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A new polar symmetry of huebnerite (MnWO_4) with ferrodistorive domains

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Abstract

Large-size single-crystal samples of huebnerite natural multiferroic MnWO_4 were analyzed by neutron and synchrotron X-ray single-crystal diffraction as well as by polarized Raman spectroscopy. Both neutron and X-ray diffraction analyses reveal polar space-group symmetry $P2$ for the nuclear structure of huebnerite via the detection of weak reflections $h0l$ ($l = \text{odd}$) forbidden for the gliding plane c . Renninger scans of the reflection 301 on the neutron single-crystal diffractometer RESI (FRM-II) could confirm the absence of the gliding plane c in both para- and antiferromagnetic states of huebnerite. The symmetry breaking could be explained by structure analyses with neutron single crystal diffraction data at 293 K revealing that two Mn atoms in $P2$ are displaced independently along the b axis from their equilibrium position at a polar point site, C_2 in $P2/c$. Micro X-ray diffraction and Raman-scattering mapping reveal a ferrodistorive domain texture in the room-temperature paramagnetic state of huebnerite, which is attributed to $P2$ domain formation through a proper $\sim 180^\circ$ rotation about the reciprocal-space axis c^* .

Introduction

Manganese tungstate (MnWO_4 ; mineral huebnerite [1]) is paramagnetic (PM) and paraelectric (PE) at RT, exhibiting a centrosymmetric monoclinic cell ($\sim 4.9 \times 5.7 \times 5.1 \text{ \AA}^3$ with $\beta \sim 91^\circ$; space group $P2_1/c$). The basic structure is comprised of chains of MnO_6 and WO_6 octahedra (**Figure 1**). On cooling the prototype structure undergoes three successive phase transitions in a narrow temperature range: from a paramagnetic to an antiferromagnetic state (AFM3) at the Neel temperature $T_N \sim 13.5 \text{ K}$, from AFM3 to another antiferromagnetic state AFM2 at $T_2 \sim 12.3 \text{ K}$, and further to antiferromagnetic state AFM1 at $T_1 \sim 8 \text{ K}$ [1, 2]. From extensive studies of the magnetic phase diagrams of MnWO_4 [3, 4] it is known that the transition temperatures and the stability regions for its PM and AFM phases are strongly dependent on the strength of external electric or magnetic fields. This compound is considered as multiferroic (MF) because the AFM2 phase exhibits a macroscopic electric polarization induced by an incommensurately modulated ordering of the elliptical spin spiral system of Mn [2 - 5].

The magnetoelectric (ME) coupling in MnWO_4 has been analyzed in the framework of two widely accepted models. The first is based on the so-called inverse Dzyaloshinskii-Moriya (IDM) interaction between two neighbouring Mn ions for which the magnetic interaction is super-exchanged via the common oxygen ligand [6]. A linear Mn-O-Mn configuration does not produce IDM. The oxygen atom can be displaced from the line of Mn-O-Mn by an elliptical spin spiral just like the spin alignment in the (a,c) -plane in AFM2 (up-up-down-down AFM ordering). The resulting IDM interaction induces a macroscopic electric polarization perpendicular to the plane confined by the Mn-O-Mn-triangle, i.e. along the crystallographic b axis [6]. The second model for the presence of electric polarisation in AFM2 is based on the spin supercurrent inducible perpendicular to the magnetic interaction of two neighbouring Mn ions [7]. Arguing with too low IDM interactions on one hand and too high spin supercurrent with respect to the ME coupling experimentally observed in AFM2 on other hand, Sakhnenko and Ter-Oganessian have suggested another model emphasizing the role of the rotating polar point site C_2 for Mn^{2+} in MnWO_4 [8]: Their magnetic spins break the inversion symmetry in $P2_1/c$ to deflect electric dipole moments from the rotating axis C_2 . The resulting spin-dependent dipole moments give rise to a nonzero macroscopic polarization along the b axis (P_y), with an estimated P_y value $\sim 17 \text{ } \mu\text{C}/\text{m}^2$ being very close to the experimentally determined value $\sim 50 \text{ } \mu\text{C}/\text{m}^2$ [4]. The occurrence of this weak electric polarization can be understood as a result of the critical softening of magnetic excitations associated with symmetry-breaking of frozen atomic displacements, as recently reported by

