

Supplementary Information

A.C. Shockley,^{1,*} F. Bert,¹ J-C. Orain,¹ Y. Okamoto,² and P. Mendels¹

¹Laboratoire de Physique des Solides, Université Paris-Sud 11, UMR CNRS 8502, 91405 Orsay, France

²Department of Applied Physics, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

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I. SAMPLE PREPARATION AND CHARACTERIZATION

¹⁷O-enriched polycrystalline samples of Na₄Ir₃O₈ were synthesized by a two steps reaction. First, we prepared Na₄Ir₃O₈ polycrystalline samples by a solid state reaction described elsewhere [1]. The obtained sample was then put in an alumina tube filled with 0.03 MPa of ¹⁷O₂, which was rapidly heated to 1020 C, kept at this temperature for 6 h, and then quenched to room temperature.

Magnetization measurements were performed in a Quantum Design MPMS periodically to verify the sample quality. From Balodhi et al [2] and Dally et al [3], we know that when Na₄Ir₃O₈ is exposed to air, the Na content gradually

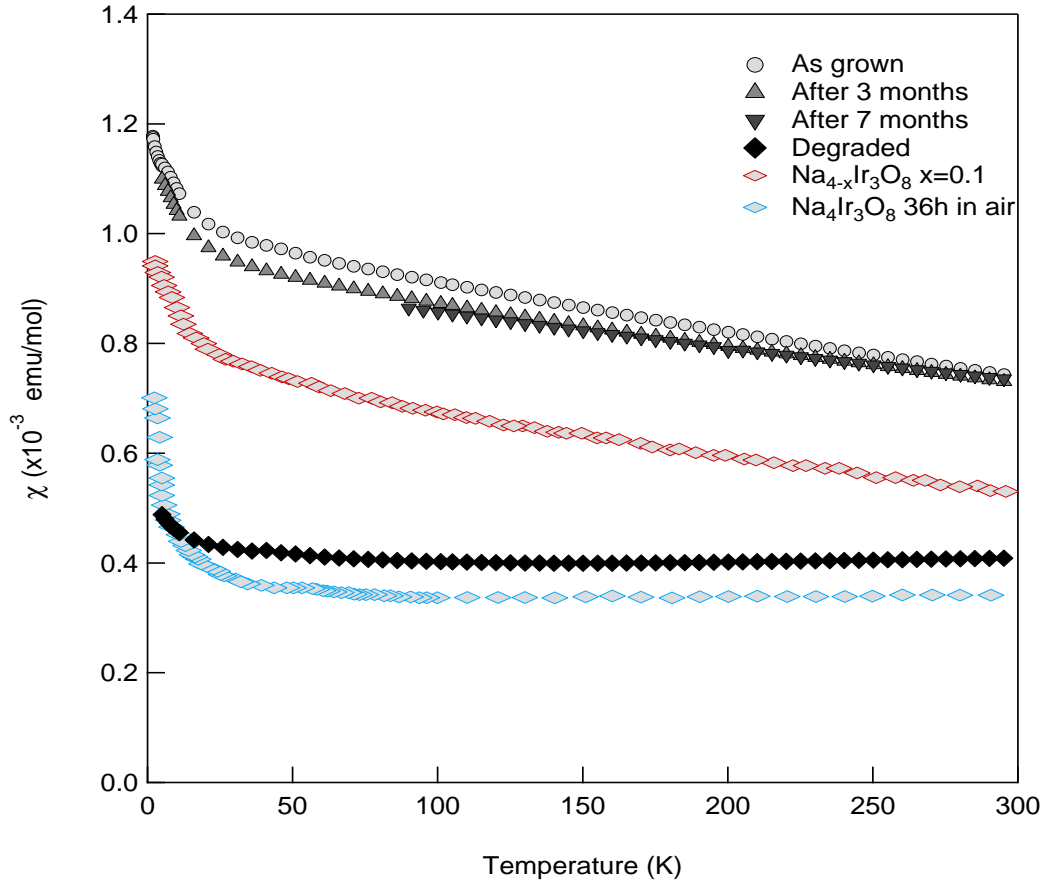


FIG. 1. Magnetization results taken at various times during the experiment. When the sample first arrived; three months later after the ¹⁷O data was taken; 7 months later after the majority of the ²³Na data was taken. Measures for the degraded Na_{4-x}Ir₃O₈, as described in the text, are also included. Data from [2] and [3] are included for the $x = 0.1$ in red outline and 36 hours exposed to air in blue outline, respectively.

