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Published in:
Physica B: Condensed Matter

DOI:
[10.1016/j.physb.2006.05.092](https://doi.org/10.1016/j.physb.2006.05.092)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2006

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Radaelli, P. G., Chapon, L., Gutmann, M., Bombardi, A., Blake, G., Schmidt, M., & Cheong, S-W. (2006). Ordering on geometrically frustrating lattices: The perspective of TOF neutron crystallography. *Physica B: Condensed Matter*, 385(10), 29-34. <https://doi.org/10.1016/j.physb.2006.05.092>

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Ordering on geometrically frustrating lattices: The perspective of TOF neutron crystallography

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Abstract

Geometrical frustration arises when geometrical constraints promote a locally degenerate ground state. A periodic system with this local geometry may “freeze” on cooling forming “ices” or remain liquid down to the lowest temperatures due to quantum effects. A third possibility is that of a structural phase transition that lowers the local symmetry and lifts the degeneracy. Two classic examples of geometrical frustration are the so-called pyrochlore lattice, which is also found in AB_2X_4 spinels, and the “ J_1 – J_2 ” model on a square lattice, which involves competing nearest- and next-near-neighbor magnetic interactions. We present recent results obtained by time-of-flight (TOF) neutron powder diffraction on orbital ordering in transition-metal spinels, leading to the concept of orbitally-driven Peierls state, and more recent data on $MoOVO_4$, a realization of the J_1 – J_2 model. A surge of interest in the so-called multiferroic materials has led to revisit the role of geometrical frustration in coupling different degrees of freedom. In this context, we present recent results on $REMn_2O_5$ obtained by neutron single-crystal and powder diffraction.

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PACS: 77.80.–e; 75.25.+z; 75.30.Fv; 61.12.–q

Keywords: Geometrical frustration; Multiferroics; Magnetic structures

1. Introduction

In many interesting physical systems, the configurations that minimize energy at the local scale cannot freely propagate throughout space, due to constraints imposed both by the nature of the interactions and by the lattice geometry—a situation that is referred to as *geometrical frustration*. Perhaps the best known example is that of three Ising spins on a triangle with antiferromagnetic (AFM) interactions, whereby only two out of the three bonds can be simultaneously satisfied, but a wealth of other examples can be found, including quasi-crystals, some classes of liquid crystals and some biological systems. Crystal lattices that are known to promote frustration for a suitable choice of the interactions are said to be *geometrically frustrating*.

Beginning with the pioneering work of Linus Pauling on water ice [1], a small number of these lattices have been the focus of experimental and theoretical research for more than 60 years. Most of the attention has concentrated on the triangular, Kagomé and square lattices (the latter with nearest and next-nearest-neighbor interactions) in 2 dimensions, and the hexagonal ice and pyrochlore lattices in 3 dimensions, both containing 2-dimensional Kagomé slabs. Interestingly, one can find profound analogies between apparently unrelated problems, such as proton ordering in ice [1], charge ordering in spinels such as Fe_4O_4 [2] and spin ordering in rare earth pyrochlores in the presence of strong on-site anisotropy [3], the commonality being provided by an identical or closely related underlying geometrically frustrating lattice.

One near-universal consequence of frustration is the suppression of the ordering temperatures much below what would be expected based on the strength of the

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interactions. On cooling, the system may eventually order, typically in a very complex pattern, or may remain disordered down to the lowest temperatures, forming either a glass or reaching an exotic, fluctuating ground state.

Systems where frustration is known to be a decisive factor in shaping the physical properties are often singled out for special interest, since they are hoped to be realizations of simple model Hamiltonians. In other cases, frustration plays a more subtle role. For example, the effect of geometrical frustration upon charge ordering has been considered for a long time the key ingredient to explain the metal–insulator (Verwey) transition in magnetite (Fe_3O_4) [4]. In the light of recent research, it is now clear that charge modulation is extremely weak at best; consequently, the role of frustration must necessarily be called into question.

Neutron scattering, both elastic and inelastic, has played a leading role in the study of ordering on geometrically frustrating lattices, due to its sensitivity to magnetic moments and to small light-atom displacements characterizing charge and orbital ordering. In this paper, we present a summary of a few of our recent results in this field, obtained by combining the unique strength of state-of-the-art, time-of-flight (TOF) neutron diffraction instruments at ISIS with synchrotron X-rays and other techniques.