Niermann et al [9]: the dynamical response of ferroelectric fluctuation at GHz frequencies above T_2 could be recorded by means of dielectric spectroscopy. The slowing down of electrically active magnetic excitations (electromagnons) at T_2 was shown for the temperature-, as well as the magnetic field-driven MF phase transition in MnWO_4 . The latter case is in particular interesting as an intermediate phase AF2' exists when applying a high-magnetic field (at least about 10 T) along the b axis [10]. This high-field phase is formed via the AF2-AF1-AF2' transition, resulting in the electrical polarization in the a axis (P_x). The ease with the field-induced change of dipole moments in MnWO_4 is attributed to the strong geometrical frustration due to exchange interactions within the zigzag Mn-chains competing with interchain interactions, according to IDM afore mentioned [10].

Concerning this topology-specific frustration, all those models have been suggested to explain the presence of non-inversion symmetry in MnWO_4 by the magnetic order. In this aspect it is worth mentioning the so-called Rashba (R2) or/and Dresselhaus (D2) effects, as suggested by Zhang and his colleagues very recently [11]: Locally limited polar point sites or non-inversion can play a crucial role for spin-orbit coupling to induce ME effects in centrosymmetric bulk crystals once the local inversion symmetry is broken. Such hidden spin polarization can allow for technological applications of multiferroic materials at low strength of external perturbation [11].

Thus, it is essential to gain a deeper insight into the behaviour of Mn at the polar site C_2 in MnWO_4 for a better comprehending of its correlated properties. From a crystallographic point of view there are two possibilities for Mn in huebnerite: 1. Two Mn positions remain symmetrically equivalent and the electric polarisation can be induced in the inversion-symmetric ($P2/c$) bulk structure only by spiral spin order, as explained by Sakhnenko and Ter-Oganessian; 2. At the polar site C_2 (0.5, y , 0.25) two Mn ions can slightly deviate about $y \pm \Delta_1$ and $y \pm \Delta_2$ respectively from the equivalent coordinate y under certain circumstances (e.g. local defects or superstructure problems). For the case $\Delta_1 \neq \Delta_2$, weak dipole moments may be created in the unit cell. Either they are averaged over the bulk crystal to display apparently the highest symmetry $P2/c$, or nonzero microscopic polarisation is realized at room temperature (RT) at the expense of symmetry breakdown. We propose that the latter case is realized in the single-crystal huebnerite sample studied here, since the experimental data unambiguously indicate that the nuclear structure has space group $P2$, which is a subgroup of $P2/c$, the widely accepted space group for paramagnetic MnWO_4 .

Experimental

Sampling, optical and chemical analysis

A huebnerite crystal sized about 20 x 10 x 10 mm³ originating from Pasto Bueno was provided by the museum *Mineralogische Staatssammlung München*. The crystallographic orientation of this huebnerite crystal was determined by Laue X-ray diffraction to prepare several thin plates cut parallel and perpendicular to the *b* axis for microscopic and chemical analyses. The main body of the crystal was saved for neutron diffraction. A series of line scans was conducted with thin huebnerite plates by electron microprobe (Cameca SX50) at 15 kV and 10 nA with a beam diameter of ~5 µm. Several elements which can be possibly found in the natural form of MnWO₄ were analyzed (Mn, W, Cu, Mo, Fe, Ca, P, Zn, Pb, As, and O) against standards MnTiO₃, metallic W, metallic Cu, metallic Mo, Fe₂O₃, apatite (for both Ca and P), sphalerite, PbS, GaAs, and wollastonite.

Synchrotron X-ray single crystal diffraction (SXRSD)

