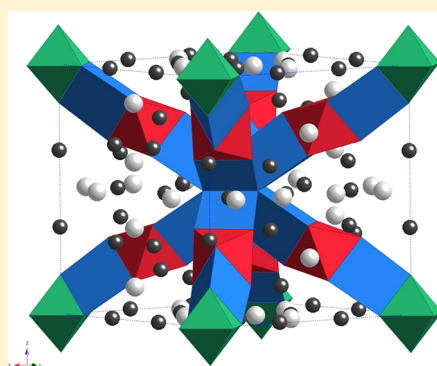


1 **Li₁₁Nd₁₈Fe₄O_{39-δ} Revisited**2 Peter D. Battle,^{*,†} Sian E. Dutton,[‡] Fernande Grandjean,^{§,||} Gary J. Long,^{||} and Katsuyoshi Oh-ishi[⊥]3 [†]Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, U. K.4 [‡]Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge, CB3 0HE, U. K.5 [§]Faculty of Sciences, University of Liège, B-4000 Sart-Tilman, Belgium6 ^{||}Department of Chemistry, Missouri University of Science and Technology, University of Missouri, Rolla, Missouri 65409-0010,
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10 **ABSTRACT:** The structure proposed for Li₁₁Nd₁₈Fe₄O_{39-δ} (Chen et al. *Inorg.*
11 *Chem.* **2012**, *51*, 8073) on the basis of diffraction and Mössbauer spectral data is
12 compared to that determined previously for Nd₁₈Li₈Fe₅O₃₉ (Dutton et al. *Inorg.*
13 *Chem.* **2008** *47*, 11212) using the same techniques. The Mössbauer spectrum
14 reported by Chen et al. has been reinterpreted. The newly refined spectral
15 parameters differ significantly from the published values but are similar to those
16 reported for Nd₁₈Li₈Fe₅O₃₉. The relative areas of the three components indicate
17 that iron cations occupy the 2*a*, 8*e*, and 16*i* sites in space group *Pm* $\bar{3}$ *n*, in
18 disagreement with the model determined from neutron diffraction by Chen et al. in
19 which only the 2*a* and 8*e* sites are so occupied. The relationship between
20 Li₁₁Nd₁₈Fe₄O_{39-δ} and Nd₁₈Li₈Fe₅O₃₉ is discussed, and it is proposed that the
21 sample prepared by Dutton et al. is a kinetic product whereas the sample prepared
22 by Chen et al. is the thermodynamically preferred product.



23 ■ INTRODUCTION

24 The crystal structure of La₁₈Li₈Rh₅O₃₉, see Figure 1, was
25 deduced from neutron powder diffraction data in 2005.¹ Chains
26 of coordination polyhedra, in which octahedral sites alternate

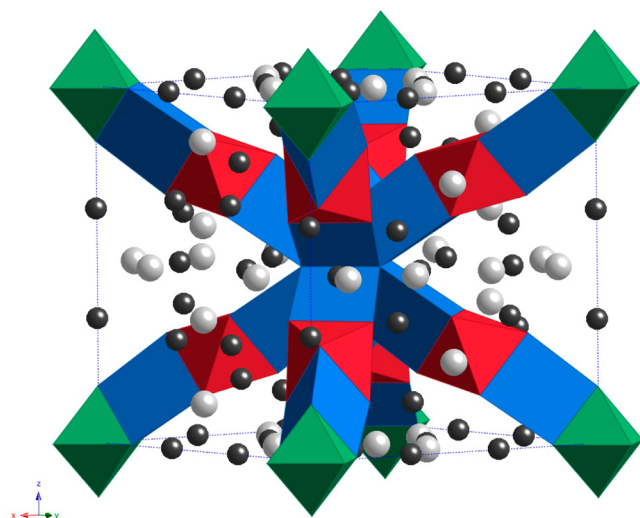


Figure 1. Cubic La₁₈Li₈Rh₅O₃₉ structure (space group *Pm* $\bar{3}$ *n*); gray circles represent oxygen, black circles La. The LiO₆ trigonal prisms are blue (16*i* site), the RhO₆ octahedra are green (2*a* site) and red (8*e*). A 2*a* site at the center of the unit cell is hidden in this view.

