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On the cover

Artist's view of a liquid of octupoles, see the related article "Neutron scattering by magnetic octupoles of a quantum liquid" by N. Gauthier, V. Porée, S. Petit, V. Pomjakushin, E. Lhotel, T. Fennel, and R. Sibille.

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The President's Page

Dear fellow neutron scientists,

Welcome to this issue of Swiss Neutron News. Let me start by thanking those who joined our recent general assembly. Being forced to hold it online prevented us from enjoying the company of colleagues and friends around an apero, but had the advantage that everyone could join without need to travel. We had two exciting presentations from the 2020 Young Scientist Prize recipients Muriel Siegwart and Jiri Ulrich, who gave very exciting presentations at our recent general assembly. I take the opportunity to congratulate them once more on their achievements. Muriel reported sophisticated neutron imaging techniques for studying fuel cells and other energy solution materials. Jiri's work on high precision nuclear data for astrophysics and geosciences represent the fields of fundamental physics using neutrons, which we wanted to encompass with the name change from Swiss Neutron Scattering Society to Swiss Neutron Science Society. In short, the scope of our interest sphere is science that relies on neutron sources.

On this topic, our umbrella organization ENSA, which I chair since beginning of 2020,

recently engaged with the EU funded BrightnESS2 project to analyze the European neutron science community with the aim of extrapolating trends and needs into the future. As part of this, we used natural language processing and machine learning to analyze neutron publications to identify domains and trends within the neutron science community. We coupled this to a survey that all of you received, and I thank those of you who took the time to answer. Within the coming year receive a second survey focused specifically on the Swiss neutron science community and impact. We are currently in an exciting time where SINQ has just been upgraded and ESS will come on-line, but where access to ILL will remain vitally important to many Swiss neutron scientists. I therefore kindly ask you to help in these efforts to map and shape the future of our scientific possibilities.

On the topic of SINQ's upgrade, it is my understanding it has been extremely successful with flux gains of 2 or better on most instruments. This is a great achievement, which everybody involved should be very proud of. Another point where we as user community can be grateful not just to PSI but to many of the neutron facilities is their efforts to enable



experiments during this unprecedented pandemic. The facilities are offering mail-in and remote experiments, which is extremely valuable to the scientific community, especially PhD students and postdocs who need results for their next career steps. I believe such neutron access solutions can be very beneficial for the total science output and for the traveling footprint of science. However, it places increased work load on the instrument scientists and facility staff. In the short term we gratefully thank them for taking on this extra burden, but in the longer term this means we must make sure that the operation budgets of facilities are adequate to optimize the total science impact.

I wish you all a healthy autumn and hope we can soon meet again in experimental halls and conference theaters,

Neutron scattering by magnetic octupoles of a quantum liquid

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Neutron scattering is a powerful tool to study magnetic structures and dynamics, benefiting from a precisely established theoretical framework. The neutron dipole moment interacts with electrons in materials via their magnetic field, which can have spin and orbital origins. Yet in most experimentally studied cases the individual degrees of freedom are well described within the dipole approximation, sometimes accompanied by further terms of a multipolar expansion that usually act as minor corrections to the dipole form factor. Here we report a unique example of neutrons diffracted mainly by magnetic octupoles. This unusual situation arises in a guantum spin ice where the electronic wavefunction becomes essentially octupolar under the effect of correlations. The discovery of such a new type of quantum spin liquid that comes with a specific experimental signature in neutron scattering is remarkable, because these topical states of matter are notoriously difficult to detect.

ON MAGNETIC NEUTRON SCATTERING

Neutrons, thanks to their spin, are employed to discern materials' magnetic properties. They are sensitive to the magnetic field produced by unpaired electrons, which can have various symmetries and properties depending on the particular atom and its crystal field environment. The magnetization density originates from both the spin and orbital distributions of open shell electrons and can be expanded in multipoles with the use of spherical harmonics. In a vast number of cases. neutron scattering results are well accounted for by considering the magnetic dipole moment of the atom - a parity-even tensor of rank 1 (axial vector). The tensors of higher odd-rank K are conventional magnetic multipoles such as the octupole (K=3) and the triakontadipole (K=5). However, their contribution to the neutron scattering form factor is usually marginal in comparison to the dipole moment.

The interaction of the magnetic multipole degrees of freedom with the neutron spin are described by the neutron-electron interaction operator $\mathbf{Q} = \exp(i\mathbf{q}\mathbf{r})(\mathbf{s} - ih/q^2 [\mathbf{q} \times \mathbf{p}])$ [1]. This operator can be expressed using spherical Bessel functions $j_n(q)$ in powers of $(\mathbf{qr})^m$ (m=0,1,2...), where q is the neutron scattering wavevector, and s, r and p are the spin, position and momentum of the electron. The first two leading terms in this expansion give the so-called 'dipole approximation'. The dominating contribution to the neutron scattering is given by the conventional radial integral $\langle i_0(q) \rangle$, which has maximum at q=0. Higher terms in the expansion of Q contain the contribution of the conventional magnetic multipole moments. The calculations of these higher-order contributions to the scattered neutron intensity is mathematically quite involved and requires the use of spherical tensors and Racah tensor algebra with the detailed procedures given in [1]. Despite this complexity, we can identify two main characteristics expected from the conventional magnetic multipoles based on the neutron-electron interaction. First, conventional magnetic multipoles give significantly smaller contribution to neutron scattering than the dipole one. Second, their form-factor is zero at q=0 with a maximum at relatively high q, and is also anisotropic. The expected signatures of magnetic multipoles are therefore a weak anisotropic signal at high q, making their experimental detection a real challenge.

Multipoles that are observable in neutron scattering must be odd under time-reversal symmetry. This includes the conventional magnetic multipoles, which are parity-even multipoles and are the main topic of this article. We note, however, that parity-odd multipoles can also exist and be observed if the atomic wavefunction does not have a well-defined parity [2-4]. These parity-odd multipoles are fundamentally different from the conventional (parity-even) magnetic multipoles. For example, the first order parity-odd multipoles are called anapoles, or toroidal moments, which are the cross products of spin s or orbital l angular momentum with the electron position r.

MULTIPOLES IN CONDENSED MATTER RESEARCH

Although a vast majority of materials with strong electronic correlations can be well

understood based on individual degrees of freedom described using the first term of the multipolar expansion, further terms are required to explain an increasing number of novel phenomena. Such multipole moments can in principle lead to the emergence of macroscopic orders that are sometimes called 'hidden' due to the challenge of determining their order parameter [5-6]. Multipoles in condensed matter correspond to anisotropic distributions of electric and magnetic charges around given points of the crystal structure - a situation that can arise at the atomic scale from spin-orbit coupling, such as for the multipoles proposed to explain a famously mysterious phase in the heavy-fermion material URu₂Si₂ [7], or at the scale of atomic clusters where the established correlations lead to the emergence of novel degrees of freedom, such as in the spin-liquid regime of Gd₃Ga₅O₁₂ [8].

As already noted, neutrons are also sensitive to odd-parity multipoles, and a number of studies have pointed to their role to explain phase transitions that break both space inversion and time reversal. This has been especially discussed in the context of magnetoelectric insulators [9-10], and in high-T_c superconductors where magneto-electric quadrupoles were proposed as the order parameter of the transition appearing in the pseudogap region [11-12].

Well characterized examples of 'hidden' orders of (conventional) multipoles exist, such as in NpO₂ or CeB₆ and its substitutional alloys Ce_{1-x}La_xB₆ [5-6]. In neptunium dioxide [13], the primary order parameter is associated with magnetic octupoles that order around 25 K in a longitudinal structure defined by three wavevectors. This structure of ordered octu-

poles was established, indirectly, using resonant X-ray diffraction through the measurement of a parasitic order of electric quadrupoles having the same structure [14,15]. In cerium hexaboride, the first correlated phase entered upon cooling in zero field below $T_Q = 3.4$ K is an antiferroquadrupolar order, which is followed by an antiferromagnetic order of dipoles at $T_N = 2.3 \text{ K} [16, 17]$. The dipole-dipole nature of the intersite magnetic interactions make the associated correlations more resistant against disorder than for the electric quadrupoles, so that T_Q decreases faster than T_N upon diluting the cerium lattice with lanthanum [18]. At some doping level, these phase transitions intersect and a new phase pocket appears, characterized by an antiferromagnetic ordering of octupoles that was measured directly using resonant X-ray diffraction [19].

The contribution of parasitic magnetic octupoles to the total magnetic scattering intensity - of mainly dipole origin, is well known in materials such as elemental holmium for instance [20]. However, the experimental results for Ce0.7La0.3B6 presented in ref. [21], where magnetic multipoles are the primary order parameter, is to the best of our knowledge a unique example in terms of ordered magnetic multipoles scattered by neutrons. Only three independent magnetic Bragg peaks were detected, but the fact that the intensity at q=6 Å⁻¹ is larger than at q=1.3 Å⁻¹ has led the authors to argue that these have octupolar origin. A later theoretical study [22] qualitatively confirms that the q-dependence of the observed peaks agrees with the calculated octupolar neutron magnetic form factor of cerium in this material.



