Crystal field excitations from Yb$^{3+}$ ions at defective sites in highly stuffed Yb$_2$Ti$_2$O$_7$

G. Sala,$^{1,2}$ D. D. Maharaj,$^2$ M. B. Stone,$^1$ H. A. Dabkowska,$^3$ and B. D. Gaulin$^{2,3,4,5}$

$^1$Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
$^2$Department of Physics and Astronomy, McMaster University, Hamilton, ON L8S 4M1 Canada
$^3$Brockhouse Institute for Materials Research, McMaster University, Hamilton, ON L8S 4M1 Canada
$^4$Canadian Institute for Advanced Research, 661 University Avenue, Toronto, ON, M5G 1M1 Canada
$^5$Department of Physics and Astronomy, McMaster University, Hamilton, ON L8S 4M1 Canada

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The pyrochlore magnet Yb$_2$Ti$_2$O$_7$ has been proposed as a quantum spin ice candidate, a spin liquid state expected to display emergent quantum electrodynamic with gauge photons among its elementary excitations. However, Yb$_2$Ti$_2$O$_7$’s ground state is known to be very sensitive to its precise stoichiometry. Powder samples, produced by solid state synthesis at relatively low temperatures, tend to be stoichiometric, while single crystals grown from the melt tend to display weak “stuffing” wherein ~ 2% of the Yb$^{3+}$, normally at the A site of the A$_2$B$_2$O$_7$ pyrochlore structure, reside as well as at the B site. In such samples Yb$^{3+}$ ions should exist in defective environments at low levels, and be subjected to crystalline electric fields (CEFs) very different from those at the stoichiometric A sites. New neutron scattering measurements of Yb$^{3+}$ in four compositions of Yb$_{2+x}$Ti$_{2-x}$O$_{7-y}$, show the spectroscopic signatures for these defective Yb$^{3+}$ ions and explicitly demonstrate that the spin anisotropy of the Yb$^{3+}$ moment changes from XY-like for stoichiometric Yb$^{3+}$, to Ising-like for “stuffed” B-site Yb$^{3+}$, or for A-site Yb$^{3+}$ in the presence of an oxygen vacancy.

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Exotic magnetic ground states of cubic pyrochlore magnets, with composition A$_2$B$_2$O$_7$, are of great topical interest, as the pyrochlore lattice is one of the canonical architectures supporting geometrical frustration in three dimensions [11,2]. Magnetism can reside at either the A$^{3+}$ site or the B$^{4+}$ site, and the magnetic moments’ anisotropy and the interactions between the moments conspire to give rise to rich ground state selection. Among the states and materials that have been of recent interest have been the classical spin ice states in Dy and Ho titanate pyrochlores [3,7], spin liquid and spin glass states in molybdate pyrochlores [8], and spin fragmentation in Nd based zirconate pyrochlores [9]. The possibility that a quantum analogue of the spin ice ground state, i.e. quantum spin ice (QSI), may exist in certain low moment pyrochlore magnets, including Yb$_2$Ti$_2$O$_7$ and Pr$_2$Zr$_2$O$_7$, has generated much excitement [10,24].

At low temperatures Yb$_2$Ti$_2$O$_7$ displays two magnetic heat capacity anomalies: a broad one near 2 K and a sharp anomaly signifying a thermodynamic phase transition near $T_C = 0.26$ K [25,29]. Below $T_C$, the ordered structure is thought to be a splayed ferromagnet with moments pointing close to the (100) directions [30,34]. However, surprisingly sample variability has been reported in this phase transition, with some studies not seeing direct evidence for the ferromagnetic ordered state [18,35–41]. Using the sharp anomaly in $C_P$ as the figure-of-merit for the phase transition, interesting systematics have been observed [28,29,42,43]. Powder samples grown by solid state synthesis at relatively low temperatures show a sharp $C_P$ anomaly and a high $T_C$, usually ~ 0.26 K [28,29,42,43]; however most single crystal studies display broader thermodynamic anomalies at much lower temperatures, often with $T_C$s around and below 0.2 K [30,31,35,40].