SXRSD was performed at the instrument F1 equipped with a four-circle-kappa single crystal diffractometer at HASYLAB (Hamburg, Germany) with a wavelength of 0.5000(3) Å (Si(111) monochromator) using a charge-coupled detector (CCD), MarCCD165 (2k x 2k pixels in Ø = 165mm). A (001)-oriented thin plate of huebnerite (~ 3 x 1 x 0.08 mm³) was used to collect SXRSD data from both each single domain and the domain boundary (**Figure 2**). For this special purpose, a high-power long focusing polarization microscope and a motorized microslit were installed additionally to ensure diffraction exactly from the selected region within the domain crystal. The thin crystal was embedded between two cellulose foils and spanned within a brass ring sample holder and then mounted on a XYZ-stage. This sample stage was set to the diffractometer fixed at $2\theta = 0^\circ$, $\omega = 0^\circ$, and $\chi = -90^\circ$ (**Supplementary 1**) in a distance of 80 mm from the CCD detector. The primary beam was oriented perpendicular to the (001) plane of huebnerite at $\varphi = 0^\circ$. Using the installed long-focusing polarization microscope the primary beam spot was coordinated to localize three different measuring points at two neighboring domains (denoted by D1 and D2) and their domain boundary (DB) (**Figure 2**). The individual regions D1, D2, and DB were exposed separately to synchrotron X-ray passing the microslit with an opening of 2 x 20 µm² for data collection. Each data set was measured with a step scan of 1° ($\Delta\varphi$) for 65 sec per frame in a small range of $-15^\circ < \varphi < 15^\circ$ to prevent the overlapping of diffraction data from individual

domains. Indexing and reciprocal plane reconstructions were executed with the software package CrysAlisPro (Agilent).

A homogeneous single-crystallite huebnerite ($0.08 \times 0.07 \times 0.02 \text{ mm}^3$) was selected for collecting SXRSD data with a high redundancy and completeness. This crystallite was prepared on a glass fiber to be mounted on a goniometer head behind a 0.7 mm (ϕ) collimator. Four different combinations of Eulerian angles were chosen for data collection in ϕ -scan mode with a crystal-detector distance of 60 mm at 293 and 100 K using a nitrogen gas open-flow cooler: 1. Run at $2\theta = 0^\circ$, $\omega = 0^\circ$, $\chi = 0^\circ$ with 2 sec/frame ; 2. Run at $2\theta = 0^\circ$, $\omega = 0^\circ$, $\chi = 0^\circ$ with 15 sec/frame ; 3. Run at $2\theta = -60^\circ$, $\omega = 0^\circ$, $\chi = 0^\circ$ with 45 sec/frame ; 4. Run at $2\theta = -60^\circ$, $\omega = 20^\circ$, $\chi = 60^\circ$ with 45 sec/frame .

Using the XDS package [12] data reduction was performed for indexing, Lorentz-polarization correction, integration, scaling, and cell parameter refinements. The obtained hkl files were corrected for oblique phosphor incidence using the program PHOSCOR [13]. An anisotropic absorption correction was done semi-empirically with direction cosines of reflections using the program SORTAV [14]. Structure solutions were performed by using the Patterson Method option of SHELXS [15]. Subsequent least-squares refinements of the atomic parameters were done with JANA2006 [16]. Reconstructions of the $h0l$ plane were done by using the program RASTM [17].

Neutron single crystal diffraction (NSCD) and Renninger scan

A large huebnerite crystal ($0.79 \times 0.66 \times 0.14 \text{ mm}^3$) cut from the bulk sample was used to collect neutron single crystal diffraction data at the instrument RESI at FRM-II (Garching, Germany). Applying a wavelength of $1.043(1) \text{ \AA}$ (Cu(422) monochromator) a set of 2D raw data was detected on a MAR345 image plate (345 mm in diameter) and processed using the program package EVAL [18]. In **Table 1** data collection and reduction parameters for NSCD collected at 298 K are summarized along with the SXRSD collected at 100 K . All single crystal diffraction data sets contain reflections $h0l$ with $l = \text{odd}$ which are forbidden to $P2/c$ (**Table 2**).

In so-called Renninger scans the crystal is rotating about the azimuthal axis (ψ) perpendicular to the (hkl) diffraction plane in order to detect its own Bragg intensity free from multiple scattering events [19]. If a symmetrically forbidden reflection appears in every ψ -scan step, symmetry breaking must be considered. For validating the truth of those reflections given in **Table 2**, a series of Renninger scan was conducted at the instrument RESI with a wavelength of $1.038(1) \text{ \AA}$ and the same huebnerite crystal sample used in the previous data collection in

NSCD. A ^3He point detector was used to discriminate intensity noises efficiently. The reflection 301 was scanned over ψ from 0° to 35° with a constant step of $2^\circ(\Delta \psi)$ at three different temperatures at 3, 10, and 13 K, based on its well-known magnetic phase transitions. Subsequently this reflection was measured continuously between 3 and 88 K to monitor its intensity variation as a function of temperature.