Inelastic neutron scattering (INS) data of Ce₂Sn₂O₇ probing the crystal-electric field levels within the ground multiplet ²F_{5/2} of Ce³⁺ (**a**) [29]. The bulk magnetic susceptibility χ [28], shown in blue as the effective magnetic moment $\mu_{eff} \propto \sqrt{\chi T}$ as a function of temperature (**b**) reveals three regimes. At high (T > 100 K) temperature μ_{eff} decreases due to crystal-field effects – a regime that is well reproduced by the calculation from the fit of the INS data [29]. At moderate (1 K <

T < 10 K) temperatures, a plateau of ~1.2 μ_B corresponds to the dipole moment of the ground state 'dipole-octupole' doublet. At low (T < 1 K) temperature, μ_{eff} decreases further under the effect of dominant octupole–octupole correlations, making the octupole moment strengthen at the expense of the dipole one, as shown in Figure 2.

A constant to all materials discussed so far is the notion of order associated with multipoles. Comparatively, far less attention has been given to the effect of multipolar fluctuations in the absence of multipolar order. We can mention, though, that a number of recent theoretical studies point to the relevance of multipole fluctuations in unconventional superconductivity [23-26], where it is proposed to induce anisotropic pairing mechanisms [27].

A central result of the present work is to demonstrate the existence of a phase of correlated yet fluctuating multipoles, in the absence of long-range order down to the lowest temperatures. This discovery is based on a number of signatures indicating the development of a correlated ground state below 1 Kelvin, corroborated by neutron scattering results consistent with the formation of a fluid-like state of magnetic octupoles. The intensity distribution is weighted to large scattering vectors, which indicates that the correlated degrees of freedom have a more complex magnetization density than that typical of magnetic dipoles in a spin liquid. Keeping the broader relevance and implications of these findings for the last section of this article, we can already mention here that, in the context of neutron scattering, Ce₂Sn₂O₇ already stands out as it appears to be the second experimental evidence of neutrons scattered by non-parasitic higher-order magnetic multipoles.

MAGNETIC MULTIPOLES IN CERIUM STANNATE

We first define the context of the present study in terms of uncorrelated degrees of freedom



Magnetic charge density calculated from the type of ground state wavefunction of Ce³⁺ determined from the fit of the neutron data in Figure 1, i.e. $|\pm\rangle = A|\pm 3/2\rangle \pm B|\mp 3/2\rangle$. The values of J_z correspond to different values of the A and B coefficients.

in the material of interest, Ce₂Sn₂O₇ [28-29]. Trivalent cerium has one f electron, with spin S=1/2 and orbital angular momentum L=3mixed into a I=5/2 ground multiplet by spin-orbit coupling, which splits into three Kramers doublets in the crystal-electric field. Transitions within this ground multiplet are easily seen in inelastic neutron scattering measurements using an incident energy E_i of 150 meV, at energy transfers $E \approx 51$ and 110 meV (Figure 1a) [29]. Intermultiplet transitions to the J=7/2 multiplet are also visible from measurements taken with higher *E*_i, but their overlap in this data make them rather ill-defined experimentally. However, the transitions within the ground multiplet are sufficient to refine the parameters of the crystal-field Hamiltonian, and these can reproduce the data at higher energy transfers as well as the bulk susceptibility at high temperature. The latter is represented in Figure 1b, where the effective magnetic dipole moment $\mu_{eff} \propto \sqrt{\chi T}$ is plotted as a function of temperature. This quantity decreases upon depopulating excited crystal-field levels when cooling, to reach an approximate plateau of ~1.2 μ_B in the range from 1 to 10 K. This value corresponds to the dipole moment calculated from the wavefunction of the ground doublet only.

The essential result of the above crystal-field analysis is that the wavefunction of the ground state Kramers doublet is of the general form $|\pm\rangle = A|\pm 3/2\rangle \pm B|\mp 3/2\rangle$, where A and B are real. Any linear combination of these $|m_{I_z} = \pm 3/2\rangle$ states is by definition an eigenstate of the Hamiltonian. The wavefunction corresponds to a so-called 'dipole-octupole' doublet [30-31]. Importantly, we point out that the moment sizes respectively associated with the dipole and octupole operators directly depend on the values of the A and B coefficients. For instance, the situation where A=1 and B=0 leads to a full dipole moment $\langle J_z \rangle = 3/2$ and a zero octupolar moment, while A=B gives $\langle J_z \rangle = 0$ but a net octupolar moment (Figure 2). A key idea of the present work on Ce₂Sn₂O₇ is that the further decrease of dipole moment, observed in μ_{eff} when cooling down in the correlated regime below 1 K, is due to dominant octupole-octupole couplings, caus-



Effective magnetic moment $\mu_{eff} \propto \sqrt{\chi T}$ (**a**) and heat capacity (**b**) as a function of temperature in the correlated regime of Ce₂Sn₂O₇ below 1 Kelvin [28-29]. The magnetization curves as a function of field are shown in panel (**c**). All experimental data are shown as open or close circles and were used to fit the dipole–dipole \mathcal{J}^{zz} and octupole–octupole \mathcal{J}^{yy} exchange parameters using the relevant Hamiltonian for 'dipole-octupole' doublets on the pyrochlore lattice.

ing the octupole moment to strengthen at the expense of the dipole one. In other words, dominant octupole–octupole interactions mix the otherwise degenerate $|m_{Jz} = \pm 3/2\rangle$ states to form new split eigenstates – the driving force being to minimize the energy of the system due to different magnetic dipole and octupole moment sizes.

SIGNATURES OF CORRELATIONS IN MACROSCOPIC MEASUREMENTS

Our investigations of Ce₂Sn₂O₇ started with measurements of the bulk magnetization and heat capacity down to very low temperature [28]. As already exemplified with the plot of μ_{eff} shown in Figure 1b, signatures of a correlated state appear in this data below about 1 Kelvin. At these temperatures, the ground state doublet is thermally well isolated from excited

crystal-field levels, and therefore is sufficient as a minimal low-energy description of the degrees of freedom. In the correlated regime, where the magnetic susceptibility increases slower than expected for a simple paramagnet, a hump is also observed in the heat capacity (Figure 3), thus further hinting at cooperative phenomena setting-in below 1 Kelvin.

The magnetization curves are also instructive, as the powder-averaged saturation at high field occurs at roughly half the value of the ground-doublet dipole moment, which is expected for Ising moments on a pyrochlore lattice due to the important noncollinear local anisotropy. The Ising anisotropy of the dipoles is also corroborated by calculations using the wavefunction determined from the analysis of the inelastic neutron scattering results. It is interesting to note that Ising moments of ~1.2 $\mu_{\rm B}$ on the pyrochlore lattice of Ce₂Sn₂O₇



Magnetic dipoles respecting the '2-in-2-out' ice rule on each tetrahedron (**a**) and octupoles obeying the '2-plus-2-minus' rule (**b**), together with their respective neutron magnetic diffuse scattering patterns (**c** and **d**) calculated in the (HHL) plane of reciprocal space using Monte Carlo simulations [29]. Note that the spin ice pattern (panel **c**) is displayed over a much larger area of reciprocal space than usual, but the typical features can be discerned in the central region.

translate into classical dipole–dipole couplings of about 0.025 K, which is small compared to the scale of the dominant interactions. This simple comparison indicates that the correlated state originates from quantum-mechanical exchange interactions [28]. All bulk measurements, as well as muon spin spectroscopy [28], exclude the presence of magnetic order in Ce₂Sn₂O₇ down to the lowest temperatures (0.02 K), and instead suggest a highly frustrated magnet. The set of bulk measurements presented in Figure 3 can be used to extract exchange constants using the relevant Hamiltonian for rare-earth pyrochlores with 'dipole-octupole' doublets, $\mathcal{H}_{DO} = \sum_{\langle ij \rangle} [\mathcal{J}^{xx} \tau_i^x \tau_j^x + \mathcal{J}^{yy} \tau_i^y \tau_j^y + \mathcal{J}^{zz} \tau_i^z \tau_j^z + \mathcal{J}^{xz} (\tau_i^x \tau_j^z + \tau_i^z \tau_j^x)]$ [30-31]. The doublet is modelled by pseudo-spin S = 1/2 operators $\vec{\tau}_i = (\tau_i^x, \tau_i^y, \tau_i^z)$, where the components τ_i^x and τ_i^z transform like magnetic dipoles while τ_i^y behaves as an octupole moment. For the sake of simplicity and in order to avoid over-parametrizing the fit, we consider $\mathcal{J}^{xx} = \mathcal{J}^{xz} = 0$, which still captures the essential physics of octupolar phases. Using meanfield calculations, the bulk magnetic properties at low temperature are employed to extract values for \mathcal{J}^{yy} and \mathcal{J}^{zz} (see Figure 3) [29]. As already explained at a qualitative level, the drop of the effective magnetic moment below 1 K can be accounted for using a dominant octupole-octupole interaction \mathcal{J}^{yy} . Although the fit is equally good for $\mathcal{J}^{yy} = +0.48 \pm 0.06$ K or $\mathcal{J}^{yy} = -0.16 \pm 0.02$ K (and a small but finite dipole-dipole coupling $\mathcal{J}^{zz} = +0.03 \pm 0.01 \text{ K}$, only $\mathcal{J}^{yy} > 0$ corresponds to a frustrated arrangement of octupoles and is able to explain the absence of phase transition. In this case, the magnetic charge density of the octupoles on a tetrahedron is constrained by a '2-plus-2-minus' ice rule (Figure 4), leading to an extensively degenerate manifold of octupole ice configurations. In the present context, 'plus' and 'minus' replace the 'in' and 'out' states characterizing dipole Ising moments on the corner-sharing lattice of tetrahedra in spin ices, and instead designate the two possible local mean-values of the octupolar operator associated with τ_i^y . We note that \mathcal{J}^{yy} <0 would imply an ordered phase of octupoles with 'all-plus-all-minus' configurations on each tetrahedron, which is not frustrated and would lead to a phase transition.