with trigonal prismatic sites, were found to occupy channels 27
within a La–O framework. The chains and channels run along 28
the (111) directions of the cubic unit cell, and the chains 29
intersect each other at (0, 0, 0) and (1/2, 1/2, 1/2). Equivalent 30
octahedral sites are located at these two points of intersection, 31
and a further, crystallographically distinct octahedral site is 32
located halfway between them. The two distinct types of 33
octahedral sites, both occupied by rhodium, are always 34
separated from each other by a prismatic site which is occupied 35
by lithium. The Rh³⁺ and Rh⁴⁺ cations, which occur in a 4:1 36
ratio in La₁₈Li₈Rh₅O₃₉, are found respectively on the 8*e* and 2*a* 37
sites of space group *Pm* $\bar{3}$ *n*; the midchain 8*e* site is significantly 38
larger than the 2*a* site at the points of intersection, and the 39
cation ordering is thus consistent with the difference in size of 40
the sites. The Li⁺ cations are located on 16*i* sites within the 41
prisms. 42

Subsequent studies^{2–7} have shown that the second-row 43
transition-metal element in Ln₁₈Li₈Rh₅O₃₉ (Ln = La, Nd, Pr) 44
can be replaced by several combinations of first-row elements 45
to form Ln₁₈Li₈M_{5-x}M'_xO₃₉ (M, M' = Mn, Fe, Co). 46
Unfortunately, the samples produced have always been 47
contaminated by the excess lithium carbonate used in the 48
synthesis. X-ray diffraction patterns collected on laboratory 49
diffractometers have not always revealed the presence of the 50
impurity phase, but it has been easily identified in neutron 51

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52 diffraction patterns. However, the crystal structure of the
53 weakly diamagnetic carbonate is known, and the presence of
54 this second phase has therefore not presented a problem in the
55 analysis of diffraction or magnetometry data collected from
56 these samples.

57 Recently⁸ Chen et al. have carried out a phase-diagram study
58 of the $\text{Nd}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--Li}_2\text{O}$ ternary system in an attempt to
59 prepare a pure sample for $Ln = \text{Nd}$, $M = M' = \text{Fe}$. They report
60 the synthesis, from a stoichiometric mixture of starting
61 materials, of a monophasic sample of composition
62 $\text{Li}_{11}\text{Nd}_{18}\text{Fe}_4\text{O}_{39-\delta}$. Dutton et al. have previously⁵ reported the
63 synthesis of $\text{Nd}_{18}\text{Li}_8\text{Fe}_5\text{O}_{39}$ contaminated, as usual, by lithium
64 carbonate. X-ray diffraction shows that the two compounds
65 have the same unit-cell parameter. Consequently, Chen et al.
66 suggest that the composition assigned to the compound
67 prepared by Dutton et al. is incorrect. This implies that 20%
68 of the iron in the reaction mixture used by the latter is in a
69 phase other than the principal product. The fact, not
70 commented on by Chen et al., that this material was studied
71 by ^{57}Fe Mössbauer spectroscopy down to 4.2 K without the
72 observation of a second iron-containing phase is therefore
73 surprising, as is the fact that the magnetic susceptibility shows
74 no deviation from paramagnetic behavior above 10 K. The use
75 of a lithium-rich formulation by Chen et al. stems from the
76 analysis of their neutron diffraction data which suggested that
77 25% of the octahedral $8e$ sites in the structure are occupied by
78 lithium rather than iron cations. Dutton et al. found an Fe:Li
79 ratio of 85:15 on this site, but with the important difference
80 that the prismatic $16i$ site was partially occupied by iron cations
81 so as to maintain the overall composition. This model was
82 consistent with both their neutron diffraction and Mössbauer
83 spectroscopic data. The remainder of the extra lithium required
84 by the composition $\text{Li}_{11}\text{Nd}_{18}\text{Fe}_4\text{O}_{39-\delta}$ is attributed by Chen et
85 al. to the partial occupation by lithium of a $24k$ site which was
86 unoccupied in the structural model proposed by Dutton et al. It
87 appears that this additional site lies only 1.57 Å from an oxide
88 ion, and only 1.599 Å from a lithium cation in one of the
89 polyhedral chains. The authors recognize this as an issue and
90 suggest that the two cation sites are not simultaneously
91 occupied, but the implied presence of vacancies on the $16i$ sites
92 and the consequences of this for the composition are not
93 discussed further.

