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Structural and Magnetic Characterization of La_2NiRhO_6

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A polycrystalline sample of the perovskite La_2NiRhO_6 has been prepared. Neutron diffraction shows the compound to be orthorhombic (space group *Pbnm*; *a*=5.5350(4), *b*=5.5529(4), and *c*=7.8305(5) Å at 5 K) with a disordered arrangement of Ni and Rh over the six-coordinate *B* sites. Consideration of the *B*–O bond lengths and the paramagnetic Curie constant suggests that the Ni and Rh cations are trivalent and low spin. Magnetization and neutron diffraction experiments show that a transition to a spin-glass phase occurs upon cooling below 12 K. © 1999 Academic Press

INTRODUCTION

Ferromagnetism has been observed in relatively few insulating mixed metal oxides containing only one element from the *d*-block of the periodic table; Pauli's exclusion principle ensures that antiferromagnets are more common than the more useful ferromagnets. In an attempt to synthesize new oxide ferromagnets we (1–3) have prepared a number of perovskite-related compounds containing two *d*-block cations with different numbers of electrons in the valence shell. The Goodenough–Kanamori rules (4) predict that there will be a ferromagnetic 180° superexchange interaction between certain pairs of alioelectronic cations, for example, d^3 and d^8 species, but our attempts to take advantage of this effect have to date been thwarted by the failure of the different elements to distribute themselves in an ordered manner over the available crystallographic sites. We have found that, as a consequence of the disordered cation distribution, long-range magnetic order is frustrated in a number of these materials, and they consequently show properties characteristic of a spin glass. More surprisingly, we have found spin-glass behavior in compounds, for example (5), Sr_2FeTaO_6, which contain a disordered arrangement of a magnetic cation and a diamagnetic cation over the six-coordinate (*B*) sites in the nonfrustrated perovskite structure, even though the concentration of Fe^{3+} in this compound is considerably above the percolation limit for cubic lattices. Our continuing search for ferromagnets has now lead us to synthesize a new perovskite phase of composition La_2NiRhO_6. The oxidation states of the transition metal cations in this compound were not obvious at the outset, with Ni^{2+}/Rh^{4+} and Ni^{3+}/Rh^{3+} both being considered possible. In a crystal structure containing an ordered cation array, the former might lead to ferromagnetism; a weak spontaneous magnetization has been observed previously (6) in the isoelectronic cation-ordered compound La_2NiIrO_6. The magnetic properties in the case of the Ni^{3+}/Rh^{3+} configuration being adopted would also be sensitive to the degree of cation ordering, but the spin state of Ni^{3+} is an additional variable which must be taken into account. The available data suggest that both Rh^{3+} and Rh^{4+} (7, 8) would be low spin and that Ni^{2+} would be high spin, but the spin state of Ni^{3+} is not as easy to predict. Ferromagnetism might occur in a chemically ordered array of low-spin $3d^7$:Ni^{3+} cations which were able to establish a cooperative Jahn–Teller distortion and undergo so-called orbital ordering. We have studied La_2NiRhO_6 by neutron diffraction to resolve these issues. Consideration of the diffraction data, together with the results of magnetometry experiments, has allowed us to establish the extent of cation ordering in La_2NiRhO_6, to discuss the oxidation states of the transition metals and to produce a description of the magnetic behavior of this compound.

EXPERIMENTAL

A black polycrystalline sample of La_2NiRhO_6 was prepared by heating a well-ground, well-pelleted, stoichiometric mixture of dry La_2O_3, NiO, and Rh_2O_3 in air at 800°C (1 day) and 1000°C (1 day), and subsequently in a gentle flow of O_2 at 1150°C (7 days), 1200°C (7 days), 1250°C (7 days), and finally 1275°C (1 day), with frequent regrindings. The temperature increases were effected at a rate of 0.1°C/min. The final product was characterized initially by X-ray powder diffraction at room temperature. Neutron powder

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diffraction data were then collected at a temperature of 5 K over the angular range $10^\circ \le 2\theta \le 150^\circ$ with a 2θ stepsize of 0.05°, $\lambda = 1.5938$ Å, on the diffractometer D2b at the Institut Laue-Langevin, Grenoble. The sample, ~7.5 g, was contained in an 8-mm diameter vanadium can. The neutron diffraction data, uncorrected for absorption, were analyzed by the Rietveld method (9) using the GSAS suite of programs (10). The background was fitted by a Chebyshev polynomial (eight parameters) and the peak shape was described by a pseudo-Voigt function (five parameters). The zero-point error, histogram scale factor, three lattice parameters, four thermal parameters, and seven positional parameters were also varied in the course of the structure refinement.

