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Evolving spin periodicity and lock-in transition in the frustrated ordered ilmenite-type $\beta$-Mn$_2$InSbO$_6$.

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Polar magnets are promising materials for new applications as multiferroics or in spintronics. In double corundum-related oxides, the cation ordering imposes a polar structure and the use of high pressure facilitates the insertion of magnetic cations into the compounds. Here we present the high-pressure synthesis of a new polar and ferrimagnetic corundum derivative Mn$_2$InSbO$_6$, which adopts the ordered-ilmenite-type structure. Neutron powder diffraction reveals that the high-temperature nearly collinear ferrimagnetic phase evolves to an incommensurate helical structure with $k_\delta = [0 \ 0 \ k_z]$ propagation vector, which then locks to the commensurate value of $k_z = 1/8$. This complex magnetic behavior is likely to be related to magnetic frustration and the polar nature of the ordered double corundum structure.

I. INTRODUCTION

High pressure and high temperature treatments of ABO$_3$ oxides promote unusual cationic arrangements and interesting physical properties.$^{[1]}$ For instance, at ambient pressure, both MnXO$_3$ with X = V and Ti crystallise in the ilmenite-type structure. They consist in hexagonal closed-packed oxygens with two-thirds of the octahedral holes filled with Mn and V or Ti in an ordered-layer fashion along the z-direction with a non-polar $R-3$ space group. Under high pressure conditions, MnVO$_3$-II shows a perovskite structure with itinerant $3d^1$ V$^{4+}$ and localised $3d^5$ Mn$^{2+}$ electrons, where the spins order in a helical magnetic structure.$^{[2]}$ MnTiO$_3$-II presents a LiNbO$_3$-type, where the cations order along the [111] direction of the cubic cell with the polar $R3$ space group. It presents multiferroic properties due to Dzyaloshinskii-Moriya exchange interactions (DM).$^{[3, 4]}$ Following explorations of the double perovskites family, with more than 600 members,$^{[4]}$ double corundum derivatives A$_2$BB’O$_6$ have demonstrated their potential for new multifunctional materials with magnetic ions into both A- and B-sites of Ni$_3$TeO$_6$ and ordered-ilmenite structural types with $R3$ polar space group.$^{[5]}$ However, despite the possible combinations, only 15 polar A$_2$BB’O$_6$ double corundum-related compounds have been reported to date. Of these, three are theoretical predictions$^{[6, 7]}$, four synthesised at ambient pressures$^{[8, 9, 10]}$ and the rest can only be stabilised under high pressure and temperature conditions$^{[11, 12, 13, 14, 15, 16, 17, 18, 19]}$ (Supplementary Table S2).

The polar lattice of double corundum-type oxides can also stimulate the formation of modulated spin structures via a mechanism described by Lifshitz invariants in a Landau free-energy expansion.$^{[20, 21]}$ This gradient energy term favours inhomogeneous magnetic states and is known to result in incommensurate magnetic ground states in MnSi$^{[22]}$ and BiFeO$_3$.$^{[23, 24]}$ Both of these compounds demonstrate rich phase diagrams including magnetic field induced skyrmion lattice$^{[25]}$ and high-temperature multiferroic properties respectively.$^{[26]}$

In this work, we present the high pressure synthesis of a new polar and magnetic double corundum oxide Mn$_2$InSbO$_6$. The compound has been found to exhibit a remarkable evolution between complex magnetic structures towards a long-period modulated ground state compatible with the mechanism promoted by the gradient Lifshitz terms.

