Powder Neutron Diffraction and Materials Chemistry/Physics Research in Canada (1949-2017)

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INTRODUCTION: THE EARLY DAYS OF DIFFRACTION AT CHALK RIVER (1949-1969)

The story of powder neutron diffraction at Chalk River is inextricably linked to the history of neutron science at Chalk River itself. Canada's interest in nuclear research grew out of our involvement in World War II and the race to harness the power of the atom. In 1942, a joint Canadian-British laboratory was built in Montreal to assist in the war effort under the leadership of the National Research Council of Canada (NRC) [1]. There were many Europeans working in Canada at the time, including the UK's John Cockcroft and France's Lew Kowarski and Hans von Halban. Kowarski and von Halban were physicists that had recently escaped Nazi occupied Germany with 200 kg of heavy water (the largest supply in the world at the time) [2]. This formed the impetus for the design of a heavy water moderated reactor with the initial goal of producing plutonium for the Manhattan project. In 1944, the Montreal research group moved to a newly built laboratory at Chalk River, Ontario, where the first reactors in Canada were being built. In 1949, the National Research Universal reactor (NRU) project began, which was a Canadian design and would form the basis for the future for Canadian neutron beam research [3]. The 135 MW reactor is a significant Canadian success story, providing not only intense neutron beams for materials research, but also medical isotopes for over 20 million people in 80 countries, and a testing ground for innovative reactor and fuel rod design projects [4].

In the 1950s, the neutron beams at the NRU reactor were being used predominantly for condensed matter physics experiments by eminent scientists such as Bertram Brockhouse, a Nobel Laureate and pioneer of the triple axis spectroscopy method [5]. Powder neutron diffraction

SUMMARY

We present a review of power neutron diffraction research in Canada from 1949-2017.

(PND) studies of materials was not developed as a broader technique outside of solid state physics until much later. In PND, the entire contents of reciprocal space are mapped onto one dimension, the Bragg angle, 2θ (or the momentum transfer, $Q = 4\pi\sin\theta/\lambda$). Prior to 1970 or so, PND was restricted to very high symmetry materials, say cubic or perhaps tetragonal, due to severe Bragg peak overlap since early instruments had at best moderate $\Delta d/d$ resolution and experiments were time consuming due to the use of "single" or point detectors. One notable interdisciplinary pioneer of PND at NRU was Professor Osvald Knop of Dalhousie University (chemistry) [6]. Osvald, a consummate crystallographer (partially trained under Linus Pauling), completed many experiments at Chalk River throughout the 1960s, in particular the first PND study of an oxide pyrochlore material, $Er_2Ti_2O_7$. Pyrochlore oxides have been of great interest to many in the Canadian physics community up to the present time [6]. The real breakthrough in neutron powder diffraction came in the late 1960s as the Rietveld method was developed along with more sophisticated computational techniques and technology [7].

THE RIETVELD REVOLUTION: 1969-1991

Hugo Rietveld (1932-2016) was a Dutch crystallographer and pioneer of neutron powder diffraction [7]. Although born in the Netherlands, he later studied physics at the University of Western Australia in Perth, obtaining his PhD in 1964. His thesis was the first single crystal neutron diffraction study in Australia (completed at the nuclear reactor HIFAR in Sydney). He then became a research officer at the Netherlands Energy Research Foundation ECN in Petten where his interest in powder diffraction was piqued during studies of uranates and other ceramics. In 1967 he finished an early version of his refinement method, and published the results in 1969 [8]. The Rietveld refinement method was born.

It took many years for the Rietveld revolution to change neutron powder diffraction. Computing facilities were rudimentary at many national laboratories, and the method required high quality neutron diffraction data with good

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resolution. However, the method has now completely changed how scientists obtain and analyze structural data in materials, and is now the gold standard in the materials science community. Rietveld's revolutionary data analysis technique — fitting of the entire diffraction profile rather than individual Bragg peaks — permitted extraction of the maximum amount of structural information from a PND pattern. In many cases, the results were comparable to those from single crystal x-ray data [9]. The importance of this technique is not to be underestimated, especially in the materials chemistry community where it can be difficult if not impossible in some cases to obtain large, high quality single crystals. The Rietveld technique changed everything, from how modern neutron scatterers take data, design instruments, and develop analysis software. For example, in the late 1970s, the construction of higher resolution or higher throughput diffractometers to take advantage of Rietveld method was made a priority by many neutron research groups and laboratories. Wide angle, multi-wire, and multi-tube detectors were rapidly designed throughout the 1980s. Another key development was the establishment of user-centred programs on a peer reviewed proposal basis to increase access to PND data. This greatly expanded the use of the technique by non-specialists and built a large user base, especially in Europe at the ILL (Institute Laue Langevin).

Compared to this rapid progress in Europe, Canada and USA were relatively late to the game with respect to powder neutron diffraction, except for the IPNS (Intense Pulsed Neutron Source) at ANL (Argonne National Laboratory). The building of a suite of powder diffractometers at the ILL started soon after the reactor was commissioned in 1967, and in the UK, ISIS (1985) also quickly adapted and advanced modern neutron diffraction techniques [10,11]. The IPNS, in comparison, began operation in 1981. Canada's first modern powder neutron diffractometer (PNDiff) was built at the McMaster Nuclear Reactor (MNR) adapting a design from the University of Missouri's neutron research group (MURI) by M.F. Collins, J.R.D. Copley, C.V. Stager, J. Couper, K. Lushington and J.E. Greedan and became fully operational in 1986 [12]. The central feature was a position sensitive detector (PSD) with a 2θ range ~ 25°/setting which travelled on the diffraction circle built originally by Brockhouse in the 1960s. Due to the low MNR power at 2MW, the dataset collection time was approximately 2 days/sample for $5° < 2\theta < 130°$, $\lambda = 1.39$ Å: [0.394 Å$^{-1} < Q < 8.19$ Å^{-1}] at a single temperature. Although somewhat impractical as a true user facility, nonetheless, ~50 papers with ~1500 citations included data from this diffractometer from 1984-1998. Highlights included the solution of the correct structure of $YBa_2Cu_3O_7$ in March 1987 (effectively tied for first with a group using the IPNS) [13]. PND was particularly useful in locating the oxygen atomic positions and in avoiding the problem of heavily twinned crystals which plagued early x-ray studies.

In the late 1980s, a proposal was put forward to upgrade the powder diffraction facilities at Chalk River by Chalk River and NSERC: the DUALSPEC suite of instruments. The initial cost estimate was $3.5 M [14]. DUALSPEC completely changed the diffraction landscape in Canada, and arguably all of North America, as it housed one of the most powerful diffractometers — the C2 instrument.

THE DUALSPEC ERA: 1991-2017

With the commissioning of DUALSPEC at NRU in 1991, a true user facility existed in Canada for the first time. Two instruments were built, C2 (PNDiff) and C5 (inelastic triple-axis spectroscopy). C2 is equipped with an 800 element multi-wire detector, with a 2θ range of 80°/per setting. With a neutron wavelength of $\lambda = 1.33$ Å $- 2.37$ Å, the angular range of $3° < 2\theta < 120°$ covered an impressive Q-range [0.14 Å$^{-1} < Q < 8.18$ Å^{-1}]. Other wavelengths such as 4 Å with a Be filter could also be used. For comparison, in 1992 at NIST (National Institute of Standards and Technology) a 32-element detector was built! Thus, by 1991, C2 was the most efficient PNDiff at a reactor source in North America. The success of C2 spawned highly successful Canadian Powder Diffraction Workshops across Canada that ran for many years. While comparisons with spallation source instruments are difficult, C2 was probably more efficient than GPPD (General Purpose Powder Diffractometer) or SEPD (Special Environment Powder Diffractometer) at IPNS. Unfortunately, the IPNS ceased to function in 2008 due to budget cuts to the Department of Energy. A comparable next generation diffractometer, POWGEN at the SNS (Spallation Neutron Source), was commissioned in 2011-2012. Thus, for approximately 20 years (1991-2011), C2 was likely the most efficient PNDiff in North American (this is certainly true if only reactor source instruments are considered). The wide range of ancillary equipment, cryostats to 3.5 K and atmosphere-controlled furnaces with a range up to 1800 °C rendered C2 a highly versatile instrument [14]. Datasets were also typically gathered in less time that other comparable diffractometers.