Crystallographic studies of the powder and single crystal samples have revealed that the powder samples are stoichiometric Yb$_2$Ti$_2$O$_7$, while the single crystals are “lightly stuffed”, and characterized by the composition Yb$_{2+x}$Ti$_{2-x}$O$_{7-y}$, with $x$ ~ 0.04 [28]. That is, a small excess of Yb$^{3+}$ ions, nominally at the crystallographic 16d or A site, are “stuffed” onto the 16c or B site where

![Diagram](image-url)
nonmagnetic Ti$^{4+}$ ions are located in pure Yb$_2$Ti$_2$O$_7$ as schematically indicated in Fig. 1. Light stuffing is also known to occur in other titanate pyrochlores [47].

It is remarkable that such a small change in stoichiometry could so strongly effect the ground state selection of a simple ordered state in a three dimensional magnetic insulator. Related phenomena has also recently been observed in the effect of hydrostatic pressure on stoichiometric Yb$_2$Ti$_2$O$_7$ samples, where ambient pressure conditions show no sign of a $\mu$SR signal for the transition, but a minimal 1 kbar (and above) applied pressure results in a clear signal for a transition near $T_C \sim 0.26$ K [48].

With weak “stuffing” able to suppress this phase transition by as much as $\sim 25\%$ [28, 31, 32], it is important to understand precisely what is at play in its ground state selection. One thing that is clear is that most single crystals of Yb$_2$Ti$_2$O$_7$ likely have Yb$^{3+}$ ions occupying not only the stoichiometric A-sites, but also B-sites. They also possess A-sites with missing oxygen neighbours. The Yb$^{3+}$ ions in defective environments are expected to experience very different crystal field effects than those at stoichiometric A-sites [49]. As these effects determine the spin anisotropy and size of the Yb$^{3+}$ moment, it is possible that the defective Yb$^{3+}$ moments and their anisotropy are very different from those displayed by stoichiometric Yb$^{3+}$ - indeed a prediction from point charge calculations of the crystal field effects on Yb$^{3+}$ have suggested that this is the case [49].

The eigenvalues and eigenfunctions associated with crystal field states can be determined using inelastic neutron spectroscopy, and these have been determined for stoichiometric Yb$_2$Ti$_2$O$_7$ and several other rare-earth based pyrochlore magnets [49, 51]. However, the equivalent measurements on Yb$^{3+}$ in defective environments in Yb$_{2-x}$Ti$_{2-x}$O$_{7-y}$ are much more difficult, as the environments occur at low density in these materials. Additionally, as we will see, the eigenvalues associated with the defective environments tend to extend to much higher energies.

Powder samples of Yb$_{2+x}$Ti$_{2-x}$O$_{7-y}$ with $x = 0.11$ and 0.18 were prepared at McMaster University and characterized using the POWGEN neutron powder diffractometer [52] at the Spallation Neutron Source of Oak Ridge National Laboratory. Our best refinement of this powder diffraction data gives $x = 0.106(4)$ and $0.176(8)$ for the highly stuffed samples with oxygen vacancies preferentially located at the O(1) site of the pyrochlore lattice, as discussed in the Supplemental Material (SM).

Inelastic neutron scattering measurements were performed on these two highly stuffed powder samples. The resulting samples were $\approx 4$ g of powder for each of the $x = 0.11$ and 0.18 samples. We studied their CEF excitations using the direct geometry time-of-flight spectrometer SEQUOIA [53] at ORNL and compared these results with earlier measurements performed [49] on the stoichiometric ($x = 0$) and lightly stuffed ($x = 0.05$) samples. The powder samples were loaded into aluminium flat plates and were sealed under He atmosphere in a glove box. An empty, aluminium flat plate with the same dimensions was prepared in a similar manner and employed for background measurements. Measurements have been performed at $T = 5$ K and 300 K, with incident energies of $E_i = 150$, 250 and 500 meV. The corresponding chopper settings selected at these energies were: $T_0 = 150$ Hz and $FC_2 = 600$ Hz, $T_0 = 120$ Hz and $FC_2 = 600$ Hz and $T_0 = 150$ Hz and $FC_2 = 600$ Hz respectively. The data were reduced with Mantid [54] and analyzed using DAVE [55] software, while we employed custom software to refine the CEF spectrum of the powder samples, as described above and in the SM.