2. Charge and orbital ordering in t_{2g} transition-metal spinels

The B-site pyrochlore lattice in transition metal spinels (general formula AB_2X_4) has for many years been regarded as a realization of geometrical frustration for both charges and spins [2]. More recently, we started to explore the implications of having the B-site accommodating partially filled t_{2g} orbitals (Fig. 1), which can interact across the

Fig. 1. Orbital ordering on the AB_2X_4 spinel structure. The B-site lattice (yellow), identical to the pyrochlore lattice, is geometrically frustrating. Chains of edge-sharing BO_6 octahedra accommodate partially filled t_{2g} orbitals.

shared octahedral edges towards which their lobes are pointing. The cases of CuIr_2S_4 ($\frac{1}{2}$ hole per site, [5]) and MgTi_2O_4 (1 electron per site, [6]) were examined in detail. Both systems undergo coupled metal–insulator and structural transitions (at 230 and 260 K, respectively), and in both cases the magnetic susceptibility drops at the transition (CuIr_2S_4 becomes completely diamagnetic). The low-temperature crystal structures display a complex pattern of subtle distortions, which could only be solved by a combination of techniques. In the case of CuIr_2S_4 , the superlattice reflections were indexed using electron diffraction, while synchrotron X-ray diffraction was employed to determine the triclinic distortion (Space Group $\text{P}\bar{1}$) of the low-temperature pseudo-tetragonal unit cell (the triclinic unit cell volume was $V = 943.263 \text{ \AA}^3$). However, even with this information, finding the correct displacement pattern for the 28 atoms in the asymmetric unit cell was a significant challenge. The medium-resolution neutron diffraction data obtained using the GEM diffractometer at ISIS (Fig. 2) proved to be essential in the early stages. A refinement in the pseudo-symmetric tetragonal unit cell (i.e., ignoring the superlattice reflections) based on those data enabled us to establish that the Ir and S atoms displaced along the $[1\bar{1}0]$ direction (i.e., along the “ribbons” of octahedra) and in the ab plane, respectively. This is consistent with the Ir ions displacing *towards* and *away from* each other in the modulated structure, and corroborated an early speculation that the drop in magnetic susceptibility might be due to the formation of spin singlets associated with $\text{Ir}^{4+}\text{--Ir}^{4+}$ dimers (Ir^{3+} is in the low-spin state with $S = 0$, see Fig. 3a). This model provided a filter for the possible normal modes of displacements, which was subsequently applied to fit the full set of medium-resolution data from GEM, and high-resolution data from HRPD (neutron) and Spring-8 (synchrotron X-ray), including superlattice reflections. The Pair Distribution Function method, based on the GEM data, was also applied to establish the degree of ordering or the low-temperature structure, which was found to be excellent. The structure solution (Fig. 3c) was indeed found to contain dimers: 8 out of the 16 Ir atoms in the triclinic unit cell form very short pairwise distances with each other ($\sim 3.0 \text{ \AA}$), whereas all the other Ir–Ir distances are normal ($\sim 3.5 \text{ \AA}$).

MgTi_2O_4 was found to display a closely related phenomenology, and was solved with the same techniques, but with an additional “twist”. Here, all the Ti sites are equivalent, accommodate one electron each (Fig. 3b) and are all dimerized. Interestingly, the pattern of dimers breaks the chiral symmetry of the spinel structure at the level of the individual tetrahedron (Fig. 3d): in other words, a tetrahedron and its mirror image cannot be made to coincide by rotation. The structure is tetragonal (Space Group $\text{P4}_2\text{1}_2$) and can be described as containing a set of “helices” of alternating short and long Ti–Ti bonds.

There is an obvious connection between the problem of dimer ordering on the frustrating B-site pyrochlore lattice

Fig. 2. Top: CuIr_2S_4 diffraction patterns as a function of temperature, as collected on GEM. There is a clear first-order transition around 230 K, accompanied by the appearance of superlattice peaks (marked with “S”). Bottom: anisotropic atomic displacement parameters for Ir, as refined in the pseudo-symmetric tetragonal space group $I4_1/amd$ on the basis of the GEM data. The enormous elongation of the U_{22} component hints at a dimerization pattern for the Ir sites.

and other “classic” problems of frustration. This is particularly clear in MgTi_2O_4 , where, each tetrahedron contains exactly one dimer, and therefore obeys an “Anderson-like” condition [2], or, if we prefer, a set of “ice-like” rules. The origin of the unique ordering patterns arising from these rules has recently been explored theoretically, from the perspective of quasi-localized [7] and quasi-itinerant [8] charge carriers (the latter referred to by the authors as an “orbitally driven Peierls state”). Also, the connection with the problem of charge ordering is being intensely investigated, in both theory and experiments.