MAGNETIC OCTUPOLE NEUTRON SCATTERING IN CERIUM STANNATE

We now turn to the observation of magnetic neutron scattering from the octupole ice state expected from the analysis of the bulk measurements. Using the powder diffractometer HRPT at SINQ, later also confirmed using D20 at ILL, a weak diffuse signal appearing at high scattering vectors was observed in high-statistics difference data between 5 K and several lower temperatures ranging from 2 K to 0.05 K (Figure 5) [29]. The intensity distribution is zero at low scattering vectors q<4 Å⁻¹ but grows and reaches a maximum around q~8 Å⁻¹, which is characteristic of higher-order multipoles.

The diffuse scattering observed in Ce₂Sn₂O₇ has several important implications, even though its wave-vector dependence cannot be studied in details due to powder averaging. First, the simple existence of this signal is likely to be an additional and good reason to think that the system is governed by quantum exchange interactions. Second, the magnitude of the signal, presented in absolute units, is in very good agreement with that expected for a ground state based on octupole ice correlations, thus giving strong support to their existence in this material. To ascertain this, the experimental data in Figure 5 is presented together with the powder average of the diffuse neutron scattering calculated for an octupole ice phase. The signal measured at 0.05 K is about two thirds of the intensity of the zero-temperature calculation, the latter assuming a full octupolar moment and the generic wavefunction of Ce3+ determined for Ce₂Sn₂O₇.

The octupole ice scattering is in general about several hundred times weaker than the value expected for spin-ice scattering, even considering the small dipole moment of Ce₂Sn₂O₇, which itself is much weaker than that of classical spin ices like Ho₂Ti₂O₇ [32]. Therefore, it remains a real challenge to measure such a weak signal, which was repeated multiple times and on two different instruments



Diffuse octupolar scattering (blue points with error bars corresponding to ±1 standard error) obtained from the difference between neutron diffraction patterns measured at 5 K and at a lower temperature indicated on each panel. Measurements were performed on HRPT (λ = 1.15 Å, dark blue points on panels **a-c**) and D20 (λ = 1.37 Å, light blue points on panel **c**). Note the large scattering vectors required to observe scattering by magnetic octupoles. The increase of octupolar moment evaluated by the temperature dependence of the integrated diffuse scattering (**d**) matches with the drop of the dipole moment measured in bulk susceptibility (c.f. Figure 3**a**). The powder average of the diffuse scattering calculated for the octupole ice and spin ice configurations is shown respectively with red and green points in panel **c**, while the solid red line represents the same calculation for the octupole ice but scaled (× 0.625) onto the experimental data. Note the different scales used to display the octupolar (left scale) and dipolar (right scale) scattering in Ce₂Sn₂O₇.

in order to exclude spurious origins of the hump observed at high q. The available neutron flux is actually not the most important instrumental characteristic to improve the statistics here, but rather a combination of well understood instrument features, background, collimation, high resolution in order to distinguish the signal from the shifts of Bragg peaks due to thermal contraction in difference patterns, and optimal choice of wavelength in order to favour a large detector angular range for the region of interest in reciprocal space.



Imaginary part of the dynamic spin susceptibility (**a**, blue points with error bars corresponding to ±1 standard error). The difference map between low (correlated) and high (uncorrelated) temperatures (**b**), summarizes the wavevector dependence of the spin excitations as a function of energy, giving evidence for a continuum of fractionalized spin excitations. The phenomenological form used to fit the spectrum (red line) happens to capture the features expected from theory for spinon excitations in a quantum spin ice (onset, peak and extent) [33,37-39].

AN OCTUPOLAR QUANTUM SPIN ICE

The exchange constants extracted from the set of bulk measurements place $Ce_2Sn_2O_7$ in the octupolar quantum spin ice regime [30-31] – a quantum liquid built up from a manifold of octupole ice configurations set by the dominant \mathcal{J}^{yy} exchange and allowed to quantum fluctuate thanks to \mathcal{J}^{zz} acting as a transverse perturbation.

In a (dipolar) quantum spin ice, excitations are expected to be of two types [33]. Gapped excitations, akin to spinons, correspond to defects created by single spin-flips in a '2-in-2-out' manifold – a quantum version of the magnetic monopoles of classical spin ice. Equivalently, in an octupolar quantum spin ice [30-31], we still expect such excitations to arise in the form of dipolar low-energy inelastic neutron scattering, because \mathcal{J}^{zz} allows

neutron-active transitions between the two states of the doublet split by \mathcal{J}^{yy} [29]. Low-energy neutron spectroscopy data of Ce₂Sn₂O₇ indeed reveal the presence of low-energy excitations that are dipolar in nature (Figure 6) [29], and their continuous character matches expectations for the fractionalized spinon excitations of a quantum spin liquid. Gapless excitations of a quantum spin ice known as 'photon' excitations, however, are expected to follow an octupolar form factor in the present case. And, given the bandwidth expected for such excitations, in the µeV range, resolving their energy spectrum using neutron scattering appears impossible in view of the incident energies of the order of 50 meV required to reach far enough reciprocal space.

The continuum is peaked around 0.05 meV, which is approximately the dominant exchange interaction \mathcal{J}^{yy} , and extends up to at least 0.3 meV, which is significantly larger. Both of these characteristics are consistent with theoretical predictions for the spinon continuum of a quantum spin ice [33,37-39]. Moreover, at the low-energy edge of the continuum, a sharp increase in the density of states is observed, which is reminiscent of the threshold predicted for quantum spin ices due to the effect of the emergent photon on

COMPARISON WITH OTHER MATERIALS

the production of spinons [39].

Recent works have focused on a related material, Ce₂Zr₂O₇, with the advantage of large single crystals being available [34-35]. However, this comes at the price of a poor control of the oxygen stoichiometry due to the difficulty to maintain a clean atmosphere at the very elevated melting temperature reached during travelling-solvent crystal growth, combined with a problem of oxidation at ambient conditions inherent to the compound [34]. Oppositely, the trivalent oxidation state of cerium can be readily stabilized in Ce₂Sn₂O₇, taking advantage of a solid state oxydo-reductive reaction during which Snº is oxidized to Sn4+ while reducing Ce4+ to the required Ce³⁺ [36]. Moreover, the oxygen stoichiometry of the stannate can be precisely determined by thermogravimetric measurements under air by following the mass gain from the sample to its oxidation product, which leads to conclude for a perfect oxygen stoichiometry within a precision of less than 1%. This contrasts with the 10 % of extra oxygen, and hence non-magnetic Ce⁴⁺ impurities, in samples of cerium zirconate [34].

Despite these differences in the quality of the samples of Ce₂Sn₂O₇ and Ce₂Zr₂O₇, a number of measurements indicate that both materials are characterized by the same quantum spin liquid ground state. These are *i*) a crystal-field analysis indicating a 'dipole-octupole' ground state doublet in both cases [29,34-35], *ii*) heat capacity data that appear consistent for the two materials [28,34-35], iii) muon spin rotation experiments indicating that both of these isostructurals retain a dynamical magnetic ground state down to 0.02 K [28,35], and iv) low-energy neutron spectroscopy experiments providing evidence for continua of dipolar spin excitations characterized by the same energy and damping in $Ce_2Sn_2O_7$ [29] and $Ce_2Zr_2O_7$ [35]. For all these reasons, it appears reasonable to think that the octupolar quantum spin ice scenario might also explain the observations of quantum spin liquid dynamics in Ce₂Zr₂O₇.