Magnetic measurements were performed using a Quantum Design SQUID magnetometer. The susceptibilities were recorded in fields of 100 G after cooling in both the zero field (ZFC) and the measuring field (FC). Hysteresis measurements were carried out at 5 and 300 K in fields between 2000 and − 2000 G after cooling the sample in a field of 2000 G.

RESULTS

The X-ray diffraction pattern of the reaction product showed it to be a monophasic, pseudocubic perovskite, with no ordering of Ni and Rh over the six-coordinate (*B*) sites. The unit cell parameters refined to the values $a = 5.5444(3)$, $b = 5.5661(3)$, and $c = 7.8383(4)$ Å in the orthorhombic space group *Pbnm*. This symmetry assignment was confirmed by a full analysis of the neutron diffraction data collected at 5 K, the results of which are presented in Tables 1 and 2 and in Fig. 1. All the Bragg peaks were accounted for by this model; no additional peaks were observed at small scattering angles (Fig. 1 inset). The marked tilting of the BO_6 (B = Ni, Rh) octahedra apparent in Fig. 2 gives an indication of the degree of departure from cubic symmetry.

The magnetic susceptibility of La_2NiRhO_6 is shown in Fig. 3. The data in the temperature range $146 \le T\,(\mathrm{K}) \le 300$ were fitted to a Curie–Weiss law with an additional term to allow for temperature-independent paramagnetism:

$$\chi = \frac{C}{T+\theta} + \alpha.$$

The fitted values of C, θ, and α were 0.84(2) cm^3 K mol^{-1}, − 95(3) K, and $5.3(3) \times 10^{-4}$ cm^3 mol^{-1}, respectively. At lower temperatures the data cannot be fitted by this simple model; the ZFC susceptibility shows a maximum at 12 K

