Non-collinear long-range magnetic ordering in HgCr$_2$S$_4$

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Abstract

The low-temperature magnetic structure of HgCr$_2$S$_4$ has been studied by high-resolution powder neutron diffraction. Long-range incommensurate magnetic order sets in at $T_N \sim 22$K with propagation vector $\mathbf{k}=(0,0,\sim 0.18)$. On cooling below $T_N$, the propagation vector increases and saturates at the commensurate value $\mathbf{k}=(0,0,0.25)$. The magnetic structure below $T_N$ consists of ferromagnetic layers in the $ab$-plane stacked in a spiral arrangement along the $c$-axis. Symmetry analysis using corepresentations theory reveals a point group symmetry in the ordered magnetic phase of 422 ($D_4$), which is incompatible with macroscopic ferroelectricity. This finding indicates that the spontaneous electric polarization observed experimentally cannot be coupled to the magnetic order parameter.

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There has been a considerable renewal of interest in multiferroic materials in the last few years, in particular in magnetoelectric oxides such as TbMnO$_3$, TbMn$_2$O$_5$, or the Kagomé staircase compound Ni$_3$V$_2$O$_8$. These systems are all improper ferroelectrics and exhibit as a common feature strong magnetic frustration due to the presence of competing interactions or geometrical constraints. Consequently, their magnetically ordered states are typically quite complex. Independent of the microscopic mechanism responsible for ferroelectricity-antisymmetric Dzyaloshinskii-Moriya interaction or symmetric exchange striction-the symmetry breaking process associated with long-range magnetic order leaves a non-centrosymmetric structural point group, allowing a macroscopic spontaneous polarization to develop below the magnetic critical temperature. Another common element of fundamental interest is the nature of magnetic ordering itself, which involves propagation vectors inside the Brillouin zone, whether the magnetic order is commensurate or not with respect to the crystalline unit cell. In all these cases, it is crucial to perform symmetry analysis using co-representation theory to determine the point-group symmetry lowering induced by magnetic ordering.

Recently, attention has been drawn to chalcogenide chromium spinels of the type ACr$_2$X$_4$ (A=Cd,Hg; X=S,Se) which are weakly ferroelectric in their magnetically ordered state and have been classify as multiferroic materials. However, the dielectric behaviors are reminiscent of relaxor ferroelectrics, in which polar domains of nanometric sizes appear below the critical temperature. Although most chalcogenide spinels are Heisenberg ferromagnets, HgCr$_2$S$_4$ shows a more complex magnetic behavior at low temperature, indicating stronger competition between short- and long-range interactions: despite a large positive Weiss temperature of 142K, indicating dominant ferromagnetic interactions, the low temperature magnetic structure found by neutron diffraction experiments corresponds to a non-collinear antiferromagnet, in agreement with recent bulk magnetization measurements. However, Weber and co-workers noted in that the true nature of the magnetic state of HgCr$_2$S$_4$ still needs some clarification due to discrepancies between recent magnetization results and the earlier neutron and optical studies. Specifically, these earlier reports claim a much higher transition temperature than that of Weber et al. Determining the exact magnetic ground state, including its symmetry properties, is of crucial importance to study the potential coupling of magnetic and ferroelectric order parameters and is the prime motivation of the present work.
In this Communication, we report a complete analysis of the magnetic structure of HgCr$_2$S$_4$ studied by high-resolution neutron powder diffraction. Our results show that $T_N = 22.5$ K, in agreement with recent magnetization and specific heat measurements and contradicting early neutron diffraction and optical studies that reported a transition temperature around 60 K. The magnetic structure is incommensurate at $T_N$, but the propagation vector rapidly evolves with decreasing temperature, becoming nearly commensurate at 1.5 K. We also report the symmetry properties of the low-temperature magnetic structure as analyzed using corepresentation theory. We find that only a single mode belonging to a two-dimensional irreducible co-representation of the little group fits the experimental data. The resulting ordered magnetic structure refined from the neutron data is a spiral with propagation vector parallel to its axis. Symmetry analysis reveals that for $\mathbf{k}$ incommensurate the structural point group associated with this magnetic configuration is 422, forbidding the development of a macroscopic polar vector at $T_N$. For $\mathbf{k} = \frac{1}{4}$ exactly, the point group symmetry is lower (222 or 2, depending on the choice of the overall phase). However, this situation is only found at very low temperatures, leading to the clear conclusion that the appearance of hysteresis loops in the electric spontaneous polarization below $70 K > T_N$ is not related to antiferromagnetic order.

