YSr$_5$Ni$_3$O$_8$—a New Nickel(I) Oxide with a Defect Sr$_2$CuO$_3$ Structure

M. James* and J. P. Attfield

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW
Interdisciplinary Research Centre in Superconductivity, University of Cambridge, Madingley Road, Cambridge, UK CB3 0HE

A stoichiometric oxide of 3d^9 nickel(I), YSr$_5$Ni$_3$O$_8$, has been prepared through the hydrogen reduction of YSr$_5$Ni$_3$O$_{11}$, resulting in a change from a tetragonal K$_2$NiF$_4$ type structure to an orthorhombic Sr$_2$CuO$_3$ arrangement in which 1/3 of the bridging oxygen atoms are missing from chains of apex-linked nickel oxide square planes.

Oxides containing d^9 transition-metal ions have been of great interest since the discovery of high T_c superconductivity through the doping of layered copper(II) oxides. Although many oxides of Cu^{2+} are known, few other d^9 ions form stable oxides, for instance, AgO contains Ag$^+$ and Ag^{3+} rather than 4d^9 Ag^{2+}.[1] The 3d^9 ion Ni$^+$ is readily stabilised by π-acceptor ligands, e.g. in Ni(PPh$_3$)$_3$X (X = Cl, Br, I), but is rarely found in an oxide environment. The only known examples are the infinite-layer phase LaNiO$_2$[2] with a square-planar coordination of oxygen to nickel, and MNa$_2$NiO$_2$ (M = Rb, K)[3] with a linear two-coordination. However, mixed Ni$^+$/Ni^{2+} oxides such as La$_{1.6}$Sr$_{0.4}$NiO$_{3.47}$[4] and LaSrNiO$_{3.1}$[5] have been prepared by the reduction of K$_2$NiF$_4$ type oxides La$_{2-x}$Sr$_x$NiO$_4$. We have recently discovered that a stoichiometric nickel(III) phase with a defect K$_2$NiF$_4$ structure, MSr$_5$Ni$_3$O$_{11}$, can be prepared for M = Y,[6] Dy, Er and Tm. In this communication we show that these phases can be reduced to new nickel(I) oxides, MSr$_5$Ni$_3$O$_8$, and we describe the crystal structure of YSr$_5$Ni$_3$O$_8$.

The thermogravimetric reduction of the nickel(III) oxide YSr$_5$Ni$_3$O$_{11}$ is shown in Fig. 1. The 30 mg sample was heated at 5 °C min^{-1} under a 5% H$_2$–N$_2$ atmosphere (58 ml min^{-1}) in a Stanton Redcroft STA-760 thermogravimetric analyser. The plateau corresponding to an average nickel oxidation state of +1 suggested the presence of a stable reduced intermediate between YSr$_5$Ni$_3$O$_{11}$ and the final decomposition products Y$_2$SrO$_4$, SrO and Ni. This reduced intermediate has been prepared by heating YSr$_5$Ni$_3$O$_{11}$ under the same atmosphere at 450 °C for 4 h. A similar intermediate is observed in the thermogravimetric reduction of MSr$_5$Ni$_3$O$_{11}$ (M = Dy, Er, Tm).
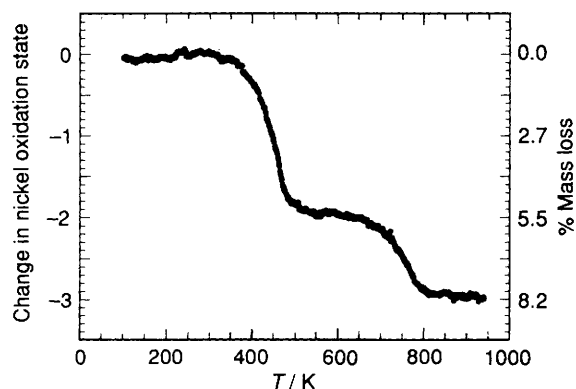
The powder X-ray diffraction profile of the reduced material was recorded on a Phillips PW1710 diffractometer, utilising Cu-Kα radiation. Data of sufficient quality for structure refinement were collected over 13 ≤ 2θ ≤ 113°, in 0.025° steps, with integration times of 11 s. A Rietveld refinement[7] of the structure was carried out with the GSAS program.[8] Small amounts of SrO, Y$_2$SrO$_4$ and Ni metal were also observed in the profile and were fitted in the refinement. The pattern of the new phase is similar to that of the original tetragonal nickel(III) phase, but with a pronounced ortho-

rhombic splitting. This suggested a Sr$_2$CuO$_3$ type structure[9] for the new phase, and the data were fitted using this model with (1/6Y + 5/6Sr) at the Sr site in space group *Immm*. A good fit was obtained from this structural model and a pseudo-Voigt peak shape function. In the final stages the O site occupancies were refined independently. The O(1) site was found to be fully occupied but vacancies were found at the O(2) site. Results of the refinement and bond distances are listed in Table 1.