To broaden the scope of the comparison to other materials as well, we can mention here that Ce³⁺ pyrochlores hold a certain degree of uniqueness in the whole zoo of candidate quantum spin liquids. Indeed, they have smaller dipole moments compared to most candidates based on rare-earths [40], thus reducing the classical dipole-dipole forces to a negligible interaction, and their ground-state doublet is well isolated - thus clearing any doubts on possible quantum processes involving low-lying crystal-field levels [41]. The Kramers nature of the ground state doublet additionally avoids complexities related to transverse fields induced by the residual amounts of structural disorder always present in any real sample [42-45]. These characteristics, together with the cooperative behavior of the 'dipole-octupole' pseudo-spins we have demonstrated and the excitation continuum we have measured, give these materials the promise to become excellent proven examples of a three-dimensional quantum spin liquid.

CONCLUSIONS AND OUTLOOK

With this experimental work demonstrating that the correlated ground state of the pyrochlore material $Ce_2Sn_2O_7$ is a quantum liquid of magnetic octupoles, we establish a fundamentally new state of matter: a quantum ice of higher-rank multipoles. This discovery is ground-breaking for several reasons that are briefly summarized below [29,46].

States of matter that are primarily driven by multipolar interactions are rare, and the octupole ice is unique among those rarities in that it is highly frustrated and likely exhibits topological order. As stated at the outset, higher multipolar interactions are known or conjectured to be the key to understanding a wider range of 'hidden' orders in condensed-matter systems, from heavy-fermion materials to, potentially, high-transition-temperature superconductors. Bringing together this area of research with the intriguing world of 'ice physics', and quantum spin liquids more generally, holds the promise to open new perspectives.

The experimental results obtained here are consistent with the realization of a topological phase in three dimensions, known as the U(1) quantum spin liquid. In Ce₂Sn₂O₇ we have demonstrated that the relative contributions of dipole and octupole moments to the ground-state wavefunction depend on temperature, and also can be tuned by an applied magnetic field. These two control knobs on the 'dipole-octupole' quantum object encoded in the local ground-state wavefunction open up intriguing prospects with a view to explore the rich physics of these quantum many-body systems.

With the recent progress in the theoretical understanding of 'dipole-octupole' pyrochlores [47-50] and of quantum spin ice in general [37-39,51-52], the prospects for Ce₂Sn₂O₇ and related materials are very encouraging. It appears likely that these will conclude to a recognized identification of a three-dimensional quantum spin liquid, in line with the historical works having introduced the concept known as 'quantum spin ice' about 15 years ago [53], with the difference, however, that the ice manifold is constructed from the magnetic octupole components of a pseudo-spin [30-31]. Experimentally, there are great challenges ahead, such as resolving the octupole ice diffuse scattering in three-dimensional reciprocal space, as well as the spinon continuum using finer energy resolution, and also understanding the field-induced dipole orders.

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Expansion of experimental infrastructure at HRPT: Stroboscopic neutron diffraction

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Abstract

A range of experimental possibilities for users of the high resolution powder diffractometer HRPT at SINQ has been extended by the stroboscopic mode of operation. A specimen whose state can be periodically modified, is being sampled continuously over many iterations, and a special binning procedure delivers then diffraction data representing the separate stages of the process by their individual diffraction patterns. Starting from some model experiments, where the position of a sample in the beam was mechanically changed in time, and could successfully be tracked back to the correct values, we have further applied the new stroboscopic method to investigate the structure changes occurring in the electrode materials of rechargeable Li-lon batteries upon fast charge and discharge. Thereby we could establish correlations between the charge/discharge rates,



Radial Collimator RC2 with a fine angular opening of 0.5, which results in a maximum footprint of the triangular transmission function of ~14 mm, during one of the routine radial collimator exchanges at HRPT.

lifetime of the batteries and the peculiarities in the evolutions of the crystal structure of the electrode materials.

Innovations at HRPT

The high-resolution neutron powder diffractometer HRPT [1] at SINQ is one of the world-leading instruments for chemical and magnetic crystallography. Conceptually designed by P. Fischer, PSI, it is producing steady scientific output since 1999. On average, approximately 30 publications in the reviewed scientific journals per year are based on the results obtained at HRPT. In many instances, HRPT has been delivering novel technical solutions that allowed to expand the range of applications of powder neutron diffraction, to improve the quality of the acquired diffraction data, or to significantly increase the efficiency of neutron beamtime usage at SINQ. Already in 2003, we have modified the radial collimator originally introduced into the neutron instrumentation in 1981 [2] and then adapted by J. Schefer and P. Fischer for powder neutron diffraction in the design of the DMC diffractometer at the reactor Saphir [3].

In its original design, the radial collimator of HRPT (produced by JJ-Xray) was featuring too weak absorption, which was resulting in visible background, especially with shorter neutron wavelengths. For the refurbished radial collimator, exact estimation of the necessary absorber density on the thin mylar foils has been done, and the painting conditions of the foils have been experimentally verified



Sample changer for room temperature measurements at HRPT. Accepting up to 8 samples, it allows to significantly increase the effectiveness of the beamtime usage, especially for campaigns with high number of samples to study. Right: a huge set of samples to be studied at HRPT (~80 in approximately 4 days): a typical case for automated exchange of samples.

through direct transmission measurements of test foils at different neutron wavelengths. The modified radial collimator RC1 suppresses now completely the contributions from sample environments typical at SINQ, for most of the reasonable geometries and counting rates. The full width at half maximum of its triangular transmission function at sample position amounts to 14 mm.

Later on, we have acquired the second radial collimator RC2 (shown in Figure 1) with a yet finer opening for angular collimation of 0.5 deg., which allows now for example to increase the peak to background ratios also for tiny samples in the presence of tight and massive sample environments, like e.g. pressure cells. In most cases, a factorwise gain in the peak to background ratio could be reached at a cost of only approximately 20% total intensity loss.

One further innovation was the use of sample changers. In 2006, we have started to use our first carousel-type sample changer for room temperatures (Figure 2). Designed by A. Bollhalder, PSI, it allows up to 8 samples to be mounted at a time and interchanged in a programmed way. This contributes to a far more effective use of the beamtime, especially for the longer measurement campaigns with many similar samples to be characterized.

A few years later (2009), our first sample changer for up to 4 samples for low temperatures down to 1.5 K has come into operation. The original idea to position the entire sample changer mechanism inside the sample chamber of the cryostat came from M. Zolliker, and the design was done by A. Bollhalder at PSI. A follow-up version of the low-temperature sample changer, the LT5 (shown in Figure 3), that is mainly being used now, accepts up to 5 samples simultaneously, and additionally allows for the sample rotation around its axis. In many cases this helps significantly reducing the unwanted preferred orientation effects, and contributes to the reliability of the structure determination and refinement. Introduction of the routine use of sample changers has dramatically improved the efficiency of the usage of beamtime, helium and manpower. A typical user experiment with several samples



(Left): LT5 sample changer with 5 samples loaded, ready for insertion into the cryostat. A sample to be measured is brought to the beam and can be rotated around its axis. Right: an illustration of the usefulness of the sample changer: a graph of sample temperature vs. time for a typical user experiment with 5 samples in 3 days without (top) and with (bottom) using the sample changer. The shaded rectangles represent times spent for sample changes and initial cooling. Using the sample changer reduces these losses from ~13 to ~3 hours for such an experiment.

to be measured at different low temperatures over a period of few days, is thereby gaining 10-20% of additionally available useful beamtime. Additionally, significant amounts of helium are saved. All HRPT sample changers are entirely based on the in-house design and production.

A smart Perl-based library of user-friendly programs has been developed over the past several years, that makes carrying out the experiments, obtaining the properly rebinned and normalized experimental data intuitively clear, and helps following the status of all the relevant aspects of the experiment most efficiently. This includes a transparent way of selecting the modes of the instrument operation, planning the time schedule of the measurements, watching the necessary hardware parameters, proper driving of motors, automatic data processing, and many more aspects of the instrument operations.

In the current contribution, we are presenting one more expansion of the capabilities of high resolution powder neutron diffractometry at SINQ: the practical implementation of the so-called stroboscopic mode of HRPT. The principal design and practical implementation of the electronics for this new HRPT option have been done at PSI by G. Theidel, U. Greuter and R. Bürge. Our recently published article [4] deals with this study in details.

The operando stroboscopic neutron diffraction mode

The reason to use the stroboscopic approach in neutron diffraction is to be able to characterize the crystal structures of possible transient states of matter during phase transitions or chemical reactions etc. The obvious principal obstacle for using neutron diffraction hereby is the vanishingly short times during which the hypothetical intermediate states of interest usually exist. Majority of the phase transformations in solid substances that would be a natural playground for neutron scattering studies, are occurring on the time scales of ps to ns. On the contrary, the phenomena occurring in mesoscopic systems are characterized by the time scales that are in some cases already closer to those we are living in. The spatially inhomogeneous (modulated on the mesoscopic scales) systems display relaxation, diffusion, transition phenomena or chemical reactions with characteristic time-scales sometimes on the order of seconds or even slower. This is where the (neutron) stroboscopic studies can find their application.