Having said all of the above, C2 exists now more or less as it was built in 1991. No significant improvements, such as installation of focusing monochromators, which had the potential to increase the flux on sample by large factors were ever implemented, in spite of significant efforts. Starting in 2007, initial design and testing of focusing monochromators was carried out. The large-area mosaics of deformed germanium crystals were expected to deliver a factor of 10 increase in flux-on-sample at both 1.33 Å and 2.37 Å. A similar improvement in detector efficiency was planned by moving from a relatively short BF_3 detector to a taller ^{3}He-based detector like the ones on the two powder instruments at OPAL, the Australian research reactor. The 15 month shutdown of NRU from technical difficulties and Chalk River scientist Lachlan Cranswick's untimely passing in 2010 were setbacks to the planned C2 improvements. Lachlan spent a considerable amount of effort making upgrades to C2 a priority. While the low-Q limit of 0.14 Å^{-1} has made C2 invaluable for studies of magnetic materials where long-period magnetic modulations are common, one major design flaw — that the maximum scattering angle is limited to ~120° (2θ) — cannot be

changed as it is set by the large monochromator drum that C2 shares with C5, the inelastic instrument that forms the other half of DUALSPEC. The main consequence of this was that the maximum $Q \sim 8.2$ Å^{-1} ($d_{min} = 0.76$ Å) placed C2 at a disadvantage compared to spallation instruments, such as POWGEN, where $d_{min} \sim 0.4$ Å ($Q_{max} \sim 15$ Å^{-1} for resolving structures). However, C2 is still a workhorse for many research groups for medium resolution applications.

Although the basic hardware remains essentially as it was built, there has been an ongoing process of upgrades to the instrument operation and sample environments. A system of macros and encoded slits combined with an ILL-designed neutron camera permit precise, and often remote, alignment of samples. It should also be noted that very important improvements in ancillary equipment were implemented fairly recently. Perhaps the two most significant were the building of a very short path length sample cell permitting studies of materials containing extremely high absorption cross section elements, such as Sm, Eu and Gd [15] and the addition of a ^{3}He (Heliox) sample cell which allows data collection to $\sim$340 mK. Concerning the former, C2 is one of a very few PNDiff at which experiments on highly absorbing samples can be done more or less routinely without resorting to a hot source. Credit here is due to the efforts of Dominic Ryan, Ian Swainson and Lachlan Cranswick.

Taking all of the above into account, C2 will be very difficult to replace as a Canadian asset for the foreseeable future.

RESEARCH AT CHALK RIVER (C2)

The great strengths of powder neutron diffraction vis à vis x-ray diffraction are: (1) the ability to detect and refine accurately the positions of light (low atomic number) atoms such as hydrogen, lithium and oxygen in the presence of heavy atoms, (2) the ability in favourable cases to distinguish between atoms of nearly the same atomic number, e.g., Fe and Mn, Sc and Ti, O and N, Yb and Lu, among many others, (3) the ability to solve and refine magnetic structures including the quantitative measurement of magnetic moments, (4) the ease of use of sample environments such as furnaces and cryostats for the study of phase transitions and in situ transformations. In the following section, highlights of some Canadian research activities using C2 will be presented.

A survey of published results using C2 over the past $\sim$20 years or so suggests that the research output fits into the following categories:

(a) Minerals, molecular solids, and related systems – hydrogen bonding in hydrates.
(b) Crystal and magnetic structures of intermetallic compounds and Fe-based superconductors. Included are Gd, Sm and Eu – based materials and mK studies.

(c) Crystal and magnetic structures of transition metal oxides. Li battery materials, low dimensional and geometrically frustrated oxides, magnetism and the Mott transition, potential multi-ferroics.
(d) Studies of hydrogen containing materials and hydrogen storage materials.

It should also be noted that Ian. P. Swainson carried out structural studies of hybrid inorganic/organic perovskites long before this became a trendy area of research.

Selected examples from each category will be described briefly.

Minerals, molecular solids and related systems

Prior to the commissioning of C2 as a part of DUALSPEC there existed a very active program in neutron powder diffraction at the Chalk River laboratory involving Brian Powell, Bruce Torrie (Univ. of Waterloo) and other collaborators. The focus was on molecular organic crystals, initially, such as acetonitrile (CH_3CN), methanol (CH_3OH) or formaldehyde (CH_2O). Inorganic solids with molecular cations and anions, their structures and phase transitions were also studied by Robin Armstrong (Univ. of Toronto) and Julian Brown (Queen's Univ.) Materials of interest included fluorite and anti-fluorites such as $(NH_4)_2PbCl_6$ and scheelite structures such as $KReO_4$. These studies were done on triple axis instruments run in double axis mode with single counters. Later, a 30 element position sensitive detector was used but still on instruments not dedicated to powder diffraction. These studies continued after the C2 commissioning and benefitted from the greatly enhanced efficiency of the 800 element C2 detector. Several substituted halo-carbons $CH_x(F,Cl,Br,I)_{4-x}$ were studied along with more complex inorganic materials such as zeolites and related porous solids in collaboration with the Tony Cheetham group at Oxford University.

The positions of H atoms and their participation in hydrogen bonding is a perennial issue in hydrated minerals. R.C. Peterson
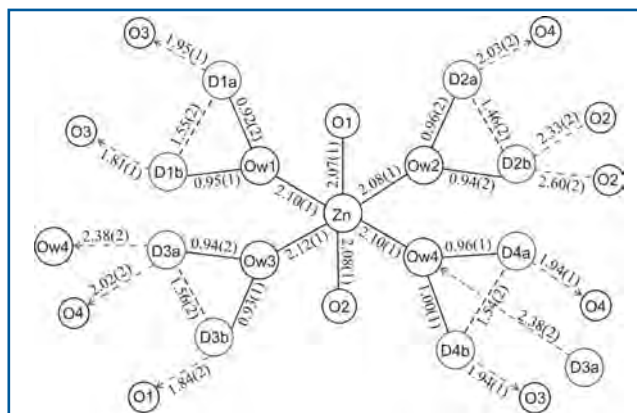

Fig. 1   The hydrogen bond network in $ZnSO_4 \cdot 4D_2O$ [22].

(Geology and Geological Engineering – Queen's University) and his group have used C2 data in the study of a number of hydrates belonging to the rozenite group of minerals, such as $ZnSO_4 \cdot 4D_2O$, $ZnSO_4 \cdot 6H_2O$ and $MnSO_4 \cdot 4H_2O$ [22]. In these materials, the Zn^{2+} and Mn^{2+} ions are in octahedral coordination which are connected by a hydrogen bonding network. While hydrogen positions derived from single crystal x-ray data were available, it was possible to obtain much more accurate and precise positions from the neutron powder data which is much more sensitive due to the cross-section of neutron-proton scattering. The results for $ZnSO_4 \cdot 4D_2O$ are shown in Fig. 1. Note the highly asymmetric nature of the D-O bonds which involve short (~0.95 Å) and long (1.9-2.3 Å) segments. In some cases, D2b and D3a in Fig. 1, a single D-ion forms a "bifurcated" hydrogen bond involving one short and two long bonds.

Crystal and magnetic structures of intermetallic compounds and Fe-based superconductors

Among the most interesting examples is very recent work on the half-Heusler intermetallic, GdBiPt, which is a candidate antiferromagnetic topological insulator [23]. These collaborators from the Univ. de Montreal, McGill and McMaster were able to solve the magnetic structure using the data in Fig. 2 to show that below $T_N = 9$K, the Gd moments are arranged in ferromagnetic planes parallel to the face diagonal of the chemical unit cell which couple antiferromagnetically to adjacent planes. Such a layered magnetic structure is thought to be a necessary criterion for realization of the antiferromagnetic topological insulating state. It should be noted that these data were collected on a 150 mg sample – small by traditional neutron scattering standards.