II. EXPERIMENTAL

Mn$_2$InSbO$_6$ sample was synthesised under high pressure-high temperature conditions. The stoichiometric proportions of Mn$_2$O$_3$, In$_2$O$_3$ and Sb$_2$O$_3$ oxides were ground under acetone to prepare the precursor mixture and treated at 5 GPa and 1373 K during 20 minutes using a Walker-type multianvil apparatus. After the reaction time, the temperature was quenched and the pressure was slowly released. High resolution powder XRD data were collected for Mn$_2$InSbO$_6$ at 80 K, 40 K, 30 K, 20 K, 17 K, 14 K,
10 K, 8 K, 6 K and 4 K in the 5° < 2θ < 40° angular range with a 0.03° step size using λ = 0.467173 Å synchrotron radiation at the BL04-MSPD beamline at ALBA light source (Barcelona, Spain). For the refinement of the SXRD data, the background was modelled with a list of experimental equidistant points afterwards refined through the linear interpolation of intermediate values and the peak shape was fitted using a Thompson-Cox-Hastings type function. Neutron powder diffraction (NPD) profiles were collected for Mn$_2$InSbO$_6$ at 2 K, 4 K, 6 K, 8 K, 10 K, 14 K, 17 K, 20 K, 30 K, 40 K and 80 K using the WISH instrument (ISIS facility, Oxford, U.K). The crystal and magnetic structures were refined using the FullProf suite [27]. The nuclear scattering was modeled in the R3 space group and the magnetic intensities were introduced in the refinement procedure using the propagation vectors formalism with k$_1$ = [0 0 0] (20 K), k$_2$ = [0 0 1/8] (2 K) and k$_3$ = [0 0 k$_z$] (intermediate temperatures). Magnetic symmetry analysis was carried out using the program BasIreps [27] for R3 space group.

Magnetic susceptibility measurements were performed on a Quantum Design XL-MPMS SQUID magnetometer under DC Zero-Field-Cooling (ZFC) and Field-Cooling (FC) conditions in the temperature range 2 K < T < 100 K under magnetic fields of 0.5 T and 0.01 T. Magnetization hysteresis loops were measured at 2 K, 10 K, 17 K, 20 K, 40 K and 60 K up to 3 T. Specific heat was measured using a Quantum Design PPMS under magnetic fields of 0 T, 3.5 T and 7 T. The dielectric response was measured on cooling with a Andeen-Hagerling Capacitance bridge at 1 kHz in a closed cycle refrigerator.

III. RESULTS AND DISCUSSION

A. Crystal Structure

Mn$_3$InSbO$_6$ prepared at ambient pressure crystallises in the Mg$_3$TeO$_6$-type structure, another corundum type derivative with R-3 centrosymmetric group (a = 8.93 Å and c = 10.71 Å) and all cations in octahedral coordination but with manganese and indium fully disordered.[28] The polycrystalline β-Mn$_2$InSbO$_6$ polymorph reported here requires high-pressure synthesis at 5 GPa and 1373 K (see Experimental Section). Initial laboratory X-ray diffraction indicated a rhombohedral cell (a = 5.38 Å, c = 14.21 Å) and a small amount of unreacted In$_2$O$_3$ (<5% wt). Rietveld analysis of combined high-resolution synchrotron X-ray (SXRD) and neutron powder (NPD) diffraction data collected at 80 K (Supplementary Fig. S1) revealed that Mn$_3$InSbO$_6$ crystallises in a double-corundum-type derivative. It presents alternating xy honeycomb layers formed by ordered Sb / Mn and disordered In / Mn octahedra sharing edges, stacked along the z axis. This structure is known as Ordered-Ilmenite-type (OIL-type).[29] The contrast between Mn, In and Sb arising from their neutron scattering lengths (Mn = -3.73 fm, In = 4.06 fm, Sb = 5.57 fm) and X-ray form factors (Z = 25, 49, 51) allowed their antisite disorder to be quantified from combined NPD and SXRD refinement. One cation layer is fully ordered with Sb and Mn (site M2) and one is fully
disordered between Mn and In (M1 and M3). The crystal structure is shown in Figure 1a and the final refinement results at 80 K are listed in Supplementary Table S3. The antisite exchange between M1 and M3 within the layer results in a larger Mn occupancy at both M1 (51.2 %) and M3 (55.5 %) sites in good agreement with the In deficiency matching the minor In2O3 secondary phase. For M2 and Sb sites, refinements suggested no disorder (antisite allowance refined to <1% with no fit improvement), so hereafter we will refer to the compound as (Mn0.5In0.5)2MnSbO6. This selective site exchange reflects the small size and charge mismatch between In3+ (rVI = 0.8 Å) and Mn 2+ (rVI = 0.83 Å) compared to that between Sb5+ (rVI = 0.6 Å)[30] and Mn2+. Bond valence sums (BVS) calculations with an interpolation method[31] result in +2.34, +2.39, +2.09, +5.10, for M1, M3, M2 and Sb in agreement with formal cationic oxidation states and anti-site disorder of (Mn0.52+In0.53+)2Mn2+Sb5+O6. The proposed formal cation oxidation states are supported by X-ray photoelectron spectroscopy (XPS) measurements (Supplementary Table S1 and Fig. S4) [32, 33, 34, 36, 37]. Bond distances and angles are registered in Supplementary Table S8.