3. Magnetic frustration in 2D and “multiferroic” behavior

The so-called J_1 – J_2 Heisenberg antiferromagnet is one of the most studied frustrated models in 2 dimensions. Here, Heisenberg spins reside at the nodes of a square lattice, and interact AFM with their nearest- (J_1) and next-nearest (J_2) neighbors. The two limiting cases of this model are

Fig. 3. Top: electronic configurations of the transition metal ions in CuIr_2S_4 (a) and MgTi_2O_4 (b). Since Cu is in the $1+$ oxidation state in the thiospinel, the valence of Ir is intermediate between $3+$ and $4+$, both in the low spin states. Bottom: the crystal structures of CuIr_2S_4 (c) and MgTi_2O_4 (d), showing the arrangement of the dimers. The diagram at the bottom of panel (d) shows how the chiral symmetry is broken.

relatively simple and well understood: when $J_1 \gg J_2$, the system orders into a simple Néel state, whereas when $J_1 \ll J_2$ the problem can be treated in terms of two decoupled interpenetrating Néel lattices, although, beyond the mean field approximation, a collinear state is stabilized by the so-called “order from disorder” mechanism (Fig. 4a). The intermediate situation near the exact frustration point $J_1 = 2J_2$ is still a matter of debate, particularly in the quantum case ($S = \frac{1}{2}$). Consequently, there is significant interest in finding experimental realizations of this model.

Recently, a family of quasi-2D vanadium oxides containing the “vanadyl” ion VO has been shown to realize the J_1 – J_2 model to a good degree. The general formula of this family is A_xVOBO_4 , where B is a tetrahedrally coordinated cation, and A is another cation (or a vacancy), so that the V valence balances at $4+$ ($3d_1$, $S = \frac{1}{2}$). V is in its typical square-pyramidal coordination with oxygen. The first task of the experimental research is to place each compound within the J_1 – J_2 phase diagram, by determining the magnetic structure and the size of the ordered moment. Interestingly, the two members of the family so far studied in detail, $\text{Li}_2\text{VOSiO}_4$ [9] and VOMoO_4 [10] seem to realize opposite ends of the phase diagram, since they order AFM in the collinear phase and in the Néel phase, respectively. Magnetic structure determination from powder data in the presence of weak moments is a task traditionally assigned

Fig. 4. a: Two realization of the J_1 – J_2 model in 2D vanadyl compounds. Bottom: realizations of the ASYNNNI model in the multiferroic compounds $REMO_3$ (b) and $REMn_2O_5$ (c). Plusses (+) and minuses (–) indicate spin directions in the commensurate AFM structure (spins are actually oriented in the ab plane).

to reactor instruments, but, in the case of $VOMoO_4$, GEM has “proven its mettle” by clearly identifying moments as small as $0.15 \mu_B$ near the phase transition (the ordered moment at low temperature is $0.4 \mu_B$). Perhaps more significant is the ability of TOF neutron powder diffraction to determine the magnetic and crystal structures simultaneously with great precision [10]. This was crucial in revealing the presence of a subtle ab plane expansion on cooling, with onset at ~ 100 K, i.e., significantly higher than the 40 K Néel temperature. Interestingly, our high-resolution synchrotron X-ray diffraction data indicate that there is no symmetry lowering.

It is natural to speculate that this anomaly may arise from exchange-striction, whereby the system, as it nears its ordering temperature, attempts to optimize the different requirements of its competing or frustrated interactions. In this respect, Fig. 4a outlines a subtle but important difference between the Néel structure (as in $VOMoO_4$) and the collinear structure (as in Li_2VOSiO_4). In the latter case, there is an *exact cancellation* of energy terms along the horizontal (positive energy) and vertical (negative energy) directions, suggesting that the system would lower its symmetry to orthorhombic (the so-called Spin Jahn–Teller effect). Conversely, in the Néel structure, all the next-nearest-neighbor interactions have uniformly the wrong configuration; therefore the system may still attempt to lower J_2 by “tuning” the crystal structure, but should not undergo a symmetry-lowering transition.