* acshoc@gmail.com

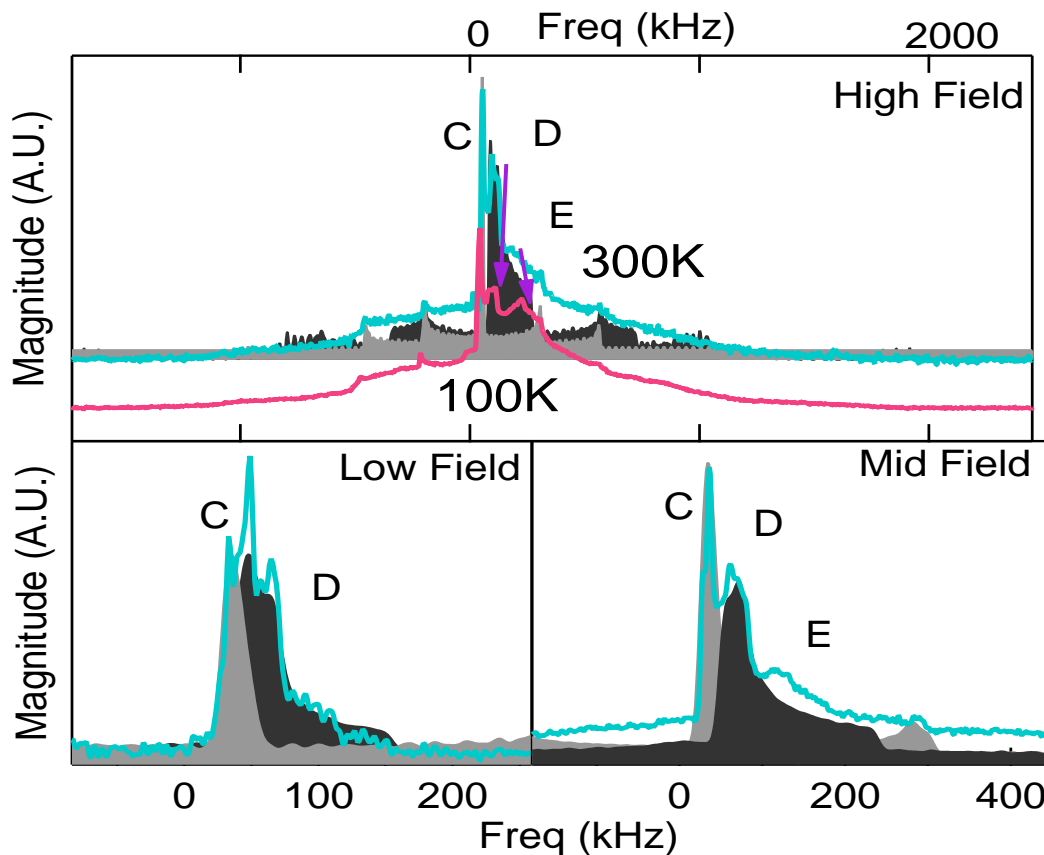


FIG. 2. The spectrum for ^{17}O , $\gamma/2\pi = 5.772$ MHz/T, taken at 21.159 MHz, 43.33 MHz, and 68.127 MHz (blue lines are 300 K, pink line is 100K). Simulations of the NMR powder spectrum are shown for peak C (light grey) and peak D (dark grey), both $\text{O}(1)$. The zero frequency is the reference position taken for O in water.

decreases over time and the magnetization is very sensitive to the Na content. For samples of $\text{Na}_4\text{Ir}_3\text{O}_8$ from different batches and measured at different times, the magnetization at 300 K is always consistent. However a slight variation is observed for $T < 250$ K. Dally et al posit that the different values of Θ_{CW} which have been reported are due to admixtures of $\text{Na}_3\text{Ir}_3\text{O}_8$ within $\text{Na}_4\text{Ir}_3\text{O}_8$. The magnetization of our sample was the same as reported in [1] and the value at 300 K dropped by 2% over a period of 7 months, the duration of the experiment. According to [2], the magnetization of $\text{Na}_{3.9}\text{Ir}_3\text{O}_8$ at 300 K is 30% lower than $\text{Na}_4\text{Ir}_3\text{O}_8$ which indicates our sample's decrease in Na content is negligible.