The availability of the Heliox sample cell enabled a study of the complex magnetic structures of $Er_3Cu_4Ge_4$. There are two Er sites (2d) and (4e) which order at different temperatures, 8K and 3.5K, respectively. While Er (2d) shows a commensurate order and a nearly full moment of $8.9(2)\mu_B$, ($g_J = 9$ for Er^{3+}) the Er(4e) ions order incommensurately with about half of the free ion moment at 1.5K. With the Heliox insert and cell, data were taken to 0.34K as shown in Fig. 3 and it was shown that the Er (4e) moments now order in a nearly commensurate manner but still with a much reduced moment. A strong diffuse component, even at 0.34K, indicates that much of the (4e) magnetic scattering is due to short range ($\xi \sim 10$ Å) spin correlations [24].

The high temperature furnace available at C2 also plays an essential role in the study of magnetic materials, especially when the effects of magnetism and chemical disorder are intertwined. In Mn_xGa ($1 < x < 2$) [25], a potential medium-cost/medium-performance hard magnet, the excess manganese substitutes on the gallium site and also carries a magnetic moment, so in the ordered state the total scattering includes comparable contributions from Mn-Ga disorder and Mn magnetism.[b] Mn and Ga are sufficiently similar in atomic number that PND provides much better contrast than x-ray powder diffraction ($b_{Mn} = -3.75$ fm; $b_{Ga} = +7.29$ fm). Diffraction data taken at 500 °C, well above T_c, established the crystal structure (confirmed by density functional theory (DFT) calculations of substitution energies). With the structure constrained, the manganese moments on both the Mn site and the substitutional (Ga) site could be determined with confidence, Fig. 4. These moments and the antiparallel coupling between them were fully consistent with DFT results, and this steady improvement in calculation accuracy combined with validation by neutron
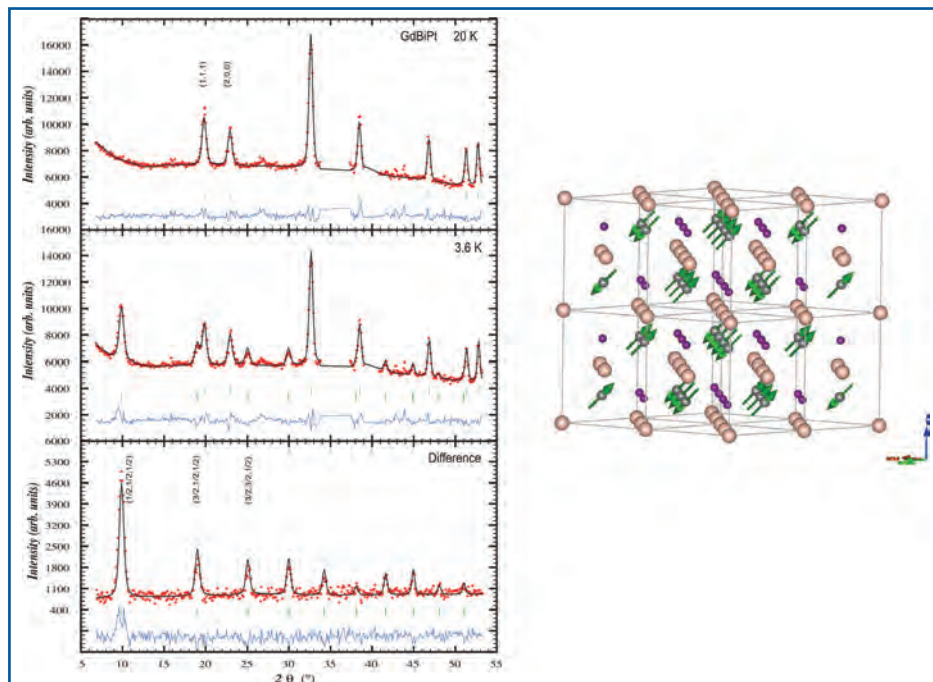

Fig. 2 (Left) C2 diffraction patterns for GdBiPt at 20K and 3.6K and the difference plot showing the magnetic peaks indexed on k = (1/2 1/2 1/2). (Right) The magnetic structure of GdBiPt. The Gd atoms are shown in gray, the Bi in pink, and the Pt in purple. The spins on the Gd atoms are oriented in ferromagnetic planes which are stacked antiferromagnetically along the magnetic propagation vector [23].
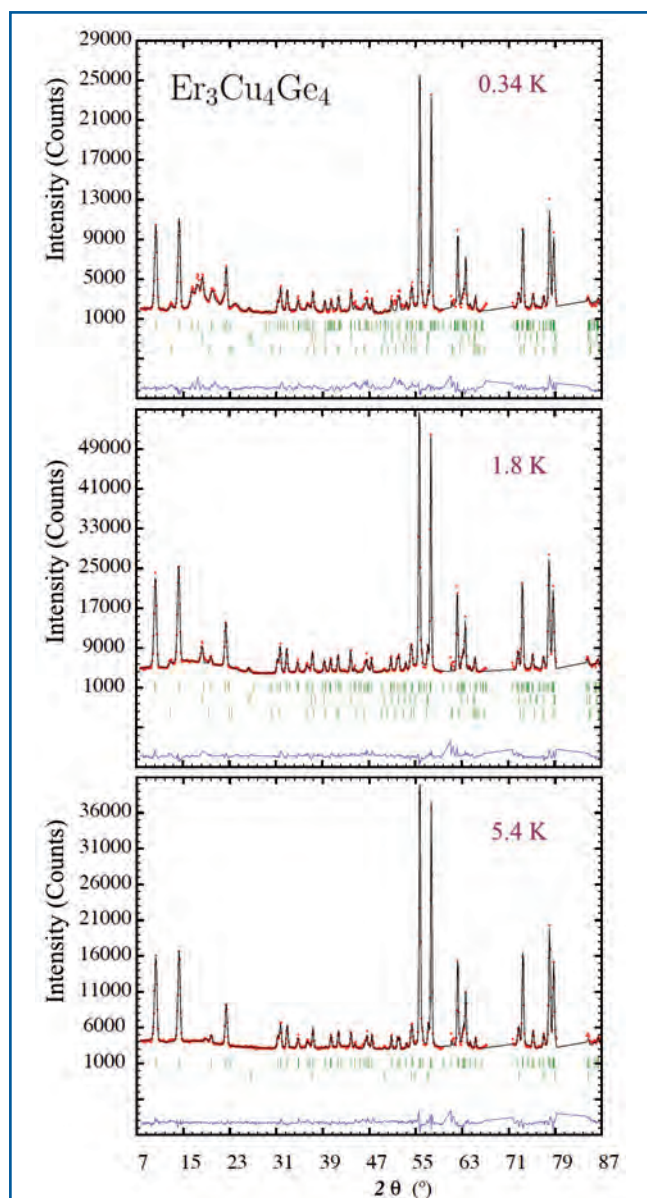
Fig. 3   C2 data for $Er_3Cu_4Ge_4$ taken with the Heliox sample cell at 0.34K (TOP), 1.8K (MIDDLE) and 5.4K (BOTTOM) [24].

scattering opens the possibility of *designing* new magnetic materials rather than blindly searching for them.