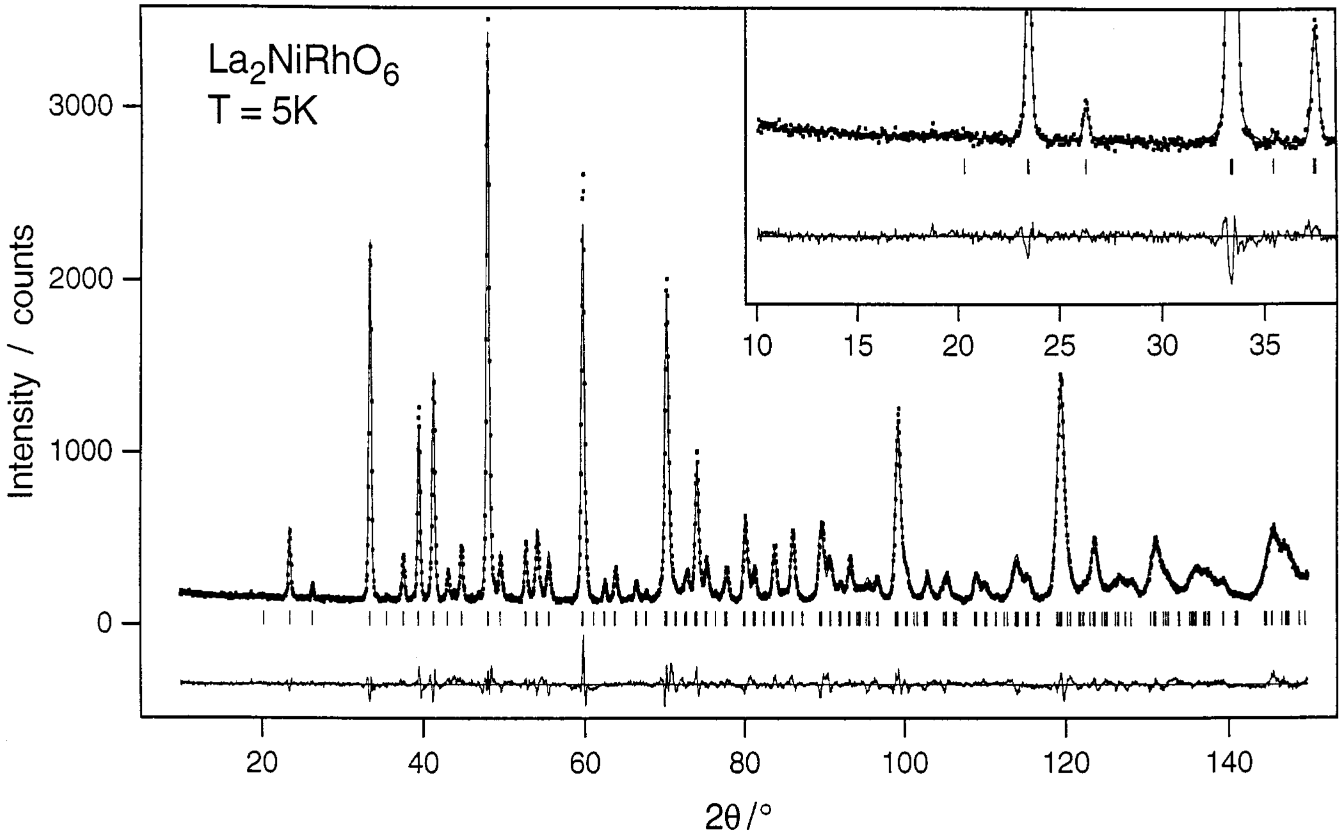

FIG. 1. Observed, calculated, and difference neutron powder diffraction profiles of La_2NiRhO_6 at 5 K. Reflection positions are marked. The inset emphasizes the absence of magnetic Bragg peaks at low angles.

TABLE 1
Structural Parameters of La_2NiRhO_6 at 5 K

Atom	Site	x	y	z	U_{iso} (Å^2)
La	4c	0.0090(7)	0.0419(3)	1/4	0.0019(4)
Ni/Rh	4b	1/2	0	0	0.0030(4)
O(1)	8d	0.2890(5)	0.2878(5)	0.0409(4)	0.0077(5)
O(2)	4c	− 0.081(1)	0.4899(6)	1/4	0.0043(7)

Note. Space group *Pbnm*, $a = 5.5350(4)$ Å; $b = 5.5529(4)$ Å; $c = 7.8305(5)$ Å; $V = 240.68(3)$ Å^3; $R_{wp} = 6.68\%$; $R_p = 5.22$; $\chi_{red} = 3.74$ for 29 variables.

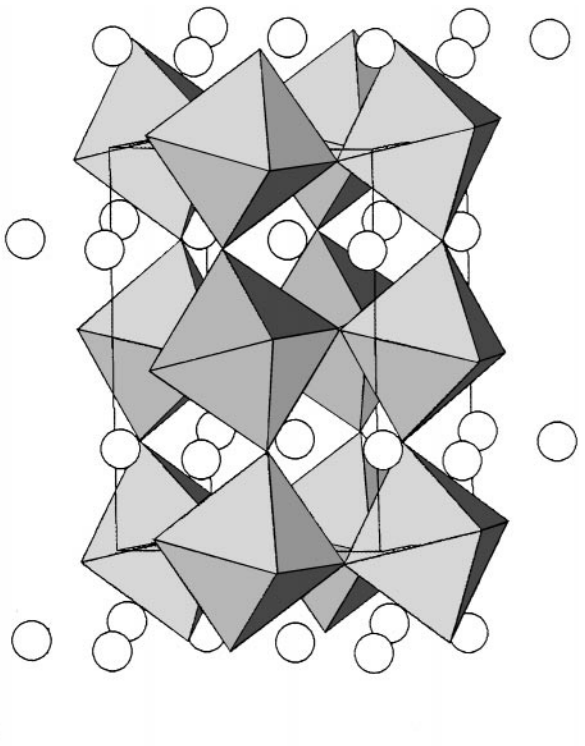

FIG. 2. Polyhedral representation of the crystal structure of La_2NiRhO_6; unfilled circles represent La^{3+}.

whereas the FC value continues to rise. The magnetization (Fig. 4) is a linear function of applied field at 300 K, but at 5 K hysteresis is present and $M(H)$ is not symmetrical about the origin.

