**Li$_{11}$Nd$_{18}$Fe$_4$O$_{39-\delta}$ Revisited**

Peter D. Battle,*† Sian E. Dutton,‡ Fernande Grandjean,§∥ Gary J. Long,∥ and Katsuyoshi Oh-ishi‡

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, U. K.
‡Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge, CB3 0HE, U. K.
§Faculty of Sciences, University of Liége, B-4000 Sart-Tilman, Belgium
∥Department of Chemistry, Missouri University of Science and Technology, University of Missouri, Rolla, Missouri 65409-0010, United States
¶Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga Bunkyo-ku, Tokyo 112-8551, Japan

**ABSTRACT:** The structure proposed for Li$_{11}$Nd$_{18}$Fe$_4$O$_{39-\delta}$ (Chen et al. Inorg. Chem. 2012, 51, 8073) on the basis of diffraction and Mössbauer spectral data is compared to that determined previously for Nd$_{18}$Li$_8$Fe$_5$O$_{39}$ (Dutton et al. Inorg. Chem. 2008 47, 11212) using the same techniques. The Mössbauer spectrum reported by Chen et al. has been reinterpreted. The newly refined spectral parameters differ significantly from the published values but are similar to those reported for Nd$_{18}$Li$_8$Fe$_5$O$_{39}$. The relative areas of the three components indicate that iron cations occupy the 2$a$, 8$c$, and 16$i$ sites in space group $Pm\bar{3}n$, in disagreement with the model determined from neutron diffraction by Chen et al. in which only the 2$a$ and 8$c$ sites are so occupied. The relationship between Li$_{11}$Nd$_{18}$Fe$_4$O$_{39-\delta}$ and Nd$_{18}$Li$_8$Fe$_5$O$_{39}$ is discussed, and it is proposed that the sample prepared by Dutton et al. is a kinetic product whereas the sample prepared by Chen et al. is the thermodynamically preferred product.

**INTRODUCTION**

The crystal structure of La$_{18}$Li$_8$Rh$_5$O$_{39}$, see Figure 1, was deduced from neutron powder diffraction data in 2005.1 Chains of coordination polyhedra, in which octahedral sites alternate with trigonal prismatic sites, were found to occupy channels within a La--O framework. The chains and channels run along the $\langle 111 \rangle$ directions of the cubic unit cell, and the chains intersect each other at $(0, 0, 0)$ and $(1/2, 1/2, 1/2)$. Equivalent octahedral sites are located at these two points of intersection, and a further, crystallographically distinct octahedral site is located halfway between them. The two distinct types of octahedral sites, both occupied by rhodium, are always separated from each other by a prismatic site which is occupied by lithium. The Rh$^{3+}$ and Rh$^{4+}$ cations, which occur in a 4:1 ratio in La$_{18}$Li$_8$Rh$_5$O$_{39}$, are found respectively on the 8$c$ and 2$a$ sites of space group $Pm\bar{3}n$; the midchain 8$c$ site is significantly larger than the 2$a$ site at the points of intersection, and the cation ordering is thus consistent with the difference in size of the sites. The Li$^+$ cations are located on 16$i$ sites within the prisms.

Figure 1. Cubic La$_{18}$Li$_8$Rh$_5$O$_{39}$ structure (space group $Pm\bar{3}n$); gray circles represent oxygen, black circles La. The LaO$_6$ trigonal prisms are blue (16$i$ site); the RhO$_6$ octahedra are green (2$a$ site) and red (8$c$). A 2$a$ site at the center of the unit cell is hidden in this view.

