2$, by maintaining a common z axis. X-ray diffraction line broadening data were consistent with plate-like crystallites of average thickness 370(50) Å along c and diameter 1100(400) Å. Some characteristic properties and chemical analysis for this phase have been reported previously (*1, 3*). Thermogravimetric analysis suggested an O/Ni ratio of 1.55 while chemical analysis gave a nickel content of 71.3(5)% and a mean Ni oxidation state of 2.65. The pyknometric density was 5.17(5) g cm^{-3}, and infrared spectra revealed the presence of three O–H bands at 3340, 1025, and 1000 cm^{-1} (Fig. 1).

0022-4596/87 $3.00

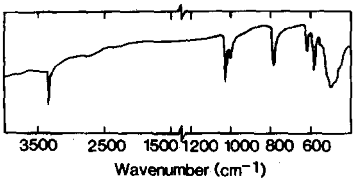

FIG. 1. Infrared spectrum of Ni_2O_3H (sample used for 4.5 K structure determination).

Results and Discussion

Neutron Diffraction, 4.5 K

Powder neutron diffraction data were recorded at 4.5 K on the D1A diffractometer, ILL, Grenoble, with the sample contained in a 16-mm-diameter vanadium can. A neutron wavelength of 1.909 Å was obtained by reflection from the 115 planes of a Ge monochromator at a takeoff angle of 122°.

Rietveld profile analysis techniques (*4*, *5*) were used for simultaneous nuclear and magnetic structure refinement using scattering lengths for Ni, O, and H of 10.3, 5.8, and −3.74 fm, respectively. The background was not refined in the program but was obtained by interpolation between a series of background values taken from regions in the observed data where there were no peaks. Weights for the profile points used in the refinement were calculated from the expression

$$[250/(I + \sigma^2)]$$

where I is the intensity measured by the counter and σ is the estimated standard deviation in the background. Profile R factors R_p and R_{wp} relate to unweighted and weighted profile points (*6*), and R_{exp} is the statistically expected value for R_{wp}.

Notwithstanding possible complications due to magnetic ordering, data were collected at 4.5 K to allow the use of a single overall thermal parameter in the initial stages of refinement and thus minimize the number of structural variables. Since the O/Ni ratio of 1.55 was incompatible with both known hydroxides, β- and γ-NiOOH, a new structure type was indicated and an initial model was proposed on the basis of X-ray diffraction data, chemical and thermogravimetric analysis, and density measurements.

The unit cell is related to that of $Ni(OH)_2$ (hexagonal, $a_h = 3.126$ Å, $c_h = 4.605$ Å) by $a = \sqrt{3}a_h$, $b = a_h$, and $c = 3c_h$, if allowance is made for slight changes due to oxidation. The unit cell thus appeared to contain 6 close-packed oxygen layers normal to c, with 2 oxygen atoms per close-packed layer. Density and thermogravimetric analysis implied approximately 8 nickel atoms per unit cell, and an overall cell content of Ni_8O_{12}, ignoring H atoms. Given the preference of Ni ions for octahedral coordination in oxide environments, the problem of determining the crystallographic structure was thus reduced to obtaining the O stacking sequence and the distribution of Ni ions within the resulting octahedral interstices. Although the stacking sequence AABBCC found in CrOOH and CoOOH (*7*) was compatible with the c parameter, it was rejected as only 6 octahedral positions would be available, and a combination of cubic (c) and hexagonal (h) layers was indicated. Consideration of the structure factors of a limited number of X-ray and neutron peak intensities suggested an ordered arrangement of Ni atoms in which every third layer of octahedral sites is fully occupied and separated from the next equivalent layer by two half-full layers. This implied the space group *Pnmn* and determined the O stacking sequence to be hcc. The nickels were in the 2*a*, 2*c*, and 4*g* sites and these will be referred to as Ni(1), Ni(2), and Ni(3) sites, respectively.

