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Structural chemistry and spin-glass behaviour of $Nd_{18}Li_8Fe_4TiO_{39}$

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ABSTRACT

$Nd_{18}Li_8Fe_4TiO_{39}$ has been synthesised and characterised by neutron powder diffraction, X-ray absorption spectroscopy, Mössbauer spectroscopy and magnetometry. The cubic structure ($Pm\bar{3}n$, $a=11.97227(8)$ Å) is based on intersecting $\langle 1\,1\,1\rangle$ chains comprised of alternating octahedral and trigonal-prismatic coordination sites. These chains lie within hexagonal-prismatic cavities formed by a Nd–O framework. The larger of the two crystallographically distinct octahedral sites, 8*e*, is occupied by iron, titanium and lithium in a ratio of 76:20:4; the smaller, 2*a*, is occupied by iron and titanium in a ratio of 79:21. The trigonal-prismatic site, 16*i*, is occupied by lithium and iron in a ratio of 98:2. The cations on the 2*a* sites are assigned as Ti^{4+} and low-spin Fe^{4+}, and those on the 16*i* sites as Li^{+} and Fe^{3+}. The 8*e* sites are thought to be occupied by Li^{+}, Fe^{3+} and Ti^{3+}. $Nd_{18}Li_8Fe_4TiO_{39}$ undergoes a transition to a spin-glass state at 4.25(5) K.

1. Introduction

The crystal structure drawn in Fig. 1 was first described in detail in an account [1] of the synthesis and characterisation of $Ln_{18}Li_8Rh_5O_{39}$ ($Ln=$La, Pr). The cubic unit cell (space group $Pm\bar{3}n$) was found to contain $\langle 1\,1\,1\rangle$ chains of alternating RhO_6 octahedra and LiO_6 prisms, with adjacent polyhedra being linked by face-sharing. The chains intersect at the origin and the body centre of the unit cell, and each chain segment occupies a hexagonal-prismatic cavity within the *Ln*–O framework. The octahedra are not all equivalent; those centred on the 2*a* sites at (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ are significantly smaller than those centred on the 8*e* sites at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and equivalent positions. The multiplicity ratio of these two octahedral sites, 1:4, is the same as the ratio of Rh^{4+}:Rh^{3+} cations in $Ln_{18}Li_8Rh_5O_{39}$ and Frampton et al. [1] therefore proposed that these mixed-valence oxides exhibit an ordered arrangement of Rh^{4+} and Rh^{3+}. Subsequent research has shown that this structure type can accommodate a wide range of chemical compositions [2–6]; rhodium may be substituted by various combinations of titanium, manganese, iron, cobalt or ruthenium, with $Ln=$lanthanum, praseodymium or neodymium.

Much of this research has been undertaken in an attempt to prepare new magnetic materials. The existence of two distinct crystallographic sites sufficiently different in size to induce the ordering of two cation species is reminiscent of the spinel structure, wherein the ordering over two sites of two cations having different magnetic moments results in ferrimagnetism. We therefore hoped that, for example, the 8*e* and 2*a* sites of $LnLi_8Fe_4MnO_{39}$ might accommodate an ordered arrangement of Fe^{3+} and Mn^{4+}, and that ferrimagnetism would consequently be observed below some Curie temperature. However, none of the compositions prepared to date has shown the requisite cation ordering. In the case of $Nd_{18}Li_8Fe_5O_{39}$, the 2*a* site is occupied only by Fe^{4+}, but a small fraction of the Fe^{3+} cations, instead of simply filling the 8*e* sites, undergoes partial site exchange with Li^{+} and consequently occupies trigonal-prismatic 16*i* sites [2]. In other cases, for example $Nd_{18}Li_8Fe_4MnO_{39}$, the same lithium/iron exchange occurs and, in addition, the 2*a* site is not exclusively occupied by one element, but by a disordered array of iron and manganese, leaving the 8*e* site occupied by a mixture of lithium, iron and manganese [3]. As a consequence of this structural disorder, and also the existence of competing superexchange interactions involving the *Ln* sublattice, many of the compounds studied, including $Nd_{18}Li_8Fe_5O_{39}$ and $Nd_{18}Li_8Fe_4MnO_{39}$, behave as spin glasses with $T_g \sim 8$ K.