The approach that we have implemented and verified at the high-resolution neutron powder diffractometer HRPT is essentially similar to the stroboscopic aliasing, whereby shining a periodic light onto the moving object may lead to obtaining a series of the seemingly static images of it. Given the "object"



Schematic representation of the stroboscopic neutron scattering experiment.

under study "moves" along repeated tracks (or the studied substance undergoes a repeating sequence of transformations), the total exposure on these slices, accumulated over many repetitions, may then get sufficient enough to produce sharp, well-illuminated images. A good introduction to the principles and a nice set of application examples of the stroboscopic neutron diffraction studies is given in ref [5].

Applied to neutron scattering, it means that if the response of a system under study is repetitive, and excursions between the two states thereof are fully reproducible, it appears possible to utilize the stroboscopic techniques, and measure the scattering response as a function both of the natural scattering variable (e.g. the scattering angle), and of time since the perturbation that would cause the transition. A schematic representation of the principle is given in Figure 4. A system under study undergoes a transition caused by "external stimulus" from "state 1" (schematically represented as a circle) to the "state 2" (square), possibly also passing through some intermediate states (triangle, stars). Later on, the system either relaxes itself, or is being driven by some other external stimulus back to the "state 1". For each of the scale units of the axis named "time since stimulus", the intensity would be very low, but having repeated the process a sufficient number of times, and combined the corresponding patterns for each of these time slices since the external stimuli causing the transition, one would hope to collect sufficient counting statistics to make the qualitative, or even quantitative conclusions on the state of the system at particular times. Hence, the hope is there to collect sound enough neutron

diffraction data to ideally refine the parameters of the crystal structures of the compounds in the intermediate states. Clear, many conditions have to be fulfilled in order the scheme to be functioning properly. The most important is that the process under study is sufficiently repetitive, otherwise the patterns corresponding to the times of "intermediate states" would no longer be really representative, in practice hindering obtaining any conclusive results. Further, there are some certain limitations on how the duration of external stimulus (of electric pulse front, or of the force application, or of the magnetic field ramp etc.) and the characteristic time of the system's response would need to correspond to each other. Ideally, it is the duration of the stimulus that needs to be much shorter. such that the uncertainties in the "time since stimulus" variable would become insignificant. For the similar reason, complications may arise for the use of time-of-flight neutron diffraction in stroboscopic mode for rather short processes. Here, the time spans of the utilized neutron pulses should be much shorter than the time scale of the process under study.

After successful preliminary tests, the first applied study followed. Stroboscopic mode of neutron diffraction has been applied to studying the crystal structure changes that occur in the Li-ion battery materials upon fast charge or discharge [4].

Applying stroboscopic neutron diffraction to operando studies on battery materials at HRPT

Li-ion technology has proven to be one of the most promising solutions for storing renewable energy [6]. Lithium-ion batteries (LIBs) are now the predominant systems to power portable tools, such as smartphones and laptops, or household appliances, and their introduction to the mobility market has already begun and continues to grow rapidly [7]. Being able to charge batteries faster is attractive, but it is known that for each battery, there is an optimal charge rate. When charged or dis-charged faster than recommended, which means using higher electric currents than those allowed, the batteries are rapidly losing their capacity. In ultimate cases, this leads to a complete degradation of their performance. Many of the mechanisms behind this performance fading are known, some are not. We have focused the use of our stroboscopic method to look into what happens microscopically to the crystal structures of battery materials during fast or even very fast charge and discharge. Neutron diffraction is established as a method of choice to study the crystal structures of battery materials [8], both due to the high penetration ability of neutrons, and in many cases - thanks to a convenient balance of the scattering powers. This allows to make qualitative conclusions, for example to determine phase

composition of the active electrode materials, and to obtain quantitative results like e.g. even to refine the Li contents in the cathode and anode materials. Thereby, the most conclusive studies are those that can be carried out insitu, or even under real operation conditions. The main challenges in such experiments are: i) the incoherent scattering of neutrons by hydrogen, of which typically a lot is contained in many of the cell components, first of all in the separators and in the electrolyte and ii) the relatively weak intensities of the neutron diffraction patterns possible to acquire at modern neutron instruments. The typical counting times in such experiments is on the order of usually at least minutes, sometimes hours.

To overcome these difficulties, specialized electrochemical cells for in-situ studies with neutrons were developed, that would be able to provide the electrochemical cycling as close as possible to the real industrial cells, while maintaining possibly highest signal to noise ratios. In practice this means bringing the most of the "useful" materials under study into the scattering position in the beam, while exclud-



Figure 5

Working principle of the stroboscopic method developed at the HRPT beamline for operando neutron diffraction acquisition on a repetitively charging and discharging cell.

ing all sources of deteriorating scattering, as much as it goes, from adding up to the unwanted background of diffraction patterns. Recently, our colleagues from the electrochemistry laboratory at PSI have developed new cells, featuring improved signal-to-noise ratio, allowing for refinement of the lithium content in the different host materials [9, 10]. This new type of cells was used in several recent studies, including for example the study of ageing mechanism of the disordered LiNi0.5Mn1.5O4 (d-LNMO) spinel cathode material by operando neutron diffraction [11]. And to address the obstacle of too low intensities from the short-living phases, smart approaches might turn helpful. Exactly for this purpose, we have applied our stroboscopic mode to collecting the operando neutron powder diffraction data in the batteries.

The data we report here were obtained from commercial cells similar to the 18650-type, that were loaded with ca. 4 grams of electroactive materials ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel vs. graphite), at different cycling rates up to 15C (4 minutes per a complete charge or discharge). Thereby at rates of 1C, 2C and 5C, the quality of the stroboscopic data was good enough to carry out sensible Rietveld refinements.

The principal realization of the operando stroboscopic neutron powder diffraction mode, applied to a typical Li-ion cell cycling at fast rate is schematically presented in Figure 5.

At the beginning of each charge (signaled by the lower cut-off voltage), a stroboscopic signal is triggering the acquisition of a new frame. One frame (one strob) corresponds to the acquisition of the diffracted neutrons during one complete electrochemical charge-discharge cycle. Within one frame, the time since the beginning of a frame is monitored, and the programmable intervals, the so-called strobo-slices (with some reasonable predefined duration) are running until the next stroboscopic signal flashes the start of the next frame. Thereby, once the potential of the cell reaches the upper cut-off voltage value, the system starts to discharge the cell; the same stroboscopic frame still running. The repetitiveness of the charge/discharge cycles is ensured through the galvanostatic (con-stant current) charge/discharge, and by permanent tracking the current and potential on the cell. During the acquisition of each frame, the diffracted neutrons are labeled with the ordinal number of the strobo-slice in which they were registered, thus each strobo-slice is effectively producing its own neutron diffraction pattern. All relevant frames are then merged in such a way that the identical strobo-slices from different strobes are binned together (100 merged frames would for example correspond to 100 electrochemical cycles of the battery). Thus, the insignificant statistics collected during a single strobo-slice in any frame contributes to an enhanced intensity diffraction pattern after a sufficient amount on frames has passed. The programmable temporal duration of the strobo-slices should be chosen in accordance with the time scales of the process under study. On a practical side, for the operando studies of the battery materials, strobo-slicing on the order of seconds seems reasonable. Most of the data we were analyzing were collected with programmed slicing of 10 s, and then binned with the slicing of 30 to 60 s.

It is worth to note that the described method is not equivalent to running many very short acquisitions one after another, and then



Color intensity maps of the evolution of intensities of some representative Bragg reflections of the main cell materials collected during operando stroboscopic NPD measurement of the first four cycles of d-LNMO vs graphite (every pattern was recorded during 1 min): (a) the (002) graphite reflection (transforming in course of charge into the (101)/(003) peaks of LiC₁₈, then into the (002) peak of LiC₁₂, and then – into the (001) peak of the LiC₆), (b) the (222) d-LNMO reflection, (c) the (112) peak of LiC₆ at ~64.5° overlapping with the (440) peak of delithiated LNMO (phase 3) at ~63.9°, the (440) peak of the half-delithiated LNMO (phase 2) at ~62.6°, and finally of the (220) peak of Al at ~63°; (d) one representative galvanostatic cycle of d-LNMO vs graphite.

binning the necessary patterns to represent a certain state of the system, because stopping one acquisition and starting another inevitably consumes time. On the contrary, during a measurement running in stroboscopic mode, data are being collected permanently, and the registered neutrons are assigned two "coordinates": a natural scattering variable (2-theta angle), and the time since beginning of charging the cell, which is serv-ing hereby as an event marker.