Initially, only the half-width parameters and cell constants were refined, but the inadequacy of this trial structure was reflected in the high weighted profile index ($R_{wp} = 26.1\%$, $R_{exp} = 3.34\%$). In addition to the obvious need to introduce H atoms, the

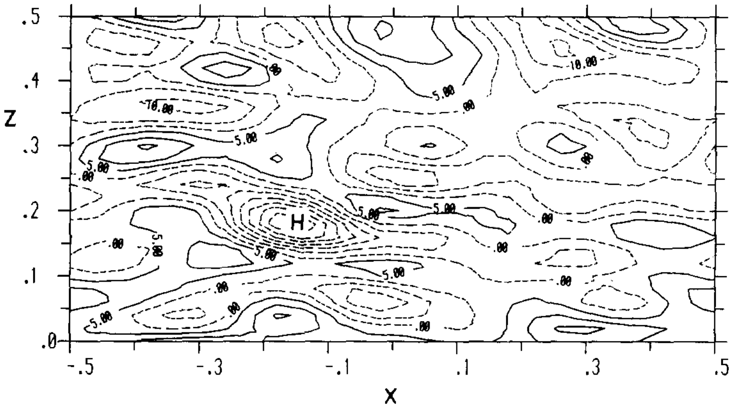

FIG. 2. Difference Fourier synthesis in the *ac* plane.

presence of the 100 and 012 reflections ($2\theta = 21.7$ and $41.7°$, respectively), which are forbidden in *Pnmn*, suggested antiferromagnetic order at this temperature. The disappearance of these peaks at ambient temperature supported this view. Due to difficulties in establishing a magnetic model in the presence of other structural uncertainties, a difference Fourier synthesis was performed at this stage in order to locate the H atoms.

A difference Fourier synthesis in the *ac* plane revealed the hydrogen location as an area of negative density at about (0.85, 0, 0.20) as is seen in Fig. 2. With the general hydrogen location fixed and the occupation number of the hydrogen treated as a variable, the magnetic properties of the material were then considered.

As there were peaks of entirely magnetic origin in the neutron diffraction data, an antiferromagnetic model was proposed for the material. A trial and error approach was adopted in order to produce an antiferromagnetic arrangement which would best fit the observed results. The most satisfactory model contained only Ni^{2+} and diamagnetic Ni^{4+} as shown in Fig. 3. The Ni^{2+} magnetic form factors used in the refinement were those determined by Alperin (*8*) for NiO. Although components of the magnetic moment along all three axes were considered, the best model incorporated a unique magnetic axis parallel to the *c* axis. This is similar to the magnetic model for $Ni(OH)_2$ (*9*) which has $+-+-$ sequences of ferromagnetic Ni^{2+} layers normal to the *c* axis. On the basis of the

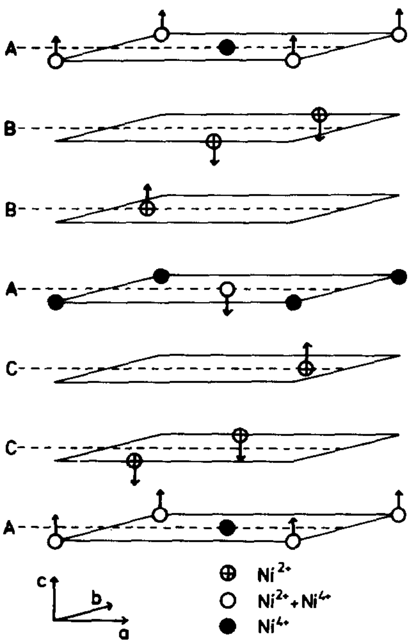

FIG. 3. Cation distribution and antiferromagnetic order.