Crystal and magnetic structures of transition metal oxides

C2 has also seen extensive use to aid in the unraveling of quite complex magnetic structures in several oxide materials. In the dugganite material, $Pb_3TeCo_3V_2O_{14}$, the magnetic Co^{2+} ions form an unusual set of trimers which in turn form a hexagonal net, Fig. 5, introducing geometric frustration. There are two magnetic phase transitions occurring at $T_{N1} = 8.6K$ and

$T_{N2} = 6.0K$. Below T_{N1} the Co spins appeared to order according to an incommensurate wave vector, $k = (0.752\ 0\ 1/2)$. A commensurate, but very odd $k = (5/6\ 5/6\ 1/2)$ appeared to describe the magnetic structure below T_{N2}, implying a magnetic cell which is 72 times the volume of the chemical cell. It was then discovered that the crystal structure was very weakly distorted to a monoclinic symmetry, P2, with a chemical supercell six times the volume of the P321 cell. Using ultra high resolution neutron data from the WISH instrument at ISIS, in combination with C2 data, it was possible to solve the magnetic structures associated with both transitions as shown in Figs. 6a and b with propagation vectors $k = (1/2\ 0 - 1/2)$ for T_{N1} and $k = (1/2\ 1/2 - 1/2)$ for T_{N2}, the directions of which are indicated by the thick arrows. In the new unit cell, the Co-trimers form isosceles triangles rather than equilateral triangles [26].

In a collaboration with S. Derakhshan (Univ. Calif. Long Beach) the magnetic structure of a new Fe oxide, $BaYFeO_4$ was solved. In spite of the apparently simple stoichiometry, the structure of this material is complex, consisting of relatively isolated columns of four membered rings consisting of corner-sharing FeO_5 square planar units and FeO_6 octahedral units, Fig. 7 [27].

Again, there are two apparent magnetic phase transitions $T_{N1} = 47K$ and $T_{N2} = 36K$. C2 data were used to solve the magnetic structures in both regimes. In the range $36K < T < 48K$, a commensurate, $k = (0\ 0\ 1/3)$ structure was found, best described as a spin density wave (SDW) with moments fixed along the b-axis. Below 36K, an incommensurate $k = (0\ 0\ 0.35)$ structure is found, best described as a cycloid with the moments now in the bc plane, Fig. 8.

Studies of hydrogen containing materials, and hydrogen storage materials

Huot *et al.* have exploited the relative ease of performing in situ PND experiments in the study of the important hydrogen storage material $Mg_2FeH(D)_6$ [28]. Structural and phase changes associated with both hydrogenation and de-hydrogenation were carried out in a specially designed sample cell. The effects of the presence of both H and D were also assessed using phase contrast (the different scattering cross-sections allows to distinguish between the two isotopes). A typical result is shown in Fig. 9 below.

CANADIAN RESEARCH AT FOREIGN SOURCES

The high quality data from the C2 powder diffractometer over the years have been complemented by Canadian research at foreign sources using techniques such as polarized neutron diffraction and nPDF methods (pair distribution function). Polarized neutron diffraction takes advantage of the spin of the neutron ($s = 1/2$) and the capability of polarizing the incoming neutron beam to

separate out the nuclear, magnetic, and spin incoherent contributions (using the XYZ technique). Canadians have mostly utilized the D7 instrument at the ILL over the last few decades, but new beamlines such as the DNS (Diffuse scattering Neutron time of flight Spectrometer) in Jülich are seeing more prominence.

One example of recent work at D7 by Canadians is on the highly correlated spin ice $Ho_2Ge_2O_7$. These materials are prepared at high pressure, and the sample size used in the polarized experiments was only 200 mg. Nonetheless, with the large Ho^{3+} moment ($\sim 10\mu_B$), the magnetic scattering can clearly be seen on D7 after a few minutes of counting time (even after the XYZ analysis), illustrating the power of modern neutron sources.

The diffuse neutron scattering can be tracked as a function of temperature, and with modern methods of Reverse Monte Carlo (RMC) modeling of the data, the development of the 2-in, 2-out Ho^{3+} spin ice structure can be determined (Fig. 10). This is crucial for investigating claims of "monopole" formation, that are effectively defects within the 2-in, 2-out short range ordered structure.

With modern RMC methods (and new software developments such as Spinvert), fits of polarized neutron diffraction data can now be used to extrapolate to single crystal data. Figure 11 illustrates the RMC fits to three different spin ices measured at D7 ($Dy_2Ti_2O_7$, $Ho_2Ti_2O_7$, and $Ho_2Ge_2O_7$ in the left panels). The corresponding magnetic scattering can be then calculated for single crystal data (right panels), and compared to each other. While single crystal polarized data is preferred over powder data, there are many compounds of interest in which single crystal growth is challenging at best (such as the high pressure pyrochlores $A_2Ge_2O_7$, A = rare earth) [29].

Neutron pair distribution function (nPDF) analysis has been used increasingly by chemists and materials scientists to study disorder in complex crystalline materials, i.e., to determine not only the average but also the local structure. This approach is often dubbed "total scattering". Data are taken to $Q > 30$ Å^{-1}, typically, and normalized by the total scattering cross section of the sample to yield the total scattering structure factor $S(Q)$ from which the pair distribution function $G(r)$ can then be obtained through a Fourier transform. Such experiments are not possible at C2 and specialized
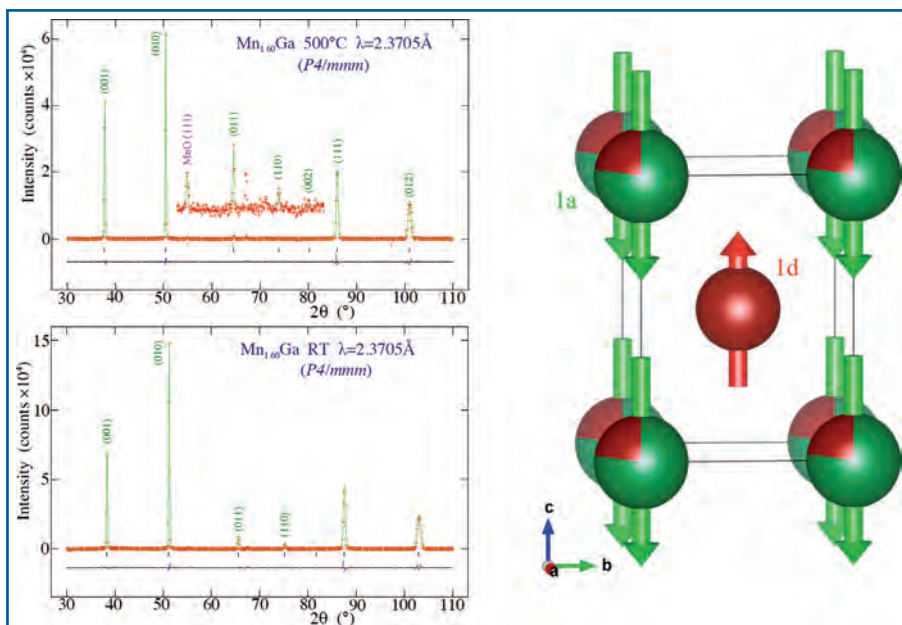

Fig. 4   (Left panels) PND patterns for $Mn_{1.60}Ga$ taken (top) at 500° C, well above T_c, to establish the crystal structure and (bottom) room temperature where the system is magnetically ordered. Note the small intensity changes at most of the peaks, especially the (011) and 110). (Right panel) The magnetic structure of $Mn_{1.60}Ga$. The Mn moment on the 1d site, ($2.45\mu_B$) fully occupied by Mn, is antiparallel to that on the 1a site ($\sim 3\mu_B$) where Mn substitutes for Ga [25].
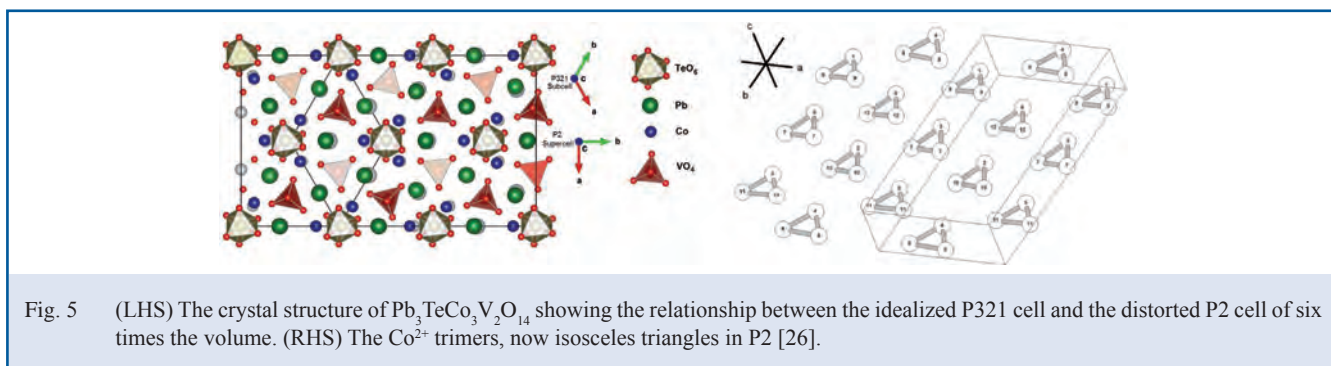