The CEFs originate primarily from the “cage” of O$^{2-}$ ions surrounding the cations, lifting the $\left(2J+1\right)$-fold degeneracy of the $J = 7/2$ ground state manifold appropriate to Yb$^{3+}$. Typical time-of-flight inelastic neutron scattering data from four powder samples of Yb$_{2+x}$Ti$_{2-x}$O$_{7-y}$, with $x = 0$, 0.05, 0.11, and 0.18 are shown at $T = 5$ K in Figs. 3, and for $x = 0.11$ and 0.18 in Fig. 4. This data has been analysed from a starting point, known as the point charge approximation [50, 59], where initial CEF transitions from the ground state are calculated based on the local symmetry of the $A$ and $B$ site Yb$^{3+}$ ions, taken from crystallographic measurements. The energies and intensities of the CEF transitions are subsequently refined to agree with the experimental data. The case for Yb$^{3+}$ is relatively straightforward as its 13 $4f$ electrons give a Hund’s rule ground state of $J = 7/2$, so it is a Kramers’ ion with at most 3 CEF transitions from the ground state.

We considered 3 local Yb$^{3+}$ environments shown in Fig. 2. These are Yb$^{3+}$ in an $A$ site environment with a full complement of 8 neighbouring O$^{2-}$ ions; in an $A$ site environment with one O$^{2-}$ vacancy (referred to as an $A'$ site); and a Yb$^{3+}$ ion in a $B$ site environment with a full complement of 6 neighbouring O$^{2-}$ ions. The $A$ site O$^{2-}$ environment consists of a cube distorted along the local [111] directions. Six O(2) ions are located on a plane perpendicular to this direction and a three-fold rotation axis. Two additional O(1) ions are located along the local [111] axis. In other titanate pyrochlores, the O(1) sites are known to have a higher probability of hosting vacancies than the O(2) sites [60], a result which we confirm here for Yb$_{2+x}$Ti$_{2-x}$O$_{7-y}$ using powder neutron diffraction, as shown in the SM. By contrast, the environment at the $B$ site is a trigonal anti-prism made of six O(2) oxygen ions. Additional local Yb$^{3+}$ environments, such as an $A$ site Yb$^{3+}$ with two vacancies, were assumed to be unlikely at the stuffing levels considered here.

Our CEF calculation followed Prather’s convention [61] and employed the Stevens’ formalism [32]. The resulting CEF Hamiltonian for Yb$^{3+}$ at all three sites
The energy eigenfunctions associated with each environment can be written as:

\[ \hat{\cal H}_{CEF} = B_2^0 \hat{Q}_2^0 + B_4^0 \hat{Q}_4^0 + B_4^3 \hat{Q}_4^3 + B_6^0 \hat{Q}_6^0 + B_6^3 \hat{Q}_6^3 + B_6^6 \hat{Q}_6^6 \]  

Here \( \hat{Q}_n^m \) are the Stevens’ operators and \( B_n^m \) the CEF parameters used to approximate the Coulomb potential generated by the ligands.

The unpolarised neutron partial differential magnetic cross-section can be written within the dipole approximation as [63]:

\[ \frac{d^2\sigma}{d\Omega dE'} = C \frac{k_f}{k_i} F^2(|Q|) S(|Q|, \omega) \]  

where \( \Omega \) is the scattered solid angle, \( \frac{k_f}{k_i} \) the ratio of the scattered and incident momentum of the neutron, \( C \) is a constant and \( F(|Q|) \) is the magnetic form factor of the magnetic \( \text{Yb}^{3+} \) ion. The scattering function \( S(|Q|, \omega) \) gives the relative scattered intensity due to transitions between different CEF levels. At constant temperature and wave vector \( |Q| \), we have:

\[ S(|Q|, \omega) = \sum_{i,i'} \sum_{\alpha,\beta} \frac{|\langle i| J_{\alpha} |i' \rangle|^2}{\sum_{\beta} e^{-\beta E_i}} \int \sum_{\beta} e^{-\beta E_i} F(\Delta E + \hbar\omega) \]  

where \( \alpha = x, y, z \) and \( F(\Delta E + \hbar\omega) = F(E_i - E_{i'} + \hbar\omega) \) is a Lorentzian function which ensures energy conservation as the neutron induces transitions between the CEF levels \( i \to i' \), that possess a finite energy width or inverse lifetime.

