Reverse Monte Carlo neutron scattering study of the ‘ordered-ice’ oxide pyrochlore Pb$_2$Ru$_2$O$_{6.5}$

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Abstract

We employ high-resolution total neutron scattering in conjunction with reverse Monte Carlo simulations to examine, in a detailed and unbiased manner, the crystal structure of the vacancy-ordered oxide pyrochlore Pb$_2$Ru$_2$O$_{6.5}$O$_0.5$ in light of its structural analogy with proton ordering in the structures of ice. We find that the vacancy and the O$^\prime$ ion are completely ordered, and that the average structure in the $F\bar{4}3m$ space group describes the vacancy ordering precisely. We complement these results with an examination of the Pb$^{2+}$ lone pair network using density functional electronic structure calculations, and a comparison of the low-temperature lattice-only heat capacity of Pb$_2$Ru$_2$O$_{6.5}$O$_0.5$ with that of other related pyrochlores.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years, pyrochlore [1] A$_2$B$_2$O$_6$O$^\prime$ compounds (also described compactly as A$_2$B$_2$O$_7$) have been explored—in cases where A is a rare-earth ion and B is a transition element—for a number of reasons, ranging from their unusual magnetic ‘spin-ice’ ground states [2] and their anomalous Hall effect behavior [3] to possible realization of magnetic monopoles [4], and because certain pyrochlore compositions, notably Y$_2$Ir$_2$O$_7$, can display electron correlation in the presence of spin–orbit coupling [5].

When pyrochlores are prepared with lone pair active ions such as Pb$^{2+}$ or Bi$^{3+}$ on their A sites, rather than rare-earth or alkaline-earth ions, one can expect interesting structural effects. An example of this is the grotesquely complicated low-temperature structure of Bi$_2$Sn$_2$O$_7$ and its numerous polymorphs that form upon heating [6, 7]. Hector and Wiggin [8] reported a low-temperature preparation of Bi$_2$Ti$_2$O$_6$O$^\prime$ in 2004; a compound which prefers to disorder extensively and locally, and remains cubic down to a temperature of 2 K rather than undergoing a phase transition to a coherently distorted ground state. This observation led to the suggestion that just as the pyrochlore lattice hinders coherent magnetic ordering [9], so too possibly are coherent lone pair induced displacements hindered in compounds such as Bi$_2$Ti$_2$O$_6$O$^\prime$ and related pyrochlores [10–12], a phenomenon dubbed ‘charge-ice’ [13] in analogy with problems of proton ordering in the structure of ice-I$_c$ and ice-I$_h$ [14, 15]. The low-temperature thermal properties [16] and detailed scattering studies [17] have supported the validity of this suggestion.

In contrast to A$_2$B$_2$O$_6$O$^\prime$ pyrochlores, which crystallize in the $Fd\bar{3}m$ space group and whose O$^\prime$ sites describe a diamond lattice, in Pb$_2$Ru$_2$O$_{6.5}$O$_0.5$ (average structure reported from Rietveld refinements of neutron [18] and synchrotron
using the electron localization function at an isosurface of 0.80. For clarity, Ru and O are not displayed in (b).

In this contribution, we employ high-resolution neutron scattering tools based on analysis using the reverse Monte Carlo method [21, 22] and least-squares refinements to establish, in a structurally unbiased manner, the extent of ordering between O’ and □. We find that the average structural description in the F43m space group of completely ordered vacancies is consistent with the results of the reverse Monte Carlo simulation of total scattering. An interesting consequence of the ordered vacancies is that the stereochemically active lone pairs on the Pb2+ ions have a location to position themselves in a completely coherent fashion as we shall show. We use this study to emphasize the importance of employing both the Bragg scattering intensity as well as the pair distribution function, $G(r)$, in the reverse Monte Carlo analysis. Finally, we examine the lattice part of the low-temperature heat capacity for local Einstein modes that have been observed in other pyrochlore compounds with incoherent lone pairs [11, 23].