TABLE I

REFINED STRUCTURAL PARAMETERS FOR Ni_2O_3H AT 4.5 K[a]

	x/a	y/b	z/c	Occupation per cell	B (Å^2)[b]
Ni(1)	0.0	0.0	0.0	2.0	0.73(2)
Ni(2)	0.0	0.0	0.5	2.0	0.73(2)
Ni(3)	0.3213(4)	0.0	0.1746(1)	3.78(1)	0.73(2)
O(1)	0.9623(5)	0.0	0.2424(2)	4.0	0.78(3)
O(2)	0.6401(6)	0.0	0.0734(2)	4.0	0.78(3)
O(3)	0.6901(6)	0.0	0.4244(2)	4.0	0.78(3)
H	0.843(1)	0.0	0.1866(4)	3.26(6)	0.9(1)

[a] Cell parameters: a = 5.073(1) Å, b = 2.909(1) Å, c = 13.927(1) Å; magnetic moments: Ni(1) = 1.49(8) B.M., Ni(3) = 1.74(5) B.M.; final R factors: $R_p = 8.95\%$, $R_{wp} = 6.13\%$, $R_{mag} = 12.95\%$, $R_{exp} = 3.30\%$.

[b] Corrected for absorption effects (*11*).

TABLE II

BOND DISTANCES AND ANGLES, 4.5 K

Ni(1)–O(2)	2.092(3) [2][a]	Ni(3)–O(1)	2.051(3) [1]
Ni(1)–O(3)	2.038(2) [4]	Ni(3)–O(1)	1.992(2) [2]
Mean Ni(1)–O	2.056	Ni(3)–O(2)	2.145(3) [1]
		Ni(3)–O(3)	2.111(2) [2]
O(2)–Ni(1)–O(3)	80.80(9) [4]	Mean Ni(3)–O	2.067
O(2)–Ni(1)–O(3)	99.20(9) [4]		
O(3)–Ni(1)–O(3)	91.05(8) [2]	O(1)–Ni(3)–O(2)	96.4(1) [2]
O(3)–Ni(1)–O(3)	88.95(8) [2]	O(2)–Ni(3)–O(3)	79.0(1) [2]
		O(1)–Ni(3)–O(1)	92.9(1) [2]
		O(1)–Ni(3)–O(3)	91.2(1) [2]
Ni(2)–O(2)	1.915(2) [4]	O(1)–Ni(3)–O(3)	89.4(1) [2]
Ni(2)–O(3)	1.893(3) [2]	O(1)–Ni(3)–O(1)	93.8(1) [1]
Mean Ni(2)–O	1.908	O(3)–Ni(3)–O(3)	87.1(1) [1]
O(2)–Ni(2)–O(3)	89.3(1) [4]		
O(2)–Ni(2)–O(3)	90.7(1) [4]	H–O(1)	0.982(6)
O(2)–Ni(2)–O(2)	98.87(9) [2]	O(1)–H . . . O(2)	2.864(4)
O(2)–Ni(2)–O(2)	81.13(9) [2]		
		O(1)–H–O(2)	175.2(5)

[a] Distances in Å, angles in degrees; the numbers of equivalent bonds per polyhedron are shown in brackets.

magnetic structure and from calculations of Ni–O distances for the model at this stage, the material was found to consist of Ni^{2+} and Ni^{4+} ions with the diamagnetic Ni^{4+} ions being in Ni(2) sites. The magnetic structure reflects the importance of the nominal 180° cation–anion–cation superexchange [Ni(1)–O(2)–Ni(3)] in the compound, as observed for many other materials.

Refinement of site occupancies revealed that the Ni(3) sites and the H sites were only partially populated. The final refinement, for which a pseudo-Voigt peak shape function and an anisotropic crystallite size broadening parameter (*10*) were used, gave a weighted profile of 6.13% (R_{exp} = 3.30%). Three isotropic temperature factors were refined, one each for Ni, O, and H. A magnetic R factor based on integrated peak intensities of pure magnetic and mixed reflections was calculated, and a value of 12.95% was obtained for the final refinement. This was considered totally satisfactory in the light of the low intensity of the magnetic profile relative to the background.