Polycrystalline HgCr$_2$S$_4$ was synthesized by combining powders of Cr (99.99%) and S (99.999%) with liquid Hg (99.9998%) mixed in a stoichiometric ratio. The mixture was sealed in an evacuated quartz tube and heated slowly to 600 °C for several days. The powder was then ground, pelletized, and sealed again for sintering at 800 °C for several weeks. Powder neutron diffraction data were collected on the high-resolution OSIRIS diffractometer at the ISIS pulsed neutron source (UK). A 1.5g sample was enclosed in a vanadium can placed in a helium cryostat. Long scans were recorded above (30K) and below (1.5K) $T_N$ to solve the magnetic structure. Shorter scans in a narrower d-spacing range (5.2-6.4Å) were recorded between 1.5K and 25.5K in 1K steps to follow the temperature dependence of the (111)+$\mathbf{k}$ Bragg peak. Rietveld refinements were performed with the program FullProF. Symmetry analysis using representation theory was performed with the help of the software MODY. Co-representation matrices and modes are obtained from the corresponding irreducible representations as described by Kovalev. Results are presented using Kovalev’s notation. We label representations as $\Gamma_i$ and corepresentations as $\tilde{\Gamma}_i$. 
TABLE I: Symmetrized in-plane basis vectors for the co-representations $\tilde{\Gamma}_5$. $\epsilon = e^{-i \frac{\pi}{2}}$, and $\epsilon^*$ is the complex conjugate of $\epsilon$. The atomic positions of Cr$_i$ (i=1,4) are given in the text.

| Atoms       | Cr$_1$       | Cr$_2$       | Cr$_3$       | Cr$_4$       |
|-------------|--------------|--------------|--------------|--------------|
| $\Gamma_5(1-1)$ | $e^{2\pi i (1,0,0)}$ | $e^{4\pi i (1,0,0)}$ | $e^{3\pi i (1,0,0)}$ | $e^{3\pi i (1,0,0)}$ |
| $\Gamma_5(1-2)$ | $e^{2\pi i (-1,0,0)}$ | $e^{4\pi i (-1,0,0)}$ | $e^{3\pi i (-1,0,0)}$ | $e^{3\pi i (-1,0,0)}$ |
| $\Gamma_5(2-1)$ | $e^{2\pi i (i,0,0)}$ | $e^{4\pi i (i,0,0)}$ | $e^{3\pi i (i,0,0)}$ | $e^{3\pi i (i,0,0)}$ |
| $\Gamma_5(2-2)$ | $e^{2\pi i (i,0,0)}$ | $e^{4\pi i (-i,0,0)}$ | $e^{3\pi i (-i,0,0)}$ | $e^{3\pi i (-i,0,0)}$ |

The neutron powder diffraction pattern collected at 30 K is consistent with the cubic crystal structure$^{15}$, space group $Fd\overline{3}m^{18}$. The high neutron absorption cross-section of Hg and reduced Q-range intrinsic to this instrument prevented us from extracting reliable thermal parameters and from probing possible off-center displacement of the Cr atoms as recently suggested$^{8}$. A detailed temperature-dependent structural investigation by X-ray diffraction is currently underway and will be reported elsewhere. At 1.5K, 12 magnetic Bragg peaks appear at low-Q in the diffraction pattern; all can be indexed with the propagation vector $\mathbf{k} = (0,0,\delta)$ (with respect to the conventional F-centered cell) in agreement with a previous study$^{10}$. $\delta \sim \frac{1}{4}$ within our experimental resolution, i.e. the periodicity of the magnetic structure is commensurate with respect to the nuclear unit-cell at 1.5 K.

The symmetry-allowed magnetic structures have been determined by co-representation analysis. Here we consider four Cr atoms in the primitive unit-cell (labelled Cr$_i$, i=1,4) respectively positioned at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, \frac{3}{4}, 0)$, $(\frac{3}{4}, 0, \frac{1}{4})$, $(0, \frac{1}{4}, \frac{3}{4})$. The remaining 12 atoms are generated by F-centering operations. The magnetic representation $\Gamma$ of dimension 12 is reduced into the direct sum of irreducible representations:

$$\Gamma = \Gamma_1^1 + 2\Gamma_2^1 + 2\Gamma_3^1 + \Gamma_4^1 + 3\Gamma_5^2$$

where the subscripts label the irreducible representations following Kovalev’s notation$^{12}$ and the superscripts refer to their dimensionality. The magnetic transition is continuous, and according to the Landau theory of phase transitions$^{16}$, should involve a single irreducible representation. Indeed, the magnetic structure is found to be consistent only with $\Gamma_5$, with modes in the $ab$-plane. The symmetrized in-plane basis vectors for the associated co-representation $\tilde{\Gamma}_5$ are reported in Table I. Only the modes labelled $\tilde{\Gamma}_5(1-1)$ and $\tilde{\Gamma}_5(1-2)$ fit
the data. Both modes correspond to spiral arrangements that only differ by their rotation direction, as seen from the sign of the imaginary part of the Fourier coefficients. The phases for atoms 1-4 are fixed by symmetry and are directly related to the fractional position along $c$ in such a way that atoms belonging to a same plane (including atoms generated by F-centering translations) have the same phase. The magnetic structure is therefore modeled by a single parameter: the magnitude of the Fourier component, i.e. the magnetic moment.