B. Magnetic Properties and Magnetic Structure

The combination of magnetic cations in M1, M2 and M3 sites and anti-site disorder for M1 and M3 gives rise to a complex magnetic behavior. Temperature dependent magnetisation measurements for (Mn0.5In0.5)2MnSbO6 in 0.01 T and 0.5 T fields (Fig. 1b) show a ferrimagnetic transition at TNI = 38(1) K and Curie-Weiss paramagnetism at higher temperatures with a paramagnetic moment of 6.1(1) µB / Mn, close to the theoretical value of 5.92 µB for localised S = 5/2 Mn2+, and a Weiss temperature of θ = −160(1) K showing that antiferromagnetic spin-spin interactions are dominant but partially frustrated (|θ| / TN ≈ 4). A further transition is evidenced in the 0.01 T magnetic susceptibility curves at TN2 = 8(1) K, where zero field and field cooled data diverge from each other. Magnetic hysteresis loops and heat capacity measurements show also transitions at TNI and TN2, see Supporting Information.

NPD data were analysed to understand the low-temperature magnetic behavior in (Mn0.5In0.5)2MnSbO6. On cooling below TNI = 38 K, magnetic diffraction intensity is observed, for instance on (003) and (101) peaks at ~ 4.7 Å and ~ 4.4 Å as shown in Figure 2a. All the magnetic diffraction peaks observed down to 17 K can be indexed with propagation vector k1 = [0 0 0]. Below Tδ = 17 K the intensity of the magnetic diffraction peaks decreases and new satellite peaks appear. Their position gradually changes, revealing a second transition with k6 = [0 0 k6] that locks-in at a third transition with k2 = 1/8 at TN2 = 8 K. The thermal evolution of k2 is shown on the right panel of Figure 2a. k2 increases from 0 to 1/8 on cooling and it evidences the gradual commensurate to commensurate (k1 to k2) magnetic transition through a continuum of helical magnetic structures. Rietveld fits of both commensurate magnetic structures are shown on difference patterns of 20 K – 40 K (k1) and 2 K – 40 K (k1 + k2) in Figure 2b left and the crystallographic details are summarised in Tables S4 and S5. Symmetry analysis allows a consistent description of the different magnetic structures. For stable refinements, the magnetic moment per Mn ion in the three different Mn sites were constrained to be the same. In the k1 = [0 0 0] phase, the strongest magnetic interactions are the direct (AFM) M-M interactions between cations.
located into face-sharing octahedra, i.e. M2-M3 (d ~ 2.9 Å). Therefore, ferromagnetic layers M1/M3 and M2 stack antiferromagnetically with the spins ordered along the [110] direction with a refined magnetic moment of 1.9(1) \( \mu_B / \text{Mn}^{2+} \) at 20 K (Figure 3a). Antisymmetric DM exchange interactions are allowed in the non-centrosymmetric space group \( R3 \). The spontaneous ferromagnetic component in this phase, observed in magnetisation measurements, probably comes from the uncompensated magnetization of the sublattices (ferromagnetic) and canting of the spins (weak-ferromagnetism). Single crystal analysis will be needed to refine the ordered moments of the three magnetic sublattices independently. However, the d\textsuperscript{5}-d\textsuperscript{5} interactions within the (00l) layers via superexchange through oxygen at ~ 90 ° should be AFM according to Goodenough-Kanamori-Anderson rules. Below \( T_\delta = 17 \text{ K} \), the interactions between the magnetically diluted M1/M3 sites strengthens and their honeycomb arrangement originates a strong magnetic frustration. This effect induces another transition, mainly in the M3 (blue) site, with a partial relief of frustration leading to spin reorientation as shown in Figure 3b. All previously reported Mn\textsubscript{2}BSbO\textsubscript{6} corundum derivatives have only two independent magnetic sites, originating the rigid rotation of the FM layers. The OIL structure of Mn\textsubscript{2}InSbO\textsubscript{6} has three independent magnetic sites, what increases the degrees of freedom and allows for the independent rotation of the spins within the honeycomb layers.