Received: October 3, 2012
Recently, Chen et al. have carried out a phase-diagram study of the Nd$_2$O$_3$−Fe$_2$O$_3$−Li$_2$O ternary system in an attempt to prepare a pure sample for Ln = Nd, M = M' = Fe. They report the synthesis, from a stoichiometric mixture of starting materials, of a monophase sample of composition Li$_{11}$Nd$_{18}$Fe$_4$O$_{39−δ}$. Dutton et al. have previously reported the synthesis of Nd$_{18}$Li$_8$Fe$_5$O$_{39}$ contaminated, as usual, by lithium carbonate. X-ray diffraction shows that the two compounds have the same unit-cell parameter. Consequently, Chen et al. suggest that the composition assigned to the compound prepared by Dutton et al. is incorrect. This implies that 20% of the iron in the reaction mixture used by the latter is in a phase other than the principal product. The fact, not commented on by Chen et al., that this material was studied by $^{57}$Fe Mössbauer spectroscopy down to 4.2 K without the observation of a second iron-containing phase is therefore surprising, as is the fact that the magnetic susceptibility shows no deviation from paramagnetic behavior above 10 K. The use of a lithium-rich formulation by Chen et al. stems from the analysis of their neutron diffraction data which suggested that 25% of the octahedral 8e sites in the structure are occupied by lithium rather than iron cations. Dutton et al. found an Fe:Li ratio of 85:15 on this site, but with the important difference that the prismatic 16i site was partially occupied by iron cations so as to maintain the overall composition. This model was consistent with both their neutron diffraction and Mössbauer spectroscopic data. The remainder of the extra lithium required by the composition Li$_{11}$Nd$_{18}$Fe$_4$O$_{39−δ}$ is attributed by Chen et al. to the partial occupation by lithium of a 24k site which was unoccupied in the structural model proposed by Dutton et al. It appears that this additional site lies only 1.57 Å from an oxide ion, and only 1.599 Å from a lithium cation in one of the polyhedral chains. The authors recognize this as an issue and suggest that the two cation sites are not simultaneously occupied, but the implied presence of vacancies on the 16i sites and the consequences of this for the composition are not discussed further.

The Mössbauer spectra recorded by Chen et al. do suggest the possible presence of some Fe$^{3+}$ on the 16i site in their sample, which would add to the uncertainty in the overall composition. The full-width at half-maximum of this spectral component, 0.194 mm s$^{-1}$, is as narrow as is permitted by the Heisenberg Uncertainty Principle and is considerably narrower than the other line widths reported by either Chen et al. or Dutton et al. This might be considered surprising in view of the structural disorder around the 16i site, although Chen et al. comment that the inclusion of this component was necessary to obtain satisfactory fits. In this paper we report our analysis of the spectrum published by Chen et al.

**RESULTS**

No further experimental work has been carried out. Rather we have digitized and refitted the experimental data shown in Figure 5 from reference 8. Unfortunately, Chen et al. failed to report the percentage transmission in their Mössbauer spectrum. We have therefore assumed that the percentage transmission was similar to that observed earlier, and we have fixed the minimum transmission at 98%. First, we fitted the experimental data with the spectral parameters constrained to be identical to the published fit parameters given in Table 4 of reference 8; we refined only the baseline and the total spectral absorption area. As expected, this leads to a fit that is virtually identical to that shown in Figure 5 of reference 8. Second, we refined the isomer shift, δ, the quadrupole splitting, ΔE$_Q$, the full width at half-maximum, Γ, and the percentage area of each of the three doublets, as well as the baseline, and the total absorption area, that is, a total of 14 parameters. This refinement used the highly robust and efficient Levenberg-Marquardt algorithm. The result of this fit is shown in the lower portion of Figure 2; the fit previously reported in reference 5 is as narrow as is permitted by the correlation matrix. Further, the reported spectral parameters may converge may be a consequence of the extensive correlations between the refined spectral parameters, as is shown by our correlation matrix. Further, the fit obtained herein for the Li$_{11}$Nd$_{18}$Fe$_5$O$_{39}$ spectrum yields spectral parameters that are very similar to those reported in

**DISCUSSION**

It is quite clear that the fit published by Chen et al. for Li$_{11}$Nd$_{18}$Fe$_5$O$_{39}$ had not properly converged. This failure to converge may be a consequence of the extensive correlations between the refined spectral parameters, as is shown by our correlation matrix. Further, the reported spectral parameters were given with more significant figures than is justified by the estimated, but not statistically obtained, accuracies. The refined fit obtained herein for the Li$_{11}$Nd$_{18}$Fe$_5$O$_{39}$ spectrum yields spectral parameters that are very similar to those reported in