Raman spectroscopy

Polarized Raman spectra were collected at room temperature in the range $15 - 1200 \text{ cm}^{-1}$ using a Horiba T64000 triple-grating spectrometer equipped with a liquid-nitrogen-cooled CCD detector and an Olympus BX41 microscope with a $50\times$ long-working-distance objective. The Raman scattering was excited with the 514.5-nm line of an Ar^+ laser (Coherent Innova 90C FreD) and 600 mW output laser power. The diameter of the laser spot on the sample surface was $\sim 2 \text{ }\mu\text{m}$ while the delivered laser power was 6.6 mW and 9.8 mW in parallel polarized (the polarization of incident light $\mathbf{E}_i$ parallel to the polarization of the scattered light $\mathbf{E}_s$) and cross polarized ($\mathbf{E}_i \perp \mathbf{E}_s$) geometry, respectively. Test measurements with lower laser power verified that there was no sample overheating during the experiments. The achieved spectral resolution was 1.9 cm^{-1} , while the preciseness in the peak positions was 0.35 cm^{-1} . First, polarized Raman spectra were collected in several scattering geometries (**Figure 3**) to detect all Raman-active phonon modes predicted by group theory in $P2/c$ as well as to check for possible peak position shifts due to LO-TO phenomena in plausible non-centrosymmetrical structures. Then, the sample was kept with the crystallographic c axis along the direction of propagation of the incident and scattered light (**Figure 3a**) and rotated about c at an angle φ from 0 to 180° in order to experimentally measure the dependence of the peak intensities on the orientation of the sample with respect to the polarization of the incident and scattered light; several spatial areas were probed that way to verify the reproducibility of the results. Next, different spatial areas were measured in the same scattering geometry, without rotating the sample, to probe if the sample is inhomogeneous with respect to the polarization intensity ratio. The measured spectra were temperature-reduced to account for the Bose-Einstein occupation factor and fitted with Lorentzians to determine the peak positions, widths and integrated intensities. Finally, a Raman mapping was performed in $Z(YX)Z$ scattering geometry (**Figure 3a**) on a relatively large sample area $600 \times 560 \text{ }\mu\text{m}^2$ with a step size $15 \times 15 \text{ }\mu\text{m}^2$.

Results and Discussion

Chemical analysis

According to the results from electron microprobe analyses there was no indication of chemical zonation or inhomogeneities within the experimental resolution. The average over 50 spatial areas measured in every 200 μm along a line reveals that our huebnerite sample consists only of W, Mn, and O without any traces of further elements (see **Supplementary 2**), giving a ratio of WO_3 : MnO = 75.7(6): 24.7(3). Thus possible chemical variations as the reason for the domain formation in huebnerite can be ruled out.

Synchrotron X-ray single crystal diffraction equipped with polarisation microscopy

At RT a thin crystal ($\sim 3 \times 1 \times 0.08 \text{ mm}^3$) shows a confined area in thickness of $\sim 360 \mu\text{m}$ with a relatively strong birefringence contrast of the small region D1 to the remaining crystal region D2 under a cross polarisation microscope (**Figure 2: left**). The typically perfect cleavage in $\{010\}$ is seen at the edge of the (001)-oriented DSC crystal. Hence, the sample orientation can be easily related to the crystallographic axes (**Figure 2: right**): the b axis is perpendicular to the cleavage form $\{010\}$, the a axis is parallel to the elongated direction of the crystal, and the c axis is parallel to the view direction. The dark region D1 (**Figure 2: left**) becomes bright when the cross Nicole is turned (**Figure 2: right**). This demonstrates that D1 and D2 are $\sim 180^\circ$ -oriented to each other about the crystallographic c axis, sharing the face (010). The D1 and D2 regions are not distinguishable under a normal parallel light microscope. Apart from the birefringence contrast of the small domain D1 to the rest area D2, the thin crystal sample looks like a single crystal plate. Hence, our sample can be regarded as a single crystal containing some cluster of microtwins and denoted as *domain-single-crystal (DSC)* hereafter.