Fig. 5   (LHS) The crystal structure of $Pb_3TeCo_3V_2O_{14}$ showing the relationship between the idealized P321 cell and the distorted P2 cell of six times the volume. (RHS) The Co^{2+} trimers, now isosceles triangles in P2 [26].

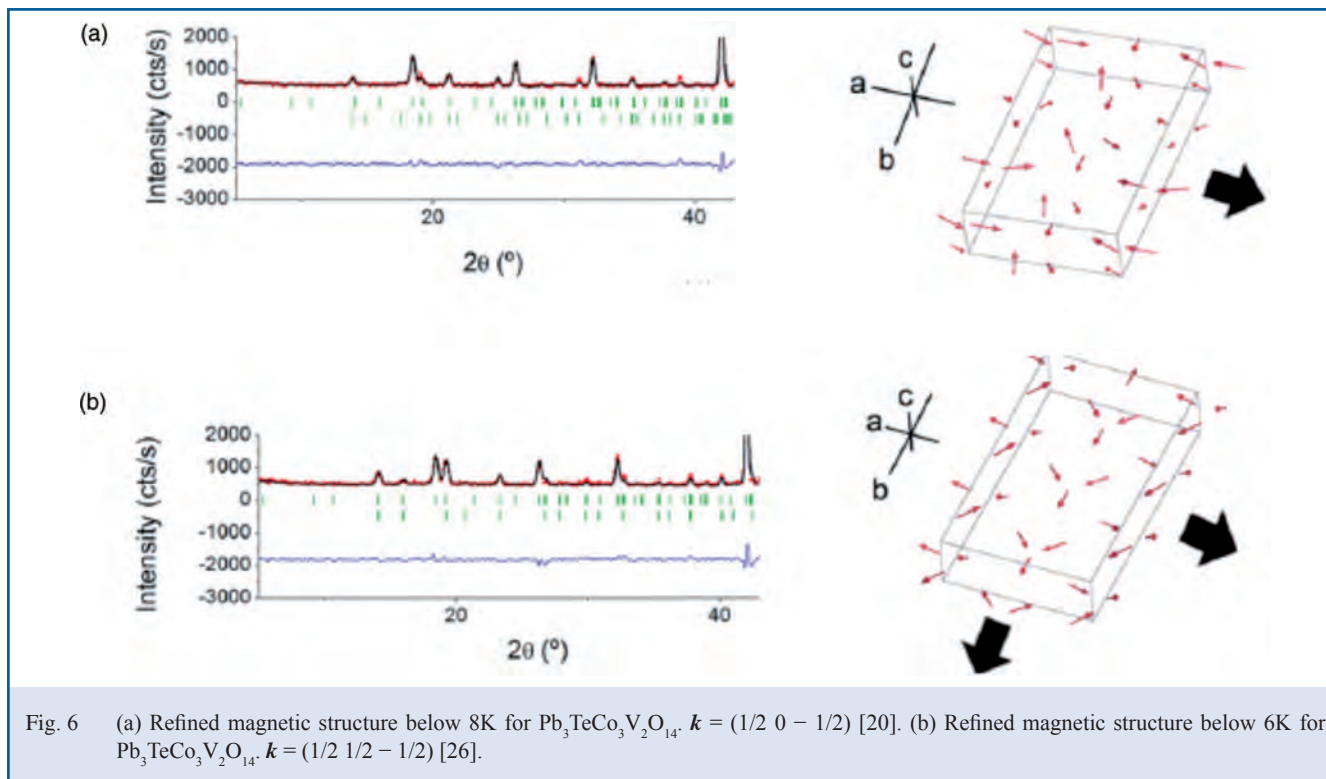Fig. 6   (a) Refined magnetic structure below 8K for $Pb_3TeCo_3V_2O_{14}$. k = (1/2 0 − 1/2) [20]. (b) Refined magnetic structure below 6K for $Pb_3TeCo_3V_2O_{14}$. k = (1/2 1/2 − 1/2) [26].
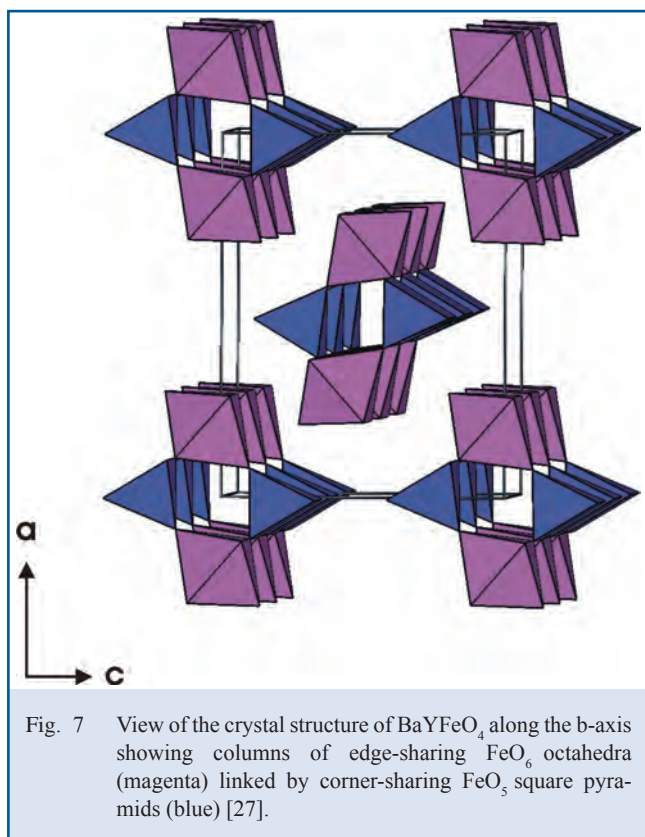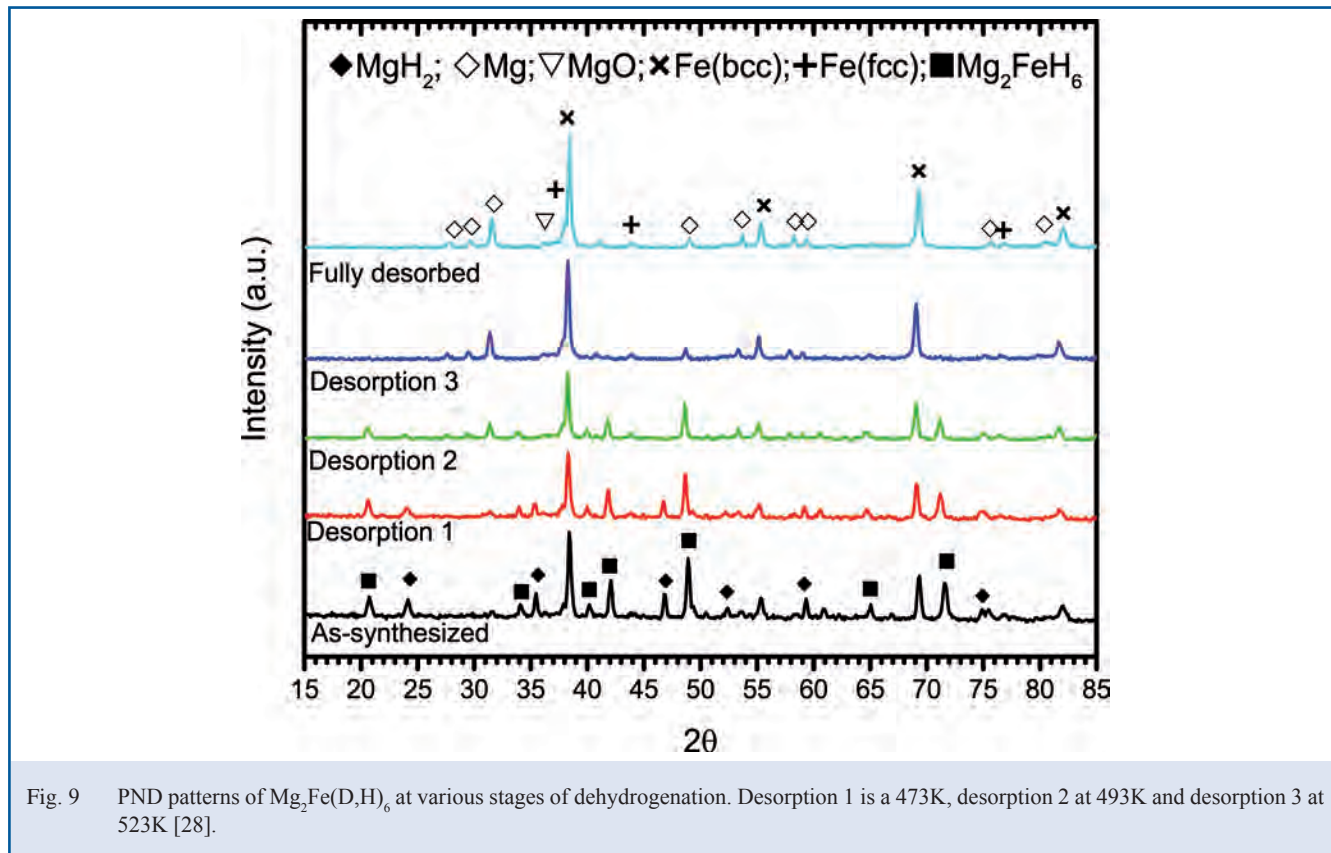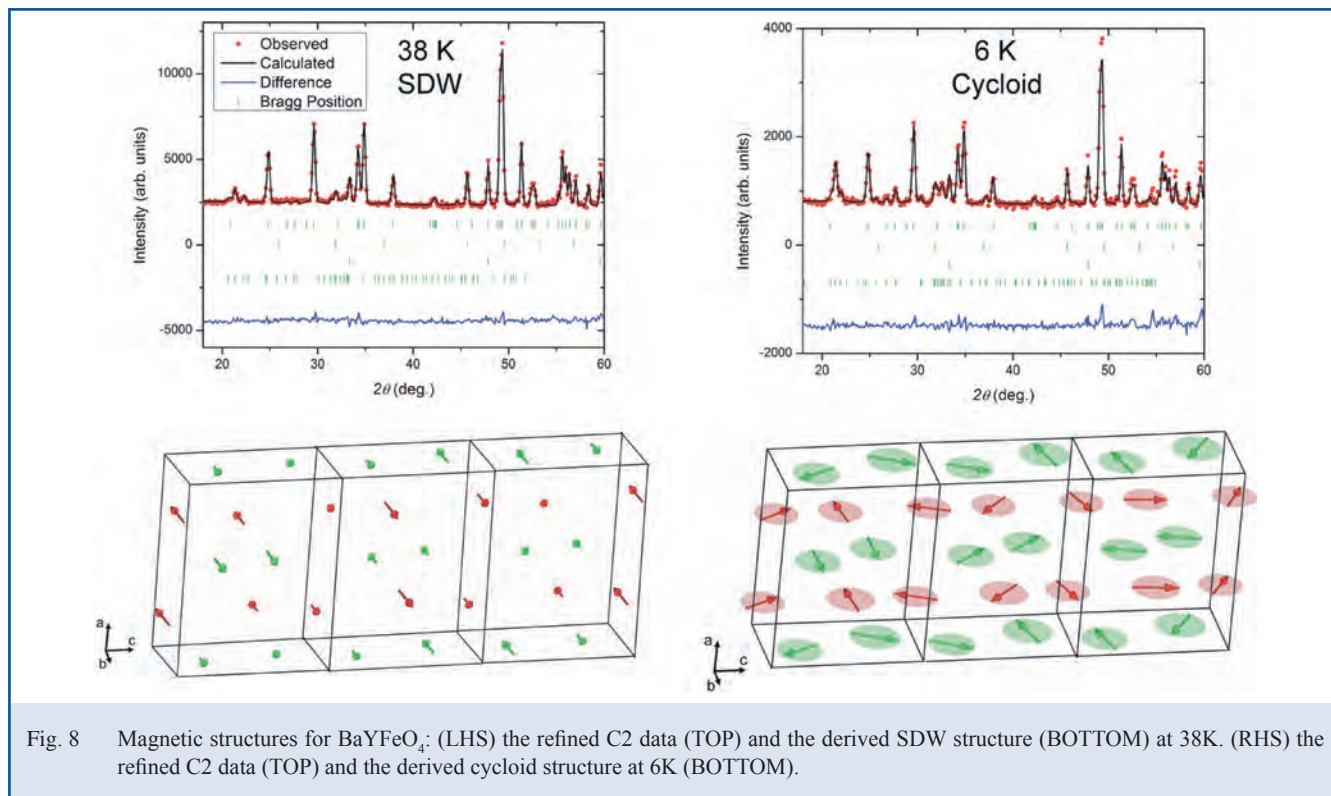