Proof-of-concept: cycling a custom-made cylindrical cell with LiNi_{0.5}Mn_{1.5}O₄ vs. graphite at 1-C rate

As a proof of concept, we investigated one of the most promising battery systems: a cell based on the redox couple $LiNi_{0.5}Mn_{1.5}O_4$

(disordered LNMO) vs. graphite. At a charge and discharge rate of 1C (1 full charge per hour), this cell can still be cycled extremely long, without losing its capacity, thus this rate still remains safe for this particular battery's performance. The stroboscopic neutron diffraction data during the first four cycles were collected with a strobo time slices of 10 seconds duration, and different time binning possibilities were tested on these data. When binned with strobo time slices duration of 1 minute, it allowed the extraction of an effective neutron powder patterns suitable for Rietveld refinement. The color intensity maps of the representative reflections of d-LNMO and graphite are plotted in Figure 6. An example of Rietveld refinement on the stroboscopic data is given in Figure 7. The full statistics thus corresponds to 4 minutes of absolute acquisition



Rietveld Refinement of the crystal structure parameters of the phases constituting the cell being charged, based upon the operando stroboscopic powder diffraction data. Experimental points, calculated profile and difference curve (at the very bottom) are shown. The three groups of lines below the main graph represent the partial contribu-tions of the calculated profiles of the phases constituting the cell, (top): C, LiC₁₂ and LiC₆ (LiC₁₈ is not present at this very stage of charge), (middle): d-LNMO half-filled and Li-poor phases 2 and 3, and (bottom): cell components: Al, Cu, and Al₂O₃.

time, but it represents just exactly 1 minute long lasting state of the cell upon charging. Rietveld refinements were carried out using multiphase model, including the phases constituting both the electrodes (cathode material d-LNMO: phases 1, 2 and 3, see later for details, and anode phases C, LiC₁₈, LiC₁₂, and LiC₆), and also the other cell materials contributing to the diffraction data: Al of the cell body and positive current collector, Cu used as negative current collector, and Al₂O₃ used as a component of the composite separator. The time dependences of the refined important crystallographic parameters of the phases of interest are presented in Figure 8. At such a fast rate, we can hardly distinguish any potential plateaus of the full cell that should be visible in the galvanostatic curves, and would be ascribed to d-LNMO and to the graphite counter electrode. The first potential plateau is generally attributed to the Mn³⁺ \rightarrow Mn⁴⁺ transition, which should represent less than 5% of the total d-LNMO charge, followed by the two potential plateaus attributed to the Ni²⁺ \rightarrow Ni³⁺ \rightarrow Ni⁴⁺ transitions.

Upon charging, the lattice of the d-LNMO shrinks, signaled by the gradual shift of the diffraction peaks to higher angles (Figure 6, panels b and c), while the Li contents in it gradually decreases, as expected [12]. After ~30 min of cycling (at approximately the half-charged state), some more dramatic changes are being observed in the diffraction peaks of the d-LNMO, as illustrated in Figure 6, panel (c) for the representative, well-isolated (222) peak. All peaks of the d-LNMO are splitting into doublets, thus signaling a phase separation into two phases (phase 2 and phase 3). Both phases 2 and 3 may sufficiently well be described as cubic with the same symmetry (*F d-3m*) as the d-LNMO. One of these two phases has an almost constant lattice parameter and presumably, a constant Li content. This stable intermediate phase emerges at the end of the first potential plateau of the transition $Ni^{2+} \rightarrow$ Ni³⁺[13. 14], and in analogy to ref. [11], we refer to it as 'phase 2'. The phase 2 appears after the extent of delithiation has reached approximately 50%, and it was reported to have a lithium content of ~0.5 by Shavanaran et al [15]. Our refinements indeed are confirming this value. The other phase ('phase 3') is actually better seen only upon further charging and the delithiation of the cathode material. The phase 3 features a lattice constant and presumably, the Li-content, that are very fast decreasing with time. This generally is in accordance with the electrochemistry and the change in oxidation state of Ni during the last potential plateau (transition $Ni^{3+} \rightarrow Ni^{4+}$). Also the phase 3 can be described as a cubic structure with the Fd-3m space group, and its refined lithium content is close to zero in the fully charged state. Both phases 2 and 3 coexist during the last potential plateau, and there seems to be a statistically significant refined redistribution

of the fractions between the phases 2 and 3, whereby the almost Li-free phase 3 is dominating in the fully charged state, as expected. The unit cell volume of d-LNMO decrease is ~5.4% during delithiation with a decrease of ~3.1% for the first nickel redox couple, and of ~2.3% for the second one; values that are generally in a good agreement with the literature [16, 17].

Quite similarly, the crystal structure changes are nicely seen in the graphite anode material. In case of graphite (Figure 6), the structural changes observed upon lithiation (charge) and delithiation (discharge) are guite similar to those seen in our previous studies [9, 11]. During the first charge, different stages of graphite lithiation (namely, stages 1L, 4L, 3L, 2, and 1), especially the principal stages LiC18 (stage 3L), LiC_{12} (stage 2) and LiC_6 (stage 1), can be clearly distinguished [18, 19]. The phase fractions of the phases constituting anode material that were calculated from the Rietveld refinements during cycling are displayed in Figure 8, along with the "normalized" unit cell volumes thereof. The exceeding amount of graphite (coming from the cell balancing) as compared to the d-LNMO cathode counterpart results in having a certain amount of the almost-non-lithiated (stage 4L) graphite at all stages of cell evolution. The galvanostatic cycling displays itself in clearly linear dependences of the mutual phase fractions of various phases of the anode material, especially clearly is this linearity seen in the mutual phase fractions of e.g. LiC_{12} and LiC_{6} , close to the maximal charge state and in the very beginning of the discharge. The dependences of the unit cell volumes of the graphite-derivative phases, presented in the Figure



Dependences of some characteristic crystal structure parameters of the cell materials on the stroboscopic time, as refined from the stroboscopic neutron diffraction data. (Left) Lattice parameters of the graphite-derivative phases in the anode, normalized to the metrics of one graphite unit cell; (middle): Evolution of the graphite derivatives' phase fractions and unit cell volumes in the anode material; (right): evolution of the refined lithium contents in the phases 1 and 3, as well as of the relative phase fractions and unit cell volumes of phases 1, 2 and 3 of the d-LNMO cathode material. All results are based on the Rietveld refinement of the neutron diffraction stroboscopic measurement. In all panels, the open symbols correspond to the non-varied (fixed) parameters. Where not seen or shown, the errors on solid symbols are smaller than the symbol sizes.

8, refer to the "normalized" unit cell constants and volumes, meaning that they have been recalculated to 2 carbon atoms, as in one unit cell of graphite.

In this first experiment, we have validated the proof of concept of applying the stroboscopic neutron diffraction to carry out operando neutron diffraction experiments and to determine the evolution of the crystal structures in battery materials at a fast rate of approximately 1C. In combination with the proper cell design, this allows hereby extracting the data sufficiently good for carrying out Rietveld refinements. However, the usage of stroboscopic mode can allow for studying even (a lot) faster phenomena, with characteristic process duration times well below a second, so in our further attempts we have opted for further pushing the limits. In particular, we have applied the stroboscopic neutron diffraction mode to directly follow the ageing mechanisms occurring in the batteries d-LiNi_{0.5}Mn_{1.5}O₄ vs. graphite cycled extremely fast: at 2C, 5C and even 15C rates.

Ageing mechanisms investigated by operando stroboscopic neutron diffraction

A similar cell, based on the d-LNMO vs graphite combination, was characterized using the operando stroboscopic neutron diffraction while being charged and discharged at 2C and 5C rates, respectively. These rates are definitely a lot faster than reasonable for this cell geometry and loading parameters, and the performance of the cell decays very fast. The electrochemical performance is presented in Figure 9. Over the first 16 cycles, a rapid fading of the specific capacity is observed, accompanied by a large increase of the overpotential, as expected for cell cycling at extremely fast rate in highly oxidative conditions (i.e. 5 V

Figure 9

Electrochemical performance of d-LNMO vs. graphite at extremely fast charge (2C) and discharge (5C) rates illustrated via the comparison of the 16 first galvanostatic curves with specific charge (a) and time (b) chosen as the x-axis. (Bottom) Contour plot representation of operando stroboscopic neutron diffraction measurement of a d-LNMO vs graphite cell cycled under conditions of extremely fast charge/discharge rates of 2C and 5C, respectively; the regions of the patterns around the (002) graphite reflection, and its corresponding counter-entities in the lithiated graphite phases, is plotted. Stroboscopic binning for this illustration is: pattern every 1 min. (c): the cycles 1-4; (d): the cycles 13-16 merged together.

Evolution of the graphite derivatives' phase fractions in the anode material, refined from the operando stroboscopic neutron diffraction data collected on a cell cycled at extremely fast rate 2C (charge) – 5C (discharge). (Top) beginning of cycling (cycles 1-4), (Bottom) end of cycling (cycles 13-16).

cathode materials) [20]. The last four cycles (13th to 16th) were already featuring a charging time clearly shorter (28.2 min) than originally planned 30 min, most probably due to the premature cell degradation occurring at extremely fast rate.