SXRSD from the two single regions D1 and D2 revealed typical single crystal diffraction patterns (**Figure 4: left**). In contrary, diffraction from their boundary region DB resolved two reciprocal lattices which are superimposed about c^* (**Figure 4: right**). The b^* axis of the domain D1 is aligned to $-b^*$ of D2 with a misfit of 7° . This relation between D1 and D2 in the reciprocal space resembles 180° -in-plane hybrid ferroelectric (FE)-AFM domains [20, 21]. None of such hybrid microtwins are expected in MnWO_4 under ambient conditions without applying external fields [20 - 25]. The magnetic transition temperature (T_N) is too far to expect frozen clusters of magnetic domains in the paramagnetic state of huebnerite at RT. A twin formation due to the symmetry lowering is described in the next sections.

SXRSD with a huebnerite single crystallite

Reconstructed SXRSD data collected at 293 K and 100 K revealed a number of weak reflections visible in the reciprocal lattice plane $h0l$ with $l = \text{odd}$ (**Figure 5**), which indicates the absence of c gliding mirror plane. These reflections cannot originate from high order contamination (i.e. $\lambda/2$ and $\lambda/3$ harmonic reflections from the Si(111) monochromator) for several reasons: their occurrence is not limited to small 2θ ranges; the structure factor of the diffraction vector from Si(222) is zero, resulting in zero intensity valid for all $\lambda/2$ reflections. Such $\lambda/2$ reflections can abnormally appear if thermal motions of Si atoms with large anharmonic terms become profound at elevated temperatures above 523K [26 - 28]. The anharmonicity in thermal motions of Si is insignificant to our data as being collected below 300K; Noting a short wavelength of $\lambda = 0.5000(3)$ Å applied in the current SXRSD work at F1, a previous study of high order contamination at F1 confirmed no harmonic reflections from a silicon single crystal when using synchrotron X-ray wavelengths shorter than 1.30 Å [29]. In conclusion, the observation of weak hkl reflections with $l = \text{odd}$ indicate a symmetry breaking from $P2/c$.

Neutron single crystal diffraction and Renninger scan

NSCD data collected at 293 K also revealed several weak forbidden reflections (**Table 2**). Renninger scans of the reflection 301 at 3, 10, and 13 K confirmed that there are no multiple scattering effects including severe secondary extinction, exhibiting no periodic disappearance of its intensity (**Figure 6**). Further intensity measurements of the 301 reflection from 3 up to 88K indicated a slight temperature-dependent loss in intensity highlighted by linear extrapolation in **Figure 7**, where the 301 reflection is expected even above RT. Indeed the NSCD data at 293K agreed with the absence of c -gliding in the huebnerite structure. Even though the current X-ray and neutron diffraction study could not provide the exact phase transition temperature to $P2/c$, there is no doubt about that the RT structure exhibits a subgroup symmetry of $P2/c$.

Structure analysis of the nuclear structure of huebnerite

In all temperature ranges from 293 K down to 3 K huebnerite has the known monoclinic unit cell with a pseudo-tetragonal metric (**Table 1**). There are three maximal non-isomorphic subgroups of $P2/c$: Pc , $P2$, and $P\bar{1}$. If the new cell would have $c' = c/2$ both symmetry groups Pm or $P2/m$ could be considered. However such a reduction in the cell volume is not valid for

our case. Considering the primitive monoclinic lattice refined and the absence of *c*-gliding plane, the acentric polar symmetry *P2* was selected as the right space group symmetry for huebnerite. The intensity statistic of normalized structure factors E_h strongly supports the space group symmetry *P2* to be the right choice, as $\langle E_h^2 - 1 \rangle = 0.768$ in SXRSD data corresponds exactly the one predicting the presence of acentric space groups, far from $\langle E_h^2 - 1 \rangle = 0.968$ typical for the inversion-symmetric case. More importantly, regarding the fact that Patterson synthesis is very sensitive to the symmetry, Patterson synthesis was successfully performed in *P2* with SXRSD data to allow a reasonable structure model holding the $MnWO_4$ topology (**Table 3**). All those *c*-plane forbidden reflections are extremely weak in the SXRSD at 293 K (**Figure 5a**) but they are relatively well resolved in SXRSD data at 100 K (**Figure 5b**). Structure refinements to SXRSD data collected at 100 K and NSCD data collected at 293 K were executed in both *P2/c* and *P2* to find out structural reasons for the dissymmetrization. The origin of the model resulted from Patterson synthesis in *P2* was shifted about (0, 0.5, 0.25) to be the same as in *P2/c* for easy comparison. Pairs of atom sites in *P2* which are symmetrically equivalent in *P2/c* are denoted as atomic site name with the subscripts a and b (**Table 3 – 8**; **Figure 8**).