A list of refined structural and magnetic parameters is given in Table I and bond lengths and angles in Table II. The structure is shown in Fig. 4 and the O–H . . . O bonding is clearly revealed in the Total Fourier section shown in Fig. 5; Fig. 6 shows the observed and calculated neutron diffraction patterns. Although the thermal parameters appear slightly high for 4.5 K

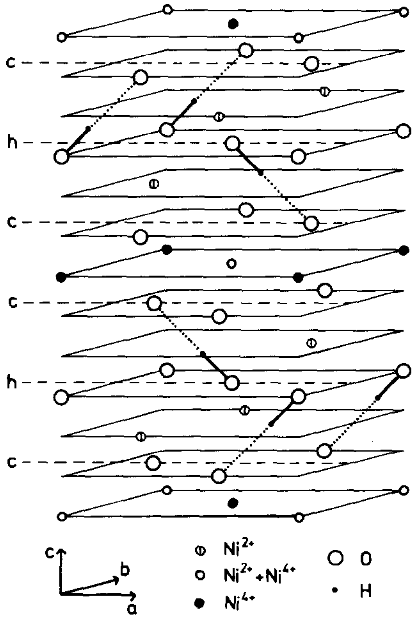

FIG. 4. Schematic representation of structure.

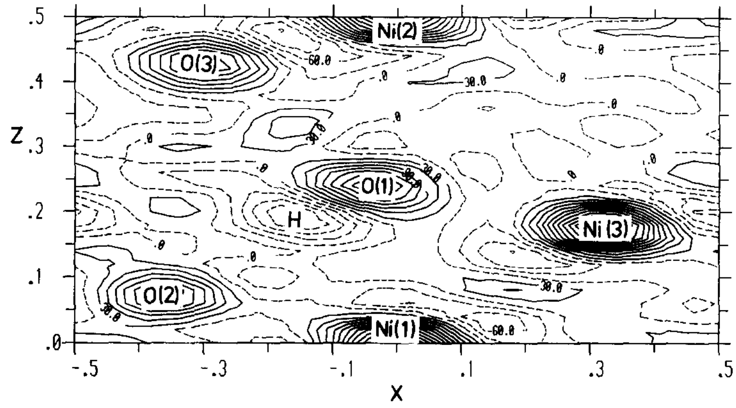

FIG. 5. Total Fourier synthesis in the *ac* plane.

data, they are compatible with a material showing disorder on two sublattices—Ni(3) and H. The final structural details are totally consistent with the observed characteristics of the material. The O/Ni ratio determined by Greaves *et al.* (*1*) of 1.55 compares well with the theoretical value of 1.54 for the model. The nickel content analysis of 71.35% compares quite well with that of 70.1% for the refined structure, and the calculated density of 5.23 g cm^{-3} is in excellent agreement with the experimental value of 5.17(5) g cm^{-3}. The Ni–O bond lengths given in Table II may be compared with the Ni–O distance in NiO of 2.088 Å (*8*) and in $LiNiO_2$ of 1.971 Å (*12*). The magnetic moments for the Ni(1) and Ni(3) sites were 1.49(8) and 1.74(5) B.M., respectively, compared with 1.81(2) B.M. reported for NiO (*8*). As would be expected, the Ni–O distances for the Ni(2) sites are less than for the other nickel sites. The Ni(1)–O distances are shorter than the Ni(3)–O distances which may reflect the presence of Ni^{4+} in the N(1) sites. This is supported by the low magnetic moment for Ni(1). If Ni(3) were purely Ni^{2+}, the mean Ni oxidation state (2.65) requires Ni(1) to comprise approximately 70% Ni^{2+} and 30% Ni^{4+}, although the less likely alternative invoking Ni^{2+} and Ni^{3+} is compatible with the data. Since the Ni(1) moment is slightly high for this interpretation, it seems more likely that Ni^{4+} occupies both Ni(1) and Ni(3) but with a strong preference for Ni(1).

The NiO_6 octahedra are all slightly distorted (Table II) in accordance with Pauling's rules (*13*). The shortest O–O distances, for example, are 2.490(4), 2.677, and 2.708 Å and are, respectively, along edges of the Ni^{4+} octahedra shared with Ni(2) [Ni^{4+}], Ni(1) [Ni^{4+} and Ni^{2+}], and Ni(3) [almost totally Ni^{2+}]. The shortest O–O distance is therefore similar to that found for the shared octahedron edges in TiO_2 (2.53 Å).