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

106 ■ RESULTS

107 No further experimental work has been carried out. Rather we
108 have digitized and refitted the experimental data shown in
109 Figure 5 from reference 8. Unfortunately, Chen et al. failed to
110 report⁸ the percentage transmission in their Mössbauer
111 spectrum. We have therefore assumed that the percentage
112 transmission was similar to that observed⁵ earlier, and we have
113 fixed the minimum transmission at 98%. First, we fitted the

114 experimental data with the spectral parameters constrained to
115 be identical to the published fit parameters given in Table 4 of
116 reference 8; we refined only the baseline and the total spectral
117 absorption area. As expected, this leads to a fit that is virtually
118 identical to that shown in Figure 5 of reference 8. Second, we
119 refined the isomer shift, δ , the quadrupole splitting, ΔE_Q , the
120 full width at half-maximum, Γ , and the percentage area of each
121 of the three doublets, as well as the baseline, and the total
122 absorption area, that is, a total of 14 parameters. This
123 refinement used the highly robust and efficient Levenberg–
124 Marquardt algorithm. The result of this fit is shown in the lower
125 portion of Figure 2; the fit previously reported in reference 5

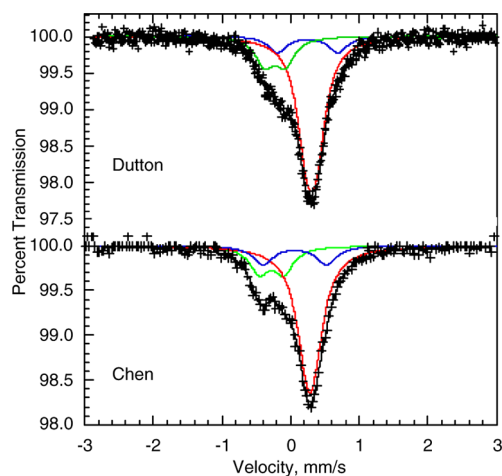


Figure 2. Room temperature Mössbauer spectra of $\text{Nd}_{18}\text{Li}_8\text{Fe}_5\text{O}_{39}$ previously published by Dutton, et al. in reference 5, top, and of $\text{Li}_{11}\text{Nd}_{18}\text{Fe}_4\text{O}_{39}$ obtained from Chen, et al. in reference 8 and fitted with three unconstrained symmetric quadrupole doublets, bottom. The vertical scale of the lower spectrum is an approximation because no scale is given in reference 8. The colors used to distinguish the three components in this figure correspond to those used for the different sites in Figure 1; the $2a$, $8e$, and $16i$ sites are in green, red, and blue, respectively.