Measurements of the ^{17}O spectrum on the degraded sample, $\text{Na}_{4-x}\text{Ir}_3\text{O}_8$, shows that the linewidth is small and does not increase down to temperatures of 1.3 K. If some admixture of Na-338 were present in our Na-438 samples, then we would expect to see well-resolved narrow peaks at 1.3 K in our Na-438 ^{17}O spectrum. Since we see no evidence of this, we do not have any admixture of Na-338 with our Na-438 sample.

The changes in the magnetization below 200 K for different Na-438 samples are still unclear; however, they do not represent large changes in the Na content in comparison with the $\text{Na}_{3.9}\text{Ir}_3\text{O}_8$.

II. SPECTRA ANALYSIS

In general, the NMR spectrum from a powder is more difficult to analyze than for a single crystal. Taking ^{23}Na with $I = \frac{3}{2}$ as an example, a single crystal spectrum would have three well-resolved lines in the presence of quadrupolar effects, which cancel only in the case of a cubic symmetry. The central line comes from the $-\frac{1}{2} \leftrightarrow \frac{1}{2}$ transition where half integer numbers refer to I_z ; the two lines on the outside are the satellites from the $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$ and $\frac{1}{2} \leftrightarrow \frac{3}{2}$ transitions. The spacing between the central and the satellite lines is of first order in the quadrupolar frequency, ν_Q , and precisely equal to it, for instance, in the case of a nucleus sitting on a three-fold symmetry axis and an external

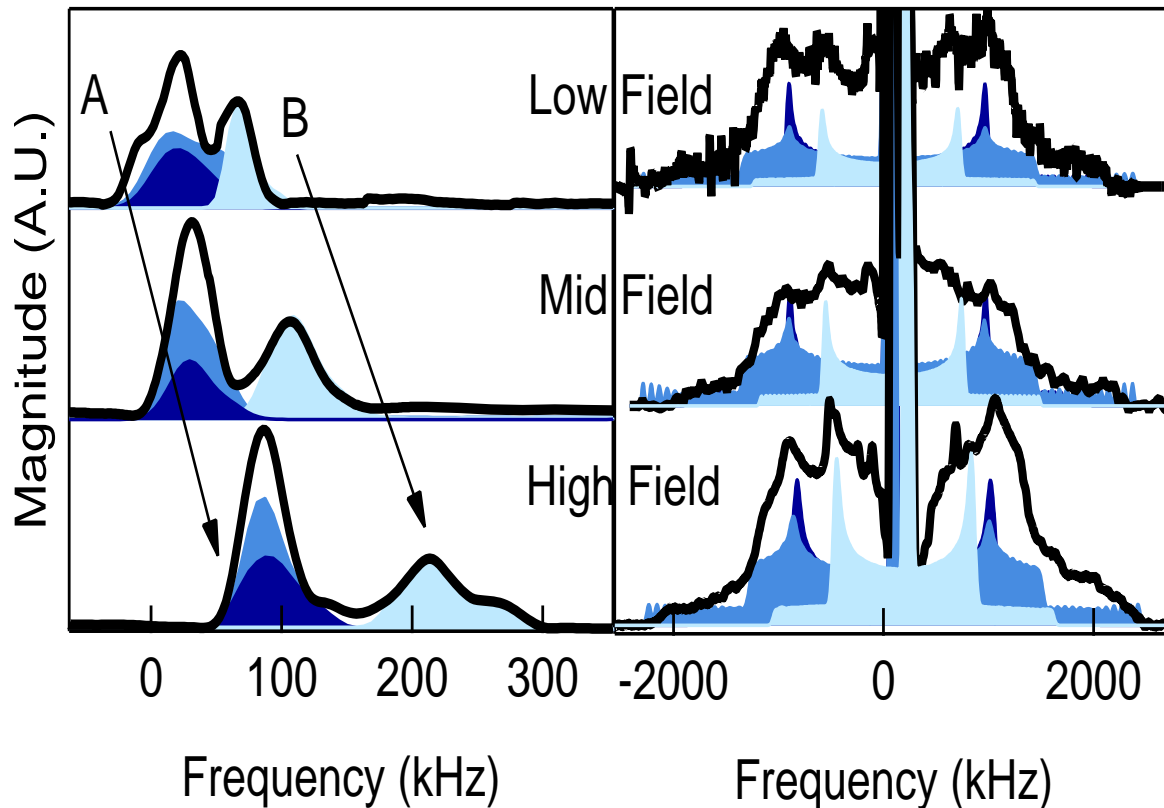


FIG. 3. The spectrum for ^{23}Na , $\gamma/2\pi = 11.772$ MHz/T, taken at 46.8 MHz -low field-, 68 MHz -mid field-, and 121.2 MHz -high field- (blue lines) (left: central; right: zoomed on the wings). Simulations of the NMR powder spectrum are shown for peak A, Na(1) in dark blue and Na(3) in blue, and peak B, Na(2) in pale blue. The zero frequency is taken for Na in a NaCl solution.