Although the studies referred to above have not produced new magnetic materials, we have made a number of interesting observations, most notably that this structure is able to stabilise cations in unusual oxidation states and spin states. In all but one of the compounds studied to date [4], the Fe^{4+} cations on the 2*a* site adopt a low-spin configuration and the magnetic susceptibility of

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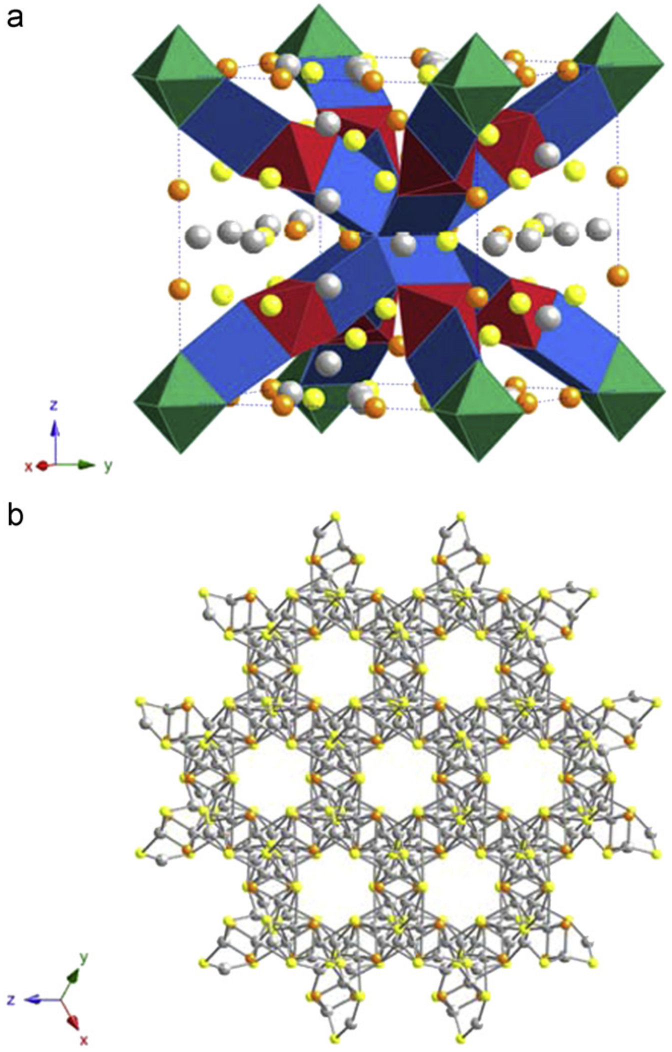

Fig. 1. (a) Polyhedral representation of the cubic (space group $Pm\bar{3}n$) structure of $La_{18}Li_8Rh_5O_{39}$; LiO_6 trigonal prisms are blue (16*i* site), RhO_6 octahedra are green (2*a*) and red (8*e*), grey circles represent oxygen (O2 and O3), yellow circles La1 and orange circles La2. (b) The La–O2–O3 framework viewed along ⟨1 1 1⟩; the polyhedral chains run through the channels. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$Nd_{18}Li_8Fe_{5-x}Mn_xO_{39}$ [3] is best interpreted by assuming that the Mn^{3+} cations on the 8*e* sites are in a low-spin state. The oxidation state Fe^{4+} is relatively rare in oxide chemistry but when it does occur the cation usually adopts a high-spin state; Mn^{3+} is not rare, but it is also usually found in a high-spin state in oxides. However, both of these cations have been shown to adopt a low-spin state under high pressure [7,8]. Similarly, Ru^{3+}, which we believe to be present in a low concentration in $Pr_{18}Li_8Fe_4RuO_{39}$ [4] and $La_{18}Li_8Rh_4RuO_{39}$ [6], has been stabilized under high-pressure conditions [9]. We have therefore proposed that the *Ln*–O framework illustrated in Fig. 1(b) exerts a significant chemical pressure on the polyhedral chains that occupy the hexagonal cavities within the framework and we have begun to explore the possibility of introducing into the octahedral sites metals that might not be expected to be compatible with the structure under normal conditions. Our initial study of titanium-containing materials focussed on cation-deficient compositions [10] and those containing no other magnetic 3*d* cations [6], but we are now able to report the magnetic properties of $Nd_{18}Li_8Fe_4TiO_{39}$.