The refinement of the neutron diffraction pattern at 1.5K is presented in Fig. 1, showing essentially perfect agreement between experimental data and model. As mentioned before, the magnetic structure shown in Fig. 2 corresponds to a simple spiral propagating along $c$ and ferromagnetic arrangements in the $ab$-plane. Within a tetrahedral Cr$_4$ unit of the pyrochlore lattice, the angle between first-neighbor spins along $c$ is $\alpha = \pi \delta / 2$, i.e. 22.5 $^\circ$ at 1.5K. The magnetic moment of 2.7(1) $\mu_B$ is slightly smaller than the expected spin-only contribution for Cr$^{3+}$, S=3/2. This value agrees well with previous studies$^{10}$ and seems to
indicate that a small fraction of the magnetic moment remain disordered at low temperature. Nevertheless, one must take this result with care due to the strong correlation between magnitude of the moment and absorption correction in the refinement.

On warming, the propagation vector deviates from $\delta = \frac{1}{4}$ at 4K, which corresponds to a monotonous variation of the angle $\alpha$, and its magnitude decreases rapidly at higher temperature (Fig. 3). It is difficult to ascribe the low temperature result where $\delta = \frac{1}{4}$ to a lock-in transition, due to the narrow temperature region in which this behavior occurs. Nonetheless, there is a clear tendency towards saturation at this value. The variation of the intensity of the $(111)+k$ magnetic reflection, presented in Fig. 3., indicates a Néel transition around 22.5K, in excellent agreement with recent specific heat results showing a lambda anomaly at 22K and the strong decrease of the magnetization at low magnetic field. However, this finding contradicts earlier neutron and optical studies suggesting the long range ordered magnetic state persists up to 60K. Also in contradiction with, the magnetic order parameter obeys a power law close to $T_N$.

When considering the origin of the magnetic structure of HgCr$_2$S$_4$ one can eliminate direct exchange at first approximation because of the much larger interatomic Cr-Cr distance with respect with analogous oxide spinels. The very nature of the magnetic structure therefore indicates that antiferromagnetic next-nearest neighbor interactions compete directly with ferromagnetic super-exchange Cr-S-Cr interactions. The parameter that seems to control the nature of the magnetic ground state is the Cr-S-Cr angle. In HgCr$_2$S$_4$ this angle is 98° at room temperature according to structural parameters derived by larger than for ferromagnetic CdCr$_2$S$_4$, for which the value is 96.9°. This is in agreement with superexchange theory since larger deviation from 90° angles, for which antiferromagnetic correlation due to electron transfer is forbidden by symmetry, will increase the orbital overlap. The apparent extreme sensitivity of magnetic structure to angle in these compounds calls for a systematic study of the magnetic properties as a function of the averaged Cr-S-Cr bond angle.

Next, we consider the ferroelectricity of HgCr$_2$S$_4$ and demonstrate that it cannot arise from coupling to the magnetic order parameter. The onset of ferroelectricity induced by symmetry breaking associated with the long-range magnetic order can be directly determined by symmetry analysis of the magnetic structure. In cases where $k$ lies inside the Brillouin zone ($k$ and $-k$ are not related by a reciprocal lattice vector), only the use of co-representation theory can capture the full symmetry properties. In Table II, we report
the matrix representatives of the symmetry operations of the little group $G_k$ (including anti-unitary operations) for the irreducible corepresentations $\tilde{\Gamma}_5$. A symmetry operator is preserved in the magnetically ordered phase if and only if it is equivalent to a lattice translation (including F-centering operations). Matrices for the proper (rotation) operations, or proper operations combined with the complex conjugation operator $K$ (anti-unitary rotations), are diagonal and therefore equivalent to a translation for $k$ incommensurate. In other words, these operations transform a basis function of the two-dimensional subspace into itself, modulo a phase factor (which is equivalent to a translation for incommensurate $k$-vectors). On the contrary, the matrices for improper operations are off-diagonal, which means that these operators are not preserved in the magnetically ordered state. From the list of symmetry operators preserved, one can deduce the structural point group 422 ($D_4$ in Schoenflies notation). Notably, this point group is inconsistent with the development of a macroscopic polar vector. In general, the point-group symmetry is lower for exactly commensurate $k$ because not all phase factors are equivalent to a lattice translation. Furthermore, anti-unitary operators may be preserved or violated depending on the overall phase factor, which cannot be determined by neutron diffraction. Here, for $\delta = \frac{1}{4}$, the point group is 2 for a generic phase and 222 for special choices of the overall phase. If the global