126 for $\text{Nd}_{18}\text{Li}_8\text{Fe}_5\text{O}_{39}$ is shown for comparison in the upper
127 portion of this figure. In this refinement, rather surprisingly, we
128 obtained a lower χ^2 value than that obtained in the first step, an
129 indication that the fit shown in Figure 5 of reference 8 is not
130 the best possible fit. More significantly, all the line widths
131 refined to normal values that are similar for the three
132 components. Further, this fit avoids the significant misfitting
133 present at both -0.2 and $+0.6 \text{ mm/s}$ in Figure 5 of Chen et al.;
134 the misfitting is primarily associated with the artificially narrow
135 line width of the doublet tentatively assigned by them to the $16i$
136 site. Our refined parameters are given at the bottom of Table 1;
137 the parameters published in references 5 and 8 are given for
138 comparison at the top and center of this table, respectively.

139 ■ DISCUSSION

140 It is quite clear that the fit published by Chen et al.⁵ for
141 $\text{Li}_{11}\text{Nd}_{18}\text{Fe}_4\text{O}_{39}$ had not properly converged. This failure to
142 converge may be a consequence of the extensive correlations
143 between the refined spectral parameters, as is shown by our
144 correlation matrix. Further, the reported spectral parameters
145 were given with more significant figures than is justified by the
146 estimated, but not statistically obtained, accuracies. The refined
147 fit obtained herein for the $\text{Li}_{11}\text{Nd}_{18}\text{Fe}_4\text{O}_{39}$ spectrum yields
148 spectral parameters that are very similar to those reported in

Table 1. Mössbauer Spectral Parameters for $\text{Nd}_{18}\text{Li}_8\text{Fe}_5\text{O}_{39}$ and $\text{Li}_{11}\text{Nd}_{18}\text{Fe}_4\text{O}_{39}$

compound	site	$\delta,^a$ mm/s	$\Delta E_Q,^b$ mm/s	$\Gamma,^c$ mm/s	area, %	assignment	ref.
$\text{Nd}_{18}\text{Li}_8\text{Fe}_5\text{O}_{39}^b$	2a	-0.229(9)	0.30(2)	0.33(2)	19.99	iron(IV)	5
	8e	0.306(1)	0.149(8)	0.332(7)	68.17	iron(III)	5
	16i	0.27(1)	0.88(3)	0.33(3)	11.84	iron(III)	5
$\text{Li}_{11}\text{Nd}_{18}\text{Fe}_4\text{O}_{39}^c$	2a	-0.296(20)	0.334(20)	0.360(20)	21.8(2.0)	iron(IV)	8
	8e	0.294(20)	0.041(20)	0.418(20)	71.6(2.0)	iron(III)	8
	16i ^d	0.077(20)	0.948(20)	0.194(20)	6.7(2.0)	iron(III)	8
$\text{Li}_{11}\text{Nd}_{18}\text{Fe}_4\text{O}_{39}^e$	2a	-0.28(3)	0.35(5)	0.34(4)	20(5)	iron(IV)	e
	8e	0.282(4)	0.08(3)	0.38(2)	65(2)	iron(III)	e
	16i	0.06(3)	0.92(7)	0.35(5)	15(3)	iron(III)	e

^aThe isomer shift is given relative to α -iron at room temperature. ^bThe 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. ^cThe proposed stoichiometry and the Mössbauer spectral parameters reported by Chen et al. in reference 8. ^dThis component was assigned by Chen et al. to a partial iron(III) occupancy of the 16i site. ^eThe best fit refinement obtained herein for the experimental Mössbauer spectral data reported by Chen et al. in Figure 5 of reference 8.

reference 5 for $\text{Nd}_{18}\text{Li}_8\text{Fe}_5\text{O}_{39}$. The major difference is the spectral area assigned to the 16i site that is larger herein than in reference 5 and accounts for the increased absorption at -0.4 mm/s in the lower spectrum in Figure 2 as compared to the upper spectrum. Consequently, the Mössbauer spectrum published by Chen et al.⁸ does not support their neutron diffraction refinement, in which iron cations occupy only the 2a and 8e sites in a ratio of 1:3. In contrast, the Mössbauer spectrum agrees very well with the iron occupancies of the 2a, 8e, and 16i sites proposed in reference 5 for $\text{Nd}_{18}\text{Li}_8\text{Fe}_5\text{O}_{39}$, but with a slightly larger occupancy of the 16i sites. Alternatively, the third doublet in blue in the lower spectrum in Figure 2 with a relative area of 15(3) % could be assigned to an undetermined iron-cation containing impurity and then the green and red doublets assigned to the 2a and 8e sites have an area ratio of 1:3.3 close to the 1:3 expected from the neutron diffraction refinement. In this case, the presence of three doublets in the Mössbauer spectrum certainly does not support the claim of purity of the samples prepared⁸ by Chen et al.