Below \( T_{N2} = 8 \text{ K} \) the magnetic structure locks-in into a commensurate state with \( k_2 = [0 0 1/8] \), in accordance with the magnetisation and heat capacity measurements (Supporting Information). The structure describes M1 – M2 – M3 layers of spins with a relative orientation of 0° ~ 170° ~ 120° between their spin directions and with a 15° rotation between slabs (Figure 3b). The refined magnetic moment of 3.2(1) \( \mu_B \) per Mn at 2 K is significantly lower than the ideal value of 5 \( \mu_B \) for \( S = 5/2 \) Mn\textsuperscript{2+} showing that frustration is still present. Magnetic diffuse scattering is present at 2 K, see Figure S3 in SI. The two magnetic structures coexist below 17 K and 11% of the \( k_1 \) phase persists at 2 K. Combined Rietveld refinements of SXRD and NPD patterns collected between 2 K and 40 K (Table S7) reveal magnetostriction in the cell parameters when the spin reorientation takes place, Figure 2b right.

**C. Dielectric properties**

The OIL-type structure of (Mn\textsubscript{1.5}In\textsubscript{0.5})\textsubscript{2}MnSbO\textsubscript{6} with polar \( R3 \) space group is expected to present a net spontaneous polarisation. However, no switching is possible since the loss of centre of symmetry comes from cation ordering and not from cooperative ion...
The variation of the permittivity and the dielectric loss \(( \tan \delta )\) thermal responses show an increase below \( T_\delta = 17 \) K, Fig. 4 (top). These variations resemble the magnetostriction observed in the cell parameters as shown in Figure 2b. The observed magnetostriction is coupled to the additional displacements of the cations along the \( c \) axis below \( T_\delta \). This ionic motion is expected to originate an increase of the polarization \(( P_s )\). The expected \( P_s \) has been estimated using a point-charge model from the experimental atomic displacements. When compared to the predicted value at 80 K \(( \sim 12 \mu \text{C/cm}^2 \) \), \( P_s \) shows a negligible change at 40 K, but it gradually increases below \( T_{N1} \) up to \( \sim 25\% \) of \( \Delta P_s \) \(( \sim 15 \mu \text{C/cm}^2 \) \) when it adopts an incommensurable magnetic structure at 14 K. This polarisation is directly related to the expansion (contraction) of \( M2 \) and Sb \(( M1 \) and \( M3 \)\) octahedra, as shown at the bottom of Figure 4, induced by the magnetic order. The octahedral distortion has been calculated in terms of their mean ellipsoid radii \(( <R> \) \) and shape \(( S \) \) parameters from Piface software \([38]\). The results, shown in Fig. S6, confirm the described cooperative evolution of the octahedral distortions resulting from the magnetic transition at \( T_{N1} \).

**Figure 4.** Thermal evolution of the dielectric response of \(( \text{Mn}_{0.5}\text{In}_{0.5})_2\text{MnSbO}_6 \) (top) showing a transition in the dielectric permittivity below 8 K. The variation in the polarization (middle), determined from the experimental atomic displacements using point-charge model calculations, evidence the onset of a weak magnetoelectric coupling at \( T_{N1} = 38 \) K which becomes progressively stronger upon cooling down to \( T_{N2} = 8 \) K. Thermal behaviour of average \(<\text{M-O}>\) bonds (bottom).

**D. Relevant Free-Energy terms**

The non-collinear orientation of the three magnetic sublattices in the helical phase (Figure 3b) strongly points to the presence of competing exchange interactions in the system. The inter-sublattice interactions are antiferromagnetic and comparable in magnitude, giving rise to magnetic frustration. Another important mechanism promoting incommensurate spin ordering is related to the polar nature of the crystal structure of \( \text{Mn}_2\text{InSbO}_6 \). This implies that the physically irreducible representation \( \text{GM}_2\text{GM}_3(\eta, \eta^* \) \) which transforms the magnetic order parameter in the high-temperature \( k=0 \) phase, allows the presence of gradient Lifshitz invariant in the Landau free-energy decomposition, \( \eta \frac{\partial \eta}{\partial \xi} - \eta \frac{\partial \eta}{\partial \zeta} \). The component of the gradient operator is transformed by the totally symmetric representation and the transformational properties of the magnetic order parameter are specified in Table S9 and S10 of the Supplemental information. This term favours an inhomogeneous magnetic state \([39, 40]\) propagating along the \( \Lambda \)-line of symmetry \(( k = 0,0,k_z \) \) and is expected to have a strong impact on the magnetic ground state in systems without strong single ion anisotropy. The mechanism involves relatively weak anti-symmetric DM exchange interactions at a microscopic level. The latter usually implies a long-period modulation. A nearly quenched orbital angular momentum expected for \( \text{Mn}^{2+} \) cations and the small value of \( k_z \) found experimentally in \(( \text{Mn}_{0.5}\text{In}_{0.5})_2\text{MnSbO}_6 \) (see Figure 2a) are both consistent with this mechanism.