Figure 2 shows a comparison of the data from the four powder \( \text{Yb}_{2+x} \text{Ti}_{2-x} \text{O}_{7-y} \) samples, using incident neutrons with \( E_i = 150 \text{ meV} \). The intensity scale has been normalized to sample mass. The stoichiometric, \( x = 0 \), and lightly stuffed, \( x = 0.05 \), powder samples show only the 3 \( A \) site CEF transitions at \( \sim 76, 81 \), and \( 116 \text{ meV} \) as previously reported [19]. As a function of increasing stuffing, \( x \), we clearly observe the growth of a new CEF at \( \sim 91 \text{ meV} \), which we will attribute to \( A' \) site \( \text{Yb}^{3+} \). A Monte Carlo calculation, shown in the SM, of the prevalence of \( A \) to \( A' \) site \( \text{Yb}^{3+} \) ions as a function of \( x \), and with \( y \) in \( \text{Yb}_{2+x} \text{Ti}_{2-x} \text{O}_{7-y} \) set to ensure charge neutrality, shows that the normalized intensity of this 91 meV CEF scales in proportion to \( x \).

The CEF spectrum at energies above 100 meV is shown in Fig. 3 for the \( x = 0.11 \) and 0.18 powder samples, as measured with \( E_i = 500\text{meV} \) neutrons. One observes clear excitations above the 116 meV CEF excitation associated with the stoichiometric \( A \) site’s most energetic CEF level. Of particular note is the well isolated CEF excitation at 358 meV which we associate with \( \text{Yb}^{3+} \) at
In conclusion, new time-of-flight neutron spectroscopy allows the possibility of detecting and distinguishing...
CEF excitations in complex real materials with relatively low levels of defective environments, and have demonstrated this for the quantum spin ice candidate pyrochlore magnet Yb$_{2+x}$Ti$_{2-x}$O$_{7-y}$. Such detailed information is particularly important for the case of Yb$_2$Ti$_2$O$_7$, as its ground state displays unusually strong sensitivity to stoichiometry. Our results specifically show Yb$^{3+}$ moments in stuffed and oxygen deficient environments display Ising anisotropy, rather than the XY local anisotropy displayed by the stoichiometric moments. Such defective Yb$^{3+}$ moments are also considerably larger than their stoichiometric counterparts, and these, at a minimum, would tend to randomize dipolar interactions. Both of these manifestations of stuffing can be important for ground state selection in real samples of Yb$_{2+x}$Ti$_{2-x}$O$_{7-y}$, and may underlie the ground state’s extreme sensitivity to stoichiometry in this family of quantum magnets.

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SUPPLEMENTAL MATERIAL: CRYSTAL FIELD EXCITATIONS FROM Yb$^{3+}$ IONS AT DEFECTIVE SITES IN HIGHLY STUFFED Yb$_2$Ti$_2$O$_7$

In this supplemental information we show the details of the crystal field calculation with which we analysed the neutron scattering data. We also highlight several details of the inelastic neutron scattering spectrum as a function of temperature. Finally we discuss sample preparation and refinement of the neutron powder diffraction data for the two highly stuffed samples of Yb$_{2+x}$Ti$_{2-x}$O$_{7-y}$.

A. Crystal Field Program

In order to analyse the neutron scattering data and fit the Crystal Electric Field (CEF) excitations we developed a calculation based on the point charge model [56] and on the Stevens’ formalism [62]. The former neglects the overlap between the orbitals and any relativistic corrections, while the latter is a mathematical tool to write an expansion of the Coulomb potential of the crystal based on the symmetries of the environment that surrounds the magnetic ion. In our samples, the magnetic rare earth ion is sitting at 3 different environments: stoichiometric A sites, oxygen deficient A’ sites and B sites. Figure 2 in the main paper shows these 3 environments. Notice that we rotated the reference system in order to align the local ⟨111⟩ direction along ẑ.