Fig. 7   View of the crystal structure of $BaYFeO_4$ along the b-axis showing columns of edge-sharing FeO_6 octahedra (magenta) linked by corner-sharing FeO_5 square pyramids (blue) [27].

instruments such as NPDF at the M. Lujan Jr. Center for Neutron Scattering at Los Alamos have been used in the past by Canadians on a wide variety of materials. With the recent highly unfortunate closure of the Lujan Center, it is not clear where Canadians will be able to travel for high quality nPDF data. While NOMAD at SNS and GEM at ISIS can be used for nPDF data collection, these instruments are not a direct substitute for NPDF. The planned DISCOVER diffractometer at SNS will likely become the best nPDF instrument in the world but it is several years from operation.

An example of the use of nPDF concerns the highly disordered material Sr_2FeMnO_5 which appears to be a cubic perovskite, Fig. 12, but with a 17% vacancy concentration on the O-site [25]. One would normally expect the vacancies to order giving the brownmillerite structure, also Fig. 12. Data from NPDF (Lujan) for this material are shown in Fig. 13. In Fig. 13a the S(Q) data to Q = 30 Å^{-1} are shown. The sharp Bragg peaks are consistent with the cubic Pm-3m cell. The inset shows that the background consists of much broader features and here is where the information on the local structure resides. The derived G(r) is given in Fig. 13b. Two fits to the nearest neighbour region, 1.5 Å-5 Å are shown in Fig. 13c (cubic perovskite – Pm-3m) and Fig. 13d (brownmillerite – Pmna). Clearly, the local structure is better modeled by brownmillerite than by the cubic average structure.