2. Experimental

A polycrystalline sample of $Nd_{18}Li_8Fe_4TiO_{39}$ was synthesised using a solid-state technique. Stoichiometric quantities of predried neodymium(III) oxide (99.99%, Alfa Aesar), iron(III) oxide (99.99%, Alfa Aesar), and titanium(IV) oxide (99.995%, Alfa Aesar) were ground together with a 50% excess of volatile lithium carbonate (AnalaR) prior to firing in pellet form at 800 °C in air for 12 h. A further 50% excess lithium carbonate was ground into the reaction mixture before it was fired again in air for 1 h, as a pellet, at 1000 °C.

The progress of the reaction was monitored by X-ray powder diffraction. High-resolution X-ray powder diffraction data for use in quantitative analysis were collected from the final product over the angular range $5 \leq 2\theta/^\circ \leq 125$. The X-ray scattering from the material is dominated by the heavy metals and consequently it was not possible to perform a full structural analysis using these data. Limited Rietveld [11] refinements were carried out using the GSAS [12] suite of programs in order to determine the unit-cell parameter. Backgrounds were fitted using a Chebyshev polynomial of the first kind and the peak shape was modelled using a pseudo-Voigt function.

The diffractometer D2b at the Institut Laue Langevin, Grenoble, France was used to collect neutron powder diffraction data using a wavelength of 1.59460(2) Å. The unit-cell parameter derived from X-ray diffraction data was used to calibrate the neutron wavelength. Data were collected over the angular range $5 \leq 2\theta/^\circ \leq 160$ with a step size $\Delta 2\theta = 0.05^\circ$ at room temperature. The sample ($\sim$0.5 g) was contained in a vanadium can of diameter 5 mm. Rietveld refinement of the structure was carried out using the FULLPROF [13] program. The background level was determined by linear interpolation between a set of background points with refinable heights. Peak shapes were modelled using a pseudo-Voigt function together with a correction for peak asymmetry.

Magnetic measurements were carried out using a Quantum Design MPMS 5000 SQUID magnetometer. The sample magnetisation was measured as a function of temperature on warming from 2 to 300 K after cooling both in zero field (ZFC) and in the measuring field of 100 Oe (FC). The isothermal magnetisation was measured as a function of field ($-50 \leq H/\text{kOe} \leq 50$) at 2, 10 and 50 K after cooling to the measuring temperature in 50 kOe. AC susceptibility data were recorded at 4 frequencies ($1 \leq \omega/\text{Hz} \leq 1000$) in a direct field of 1.96(1) Oe, measured using a gadolinium(III) oxide standard, and an oscillating field of amplitude 3.5 Oe over an appropriate temperature range with $\Delta T = 0.1$ K.

X-ray absorption experiments were conducted on beamline B18 at the Diamond Light Source [14]. XANES spectra were collected at the iron *K*-edge of $Nd_{18}Li_8Fe_4TiO_{39}$ and the isostructural compounds $Nd_{18}Li_8Fe_5O_{39}$ and $La_{18}Li_8Fe_5O_{39}$. Data were also collected on Fe_2O_3 (99.99%, Alfa Aesar) as a standard. All samples were diluted with an appropriate amount of cellulose and pressed into a pellet which was held in a pulse tube cryostat at 1.5 K. The measurements were performed in fluorescence mode using a high-rate, nine-element germanium solid-state detector system. A titanium metal foil was used to calibrate the energy scale of the spectrometer at the Ti *K*-edge, 4.966 keV. Energy steps as small as 0.35 eV were employed near the absorption edges with a counting time of 1 s per step. The program Athena was subsequently used for background correction and normalisation [15].

The iron-57 Mössbauer spectra of $Nd_{18}Li_8Fe_4TiO_{39}$ have been measured between 25 and 295 K with a constant-acceleration spectrometer which utilised a rhodium-matrix cobalt-57 source and was calibrated at 295 K with α-iron powder. The Mössbauer spectral absorber contained 20 mg cm^{-2} of the sample powder mixed with boron nitride. The ideal thickness of the Mössbauer absorber is limited to this value because of the strong non-resonant