In general the Coulomb potential of the crystal can be expressed using a linear combination of tesseral harmonics as follows,

$$V(x, y, z) = \sum_{n=0}^{\infty} \sum_{m} \frac{1}{4\pi\epsilon_0} \sum_{R_j} \frac{r_j^n}{R_j^{n+1}} Z_{nm}(x_j, y_j, z_j)Z_{nm}(x, y, z).$$  \hspace{1cm} (5)

Here $q_j$ is the charge of the ligand, $R_j$ is the position of the ligand and $Z_{nm}(x_j, y_j, z_j)$ is the tesseral harmonic [56]. If we centre our reference system on the magnetic ion, we can rewrite the previous equation in this way,

$$V(x, y, z) = \frac{1}{4\pi\epsilon_0} \sum_{n} \sum_{m} r^n \gamma_{nm} Z_{nm}(x, y, z),$$  \hspace{1cm} (6)

where for $k$ ligands,

$$\gamma_{nm} = \sum_{j=1}^{k} \frac{q_j}{R_j^{n+1}} \frac{4\pi}{2n+1} Z_{nm}(x_j, y_j, z_j).$$  \hspace{1cm} (7)

Equation 7 gives the coefficients of the linear combination of the tesseral harmonics. For every point group, only a few terms in the expansion are non zero (see Ref. [59]), and these terms coincide with the number of Stevens Operators we use in our Hamiltonian.

The point group of both the scalenohedron and the trigonal anti-prism is $D_{3d}$ and thus, following Prather’s convention [61], only the terms $Z_{20}, Z_{20}, Z_{43}, Z_{56}, Z_{66}$ and $Z_{66}$ survive in our expansion. This convention states that the highest rotational $C_3$ axis of the system must be rotated along ẑ and one of the $C_2$ axis along ŷ, assuring in this way that we have the minimum number of terms in the Coulomb expansion.

Finally we can use the so called “Stevens Operators Equivalence Method” to evaluate the matrix elements of the crystalline potential between coupled wave functions specified by one particular value of the total angular momentum $J$. This method states that, if $f(x, y, z)$ is a Cartesian function of a given degree, then to find the operator equivalent to such a term one replaces $x, y, z$ with $J_x, J_y, J_z$ respectively, keeping in mind the commutation rules between these operators. This is done by replacing products of $x, y, z$ by the appropriate combinations of $J_x, J_y, J_z$, divided by the total number of combinations. Note that, although it is conventional to use $J$ or $L$ in the equivalent operator method, all factors of $\hbar$ are dropped when evaluating the matrix elements.

As we are studying the ground state (GS) of a rare-earth system, without an external field applied, $S^2, L^2, J^2$ and $J_z$ are good quantum numbers. Thus the Crystal Field Hamiltonian can now be written as:

$$H_{CEF} = const. \sum_{nm} \left[ \frac{e^2}{4\pi\epsilon_0} \gamma_{nm} \langle r^n \rangle \theta_n \right] O_n^m = \sum_{nm} \left( A_n^m \langle r^n \rangle \theta_n \right) B_{nm} O_n^m,$$  \hspace{1cm} (8)

where $γ_{nm}$ is the same coefficient as in Eq. 7, $e$ is the electron charge, $ε_0$ is the vacuum permittivity, $⟨r^n⟩$ is the expectation value of the radial part of the wave function, $θ_n$ is a numerical factor that depends on the rare earth ion [56], const. is a constant to normalize the tesseral harmonics and $O_n^m$ are the Stevens Operators.
The terms $A_{m}^{n}(\rho^{n})\theta_{\alpha}$ are commonly called Crystal Field Parameters, and they coincide with the parameters we fit in our calculation. A general form of the Hamiltonian for our system is therefore:

$$H_{CEF} = B_{20}O_{2}^{0} + B_{40}O_{4}^{0} + B_{43}O_{4}^{3} + B_{60}O_{6}^{0} + B_{63}O_{6}^{3} + B_{66}O_{6}^{6}.$$  \hspace{1cm} (9)

It is easy to verify that the equations are not linear, so we cannot write a closed system to solve the problem and identify a unique solution. We thus decided to use our Hamiltonian as a function of six CEF parameters, that are simultaneously fit to quantities of interests such as the energy of the excitations, the spectrum and the relative intensities of the levels. The quantity that the calculation minimizes is:

$$\chi^{2} = \sum_{i} \frac{(\Gamma_{obs}^{i} - \Gamma_{calc}^{i})^{2}}{\Gamma_{calc}^{i}},$$ \hspace{1cm} (10)

where $\Gamma_{calc}^{i}$ is the calculated quantity of interest and $\Gamma_{obs}^{i}$ is the observed quantity. Following this spirit, the logic of the calculation is the following:

1. Starting with an initial set of CEF parameters, that can be calculated from first principles or taken from literature, we diagonalize our CEF Hamiltonian.