DISCUSSION

The achievement of a successful structure refinement in space group *Pbnm*, in which all the B sites are crystallographically equivalent, demonstrates that the distribution of Ni and Rh is disordered in the new perovskite La_2NiRhO_6. This contrasts with the ordered distribution of Ni and Ir found in La_2NiIrO_6, perhaps surprisingly in view of the marked similarities in the chemistry of second- and third-row transition metals from the same group of the periodic table. We take this as evidence, albeit inconclusive, that the cation oxidation states differ in the two compounds. More substantive evidence comes from a consideration of the bond lengths (Table 2) around the six-coordinate Ni/Rh cations, which show an insignificant variation from 2.005(3) to 2.012(3) Å, with a mean value of 2.009 Å. If La_2NiRhO_6 contained Ni^{2+}/Rh^{4+}, we would expect to observe a mean bond length which was intermediate between typical Rh^{4+}–O and Ni^{2+}–O distances. The former is not well determined, but the values of 2.026(5) and 2.052(6) Å found recently (7) in X-ray powder diffraction studies of relatively simple structures are both significantly longer than the mean bond length in La_2NiRhO_6, as is the better established Ni^{2+}–O distance of ~ 2.04 Å (11). The fact that both component distances are longer than their supposed mean indicates that Ni^{2+}/Rh^{4+} can not be the correct assignment of oxidation states. We are therefore lead to the oxidation state assignment Ni^{3+}/Rh^{3+}. The lower charge on Rh will lead to Rh–O bond lengths somewhat longer than those refered to above, and values spanning the range 2.054(5)–2.125(5) Å were found in a recent powder diffraction study of Sr_3LnRhO_6 oxides (12). A Ni–O distance of 1.94–1.95 Å has been reported (13) in LnNiO$_3$ (Ln = Pr, Nd, Sm), which contains low-spin Ni^{3+}. It is therefore reasonable for an oxide containing a disordered arrangement of low-spin Ni^{3+} and Rh^{3+} to show a mean B–O distance of 2.009 Å, as observed. We note that to achieve this mean distance in a Ni^{2+}/Rh^{4+} compound, the Rh–O bond length would have to be ~ 1.98 Å, a value which is significantly shorter than those observed to date. Further support for the assignment of oxidation states as Ni^{3+}/Rh^{3+} comes from the results of our susceptibility measurements, with the observed Curie constant (0.83 cm^3 mol^{-1}) being close to the values (0.63, 0.66) measured for $YNiO_3$ and $LuNiO_3$, respectively (14). However, as was pointed out by Demazeau *et al.*, these values are somewhat higher than the ideal value for a cation with $S = 1/2$ (0.375). This was originally taken as an indication that the localized electron model is not truly applicable to these compounds, an interpretation that was subsequently confirmed by the observation of a

TABLE 2
Bond Distances (Å) and Bond Angles (°) for La_2NiRhO_6 at 5 K

La–O(1)	2.636(3)	× 2	Ni/Rh–O(1)	2.005(3)	× 2
	2.434(4)	× 2		2.012(3)	× 2
	2.750(3)	× 2		2.009(1)	× 2
La–O(2)	2.537(4)		shortest O–O	2.832(5)	
	2.390(6)				
Ni/Rh–O(1)–Ni/Rh	154.7(2)		Ni/Rh–O(2)–Ni/Rh	154.2(3)	

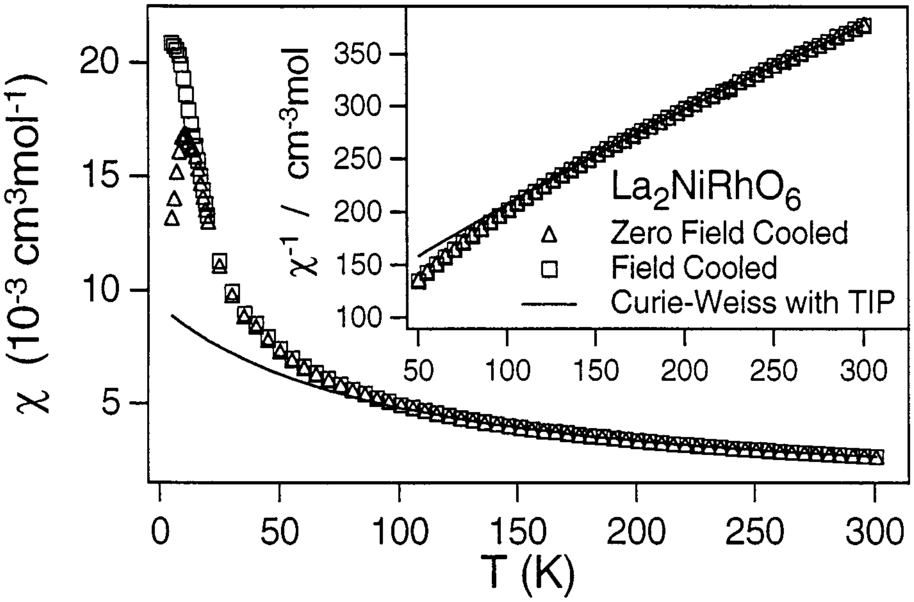

FIG. 3. Molar magnetic susceptibility and (inset) inverse susceptibility of La_2NiRhO_6 as a function of temperature.