The fact that the material contains Ni^{2+}

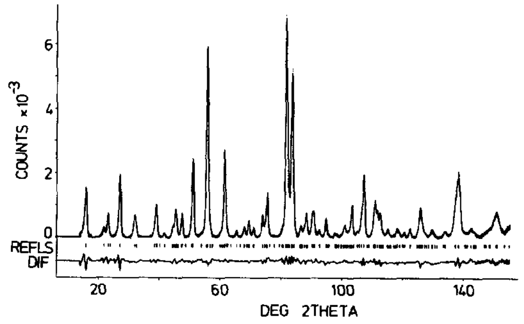

FIG. 6. Observed (dots), calculated (solid line), and difference profiles for 4.5 K data; reflection positions are indicated by vertical bars.

TABLE III

REFINED STRUCTURAL PARAMETERS FOR Ni_2O_3H AT 298 K[a]

	x/a	y/b	z/c	Occupation per cell	B (Å^2)[b]
Ni(1)	0.0	0.0	0.0	2.0	0.89(3)
Ni(2)	0.0	0.0	0.5	2.0	0.89(3)
Ni(3)	0.3207(5)	0.0	0.1749(1)	3.78(1)	0.89(3)
O(1)	0.9632(6)	0.0	0.2417(3)	4.0	1.08(4)
O(2)	0.6408(7)	0.0	0.0737(2)	4.0	1.08(4)
O(3)	0.6933(7)	0.0	0.4252(2)	4.0	1.08(4)
H	0.845(1)	0.0	0.1871(5)	3.47(7)	1.7(2)

[a] $a = 5.082(1)$ Å, $b = 2.913(1)$ Å, $c = 13.942$ Å, $R_p = 11.01\%$, $R_{wp} = 7.15\%$, $R_{exp} = 6.10\%$.

[b] Corrected for absorption effects (*11*).

and Ni^{4+} rather than Ni^{2+} and Ni^{3+}, although initially surprising, can be rationalized by the high crystal field stabilization energies of octahedral Ni^{4+} (low spin) and Ni^{2+} (high spin). This situation, however, appears unusual and definitive structural data of this type has not previously been reported for oxides containing nominally Ni^{3+}, although suggestions that $Ba_2Ni_2O_5$ may contain Ni^{2+} and Ni^{4+} have been made (*14*).

Neutron Diffraction, 298 and 473 K

Due to the very unusual electronic nature of this phase at 4.5 K, experiments were performed at higher temperatures to examine the possibility of electron configuration changes at or above the Néel temperature. After analysis, insufficient material was available for this study and a new sample was prepared. Neutron diffraction data ($\lambda = 1.9575$ Å) were collected at 298 and 473 K. Summaries of the refined structural parameters R_p and R_{wp} for Ni_2O_3H at 298 and 473 K are given in Tables III and IV, respectively, and plots of the observed and calculated profiles are given in Fig. 7a and b. The magnetic ordering evident at 4.5 K had disappeared although residual short-range magnetic order was detectable at 298 K.

TABLE IV

REFINED STRUCTURAL PARAMETERS FOR Ni_2O_3H AT 473 K

	x/a	y/b	z/c	Occupation per cell	B (Å^2)[b]
Ni(1)	0.0	0.0	0.0	2.0	1.18(3)
Ni(2)	0.0	0.0	0.5	2.0	1.18(3)
Ni(3)	0.3214(5)	0.0	0.1749(1)	3.78(1)	1.18(3)
O(1)	0.9668(6)	0.0	0.2429(3)	4.0	1.15(4)
O(2)	0.6419(7)	0.0	0.0737(2)	4.0	1.15(4)
O(3)	0.6888(7)	0.0	0.4244(2)	4.0	1.15(4)
H	0.847(1)	0.0	0.1849(5)	3.42(8)	2.3(2)

[a] $a = 5.090(1)$ Å, $b = 2.918(1)$ Å, $c = 13.978(3)$ Å, $R_p = 12.29\%$, $R_{wp} = 7.55\%$, $R_{exp} = 6.48\%$.