2. The eigenvalues are rescaled respect to the GS energy and we calculate and normalize the intensities and the CEF spectrum.

3. $\chi_{tot}^{2} = \chi_{energy}^{2} + \chi_{intensity}^{2} + \chi_{spectrum}^{2}$ is calculated using Eq. 10.

4. The procedure is iterated using another set of CEF parameters in order to minimize $\chi_{tot}^{2}$ until we converge on a solution which best estimates the experimental results.

The minimization algorithm is robust and it assures the convergence towards a global minimum. The final CEF parameters are then used to calculate the spectrum for a direct comparison with the data set. Table I shows the best CEF parameters which were found minimize $\chi^{2}$ in the fitting procedure along with the energy eigenvalues corresponding to the CEF excitations of Yb$^{3+}$ ions out of the ground state at the $A$, $A'$ and $B$ sites.

| Crystal Field Parameters (meV) |
|--------------------------------|
| $B_{2}^{A}$ | $B_{2}^{A'}$ | $B_{2}^{B}$ |
| 1.1 | -3.9860 | -4.8744 |
| $B_{4}^{A}$ | $B_{4}^{A'}$ | $B_{4}^{B}$ |
| -0.0591 | -0.002186 | -0.1407 |
| $B_{4}^{A}$ | $B_{4}^{A'}$ | $B_{4}^{B}$ |
| 0.3258 | 1.0655 | 1.47542 |
| $B_{6}^{A}$ | $B_{6}^{A'}$ | $B_{6}^{B}$ |
| 0.00109 | 0.001533 | -0.004862 |
| $B_{6}^{A}$ | $B_{6}^{A'}$ | $B_{6}^{B}$ |
| 0.0407 | 0.049192 | -0.1117 |
| $B_{6}^{A}$ | $B_{6}^{A'}$ | $B_{6}^{B}$ |
| 0.00727 | 0.01666 | 0 |

| Calculated Spectrum (meV) |
|---------------------------|
| 0.0 (d) | 0.0 (d) | 0.0 (d) |
| 76.72 (d) | 90.17 (d) | 130.98 (d) |
| 81.76 (d) | 161.38 (d) | 181.79 (d) |
| 116.15 (d) | 179.36 (d) | 358.14 (d) |

TABLE I. Refinement of the CEF parameters and energy eigenvalues at each of the three Yb$^{3+}$ sites, from fits to the inelastic spectra data set at the three sites and relative energy levels. All energy eigenvalues are doublets (d), as required by Kramers’ theorem.

B. Temperature Evolution of the Crystal Field Excitations

Crystal field excitations have several important characteristics: as single ion properties the CEFs tend to be dispersion-less and the Q-dependence of their intensities is largely determined by the magnetic form factor of the magnetic ion involved. They also display temperature dependence that reflects the population distribution of the CEF levels. Given that the lowest energy CEF excited state is at $\sim 76$ meV, and thus for all temperatures below room temperature, we expect no states above the ground state to be thermally populated. These features can be used...
to distinguish the real CEF levels from the background and from other elementary excitations, particularly phonons. In figure 6 we show the comparison of the CEF spectrum at $T = 5$ K (top panels) and $T = 200$ K (bottom panels) with an incident energy $E = 250$ and $500$ meV $x = 0.11$ and $x = 0.18$ samples.

As the temperature is increased the spectrum becomes broader in energy, in agreement with previous observations by Gaudet et al [49]. As mentioned above, this is not a thermal population effect but the result of the CEFs acquiring finite lifetimes, due to interactions with other excitations, notably phonons. With the exception of the $A$ site Yb$^{3+}$ CEF excitations, the normalized intensity of the inelastic features in the spectrum are stronger for the $x = 0.18$ stuffed sample than for the $x = 0.11$ sample, as expected, reflecting the higher level of stuffing.

The feature at $\sim 170$ meV is not a CEF level since its intensity does not change with the temperature. By contrast the shape of the peak at $\sim 179$ meV becomes very broad at 200 K consistent with the presence of two levels ($A'$ and $B$ transitions) close to each other.

The highest energy CEF feature at indicative of Yb$^{3+}$ at $\sim 358$ meV is due to stuffed $B$ site Yb$^{3+}$. This level has been previously predicted in Ref [49] and is now experimentally observed. The relatively high energy of this CEF is due to the fact that the oxygen ions surrounding the Yb$^{3+}$ at $B$ sites are closer to the Yb$^{3+}$ ions than is the case for either $A$ or $A'$ site Yb$^{3+}$.