field applied along this axis. On a general stand the central line position is affected in second order by quadrupolar effects whereas on satellite lines this comes into first order. The general expressions can be found in [4]

In a powder sample one averages over all the orientations of the unit cell with respect to the direction of the applied field. The central line does not appear any more as a well symmetric line but has a complicated shape governed by the parameters of the Hamiltonian, namely the hyperfine tensor defined by isotropic, anisotropic and axial components, K_{iso} , K_{ani} , K_{ax} and the quadrupolar tensor defined by the quadrupolar frequency and the asymmetry parameter, ν_Q , and η . Peak D in the ^{17}O spectrum (the dark grey line in Fig. 2) is a good example of an unusual central line-shape due to a powder pattern. For the satellites, the powder average smears out the well defined peaks, leaving a sharp singularity surrounded by shoulders which are sometimes referred to as wings. Peak B in the ^{23}Na spectrum (the light blue line in Fig. 3) is a good example. The shape of the central line is highly field dependent while the distance between first order quadrupolar wings are field independent. Taking spectra at several different fields can help to determine the parameters of the Hamiltonian mentioned earlier.

In order to understand the ^{23}Na and ^{17}O spectrum, we took the data at low, mid, and high fields, as shown in Fig. 2 and 3. For the ^{17}O , the high field has a complete set of points; the mid field only has the wings for the higher frequencies; the low field did not have a good enough resolution to pick up the wings. Three components are important: the first order quadrupolar parts which compose the wings and the second order quadrupolar parts and the shift tensor which split the central peaks. The shape of the wings constrains the value of the quadrupolar frequency, ν_Q , while the shape of the central peaks constrains the value of the asymmetry parameter, η and the anisotropic shift.

For the ^{17}O spectrum, we know that one of the sites, O(1,C) is on a three-fold symmetry axis and therefore $\eta=0$. This condition leads to four evenly spaced and narrow singularities in the wings, as shown in the grey simulation. These peaks match with the narrowest central peak which was assigned to O(1,C). The lowered symmetry for the O(1,D) site leads to a more complicated and much broadened spectral shape. In order to reproduce the central

Site	A_{hf} (kOe/ μ_B)	K_0 (%)	K_{iso} (%)	K_{ani} (%)	K_{ax} (%)	ν_Q (kHz)	η (no units)
Na(1)	N/A	N/A	0.08	0.02	0	2330	0.2
Na(2)	4 ± 2	0.05 ± 0.01	0.17	0.02	0.03	1320	0
Na(3)	-0.9 ± 0.3	0.04 ± 0.01	0.07	-0.03	0	1900	0
O(C)	-5.5 ± 0.4	0.11 ± 0.05	0.094	0.03	0	510	0
O(D)	-6.5 ± 0.5	0.19 ± 0.05	0.279	0.241	-0.05	895	0.94

TABLE I. Nuclear Hamiltonian parameters for all of the sites as described in the SI and the main text. The values given without error bars are one set of best values but might not be unique. The zero value for η of O(C) are constrained by symmetry considerations limited to the first neighbors environment.

spectrum in both the high and low field limits, η and the anisotropic shift needed to be quite high. The mid-field spectra was used to check the consistency of the simulations. Having an estimation of these values may be useful for comparison with future theoretical simulations, as for Sr_2RuO_4 [5]. Because the central peak of O(2,E) was very distributed, we did not attempt a simulation. The intensity of the simulations was not adjusted to reflect the expected intensity of the individual sites.

For the ^{23}Na spectrum, the situation is much more complex due to the 75% partial occupancy of Na(2) and Na(3). For the high field, the signal disappears completely at the edge of the wings which sets a limit on $2\nu_Q$ giving $\nu_Q = 2330$ kHz. The simulation shown in Fig. 3 was constrained to reproduce the central peaks for the three different fields. However, this simulation is not a unique solution; in particular, we are able to reproduce some parts of the wings but not all. A better simulation could be produced assuming more than the three ^{23}Na sites indicated by the crystal structure. Since the first nearest neighbors are all O sites, perhaps the ^{23}Na sites are sensitive to the distribution of the second nearest neighbors which include both Na and Ir.