The coupling between magnetic ordering and lattice distortion has recently become an extremely topical

subject, due to the “revival” of the magneto-electric effect, particularly in the class of materials known as “multi-ferroics”. Here, magnetic and displacive order parameters are coupled in such a way as to yield a spontaneous polarization in the magnetically ordered phase. Application of a magnetic field can therefore affect the electric polarization, often in a very dramatic way, by means of coupling to the magnetic structure.

Two families of Mn oxides have attracted particular attention: the $REMnO_3$ perovskites [11], and the $REMn_2O_5$ compounds [12], where one can change the direction or even reverse completely the sign of the electrical polarization upon application of a magnetic field at low temperatures. Interestingly, both systems are magnetically frustrated, and both bear the same relation to the J_1 – J_2 model, as shown in Fig. 4, in that they are realizations of the *asymmetric* next-nearest-neighbor interaction (ASYNNNI) model, which can be derived from the J_1 – J_2 model by making J_2 inequivalent in the two orthogonal directions. In $REMnO_3$ (RE = rare earth), the enhanced next-nearest-neighbor coupling with respect to the well-known case of $LaMnO_3$ is due to the increased rotation of the octahedra, which also weakens the *ferromagnetic* interaction J_1 [13]. In $REMn_2O_5$, the connection with the ASYNNNI model is less direct, but emerges after considering the more complex pattern of interactions in the orthorhombic crystal structure (Fig. 5).

$REMn_2O_5$ contains equal proportions of Mn^{3+} and Mn^{4+} , in pyramidal and octahedral coordination, respectively. Along the c -axis, the $Mn^{4+}O_6$ octahedra form edge-sharing chains, intersected by Mn^{3+} and RE planes between pairs of Mn^{4+} sites. The $Mn^{3+}O_5$ pyramids share one edge with each other and the remaining three corners with $Mn^{4+}O_6$ octahedra. Overall, the picture of the magnetic interactions is quite complex, with at least 5 distinct coupling constants (and probably more) being important in establishing the magnetic structures. Nevertheless, the problem can be significantly simplified by the observation that the pyramid-pyramid interaction and the pyramid-octahedra interaction through the pyramid apex are dominant and AFM, so that the magnetic structure is always close to be a collection of AFM zig-zag chains running along the a -axis (Fig. 4c). Although this basic motif is respected across the rare earth and temperature series, the magnetic phase diagram is quite complex, with regions of incommensurability along both the a - and the c -axis.

From Fig. 4c, it is easy to see that in a “perfect” commensurate AFM structure there is an exact cancellation of the nearest-neighbor energy terms, since there is an equal number of terms of the same magnitude and opposite sign containing J_1 , a situation similar to that of Li_2VOSiO_4 . It is therefore possible that the energy could be lowered through the spin Jahn–Teller effect, and that the observed ferroelectric polarization could result from the associated lattice distortions. This would establish a direct link between frustration and ferroelectricity.

Fig. 5. Projections of the REMn_2O_5 crystal structure in the ac (top) and ab (bottom) planes.

Magnetic energy could also be lowered through incommensurability, and the two mechanisms could either compete or coexist.

A neutron powder diffraction study performed on TbMn_2O_5 using GEM has evidenced a remarkable correlation between changes in the magnetic structure and anomalies in the dielectric constant and/or the electrical polarization [14,15] (Fig. 6a; the dielectric constant and polarization data can be found in [12]). Incommensurate and/or 2-dimensional magnetic ordering is first observed at T_1 , coinciding with a rise of the dielectric constant ϵ . The sample first becomes weakly ferroelectric at T_2 , the onset of *commensurate* AFM ordering with propagation vector $(\frac{1}{2}, 0, \frac{1}{4})$. The electrical polarization saturates between T_2 and T_3 , then suddenly drops almost to zero, at T_3 , associated with a rarely observed first-order *de-locking* of the magnetic structure into an incommensurate phase with propagation vector $(\frac{1}{2} - \delta_x, 0, \frac{1}{4} + \delta_z)$. The propagation

Fig. 6. Top: thermo-diffractogram from neutron powder diffraction data collected on GEM on *cooling*, showing of the evolution of the TbMn_2O_5 magnetic structure. Bottom: Rietveld refinement plot of the commensurate magnetic structure at 27 K (the data shown are from the 30° bank).

vector changes continuously on cooling, reaching $\delta_x \sim 0.02$ and $\delta_z \sim 0.07$ at low temperatures. An increase of the intensity of the magnetic Bragg peaks due to Tb moment ordering is observed around $T_4 \sim 10$ K, associated with a rapid increase of the electrical polarization.