![Figure 6](image)

**FIG. 6.** (color online) *Temperature dependence of the inelastic neutron scattering from crystal field excitations:* – Comparison of the normalized intensities of the inelastic neutron spectrum at $T = 5$ K (top panels) and $T = 200$ K (bottom panels) for incident energies $E_i = 250$ and $E_i = 500$ meV. The feature at $\sim 170$ meV is not a CEF level since its intensity does not change with the temperature. By contrast the shape of the peak at $\sim 179$ meV broadens at 200 K, compared with 5 K, consistent with the presence of two CEF levels (due to $A'$ and $B$ transitions) close to each other in energy. The inelastic peak at $\sim 358$ meV arises due to Yb$^{3+}$ at $B$ sites.
C. Sample preparation and characterization of the two highly stuffed Yb$_{2+x}$Ti$_{2-x}$O$_{7-y}$ samples

1. Sample preparation

Two single-crystals of Yb$_{2+x}$Ti$_{2-x}$O$_{7-y}$ with composition, $x = 0.11$ and $x = 0.18$ and dimensions $5\, \text{mm} \times 6\, \text{mm} \times 6\, \text{mm}$, were prepared by solid state reaction between pressed powders of Yb$_2$O$_3$ and TiO$_2$ which were sintered at 450 °C for 15 hours with warming and cooling rates of 100 °C/h. The sample preparation and characterization of the stoichiometric, $x = 0$, and $x = 0.05$ powders of Yb$_{2+x}$Ti$_{2-x}$O$_{7-y}$ are described elsewhere [28]. The purity of the starting powders of Yb$_2$O$_3$ and TiO$_2$ was close to 99.999%. To produce these highly stuffed, $x = 0.11$ and 0.18, samples of Yb$_2$Ti$_2$O$_7$, a higher ratio of Yb$_2$O$_3$ to TiO$_2$ was used in comparison to what is conventionally used in order to produce stoichiometric samples of Yb$_2$Ti$_2$O$_7$. The two single-crystals were grown at McMaster University by utilizing the floating zone image furnace technique, which is described elsewhere [64]. The growths were conducted in O$_2$ gas with no overpressure and the growth rates were 7 mm/h and 8 mm/h for the $x = 0.11$ and $x = 0.18$ samples, respectively. The single-crystal samples were then pulverized using a Pulverisette 2 mortar grinder for 30 minutes each.

2. Refinement of neutron powder diffraction data

We discuss the results of our refinement for neutron powder diffraction data collected at POWGEN [52] at $T = 300\, \text{K}$ in table II for the $x = 0.11$ and $x = 0.18$ stuffed samples. This refinement was performed using the crystallographic refinement software JANA2006 [65]. Note that the pure $x = 0$ and lightly stuffed $x = 0.05$ stuffed samples have previously been characterized by powder diffraction techniques in Ref. [28].

The neutron diffraction powder spectra and best fits to the data are shown in figure 7. The cell parameters arising from this refinement for the $x = 0.11$ stuffed sample is $a = 10.063(4)\, \text{Å}$, while for the $x = 0.18$, $a = 10.080(7)\, \text{Å}$. Table II highlights the systematic increase of the unit cell parameter, $a$, for all samples compared in this study. The fact that the length of the unit cell gets bigger as the stuffing, $x$, increases is a direct consequence of the oxygen vacancies: the Coulomb repulsion of the cations left unshielded by the vacancy tends to push all the ions away from each other increasing the size of the unit cell. Moreover our refinement showed that these vacancies are mainly located on the O(1) sites of the pyrochlore lattice, confirming the analysis in Ref. [60]. The refined chemical formula for the two compounds are Yb$_{2.106}$Ti$_{1.894}$O$_{6.952}$ and Yb$_{2.176}$Ti$_{1.824}$O$_{6.883}$ giving a stuffing of $x = 0.11$ and $x = 0.18$ respectively, in agreement with the approximate stoichiometry of the starting materials used in the crystal growth.