These results indicate that YSr$_5$Ni$_3$O$_{11}$ can be reduced to YSr$_5$Ni$_3$O$_8$ without decomposition. This structure is therefore notable for stabilising a complete range of nickel oxidation states between +1 and +3. No Y/Sr ordering is apparent within these compounds. The fully oxidised phase has a tetragonal K$_2$NiF$_4$ type structure with $\frac{1}{6}$ oxygen vacancies within the xy plane. Reduction to YSr$_5$Ni$_3$O$_8$ removes a further $\frac{2}{3}$ of these oxygens, resulting in a structural change to the Sr$_2$CuO$_3$ type (Fig. 2) in which the sites at (0, 1/2, 0) are vacant and Cu is in square-planar coordination. The refined O(2) site oxygen occupancy shows that the remaining $\frac{1}{3}$ vacancies in YSr$_5$Ni$_3$O$_8$ are at this site which reduces the average nickel coordination number to 3$\frac{1}{3}$. The high concentration of oxygen vacancies at the O(2) site could result in superstructures of isolated linear NiO$_2$ units and linked NiO$_4$ square planes, as is found in the analogous chains in YBa$_2$Cu$_3$O$_{6+x}$ for intermediate values of x, e.g. $x = 0.4$.[10] No superstructure within YSr$_5$Ni$_3$O$_8$ is evident in our powder X-ray studies and electron microscopy will be used to investigate this possibility further.

Fig. 1 Thermogravimetric reduction of YSr$_5$Ni$_3$O$_{11}$ shown as percentage mass loss and the equivalent change in average nickel oxidation state
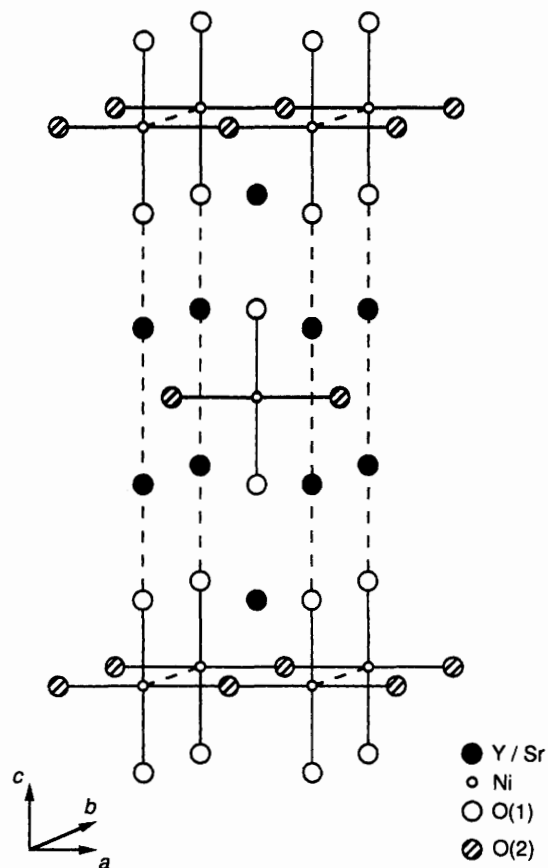
Table 1 Profile and structural parameters and interatomic distances from the refinement of YSr$_5$Ni$_3$O$_8$ in space group *Immm*, with esds in parentheses

Cell dimensions/Å

$a = 3.8030(2)$	$b = 3.5233(2)$	$c = 12.5424(6)$

Profile data

No. of reflections = 44, No. of points = 4000, No. of parameters = 21

$R_{WP} = 0.040$, $R_P = 0.029$, $R_F = 0.059$,

Atomic parameters

Atom	Symmetry position	x	y	z	Site occupancy
Ni	2a	0	0	0	1.0
Sr	4i	0	0	0.3553(1)	0.833
Y	4i	0	0	0.3553	0.167
O(1)	4i	0	0	0.1565(6)	1.0
O(2)	2b	0.5	0	0	0.72(1)

Overall $U_{iso} = 0.0123(5)$ Å^2

Interatomic distances/Å

Ni–O(1)	×2	1.963(8)
Ni–O(2)	×1$\frac{1}{3}$	1.901(1)
Mean Ni–O	×3$\frac{1}{3}$	1.938(6)

Y/Sr–O(1)	×4	2.596(1)
Y/Sr–O(1')	×1	2.493(7)
Y/Sr–O(2)	×1$\frac{1}{3}$	2.529(1)
Mean Y/Sr–O	×6$\frac{1}{3}$	2.566(3)

Fig. 2 The structure of $YSr_5Ni_3O_8$ showing chains of apically linked NiO_4 square planes along the a direction

To verify that the disordered Ni–O coordination environment is consistent with Ni^+, a bond-valence calculation was carried out using the method of Brown and Altermatt,[11] in which the valence contribution of each Ni–O bond of length r_i is $e^{(r_0 - r_i)/0.37}$. A value of $r_0 = 1.50$ Å was derived from the bond lengths in the nickel(I) oxides $LaNiO_2$[2] and MNa_2NiO_2

$(M = Rb, K)$,[3] and this gave a total calculated valence of 1.03 for the Ni environment in $YSr_5Ni_3O_8$.

The magnetic susceptibility of the reduced sample was measured on a Quantum Design SQUID magnetometer in applied fields between 0.05 and 5.0 T. $YSr_5Ni_3O_8$ was found to be paramagnetic between 6 and 300 K, but the effective magnetic moment could not be derived due to the presence of ferromagnetic Ni metal in the sample.

Both $YSr_5Ni_3O_8$ and $LaNiO_2$ result from low-temperature hydrogen reductions of their nickel(III) analogues, although the former compound requires less stringent conditions than the latter. These two nickel(I) oxides are isostructural and isoelectronic with simple copper(II) oxides such as Sr_2CuO_3 and infinite-layer type $SrCuO_2$, respectively, suggesting that reduced nickel oxide analogues of the high-T_c copper oxides could be prepared if appropriate oxidised precursors or other synthetic routes can be found. These materials will tend to be more insulating than the corresponding copper oxides, as the Ni3d–O2p energy difference is greater than the Cu3d–O2p separation, but experimental observations of their electronic properties will nevertheless be of interest.

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