It is very likely that frustration of the Heisenberg symmetric exchange and the antisymmetric interactions imposed by the polar structural distortions are both engaged into formation of the low-temperature modulated ground state. The former mechanism defines the relative magnetic phases of Mn spins between the three symmetry inequivalent sites \( M1, M2 \) and \( M3 \) (three sublattices) and the latter promotes the slow global spin rotation along the \( c \)-axis. A possible reason why the modulated state does not develop below the first transition at \( T_{N3} = 38 \) K is a partial lifting of the frustration via adopting different magnitudes of the ordered moments for the distinct sublattices. In other words, the system can control the level of the frustration by varying the ordered moments of the sublattices, and fixing them
at certain ratios. This degree of freedom, affecting both symmetric and anti-symmetric exchange, is available only at temperatures close to the transition, where the spins are far from saturation, and it is expected to vanish at lower temperatures. Note, this assumption can explain the magnetisation observed in $M$ vs $H$ hysteresis loops and the plateau in the temperature dependence of the ordered moment in the $15 < T < 30$ K range (Fig. 3c). However, single crystal neutron diffraction will be needed in order to refine the magnetic moments of the three sublattices independently.

The lock-in transition with the commensurate value $k_z = 1/8$ implies an activation of the free-energy invariant that selects the commensurate value for the propagation vector $[4 1]$ In the case of $(\text{Mn}_{0.5}\text{In}_{0.5})_2\text{MnSbO}_6$, analysis of the allowed free-energy terms revealed that the lock-in invariant indeed exists and it involves the order parameter components in an unprecedented 24th power, $\rho^{24+}\rho^*^{24+}\xi^{24+}\xi^*^{24+}$. Here, $\rho$, $\rho^*$ and $\xi$, $\xi^*$ are components of the complex magnetic order parameters of the modulated ground state, describing helices with opposite chirality (see Tables S9 and S10 in the Supplemental Information). This is a remarkably high-power term and to the best of our knowledge, $(\text{Mn}_{0.5}\text{In}_{0.5})_2\text{MnSbO}_6$ is a unique example where lock-in takes place at such a small value of the propagation vector and implies a periodicity of ~114 Å (note that $k_z = [0 0 1/8]$ in the hexagonal setting of the rhombohedral cell corresponds to $k_z = [1/24 1/24 1/24]$, in the primitive setting).

**IV. CONCLUSIONS**

$(\text{Mn}_{0.5}\text{In}_{0.5})_2\text{MnSbO}_6$ OIL polymorph was synthesised under high pressure and high temperature conditions, stabilising a partial Mn/In cation order. This polymorph exhibits a sequence of magnetic phase transitions at 38 K, 17 K and 8 K. The first one gives rise to a commensurate magnetic structure with propagation vector $k_1 = [0 0 0]$, where the Mn$^{2+}$ spins are arranged into honeycomb ($M1$ and $M3$ sites) and triangular ($M2$) sublattices with a net ferromagnetic component. The second transition results in an incommensurately modulated state with $k = [0 0 k_3]$, which locks into the commensurate value $k_3 = 1/8$, below 8 K. The complex magnetic behavior is likely to be associated with magnetic frustration of the symmetric Heisenberg exchange and the polar nature of the crystal structure promoting DM interactions. The role of the anti-symmetric interactions in formation of the modulated ground state of $(\text{Mn}_{0.5}\text{In}_{0.5})_2\text{MnSbO}_6$ is likely to be similar to that in other notable non-centrosymmetric magnets like skyrmion-forming MnSi and multiferroic BiFeO$_3$.

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