FIG. 2: Left: Magnetic structure at 1.5K showing a spiral arrangement of ferromagnetic layers in the $ab$-plane. Only Cr atoms/spins are shown as grey spheres/arrow s. Cr atoms are connected by thin grey lines showing the underlying pyrochlore lattice. Two unit-cells along the $c$-direction are represented. Right: Spin-configuration within an isolated tetrahedral Cr$_4$ unit.
FIG. 3: Upper panel: Integrated intensity of the (111)+k magnetic Bragg peak versus temperature. The solid line is a guide to the eyes. Lower panel: temperature dependence of the propagation vector component $\delta$ as a function of temperature. The dotted line indicates the commensurate value $\delta = \frac{1}{4}$.

The condition for ferroelectric order in non-collinear magnets has also been recently discussed phenomenologically by M. Mostovoy\textsuperscript{17}. Mostovoy has shown that magnetically induced ferroelectric order can develop in non-collinear magnets only if the vector product between the spin rotation axis $e$ of the magnetic structure and propagation vector $k$ is nonzero, a condition obviously not fulfilled here since $k$ and $e$ are collinear.

The origin of ferroelectricity and associated phenomenal magnetoelectric properties in HgCr$_2$S$_4$ remains an open question. We have demonstrated conclusively that, symmetry breaking of the magnetic structure does not support a ferroelectric state. However, it has been shown that hysteresis loops of the electric polarization appear below $\sim 70K$. It is possible that the ferroelectric state could be coupled to short-range ferromagnetic correla-
tions developing around the same temperature. The presence of nano-polar regions is in agreement with this picture. However in this scenario, one might expect an abrupt decrease of the spontaneous polarization below the magnetic ordering transition, due to the strong reduction of ferromagnetic fluctuations. This is apparently inconsistent with experimental observation, since Weber et al. report that hysteresis loops become more pronounced with decreasing temperature. In the light of this temperature variation, it would be particularly interesting to study a direct signature of short-range ferromagnetic order with small angle neutron scattering to explain why ferroelectric order persists below $T_N$. Additionally, a detailed temperature dependence of the spontaneous polarization is needed to explore the exact nature of ferroelectric ordering.

In summary, we find that non-collinear magnetic ordering develops at 22.5K in HgCr$_2$S$_4$ with a spiral structure. Analysis with corepresentation theory shows that magnetic symmetry breaking is inconsistent with the development of a macroscopic polar vector, suggesting another mechanism—such as coupling to short-range ferromagnetic order—as the link between magnetic and electric properties in this material.

\begin{table}[h]
\centering
\begin{tabular}{|c|cccccccc|}
\hline
Coreps & $h_1/Kh_{25}$ & $h_4/Kh_{28}$ & $h_{14}/Kh_{38}$ & $h_{15}/Kh_{39}$ & $h_{26}/Kh_2$ & $h_{27}/Kh_3$ & $h_{37}/Kh_{13}$ & $h_{40}/Kh_{16}$ \\
\hline
$\Gamma_5$ & \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} & \begin{pmatrix} i\epsilon & 0 \\ 0 & i\epsilon \end{pmatrix} & \begin{pmatrix} -i\epsilon & 0 \\ 0 & i\epsilon \end{pmatrix} & \begin{pmatrix} 0 & \epsilon \\ \epsilon & 0 \end{pmatrix} & \begin{pmatrix} 0 & -\epsilon \\ -\epsilon & 0 \end{pmatrix} & \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} & \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \\
\end{tabular}
\caption{Matrix representatives of the irreducible co-representation $\tilde{\Gamma}_5$ of the little group $G_k$ (space group $G = Fd\bar{3}m$ and $k = k_6 = (0 \ 0 \ \delta)$). The labels for symmetry operations and numbering of the irreducible representations follow Kovalev’s notation. Matrices for unitary (h) and anti-unitary (Kh) symmetry operations are given on the first and second row, respectively. $\epsilon = e^{-i\pi\delta}$}
\end{table}

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