Thus, in order to get insights into the ageing mechanisms, we have produced two separate stroboscopic datasets: the cycles 1-4 (when the materials and components of the cell were fresh and undamaged) and cycles 13-16 (when the electrochemical performance faded drastically) were merged with merging times of 1 minute, thus producing for both cases 42 datasets. Also for these data, we were able to carry out Rietveld refinements,

upon having fixed and/or constrained a reasonable number of parameters. One of the features, seen even by eyes in the color intensity maps in the bottom panel of Figure 9, is that for the strongly faded electrochemical performance (cycles 13-16), the fully-lithiated LiC₆ phase appears at earlier times, and its maximal intensity is getting weaker, compared to the fresh, undamaged cell (cycles 1-4). The Rietveld refinements are indeed directly confirming these hypotheses. As can be deduced from Figure 10, in the beginning of cycling at 2C-5C rates, the LiC₆ phase appears in the 19th minute of charge, reaches a maximum weight portion of 26(1)% of all the anode material, and disappears after the 34th minute. On the

contrary, in the end of cycling (cycle 13th-16th), when the electrochemical performance is already significantly faded, LiC₆ is already seen in the 15th minute, but its amount in the "fully charged" state only reaches 21(1)% at maximum. In the discharge process, the fully lithiated LiC₆ phase also disappears much faster - already after the 32nd minute (i.e. just 2 minutes after the beginning of discharge), and it is no longer seen in the stroboscopic diffraction data at later times. With progressing ageing caused by fast rate, the material of the graphite anode becomes on overall "more" lithiated, indicating that we are "using" more of the fresh graphite, that is initially available in a slightly excess amount in agreement with the cell balancing, and that lithium kinetics in it is becoming slower. Further, unlike in case of the cycling at ~1.1C rate, the isle of existence of the stage 3L (LiC₁₈ phase) is hardly distinguishable on charge and is almost absent in the very fast discharge processes indicating a modification of the electrochemical process at fast rate. What is rather observed in this fast discharge is a seemingly continuous transformation of the LiC₁₂ phase into graphite, and special care needs to be taken in order to keep refinements stable and reliable: the lattice and other relevant structure parameters of the phases under consideration need to be reasonably constrained. One should therefore rather consider the sum of the phase fractions of the LiC12 and LiC18 phases as a more reliably determined value than the individual phase fractions thereof in Figure 10 for the times between ~33 and ~40 minutes. Also, the increasing overpotential occurring during fast charge/discharge means that the voltage approaches the potential of lithium reduction; thus, lithium ions might start to plate instead of being inserted into the graphite [21]. Therefore, one of the reasons for the observed performance fading of performance could be lithium plating, which is known to be related to high irreversible charge 'loss' and battery failure (due to Li dendrites) [22].

Thus, even such short-living states in the battery materials can be studied *operando*, and our stroboscopic mode offers the possibility to do so quite effectively.

Exploring the really fast cell discharge with stroboscopic neutron diffraction

We have further applied the operando stroboscopic neutron diffraction mode of HRPT to probe the fading of electrochemical cell at yet faster cycle rate. This additional experiment was performed with a similar cell assembled with the same d-LNMO vs. graphite combination, at an ultra-fast discharge rate of 15C (one discharge in only ~4 minutes) following after the charge done at ~1.3C rate. The stroboscopic data were binned into neutron patterns every 15 s over the duration of in total 22 charge-discharge cycles. At these high rates, the cell performance fading is happening very fast. Figure 11 shows the evolution of the patterns in the vicinities of the (002) graphite reflection and of the (222) d-LNMO reflection for the time just at the end of the charge (time stamped with minutes 40 onward up to 45) and during the discharge (45.0 to 49.5 min). As one can see, the structural changes in d-LNMO are similar at a rate of 15C to those at a rate of 1C (Figure 11).

In the anode material, however, the transition from stage 2 (LiC_{12}) to graphite hap-

Contour plot representation of operando stroboscopic neutron diffraction measurement of d-LNMO vs graphite cell at 1.33C/15C rates (for charge/discharge, respectively): (left) the (002) graphite reflection and the corresponding reflections of the graphite derivative phases, and the (222) d-LNMO reflection (patterns recorded every 15 s), (right) the galvanostatic cycle. Only the time close to an end of charge and the full rapid discharge are shown.

pens differently at 15C compared to slower rates (e.g. at 1C, as shown in Figure 6, or at C/25, as can be seen in the Figure 4 of our previous paper [11]. Indeed, at 15C rate, the stage 3L (LiC₁₈ phase) is not detected in the discharge process at all, while it clearly is visible in slower charge or discharge processes. Finally, the appearance of graphite phase and the disappearance of stage 2 is taking much less time at fast rates. These differences in behavior could be explained by i) the difference of electrode loading (to reduce the fading of the electrochemical performance, the electrodes were loaded with twice less material than in the previous experiments and the charging rate was limited to 1.3C rate), ii) some inhomogeneous reactions inside the electrode and, iii) the greater lithium diffusion coefficients in the stage 3L, and 4L graphite as compared to the

stages 1 and 2. This behavior was predicted in the literature with a so-called 'shrinking-annuli' model [19], and our current study might be considered an experimental support for it.

Conclusions

The range of experimental possibilities at HRPT diffractometer has been extended by the stroboscopic mode of operation. This option allows in favorable cases to access the quantitative crystal structure characterization for the short-living intermediate phases in chemical processes or phase transformations. Allowing potentially the time binning down to ~10 ms, it has so far been successfully used to collect data with time resolutions of below 1 minute on real samples, suitable for conclusive Rietveld refinements.

We have applied the stroboscopic neutron diffraction mode to push the limits of time resolution in operando neutron diffraction studies on battery materials. We followed the structural evolution of the cathode and anode materials of Li-ion batteries at a fast rate of up to 5C by carrying out Rietveld refinements on the operando neutron diffraction data, and up to a rate of 15C gualitatively. We were able to compare the d-LNMO versus graphite couple at 1C and 15C rates, and thereby to shed light onto the fading mechanisms occurring at fast rates. It is likely that the limitations in Li diffusion rates for the stages 1 and 2 of lithiated graphite (seen in diffraction as LiC₆ and LiC₁₂ phases) hinder the formation of the intermediate LiC18 phase at higher rates: 2C, and especially at 5C and 15C, and contribute to the premature battery failure (electrolyte degradation, Li plating, etc.). Further, higher charge rates seem to shift Li balance from the cathode to the anode, and the time domain of existence of the fully charged LiC₆ phase also expands at higher charge rates.

This stroboscopic mode of collecting the neutron diffraction data, which essentially is

binning the partial low-intensity data from various repetitions of a process into enhanced intensity patterns representing the statistics over many cycles, offers new possibilities for research into the reproducible changes occurring in solid diffracting materials during the rather short times, otherwise hardly accessible by regular neutron diffraction techniques.

Acknowledgements

All smart technical solutions that are expanding the experimental possibilities and making the use of HRPT diffractometer so convenient and user-friendly, have been designed and built internally at PSI. We are extremely thankful to the scientific, engineering and technical staff at PSI who have over the years contributed to these developments: Peter Keller, Alex Bollhalder, Dieter Graf, Roman Bürge, Markus Zolliker, Mark Könnecke of the Laboratory for Neutron and Muon Instrumentation, Gerd Theidel and Urs Greuter at the Electronics group of the Laboratory for Particle Physics, and many other colleagues.

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Announcements

SGN/SSDN Members

Presently the SGN/SSSN has 204 members. New members can register online on the SGN/SSSN website: http://sgn.web.psi.ch

SGN/SSSN Annual Member Fee

The SGN/SSSN members are kindly asked to pay their annual member fees. At the general assembly 2013 of the society, the fee has been increased from CHF 10 to **CHF 20**. It can be paid either by bank transfer or in cash during your next visit at PSI. The bank account of the society is accessible for both Swiss national and international bank transfers: Postfinance: 50-70723-6 (BIC: POFICHBE), IBAN: CH39 0900 0000 5007 0723 6.

The SGN/SSSN is an organisation with tax charitable status. All fees and donations payed to the SGN/SSSN are **tax deductible**.

PSI Facility News

Recent news and scientific highlights of the three major PSI user facilities SLS, SINQ and

SµS can be found in the **quarterly electronic newsletter** available online under: https://www.psi.ch/science/facility-newsletter

SINQ Upgrade

Because of the Corona-virus situation, the startup of SINQ was delayed until middle of July 2020. The instruments SANS-I, TASP, FOCUS, MORPHEUS, NARZISS, and ORION have resumed operation with upgraded guides. The spectrometer CAMEA has also received an upgrade and has joined the second half of the user cycle. Flux measurements have shown that the upgrade of the neutron guides has resulted in the expected gains in flux on these instruments. The diffractometer DMC and the reflectometer Amor are both being rebuilt and will be included in the user program in 2021.

The instruments HRPT, EIGER, BOA, ZEBRA, POLDI, ICON, and NEUTRA have not received an upgrade and have resumed operation with unchanged performance.

Experiments with external users present at SINQ have started in September 2020. As the Corona situation is quickly evolving and users from countries with increased Corona risk cannot travel to PSI, some experiments may be postponed to the next year.