| Atom | $x$ | $y$ | $z$ | Site | Occupancy | $a$ (Å) |
|------|-----|-----|-----|------|-----------|---------|
| Yb   | 0.625 | 0.625 | 0.625 | 1bd | I         | 10.063(4) |
| Ti   | 0.125 | 0.125 | 0.125 | 16c | 0.947(2)  |         |
| Yb   | 0.125 | 0.125 | 0.125 | 16c | 0.053(2)  |         |
| O(2) | 0.043(4) | 0.25 | 0.25 | 48f | 0.994(4)  |         |
| O(1) | 0.5  | 0.5  | 0.5  | 8b  | 0.988(3)  |         |

TABLE II. This table summarizes Rietveld refinement results obtained from neutron powder diffraction experiments conducted at POWGEN [52] on the two highly stuffed samples of Yb$_2$(Ti$_{2-x}$Yb$_x$)O$_{7-y}$ with $x = 0.11$ and $x = 0.18$ at $T = 300\, \text{K}$.

| Degree of stuffing, $x$ | $a$ (Å) |
|------------------------|---------|
| 0.000(1)               | 10.020(3) |
| 0.046(4)               | 10.029(4) |
| 0.106(4)               | 10.063(4) |
| 0.176(8)               | 10.080(7) |

TABLE III. The table shows results from Rietveld refinement for the degree of stuffing $x$ and the lattice parameter $a$ for the four compounds of Yb$_2$(Ti$_{2-x}$Yb$_x$)O$_{7-y}$ studied. The values disclosed for the lattice parameters of the pure compound $x = 0.000(1)$ and stuffed compound with $x = 0.046(4)$ are the refined values at $T = 250\, \text{K}$ and were retrieved from Ref. [28]. The values of the lattice parameter obtained for the $x = 0.106(4)$ and $x = 0.176(8)$ were those obtained for the $T = 300\, \text{K}$ neutron diffraction data sets disclosed in table II.
Assuming that oxygen atoms are removed at random, we can perform a simple Monte Carlo (MC) simulation to calculate the relative preponderance of $A$ to $A'$ sites in the lattice as a function of the stuffing level, $x$. Assuming that each $A$ and $A'$ site contributes independently to the intensity of the spectrum, we can argue that the intensity of the transition at 90 meV should be proportional to this ratio.

For this calculation we created a supercell consisting of $64 \times 64 \times 64$ unit cells filled with random vacancies located only at the O(1) position. Due to the symmetry of the pyrochlore lattice each Yb$^{3+}$ ion at an $A$ site has only two O(1) ions as first nearest neighbour, thus we calculated how many ions have no vacancies and how many are affected by the stuffing. The calculation was repeated for 10000 realizations of disorder. We show in figure 8 the results of this analysis, with the conclusion that the transition at 90 meV originates from $A'$ sites, and its intensity is directly proportional to the number of vacancies in the system.

**FIG. 7.** (color online) Rietveld refinement of the Yb$_{2+x}$Ti$_{2-x}$O$_{7-y}$ stuffed crystals: – The Rietveld refinement has been performed assuming oxygen vacancies on the O(1) sites of the pyrochlore lattice, consistent with Ref. [60]. This model gives a good agreement with the experimental data with an $R = 5.1$ and $R = 5.2$ for the two crystals. The refined chemical formula for the two compounds are Yb$_{2.106}$Ti$_{1.894}$O$_{6.952}$ and Yb$_{2.176}$Ti$_{1.824}$O$_{6.883}$ giving a stuffing volume of $x = 0.11$ and $x = 0.18$ respectively, consistent with the approximate stoichiometry of the starting materials in the crystal growth. The unit cell parameter for the $x = 0.11$ stuffed sample is refined to be $a = 10.063(4)$ Å, while that for the $x = 0.18$ is refined to be $a = 10.080(7)$ Å.
FIG. 8. (color online) Preponderance of $A$ and $A'$ sites within the pyrochlore lattice as a function of stuffing: – (a) Projection of the $64 \times 64 \times 64$ supercell used in the Monte Carlo simulation is shown. The orange dots represent oxygen ions removed from the calculation. (b) Histogram showing the distribution of $A$ (blue line) and $A'$ sites (green line) in the lattice as a function of the stuffing. The red points represents the experimental intensities of the 90 meV CEF level extrapolated using the pure compound as background. This agreement confirms that this 90 meV CEF transition originates from an $A'$ site.