metal–insulator transition in $PrNiO_3$ (13). The interactions between Ni^{3+} cations are apparently strong enough to produce antiferromagnetic ordering in $YNiO_3$ and $LuNiO_3$ ($T_N = 145$ and 130 K, respectively) (14), but the hysteresis observed in the magnetization of La_2NiRhO_6 and the absence of magnetic Bragg peaks in the neutron diffraction data show that 50% dilution of the magnetic sublattice by diamagnetic Rh^{3+} is enough to eliminate long-range ordering above 5 K. It is clear that we have not achieved our goal of producing a cation-ordered compound which shows long-range magnetic order at low temperatures, although the value of the Weiss temperature ($\theta = -95$ K) indicates that significant magnetic interactions are present. The maximum in the ZFC susceptibility data in Fig. 3 shows that a magnetic transition occurs at 12 K, but the divergence of the ZFC and FC data, the displaced hysteresis loop measured at 5 K, and the neutron data all indicate that the low- temperature phase is a spin glass rather than an

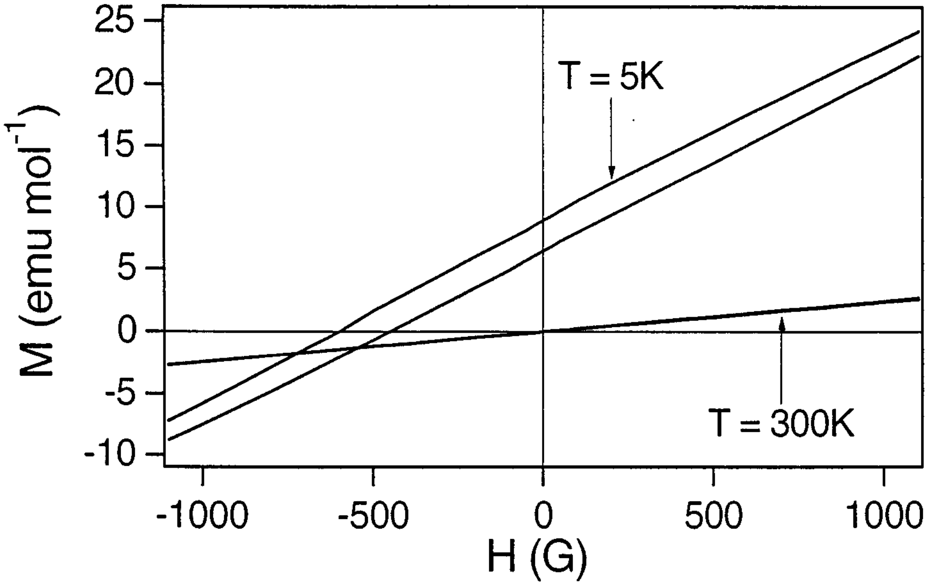

FIG. 4. Molar magnetisation as a function of field for La_2NiRhO_6, measured over the range $-2 < H$ (kG) < 2 at 300 and 5 K after cooling in 2 kG.

antiferromagnet. Similar behavior has been reported in other magnetically diluted perovskites with disordered *B* sites, for example, Sr_2FeTaO_6 (5, 15). However, it remains surprising that cation disorder is enough to produce spin-glass behavior in a nonfrustrated structure when the concentration of magnetic cations is well above the percolation limit. We have previously ascribed the effect to competition between nearest-neighbor and next-nearest-neighbor interactions, but in the case of La_2NiRhO_6 it may be that the disorder amongst the magnetic interactions is increased by local structural distortions which are brought about by the Jahn–Teller active $t_{2g},^6e_g^1$ electronic configuration of low-spin Ni^{3+}. A more extensive program of magnetometry, including ac measurements, would facilitate a more detailed discussion of the low-temperature phase.

CONCLUSION

We have presented evidence which suggests that La_2NiRhO_6 should be considered as a compound of Ni^{3+} and Rh^{3+} (rather than Ni^{2+} and Rh^{4+}) which shows spin-glass-like behavior below 12 K. The assignment of oxidation states is based on data from magnetometry and diffraction experiments. This result might be considered surprising, given that many Ni^{3+} compounds can only be prepared under a high pressure of oxygen (14). However, it has been shown that Ni^{3+} can be stabilized at 1 atm O_2 in the presence of basic cations, for example, Sr^{2+} (16, 17) or La^{3+} (13). It may well be that our insistence on the use of integer oxidation states is hindering our understanding of this compound.

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