![Image](image-url)
The isomer shift is given relative to α-iron at room temperature. The relative spectral areas of the three components have been constrained to agree exactly with the iron occupancies obtained from neutron diffraction refinements reported by Dutton et al. in reference 5. The proposed stoichiometry and the Mössbauer spectral parameters reported by Chen et al. in reference 8. This component was assigned by Chen et al. to a partial iron(III) occupancy of the 16i site. The best fit refinement obtained herein for the experimental Mössbauer spectral data reported by Chen et al. in Figure 5 of reference 8.

### Table 1. Mössbauer Spectral Parameters for Nd\(_{18}\)Li\(_8\)Fe\(_3\)O\(_9\) and Li\(_{11}\)Nd\(_{18}\)Fe\(_4\)O\(_9\)

<table>
<thead>
<tr>
<th>compound</th>
<th>site</th>
<th>(\delta, \text{mm/s})</th>
<th>(\Delta E_{Q}, \text{mm/s})</th>
<th>(\Gamma, \text{mm/s})</th>
<th>area, %</th>
<th>assignment</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd(_{18})Li(_8)Fe(_3)O(_9)</td>
<td>2a</td>
<td>-0.229(9)</td>
<td>0.30(2)</td>
<td>0.33(2)</td>
<td>19.99</td>
<td>iron(IV)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>8e</td>
<td>0.306(1)</td>
<td>0.149(8)</td>
<td>0.332(7)</td>
<td>68.17</td>
<td>iron(III)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>16i</td>
<td>0.27(1)</td>
<td>0.88(3)</td>
<td>0.33(3)</td>
<td>11.84</td>
<td>iron(III)</td>
<td>5</td>
</tr>
<tr>
<td>Li(<em>{11})Nd(</em>{18})Fe(_4)O(_9)</td>
<td>2a</td>
<td>-0.296(20)</td>
<td>0.334(20)</td>
<td>0.360(20)</td>
<td>21.8(2.0)</td>
<td>iron(IV)</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>8e</td>
<td>0.294(20)</td>
<td>0.041(20)</td>
<td>0.418(20)</td>
<td>71.6(2.0)</td>
<td>iron(III)</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>16d</td>
<td>0.077(20)</td>
<td>0.948(20)</td>
<td>0.194(20)</td>
<td>6.7(2.0)</td>
<td>iron(III)</td>
<td>8</td>
</tr>
<tr>
<td>Li(<em>{11})Nd(</em>{18})Fe(_4)O(_9)</td>
<td>2a</td>
<td>-0.28(3)</td>
<td>0.35(5)</td>
<td>0.34(4)</td>
<td>20(5)</td>
<td>iron(IV)</td>
<td>(\epsilon)</td>
</tr>
<tr>
<td></td>
<td>8e</td>
<td>0.282(4)</td>
<td>0.08(3)</td>
<td>0.38(2)</td>
<td>65(2)</td>
<td>iron(III)</td>
<td>(\epsilon)</td>
</tr>
<tr>
<td></td>
<td>16i</td>
<td>0.06(3)</td>
<td>0.92(7)</td>
<td>0.35(5)</td>
<td>15(3)</td>
<td>iron(III)</td>
<td>(\epsilon)</td>
</tr>
</tbody>
</table>

**CONCLUSION**

Although it is easy to accept that the samples prepared by the two groups have different compositions, it is not obvious that the composition assigned by Dutton et al. to their sample is incorrect. The samples prepared by Chen et al. were heated for 12–24 h at 950 °C, whereas Dutton et al. synthesized their samples by heating at 950 °C for only 1 h. It is thus possible that the sample prepared by Dutton et al. is a kinetic rather than thermodynamic product.

**REFERENCES**