2. Experimental and computational methods

The sample for neutron scattering was obtained by careful crushing and grinding of Pb$_2$Ru$_2$O$_6$O’$_{8.5}$ single crystals, whose average structure by synchrotron x-ray Rietveld refinement and whose electrical transport properties have been previously reported [19]. Time-of-flight (TOF) total neutron scattering was carried out at the NPDD instrument at Los Alamos National Laboratory at 300 and 15 K. Rietveld refinement was performed with the EXPGUI front end for GSAS [24]. Extraction of the PDF $G(r)$ with PDFGetN [25] used $Q_{\text{max}} = 35$ Å$^{-1}$. Reverse Monte Carlo simulations were run using RMCProfile version 6 [22] and a $6 \times 6 \times 6$ unit cell with 18 144 atoms. These simulations were simultaneously constrained by the Bragg profile and the $G(r)$. Multiple runs were performed and averaged when necessary to obtain the most accurate representation of the fit to data. First-principles electronic structure visualization made use of the linear muffin-tin orbital orbital method within the atomic sphere approximation using version 47C of the Stuttgart TB-LMTO-ASA program [26]. More details of such calculations in Pb- and Bi-based pyrochlore oxides can be found in [13].

3. Results and discussion

The result of Rietveld refinement using neutron TOF scattering is shown in figure 2. No impurities are present, and the F43m unit cell provides an excellent fit, with details into the high-$Q$ range reproduced past $Q = 12$ Å$^{-1}$. This model contains Pb atoms that are shifted off the ideal pyrochlore A site into a 16e position at $(x, x, x)$. The O’ anions occupy 4d sites. Details of the structure obtained from Rietveld refinement of the 300 and 15 K data are displayed in table 1. All atoms refine to their full occupancy and all the isotropic thermal parameters from the refinement refine to acceptable values.

With the ideal, average structure, density functional calculations can be performed, and used to locate the lone pairs on Pb$^{2+}$ [27] using the electron localization function (ELF) [28, 29]. Figure 1(b) displays the lone pair network,
Table 1. Average structural parameters for Pb2Ru2O6O₂ obtained from Rietveld refinement of TOF neutron diffraction data in the space group F43m (No. 216). a = 10.250 17(2) Å at 300 K and a = 10.227 75(2) Å at 15 K. All sites refine to full occupancy.

| Atom | Site | x     | y     | z     | Uiso (Å²) |
|------|------|-------|-------|-------|-----------|
| Pb   | 16e  | 0.8766(1) | x     | x     | 0.0117(1) |
| Ru   | 16e  | 0.3748(1) | x     | x     | 0.0057(1) |
| O1   | 24f  | 0.3053(2) | 0     | 0     | 0.0105(4) |
| O2   | 24g  | 0.4502(2) | 1/2   | 1/2   | 0.0082(3) |
| O'   | 4d   | 1/2   | 1/2   | 1/2   | 0.0089(3) |
| □    | 4a   | 0     | 0     | 0     | —         |

| Atom | Site | x     | y     | z     | Uiso (Å²) |
|------|------|-------|-------|-------|-----------|
| Pb   | 16e  | 0.87725(8) | x     | x     | 0.00377(8) |
| Ru   | 16e  | 0.3747(1) | x     | x     | 0.00299(8) |
| O1   | 24f  | 0.3039(1) | 0     | 0     | 0.0063(2) |
| O2   | 24g  | 0.4504(1) | 1/2   | 1/2   | 0.0042(3) |
| O'   | 4d   | 1/2   | 1/2   | 1/2   | 0.0051(2) |
| □    | 4a   | 0     | 0     | 0     | —         |

Manually altering the Pb positions or O’ ordering in the model reveals that both of these values are strongly constrained by the data. In figure 3 the effect on the goodness-of-fit χ² is plotted as a function of Pb displacement. For an ideal pyrochlore cell, the Pb would lie at the left-most end of the plot with x = 1/2 = 0.875. Refinements at T = 15 and 300 K both suggest Pb positions near 0.877, which are about 0.04 and 0.03 Å displaced, respectively, off their ideal sites and away from the nearby O’.