The structure at 293 K refined in *P2* shows two basic differences with respect to *P2/c*: the sites Mn_a and Mn_b in *P2* are differently shifted from their position equivalent in *P2/c* (**Table 4**), pointing that they are symmetrically independent on each other (**Table 5**). This is valid for all atom pairs in *P2*. On the other hand, both Mn_a and Mn_b are shifted in the positive *b* direction from their position equivalent in *P2/c* while all other atoms are in the opposite *b* direction (**Figure 9a**). The oxygen atom pairs $O1_a-O1_b$ and $O2_a-O2_b$ in *P2* show such alternating shifts in the *a*- and *c*-direction (**Figure 9b and -9c**) that their average sites are near to the respective equivalent sites O1 and O2 in *P2/c* (**Table 4**). The net atomic shift Δy in the polar *b* direction in *P2* explains the reason for the symmetry lowering from *P2/c* down to *P2*. The dipole moments derived from very small Δy values (**Table 5**) may be too weak to be detected in macroscopic polarisation measurements. However, based on the structure analysis of NSCD -data collected at 293 K, the nuclear structure should have a subtle electric polarization at RT. The volume ratio of D1 and D2 was refined to be 0.16 (4): 0.84(4) in the large single crystal (0.14 x 0.66 x 0.79 mm³) used in NSCD.

Structure refinements to the SXRSD data collected at 100 K were performed by fixing one atomic position, i.e. W_a in *P2* was fixed to the coordinate for W site in *P2/c* (**Table 6**). Otherwise the correlation between the atomic parameters for W atoms and O exceeded 90%,

due to the high X-ray scattering powder contrast between W and O. In the case of neutron diffraction, the average coherent neutron scattering length W ($b_c = 4.86(2)$ fm) is lower than that of O ($b_c = 5.803(4)$ fm) [30]. It should be reminded that the electron density distribution is determined by X-ray diffraction but the arrangement of the atomic nuclei by neutron diffraction. Therefore, care should be taken when comparing the results from both techniques. For the dominant X-ray scatterer W, which site was constrained, we supposed the structure analysis with the SXRSD data at 100 K did not show a clear distinction between $P2/c$ and $P2$ when considering refined atomic positions (**Table 6**) or thermal atomic displacement parameters (**Table 7**). As a consequence, the evaluated atomic shifts in the polar subgroup from those in the centric super group are insignificant (**Table 8**) although the data collection temperature was much lower than the case for NSCD data at 293K. At most, the refined structure at 100 K displays a distinguishable atomic pair O_{2a} - O_{2b} displaced independently from each other (**Table 8**). From structure refinements to the SXRSD data at 100K from a small crystallite ($0.08 \times 0.07 \times 0.02$ mm³) the volume ratio of D1 and D2 was determined to be 0.05 (2): 0.95(2).

Having the polar symmetry $P2$ for each single domain, the two domains D1 and D2 are uniaxially oriented in the opposite b axis to form 180°-in-plane ferrodistorive (FD) domains. In **Figure 10** the atomic arrangements in each single domain structure are illustrated with atomic shifts in the b direction from respective equivalent positions in $P2/c$. At the domain boundary the non-polar symmetry $P2/c$ can be recovered. As a result of an antiferroelectric arrangement of domains pairs parallel to the polar axis b , the polar effect would be further suppressed at the domain boundary. From the crystallographic point of view, the formation of 180°-in-plane FD domains in hubnerite is regarded as a consequent appearance of the hidden polar site C_2 for Mn atoms [11]. This observation completely contradicts to numerous studies convincing that: 1. the nuclear structure of $MnWO_4$ crystallizes in $P2/c$ exclusively, and 2. the electric polarisation is induced only by the helix-like antiferromagnetic order in the AFM2 state [8] but not in the PM state of huebnerite. Concerning its relevant multiferroic property, the magnetically induced electric polarisation around Mn_a - $O1_a$ - Mn_b - and Mn_a - $O1_b$ - Mn_b -triangles (**Figure 8**) has to be reinvestigated due to the existence of intrinsic dipole moments after breaking the bulk symmetry.