There is one further aspect of the model proposed by Chen et al. that should be considered carefully. Although they claim to have prepared monophasic samples, they state that the sample used in their neutron diffraction experiment contained 1.9 wt % LiFeO_2 . As a result of the large difference in relative molecular mass between the impurity and the principal phase, this corresponds to a molar ratio of $\sim 1:1.38$. The composition of the sample from which the structural model is derived therefore differs significantly from the ideal formulation. Unfortunately, the impurity was not detected in their preliminary X-ray studies. The neutron diffraction pattern shown by Dutton et al. reveals no such impurity, and the Mössbauer spectra they present do not show a component that is consistent with the hyperfine parameters reported previously^{9,10} for LiFeO_2 or NdFeO_3 , the two most likely iron-containing impurities. We estimate the detection limit of these spectra to be $\leq 3\%$. Furthermore, when Dutton et al. attempted to prepare $\text{Nd}_{18}\text{Li}_8\text{Co}_5\text{O}_{39}$ they detected a 2.6 wt % (1:1 molar) LiCoO_2 impurity by in-house X-ray diffraction and subsequently prepared a monophasic sample of $\text{Nd}_{18}\text{Li}_8\text{Co}_4\text{O}_{39}$. This suggests that the samples of Dutton et al. were subjected to a particularly rigorous check for impurities, and that had 20% of the iron in their reaction mixture been in a second phase it is likely that it would have been identified.

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.

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Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Frampton, P. P. C.; Battle, P. D.; Ritter, C. *Inorg. Chem.* **2005**, *44*, 7138.
- (2) Battle, P. D.; Dutton, S. E.; Thammajak, N.; Grandjean, F.; Sougrati, M. T.; Long, G. J.; Oh-ishi, K.; Nakanishi, S. *Inorg. Chem.* **2010**, *49*, 5912.
- (3) Battle, P. D.; Dutton, S. E.; van Daesdonk, P. A. *J. Solid State Chem.* **2010**, *183*, 1620.
- (4) Battle, P. D.; Dutton, S. E.; Grandjean, F.; Long, G. J.; Thammajak, N.; Wisetsuwannaphum, S. *J. Solid State Chem.* **2011**, *184*, 2580.
- (5) Dutton, S. E.; Battle, P. D.; Grandjean, F.; Long, G. J.; Oh-ishi, K. *Inorg. Chem.* **2008**, *47*, 11212.
- (6) Dutton, S. E.; Battle, P. D.; Grandjean, F.; Long, G. J.; van Daesdonk, P. A. *Inorg. Chem.* **2009**, *48*, 1613.
- (7) Dutton, S. E.; Battle, P. D.; Grandjean, F.; Long, G. J.; Sougrati, M. T.; van Daesdonk, P. A.; Winstone, E. *J. Solid State Chem.* **2009**, *182*, 1638.
- (8) Chen, Y.; Reeves-McLaren, N.; Bingham, P. A.; Forder, S. D.; West, A. R. *Inorg. Chem.* **2012**, *51*, 8073.
- (9) Cox, D. E.; Shirane, G.; Flinn, P. A.; Ruby, S. L.; Takei, W. *J. Phys. Rev.* **1963**, *132*, 1547.
- (10) Eibschutz, M.; Shtrikman, S.; Treves, D. *Phys. Rev.* **1967**, *156*, 562.