Moving fractional O’ occupancy onto the 4a vacant □ site in our model is equivalent to introducing site disorder, where having full occupancy on both sites would mimic the O’ sublattice of the full pyrochlore structure. The effect of increasing O’ occupancy on the □ site (with corresponding decrease at the O’ 4d position and using the same Uiso value) is seen in figure 3(b). Again, any occupancy on 4a results in an increased χ², implying that Bragg scattering supports O’ being fully ordered, even at 300 K. This strong proclivity to order the O’ and, in turn, the Pb displacements, is seen in related solid solutions Pb₂₋ₓLnₓRu₂O₇₋ₓ (Ln = Nd, Gd) which can tolerate only a small amount (x < 0.2) of A-site substitution before the disorder drives formation of a separate Fd3m phase [31].

The quality of the fit to the Rietveld-refined structure and the stabilities of the Pb position and O’ ordering provide evidence that Pb₂Ru₂O₆O₂ appears structurally to be consistent with the unit cell, unlike the full-O’ pyrochlores such as Bi₂Ti₂O₆O’, where the difficulty in accommodating the lone pairs results in incoherent structural disorder and off centering. In Bi₂Ti₂O₆O’, local structure analysis reveals details of

Figure 2. The neutron TOF Rietveld refinement for Pb₂Ru₂O₆O₂ at T = 15 K confirms the F43m space group. The data are presented in two panels to emphasize the Q range and the quality of the fit.

Figure 3. In (a), moving Pb off of its refined position at x = 0.8766 results in a poorer fit, seen from the poorer fit (larger χ²) for data acquired at 15 and 300 K. In (b), O’ occupancy perfectly ordered (left) and increased to simulate disorder spilling onto the vacant sites. Again, even small amounts of disordered O’ give a poorer Rietveld refinement.

visualized for an isosurface value of ELF = 0.80. The lone pairs on Pb²⁺ are seen to coherently dispose themselves in the direction of the □. It is interesting to note that while lone pairs are known to possess a volume that is comparable to that of the oxide anion, the lone pair to nucleus (of Pb²⁺) distance is significantly smaller than the distance from Pb²⁺ to O’. Hence, the lone pairs are not actually located in the vacant □ site at 4a(0, 0, 0). This is in keeping with the empirical findings of Galy, Andersson and others [30]. It is instructive to compare this ordered lone pair arrangement with what is seen in ‘charge-ice’ Bi₂Ti₂O₆O’. In Bi₂Ti₂O₆O’, which has no vacant site, the lone pairs are obliged to displace perpendicular to the O’−A−O’ axis, and they do so incoherently, with profound structural and thermodynamic consequences [13, 16, 17].

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the short-range structure that are difficult to determine from average structure probes that rely on Bragg scattering alone. In a system such as Pb$_2$Ru$_2$O$_6$O$_{0.5}$, where structural frustration should be removed by O‘ ordering, it is of interest to ask whether the local structure exhibits any hallmarks of a disordering that is not seen in the Bragg scattering/Rietveld analysis.

Reverse Monte Carlo fits to the neutron TOF total scattering are shown in figure 4. The Bragg profile retains the long-range periodicity and average atomic displacement parameters of the structure, while the $G(r)$ constrains pairwise distances and reproduces the local structure. By simultaneously fitting both datasets, we are left with a large supercell that provides a snapshot of the material. Structural details of this model can be analyzed statistically to determine the precise local tendencies supported by the experimental data.

The partial pair distribution functions in figure 5(a) display the Pb–O′ distances in the unit cell $n_{Pb-O'}(r)$ and the distances of Pb to the vacant site $n_{Pb-□}(r)$. The shift versus $r$ shows that the Pb–O′ distances are longer, so the Pb nuclei have displaced off their ideal site toward the vacant □ position. This distribution is roughly centered on the Pb–O′ distance of 2.25 Å from Rietveld refinement at $T = 15$ K.