Once again, the ability to perform a simultaneous, high-quality refinement of both crystal and magnetic structures (Fig. 6b) with fine temperature sampling was crucial in establishing an initial picture of the physics of REMn_2O_5 . In this case, powder data and single-crystal data obtained on GEM and SXD, respectively, were combined to maximum advantage. In particular, the *commensurate* magnetic structure was solved, and found to lack a center of symmetry, compatible with an overall electrical polarization along the b direction, as observed experimentally. Furthermore, the atomic displacement parameters of the pyramidal Mn^{3+} were found to increase significantly in the magnetically ordered phase.

These observations enabled us to build a microscopic picture of the development of the electrical polarization in the commensurate magnetic phase. The exact cancellation of J_1 energy terms is *lifted* by the development of

Fig. 7. Temperature and magnetic field dependence of the 5.3 Å magnetic Bragg peak of TbMn_2O_5 . Here, the data were collected on *warming*, to match [12].

displacements of the Mn^{3+} ions along the axis of the pyramid, whereby the strength of the interaction is increased or reduced to optimize the magnetic and elastic energies at each pair of sites. The resulting displacement pattern is mostly antiferroelectric, but with a small, non-vanishing net polarization along the b -axis, consistent with the magnetic symmetry.

The situation with the low-temperature incommensurate phase is considerably more complex. There is strong evidence that this phase is ferroelectric not only in TbMn_2O_5 , but also in YMn_2O_5 , thereby ruling out rare earth magnetism as the sole responsible for this effect. It is noteworthy that, for YMn_2O_5 , the electrical polarization changes sign upon entering the incommensurate phase [16], a crucial effect to explain the polarization reversal in applied magnetic field (see below). It has also been shown quite conclusively on the basis of single-crystal data that the magnetic structure is a spin density wave rather than a helical structure [17]. This creates a problem, since a spin density wave could retain an overall center of symmetry (with or without time reversal), thereby excluding the possibility to develop a net polarization. One possible solution comes from the observation that the spin-density wave is composed of several independent waves on different sites and along different directions, which are unrelated by symmetry.

The most spectacular manifestation of multiferroic behavior in REMn_2O_5 is the reversal of the electrical polarization upon application of a magnetic field at low temperatures. There is also a strong field dependence of the electrical polarization near T_3 : in fact, application of an external magnetic field shifts the cross-over from high to low polarization states to higher temperatures, thereby *suppressing* the polarization at constant temperature. Neutron diffraction data collected on GEM as a function of field have provided the explanation for both effects. At low temperatures, the Tb lattice was found to be very soft,

so that Tb spins readily align parallel to the applied field and no longer participate in the spin density wave. We have therefore hypothesized that, at high fields, the only contribution to the polarization is provided by the Mn sublattice, and this component is aligned *antiparallel* to the original polarization direction, as in the case of YMn_2O_5 . Very recently, we were also able to clarify the origin of the high-temperature multiferroic behavior. Fig. 7 shows the evolution of the 5.3 Å magnetic Bragg peak as a function of temperature and field. The data are clearly consistent with an upward shift of the transition temperature T_3 . The incommensurate phase is therefore stabilized as a function of field, consistent with the fact that this phase has a higher ordered moment with respect to the commensurate phase.

4. Conclusions

The study of charge, magnetic and orbital ordering on geometrically frustrating lattices has always been an important theme in solid-state research. Recently, this topic has received an increasing amount of attention, as the development of satisfactory theories is deemed capable of providing not only the solution to a series of long-standing problems, but also an interesting connection with “functional-like” behaviors, such as the magneto-electric effect. We have tried to show how the increased power of time-of-flight powder instrumentation, particularly the excellent resolution in both real and reciprocal space combined with a wide range of scattering vectors, has been harnessed to provide insight into several systems based on a geometrically frustrating lattice.

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