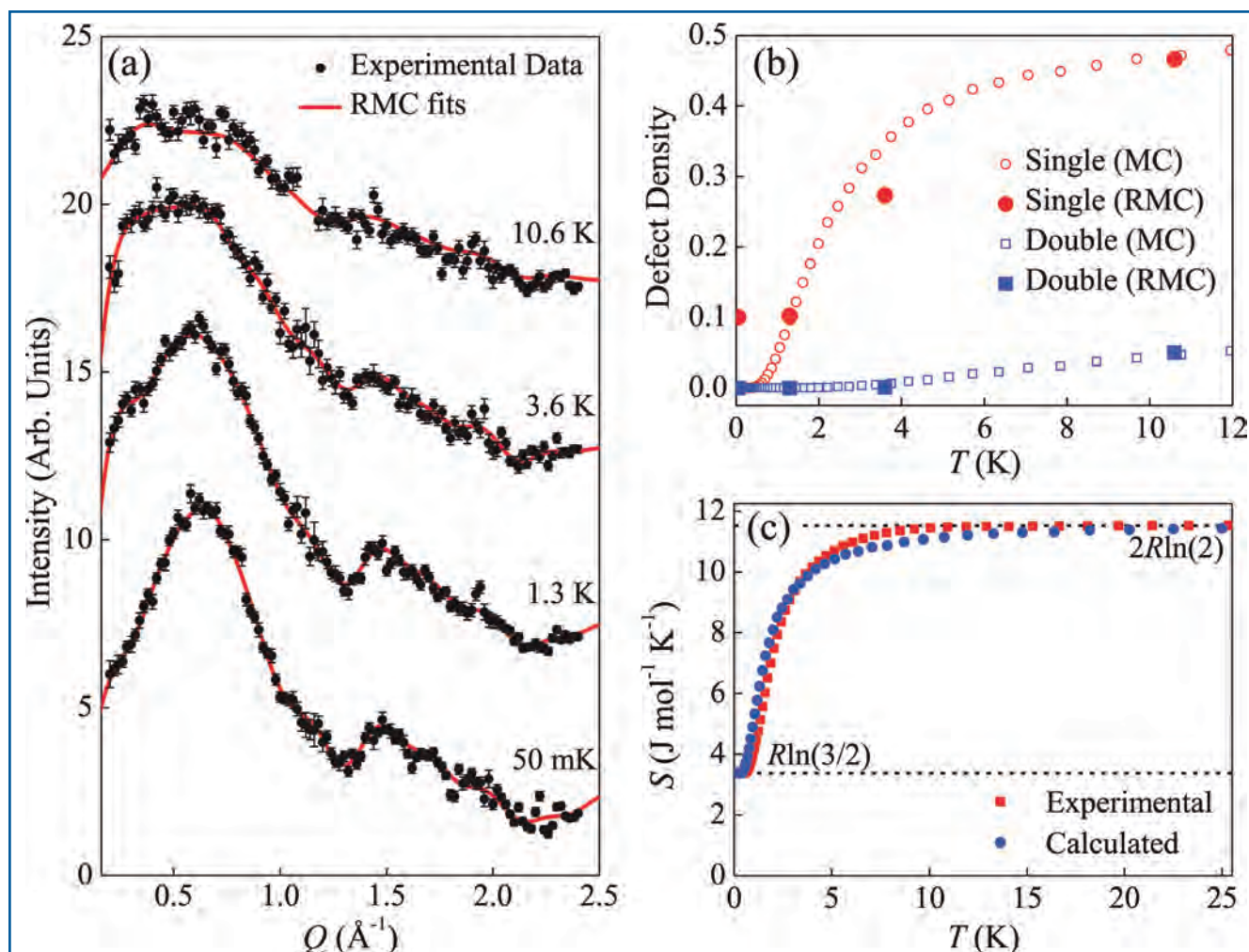Fig. 8   Magnetic structures for BaYFeO$_4$: (LHS) the refined C2 data (TOP) and the derived SDW structure (BOTTOM) at 38K. (RHS) the refined C2 data (TOP) and the derived cycloid structure at 6K (BOTTOM).

Fig. 9   PND patterns of Mg$_2$Fe(D,H)$_6$ at various stages of dehydrogenation. Desorption 1 is a 473K, desorption 2 at 493K and desorption 3 at 523K [28].

Fig. 10   (a) Temperature variation in the magnetic diffuse scattering of $Ho_2Ge_2O_7$ with RMC fits. (b) Density of ice-rules defects as a function of temperature for $Ho_2Ge_2O_7$. (c) Comparison of theoretical magnetic entropy for $Ho_2Ge_2O_7$ with experimental results [29].