Partial pair distribution functions can also reveal ordering on the O′ sublattice when vacancy ‘atoms’ with zero scattering cross-section are placed on the vacant O′ positions. The vacancies are freely allowed to swap with O′ during the RMC simulation. For a simultaneous fit to Bragg peaks and the $G(r)$, ordering is retained: the $r = 4.45$ Å nearest-neighbor distance between occupied and vacant O′ sites has no intensity for the $n_{O'-O'}(r)$ distribution in figure 5(b), indicating that no two O′ atoms share neighboring sites. However, if the RMC simulation is performed as a fit to the $G(r)$ only (and the Bragg profile is ignored) then the O′ ordering begins to melt and O′ can be found on the vacancy sites, as seen in figure 5(c). Both models are, at some level, ‘correct’ because they reproduce the respective experimental data. However, the data guiding the $G(r)$-only fit are incomplete. The O′ ordering prescribed by the Bragg pattern and verified in figure 3(b) is unambiguous, so the fully ordered case is confirmed. Because RMC is a stochastic technique, it reveals that the $G(r)$ alone does not contain sufficiently robust information about the O′ occupancy to prevent O′ from spilling onto disordered sites. Only when the additional Bragg constraint is applied is the fully ordered model reproduced from the data.

Finally, it is of interest to see whether the ordered arrangement of Pb$^{2+}$ ions and their associated lone pairs results in distinctly different low-temperature heat capacity behavior in Pb$_2$Ru$_2$O$_6$O$_{0.5}$ when compared to a compound with disordered lone pairs such as Bi$_2$Ti$_2$O$_6$O′. We display such a comparison in figure 6. The scheme used to display the scaled heat capacity, $C_p/T^3$, versus $T$ allows local Einstein-like modes to be distinguished [33], and the temperature of the peak(s) can be read off as energies of the Einstein mode. Liu and Löhnjesen [34] have suggested a general scaling law wherein the lower the temperature at which $C_p/T^3$ displays a maximum, the larger the peak height as well. They have made such correlations for a number of amorphous and crystalline systems, and Bi$_2$Ti$_2$O$_6$O′ (with its highly disordered Bi$_2$O′ network [17]) displays, of all studied crystalline systems, one of the lowest peak temperatures and largest peak amplitudes. In contrast, we see from figure 6 that in Pb$_2$Ru$_2$O$_6$O$_{0.5}$ (using published data from [19] after
subtracting the electronic $\gamma T$ contribution) the peak occurs at significantly higher temperatures and is significantly smaller in amplitude. It is nonetheless larger than what is seen for $Y_2\text{Ti}_2\text{O}_7$ [32] which has no lone pairs. The question is why, in any event, the trend seen in figure 6 is consistent with the finding that Pb$_2$Ru$_2$O$_{6.5}$ has a well-ordered network of A-site atoms unlike Bi$_2$Ti$_2$O$_6$O$'$.

4. Conclusions

Our study of the ordered-ice pyrochlore Pb$_2$Ru$_2$O$_{6.5}$ has found that Rietveld refinements dictate O$'$–□ occupancy to be fully ordered, and Pb$^{2+}$ is displaced toward O$'$ (0.04 Å at $T = 15$ K). This ordering implies that Pb$_2$Ru$_2$O$_{6.5}$ does not possess the same geometric frustration seen in fully occupied A$_2$B$_2$O$_7$ pyrochlores with lone pair active cations on the A sites. To compare Pb$_2$Ru$_2$O$_{6.5}$ to those systems, where local structure analysis provide a view of incoherent distortions, we performed RMC simulations which revealed the presence of coherent Pb$^{2+}$ off centering only. Simultaneous fits to the Bragg intensity and $G(r)$ are required to reproduce the vacancy ordering, which is not strongly constrained by the $G(r)$ alone. First-principles calculations and heat capacity measurements corroborate to show that the O$'$– □ ordering provides an outlet for (and perhaps is constrained by) the pointing of lone pairs into vacant 4a positions.

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Figure 6. Lattice-only heat capacity, with the electronic contribution subtracted, of Pb$_2$Ru$_2$O$_{6.5}$, displayed in a manner that emphasizes the Einstein-like features at low temperatures. For comparison, the similarly scaled heat capacities of ‘charge-ice’ Bi$_2$Ti$_2$O$_6$O$'$ (from [16]) and of pyrochlore Y$_2$Ti$_2$O$_7$ (taken from [32]), which does not have lone pairs, are also displayed.
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