[b] Corrected for absorption effects (*11*).

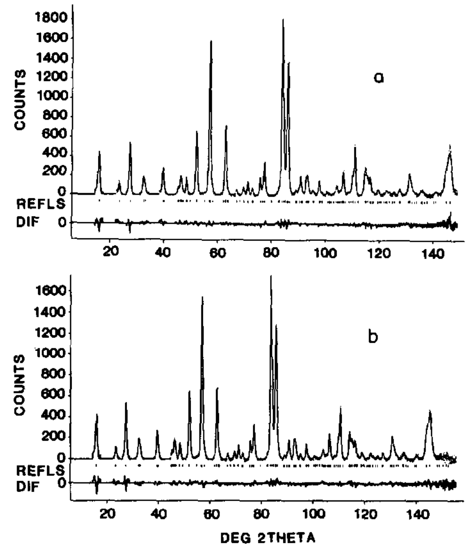

FIG. 7. Observed, calculated, and difference profiles at 298 K (a), and 473 K (b).

As can be seen from the tables of refined structural parameters for Ni_2O_3H at 298 and 473 K, there is little structural change with increasing temperature. Bond lengths in Ni_2O_3H at 4.5, 298, and 473 K are given in Table V. Since the Ni(2)–O distances are considerably shorter than for the other two sites and little increase is observed for Ni(2)–O distances with increase in temperature, Ni(2) sites are clearly still Ni^{4+}. The most significant result arising from the

TABLE V

BOND DISTANCES IN Ni_2O_3H

Bond type	Bond distance (Å) 4.5 K	298 K	473 K	Number of equivalent bonds to cation
Ni(1)–O(2)	2.092(3)	2.095(3)	2.094(3)	2
Ni(1)–O(3)	2.038(2)	2.043(2)	2.042(2)	4
Mean Ni(1)–O	2.056	2.060	2.059	
Ni(2)–O(2)	1.915(2)	1.920(2)	1.927(3)	4
Ni(2)–O(3)	1.893(3)	1.876(3)	1.904(2)	2
Mean Ni(2)–O	1.908	1.905	1.919	
Ni(3)–O(1)	2.051(3)	2.041(4)	2.041(4)	1
Ni(3)–O(1)	1.992(2)	2.000(3)	1.998(3)	2
Ni(3)–O(2)	2.145(3)	2.153(4)	2.159(4)	1
Ni(3)–O(3)	2.111(2)	2.119(2)	2.124(3)	2
Mean Ni(3)–O	2.067	2.072	2.074	
H–O(1)	0.982(6)	0.968(8)	1.011(8)	

higher temperature refinements is, therefore, that even at 473 K, the nickel in Ni_2O_3H still prefers to be present as Ni^{2+} and Ni^{4+}. The ambient temperature infrared spectra of Ni_2O_3H are consistent with the proposed structure. The band at 3340 cm^{-1} corresponds to the O–H stretching frequency for this phase. From published curves (*15*) of O–H stretching frequencies vs O–H and O–O distances for hydrogen bonded systems, the frequency of the O–H stretch for this material is in keeping with a bond length of ≤ 1 Å as is found in Ni_2O_3H. The two bands at 1025 and 1000 cm^{-1} are considered to be O–H bending frequencies and their positions are consistent with hydrogen bonds in other oxide systems (*16*). The appearance of two O–H bending frequencies, while initially surprising given that there is only one H site in this phase, can be rationalized by the defect structure. For the 4.5 K material (Fig. 1) approximately 20% of the H sites are vacant and each site is 2.9 Å distant from neighboring sites. Statistically, ~$\frac{1}{3}$ of all hydrogen for this material will be in a site next to a vacancy which could affect the O–H bending frequency. The observation that the 1025 cm^{-1} band is approximately twice the intensity of the 1000 cm^{-1} band (Fig. 1) supports this interpretation.