A second call for proposals in 2020 was cancelled due to the delayed restart of SINQ. The deadline for proposals for the 1st cycle of 2021 is Nov. 15, 2020. Please visit the page https://www.psi.ch/sinq/call-for-proposals to obtain the latest information.

Registration of publications

Please remember to **register all publications either based on data taken at SINQ, SLS, SµS or having a PSI co-author** to the Digital Object Repository at PSI (DORA): www.dora.lib4ri.ch/psi/ Please follow the link 'Add Publication'.

Open Positions at SINQ and ILL

To look for open positions at SINQ or ILL, have a look at the following webpages: https://www.psi.ch/pa/stellenangebote https://www.ill.eu/careers/all-ourvacancies/?L=0

PhD positions at ILL

The PhD program of the Institut Laue-Langevin, ILL, is open to researchers in Switzerland. Consult the page https://www.ill.eu/science-technology/ phd-students/home/ for information on the PhD program of ILL or get in contact with the managers of the program using the email address phd@ill.fr. The Swiss agreement with the ILL includes that ILL funds and hosts one PhD student from Switzerland.

Winners of the Young Scientist Prize 2020 of the Swiss Neutron Science Society, sponsored by SwissNeutronics

The Young Scientist Prize 2020 of the society is awarded to a young researchers for their outstanding achievements using neutron radiation in the framework of their PhD theses. The prize was awarded at the virtual Annual Assembly of the society, 29.10.2020.

The prize of 2020 is split and awarded to:

Dr. Muriel Siegwart

in recognition of her outstanding work on "Neutron transmission imaging of fuel cells using time-of-flight and dark-field imaging".

^{and to:} Dr. Jiri Ulrich

in recognition of his outstanding work on "High precision nuclear data of Mn-53 for astrophysics and geosciences".

Young Scientist Prize 2021 of the Swiss Neutron Science Society, sponsored by SwissNeutronics

Call for Nominations

The Swiss Neutron Science Society hereby announces the call for nominations for the 8th Young Scientist Prize of the Swiss Neutron Science Society.

In 2021, the prize will be awarded to a young scientist in recognition of a notable scientific achievement in the form of a PhD thesis that was awarded within two years of the announcement of the call, or to a nominee with an exceptional track record in neutron science established within 5 years after her/his PhD degree. The science should include the use of neutron radiation, and eligible nominees should have a clear affiliation with Swiss neutron science (be member of the Swiss Neutron Science Society, be based in Switzerland, or have conducted experiments at Swiss neutron facilities). The PhD must have been awarded within two years of the announcement of this call. The prize amounts to 1'000 CHF and is sponsored by SwissNeutronics.

Nominations for the prize should be submitted to the Swiss Neutron Science Society: sgn@psi.ch The deadline for nominations is January 31st, 2021.

Nominations should include:

- Nomination letter including the motivation for the award
- CV and publication list of the nominee
- Digital copy of the nominated work (PhD thesis)
- Letter documenting the acceptance of the nomination by the nominee
- Letters of support from authorities in the relevant field are accepted

Nominations for the prize will be treated confidentially. Nominations for the prize will be evaluated by a selection committee appointed by the board of the Swiss Neutron Science Society. The nominations will be acknowledged, but there will be no further communication. More information is available online: https://sgn.web.psi.ch/sgn/young_scientist_prize.html.

Conferences and Workshops 2020 and beyond

An updated list with online links can be found here: http://www.psi.ch/useroffice/conference-calendar

November 2020

EGI conference 2020: Federated infrastructures for connected communities November 2-4, 2020, online

European Photon and Neutron EOSC Symposium and PaNOSC & ExPaNDS Annual Meeting November 9-11, 2020, online

15th International Workshop on Spallation Material Technology November 9-13, 2020, Lund, Sweden -Rescheduled for 2022

P12 User Workshop November 17-18, 2020, online

CCG Autumn Meeting 2020 November 18, 2020, online i2ns Workshop on Innovative Inelastic Neutron Scattering November 23-25, 2020, Autrans Méaudre en Vercors, France

LEAPS Plenary Meeting November 24-26, 2020, Barcelona, Spain

ICREN 2020: 3rd International Conference on Renewable Energy November 25-27, 2020, online

A2IC 2020: Artificial Intelligence International Conference November 30 - December 2, 2020, online

VNSS: First Virtual Neutron Scattering School November 30 - December 4, 2020, online

December 2020

MLZ User Meeting 2020 December 8-9, 2020, Munich, Germany and online

German Neutron Scattering Conference 2020 December 9-10, 2020, Munich, Germany and online

Virtual BESSY@HZB User Meeting December 10, 2020, online

January 2021

16th SOLEIL Users' Meeting January 21-22, 2021, Gif-sur-Yvette, France

February 2021

ESRF User Meeting 2021 February 8-10, 2021, Grenoble, France

HERCULES 2021 - European School February 22 - March 26, 2021, Grenoble, France

March 2021

IFF spring school 2021: Quantum Technology March 1-12, 2021, Jülich, Germany

April 2021

Imaging Materials with X-Rays—Recent Advances with Synchrotron and Laboratory Sources April 18-23, 2021, Seattle, WA, USA

ECHC 2020 - XXIX European Colloquium on Heterocyclic Chemistry April 26-29, 2021, Rouen, France

May 2021

10th International Conference of the Hellenic Crystallographic Association May 14-16, 2021, Athens, Greece

EMBO workshop on Molecular Neurobiology May 21-25, 2021, Heraklion, Crete, Greece

SIAM Conference on Mathematical Aspects of Materials Science May 24-29, 2021, Bilbao, Spain

June 2021

2021 Annual MLZ Conference: Neutrons for Life Sciences June 8-11, 2021, Lenggries, Germany

2nd COMPPÅ Symposium on Membrane Protein Production and Analysis June 9-11, 2021, New York, USA

SXNS16: 16th International Conference on Surface X-ray and Neutron Scattering June 14-18, 2021, Lund, Sweden EPDIC17 - The European Powder Diffraction Conference June 15-18, 2021, Sibenik, Croatia

PSI Master School 2021 June 21-25, 2021, Villigen, Switzerland

ACS meeting: 37th National Medicinal Chemistry Symposium June 27-30, 2021, New York, NY, USA

AFC 2020: Congress of the French Association of Crystallography June 29 - July 2, 2021, Grenoble, France

July 2021

ICNS 2021: International Conference on Neutron Scattering 2021 July 4-8, 2021, Argentina

15th International Conference on Muon Spin Rotation, Relaxation and Resonance July 4-9, 2021, Parma, Italy

ECS 6: Sixth European Crystallographic School July 4-10, 2021, Budapest, Hungary

August 2021

IUCr2020 Computing School August 9-14, 2021, Nove Hrady, Czech Republic School on SAXS/SANS and BioSAXS/ BioSANS data analysis August 11-13, 2021, Kutná Hora, Prague, Czech Republic

Electron Crystallography School - 3D Electron Diffraction/MicroED Bridging Small Molecule and Macromolecular Crystallography August 11-14, 2021, Tabor, Czech Republic

TOPAS Intensive Course August 12-14, 2021, Prague, Czech Republic

25th General Assembly and Congress of the International Union of Crystallography (IUCr) August 14-22, 2021, Prague, Czech Republic

PSI Condensed Matter Camp August 16-20, 2021, Zuoz, Switzerland

ECM33: 33rd European Crystallographic Meeting August 24-28, 2021, Versailles, France

RIXS-REXS 2020: Workshop on Resonant Elastic and Inelastic X-ray Scattering 2020 August 25-27, 2021, Port Jefferson, NY, USA

JCNS Laboratory Course 2021 August 30 - September 10, 2021, Jülich and Garching, Germany

September 2021

Diffusion Fundamentals IX September 7-10, 2021, Krakow, Poland 9th International Conference on Electron Tomography September 12-15, 2021, Egmond aan Zee, The Netherlands

MUST2021: The International Conference on Molecular Ultrafast Science and Technology September 12-16, 2021, Grindelwald, Switzerland

XTOP2020: 15th Biennial Conference on High-Resolution X-Ray Diffraction and Imaging September 12-17, 2021, Minsk, Belarus

COHERENCE 2021: International Conference on Phase Retrieval and Coherent Scattering September 13-16, 2021, Shanghai, China

Big Science Business Forum 2021 September 28 - October 1, 2021, Granada, Spain

October 2021

School of Solid State Physics: Dynamics of Electrons in Atomic and > Molecular Nanoclusters October 24-30, 2021, Erice, Italy

December 2021

Italian Crystal Growth - Crystal Growth: From Theory to Application December 16-17, 2021, Torino, Italy January 2022

Third Pan African Conference on Crystallography January 17-22, 2022, Nairobi, Kenya

May 2022

LEAPS meets Quantum Technology Conference May 16-20, 2022, Erice, Italy

QENS/WINS 2022 May 23-27, 2022, San Sebastian, Spain

Editorial

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