III. STRUCTURE

We have included several different perspectives of the crystal structure to help the reader with visualization. As mentioned in the text, the basic unit cell is a pyrochlore lattice, Fig. 4 (i). The surrounding environment of the three ^{23}Na crystallographic sites are shown in Fig. 4 (ii), (iii), (iv). If we were just considering the first nearest neighbors (n.n.), the difference between the Na(1,2,3) sites seems negligible. But considering the second n.n., we should expect to see a considerable difference due to local environments leading to non-zero values of η .

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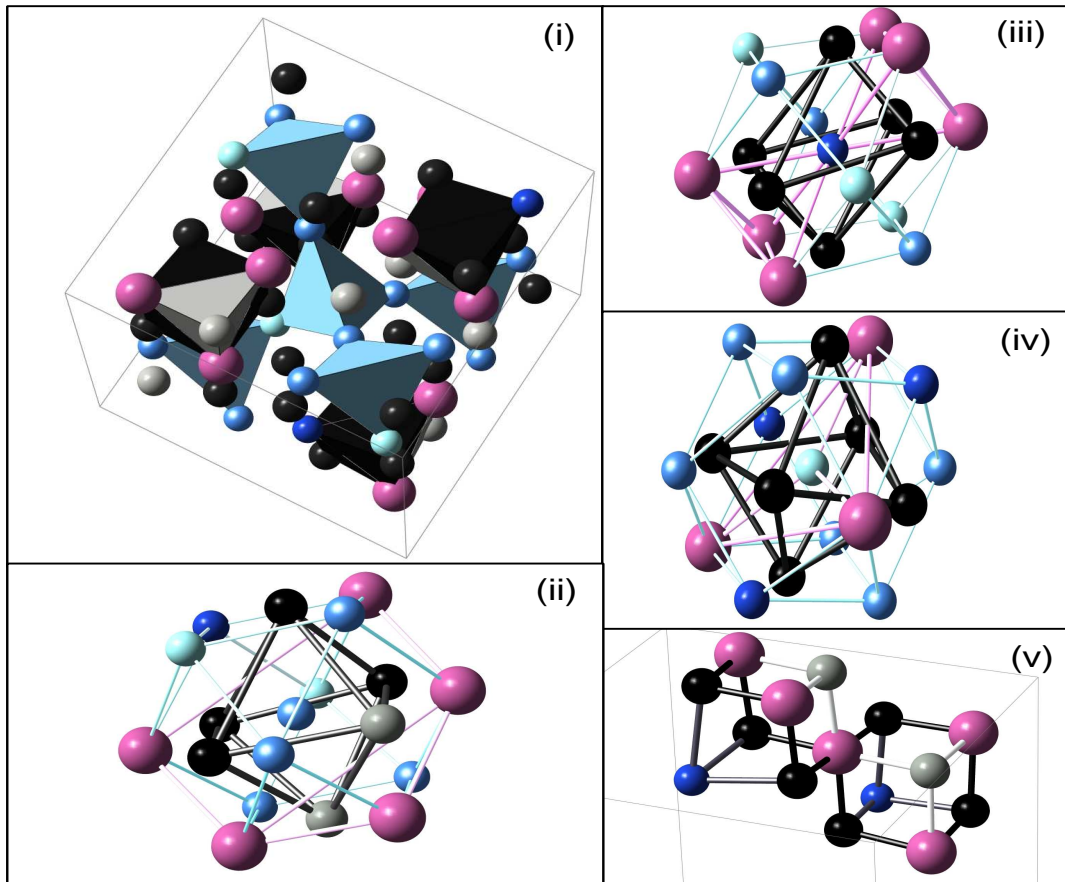


FIG. 4. (i) The unit cell with four distorted cubes of Ir (pink), Na(1) (dark blue), O(2) (black) and O(1) (grey) and five tetrahedra of Na(2) (pale blue) and Na(3) (blue). The first nearest neighbors (n.n.) form a distorted octahedron of O around the Na and the second n.n form a distorted tetradecagon of Na and Ir: (ii) the Na(3) site is surrounded by O(1) (four) and O(2) (two) and then Ir (five), Na(1) (one), Na(2) (two) and Na(3) (four). (iii) the Na(1) site is surrounded by O(2) and Ir (six), Na(2) (three) and Na(3) (three). (iv) the Na(2) site is surrounded by O(2) and Ir (three), Na(1) (three) and Na(3) (six). (v) Local environment of two corner-sharing Ir triangles.