Madelung Constant Calculations

In order to evaluate the acceptability of the structural model over the temperature

TABLE VI

MADELUNG AND DIPOLE POLARIZATION ENERGIES

Cation charge distribution Ni(1)	Ni(2)	Ni(3)	Temperature for structural parameters	Madelung energy (kcal $mole^{-1}$)	Dipole polarization energy (kcal $mole^{-1}$)[a]
4	2	2	4.5	3833	453
2	4	2	4.5	3935	567
2.5	2.5	2.5	4.5	3756	345
2	3	2.5	4.5	3799	389
4	2	2	298	3842	488
2	4	2	298	3949	602
2.5	2.5	2.5	298	3764	374
2	3	2.5	298	3809	418
4	2	2	473	3814	410
2	4	2	473	3910	512
2.5	2.5	2.5	473	3751	355
2	3	2.5	473	3779	337

[a] Assuming polarizabilities of zero for cations, 2.4 $Å^3$ for O^{2-}.

range considered with respect to purely ionic considerations, electrostatic energy calculations (*17*) were performed. The refined positional parameters of Tables I, III, and IV were used in the calculations. Madelung energies and dipole polarization energies were computed for stoichiometric Ni_2O_3H (mean Ni oxidation state 2.5, all sites with full occupancy) using the following models:

(1) Ni^{4+} in Ni(1) sites and Ni^{2+} in Ni(2) and Ni(3) sites,

(2) Ni^{4+} in Ni(2) sites and Ni^{2+} in Ni(1) and Ni(3) sites,

(3) Ni with an average oxidation state of 2.5 in Ni(1), (2), and (3) sites,

(4) Ni^{2+} in Ni(1) sites, Ni with an average oxidation state of 3 in Ni(2) sites, and Ni with an average oxidation state of 2.5 in Ni(3) sites.

The results (Table VI) imply that for all three temperatures considered, the computations support case (2) with Ni^{2+} and Ni^{4+} only, the Ni^{4+} in Ni(2) sites. This case gave a Madelung energy about 3% higher than the other models and is in complete agreement with the neutron diffraction results.

Acknowledgments

We thank SERC for financial assistance, and SERC and Lucas Research Centre for providing a CASE Award (A.M.M.). The provision of neutron diffraction facilities and technical assistance by ILL is gratefully acknowledged.

References

1. C. Greaves, A. M. Malsbury, and M. A. Thomas, *Solid State Ionics* **18/19,** 763 (1986).
2. D. Louer and M. Louer, *J. Appl. Crystallogr.* **5,** 271 (1972).
3. C. Greaves, M. A. Thomas, and M. Turner, *Power Sources* **9,** 163 (1983).
4. H. M. Rietveld, *Acta Crystallogr.* **22,** 151 (1967).
5. H. M. Rietveld, *J. Appl. Crystallogr.* **2,** 65 (1969).
6. R. A. Young and E. Prince, *J. Appl. Crystallogr.* **15,** 357 (1982).
7. A. F. Wells, "Structural Inorganic Chemistry," 5th ed., Oxford Univ. Press, Oxford (1984).
8. H. A. Alperin, *J. Phys. Soc. Japan* **17**(3), 12 (1961).
9. A. Szytula, A. Murasik, and M. Balanda, *Phys. Status Solidi B* **43,** 126 (1971).
10. C. Greaves, *J. Appl. Crystallogr.* **18,** 48 (1985).
11. A. W. Hewat, *Acta Crystallogr.* **A35,** 248 (1979).
12. M. G. S. R. Thomas, D.Phil. thesis, Oxford University (1985).
13. L. Pauling, "Nature of the Chemical Bond," 3rd ed., Cornell Univ. Press, Ithaca, NY (1960).
14. J. J. Lander, *Acta Crystallogr.* **4,** 148 (1951).
15. A. Novak, *Structure and Bonding* **18,** 177 (1974).
16. P. G. Dickens, S. Crouch-Baker, and M. T. Weller, *Solid State Ionics* **18/19,** 89 (1986).
17. J. W. Weenk and H. A. Harwig, *J. Phys. Chem. Solids* **38,** 1047 (1977).