SUMMARY AND FUTURE OUTLOOK

Chalk River laboratories has had a long and fruitful history of neutron powder diffraction research over the last five decades. The development of DUALSPEC and in particular of the C2 diffractometer brought Canada into the upper echelons of materials research. In a relatively short period of time, hundreds of papers were published using C2 with thousands of citations on a wide variety of materials. With the future of Chalk River and neutron scattering in Canada uncertain, it is unclear how Canadian scientists will proceed in powder diffraction research. One proposal is to resurrect PNDiff at the McMaster Nuclear Reactor. This would involve a single PSD covering 120°-150° in 2θ. With a proposed power increase to 5MW and the use of focusing monochromators, the new powder diffractometer might approximate the capabilities of C2. Even with this possibility, it is clear that for neutron scattering to survive as a discipline in Canada, there will have to be involvement in other foreign neutron sources at least in the short term. With the new Canadian Neutron Initiative (CNI), this may take place in the form of instrument development at foreign sources (such as DISCOVER at Oak Ridge National Laboratory) [32], membership in European neutron sources (such as the ILL and ESS – the European Spallation Source), or some combination that would enable Canadians to succeed. It would be unfortunate if we, as a community, could not promote our legacy in powder neutron diffraction and maintain our strengths on the world stage.
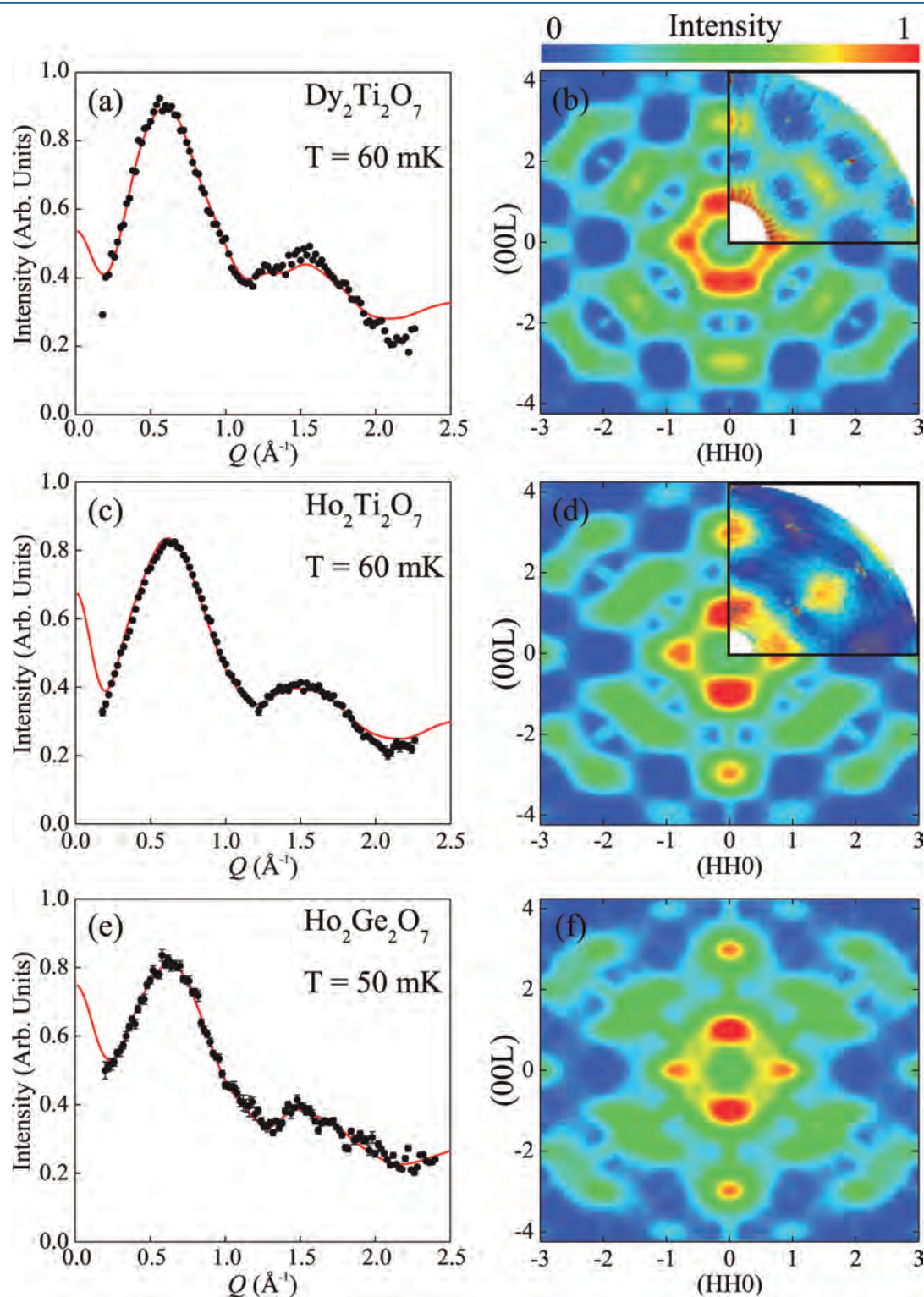
Fig. 11   Left: Fits to experimental powder magnetic data for the spin ice materials (a) $Dy_2Ti_2O_7$ (c) $Ho_2Ti_2O_7$ and (e) $Ho_2Ge_2O_7$. Fits are shown for an average of 64 independent refinements. Right: Single-crystal magnetic scattering predicted from RMC configurations for (b) $Dy_2Ti_2O_7$, (d) $Ho_2Ti_2O_7$, (f) $Ho_2Ge_2O_7$. The insets to figures (b) and (d) show one quadrant of magnetic scattering from single crystalline $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$, respectively [29].
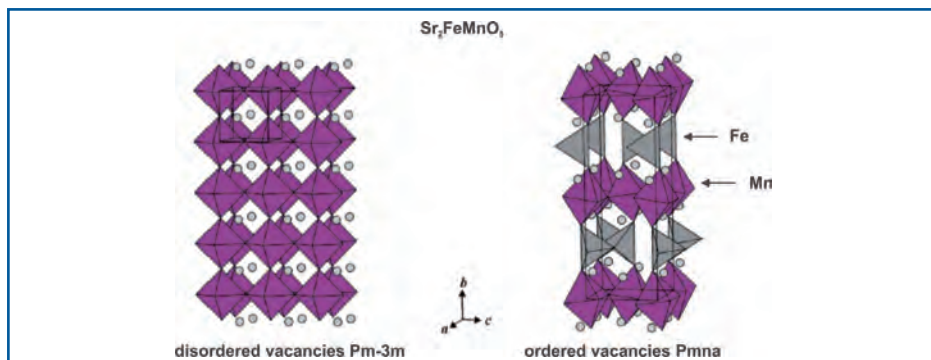
Fig. 12   (left) The cubic disordered perovskite structure (Pm-3m) for Sr_2FeMnO_5. At the centres of the violet octahedra reside the disordered Fe/Mn ions with oxygen ions at the vertices. 17% of these vertex sites will be randomly vacant. (right) An ordered brownmillerite structure (Pmna) in which the oxide vacancies, Fe and Mn ions all order resulting in layers of alternating corner sharing octahedral layers (Mn) and corner sharing tetrahedral chains (Fe). The Ca ions are shown as grey spheres. The unit cells for both cases are outlined.
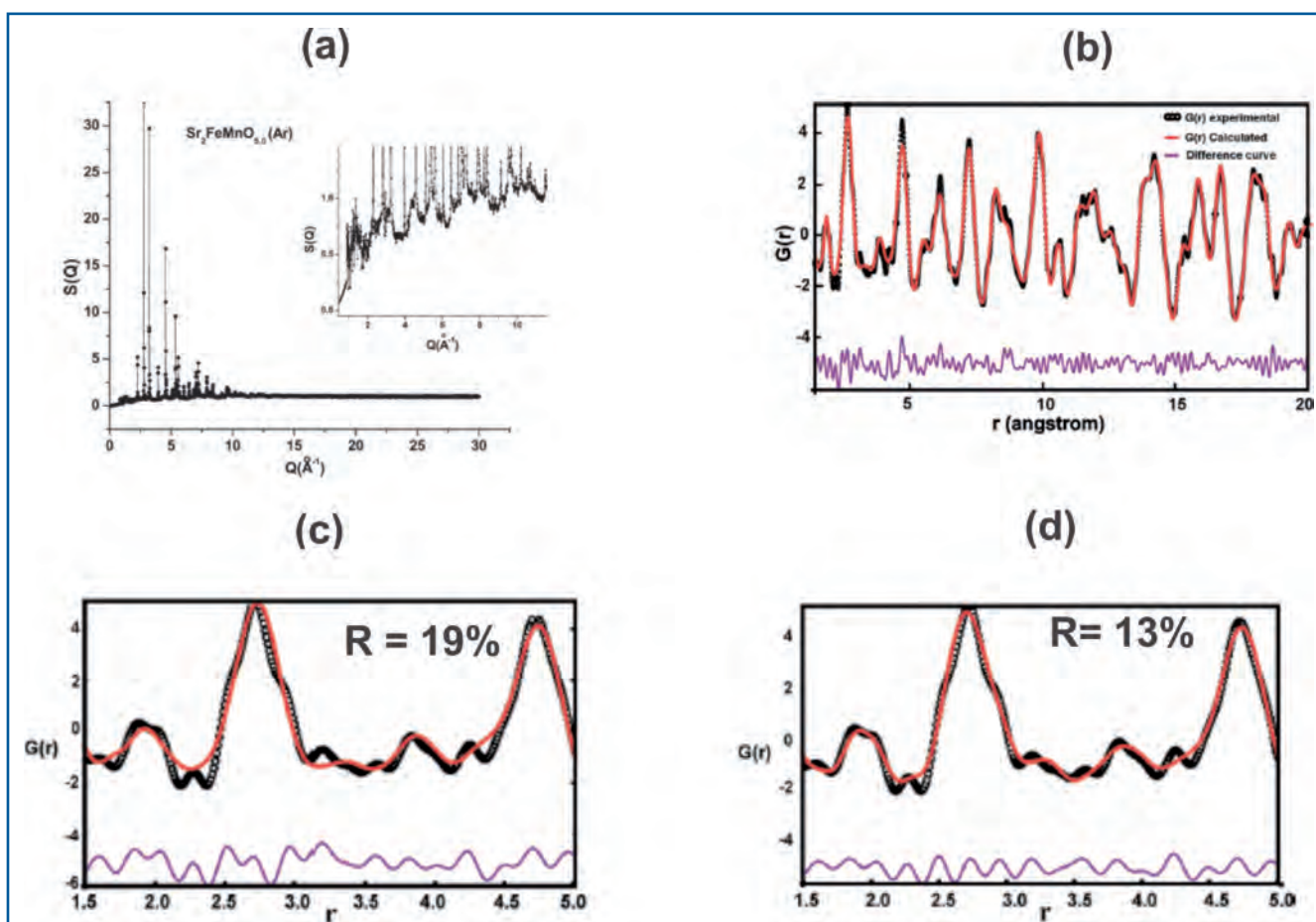
Fig. 13   (a) The S(Q) out to 30Å^{-1}. The inset shows broad features of the background upon which sharp Bragg peaks, consistent with Pm-3m symmetry, are superimposed. (b) The G(r) obtained by Fourier transform of S(Q). (c) Fit of the G(r) to a cubic local model. (d) Fit of the G(r) to a brownmillerite local model.

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