Raman spectroscopy

Raman-scattering experiments were performed on the DSC sample. According to group theory, MnWO_4 with $P2/c$ symmetry exhibits 18 Raman active modes ($8A_g + 10B_g$) and 15 IR-active modes ($7A_u + 8B_u$) [31]. The non-zero polarizability-tensor components of A_g modes are α_{xx} , α_{yy} , α_{zz} , and α_{xz} (unique axis b), whereas those of B_g modes are α_{xy} , and α_{yz} . Polarized Raman spectra in different scattering geometries are shown in **Figure 11**. As can be seen, all modes predicted by group theory are detected at room temperature. The strong A_g mode at 884.8 cm^{-1} produces an intense Raman peak in the cross polarized spectra, similar to the reported data on synthetic MnWO_4 single crystals [32]. Also, the positions of the Raman peaks measured in this study match very well the previously reported data [32 - 34], i.e. the overall Raman signature of our natural MnWO_4 sample is the same as that of synthetic single crystals. In the case of lower-symmetry monoclinic phase, if the structure is non-centrosymmetrical, e.g. $P2$ or Pc , all phonon modes will become simultaneously Raman- and IR-active and additional Raman peaks may be observed. We have detected two additional Raman signals below 890 cm^{-1} in cross polarized spectra (**Figure 11**), but their positions do not match well the reported IR-peak positions of MnWO_4 [35]. The additional Raman peaks near 642 and 784 cm^{-1} most probably arise from combination modes of type $A_g + B_g$ or $A_u + B_u$. However, a subtle peak shift towards higher wavenumbers of all A_g modes measured in $\bar{Z}(YY)Z$ with respect to their positions in the other scattering geometries was observed (**Figure 12**). Such orientation dependence of the phonon wavenumbers ω is typical of uniaxial or biaxial non-centrosymmetric crystals [36]. Depending on the direction of the phonon wavevector $\mathbf{q}$ with respect to the direction of phonon polarization $\boldsymbol{\mu}$, a certain phonon mode can appear as transverse optic TO ($\mathbf{q} \perp \boldsymbol{\mu}$) or longitudinal optic LO ($\mathbf{q} \parallel \boldsymbol{\mu}$) with $\omega_{LO} > \omega_{TO}$. In the case of polar crystal classes polar modes that are fully symmetrical irreducible representations have polarization $\boldsymbol{\mu}$ along the direction of the net polarization $\mathbf{P}$, and the corresponding LO-TO wavenumber difference is indicative of the magnitude of $\mathbf{P}$. The wavenumber shift observed in the natural MnWO_4 single crystal studied here is between 0.6 and 1 cm^{-1} , i.e. it approaches the experimental precision of our set-up. However it is firm for all peaks assigned to A_g in $P2/c$ and it is not observed for the B_g -type peaks, indicating that the orientation dependence of the A_g -type peak wavenumbers is not an experimental artifact. The phonon polarization $\boldsymbol{\mu}$ of A modes in $P2$ is along b , whereas that of A' modes in Pc is in the plane perpendicular to b . Therefore, for $P2$ one should expect to observe LO shift in $\bar{Y}(ZZ)Y$. Such a shift was not experimentally observed, indicating the rather small unit-cell

polarization of $P2$. This is in accordance to extremely weak c -plane forbidden reflections which have been overlooked in numerous studies of MnWO_4 .

The Raman data however suggest that the structure possess a net polarization with a non-zero z -component. Since the diffraction data rule out Pc as a possible space group, the Raman results can be explained assuming a further lowering of the symmetry to a triclinic $P1$ space group at the local length scale of a few unit cells. It is worth noting that a triclinic phase of MnWO_4 has been observed at high pressures but the structure was refined in non-polar symmetry $P\bar{1}$ [37, 38]. This high-pressure phase characteristically gives rise to the strongest and highest frequency A_g mode at 871 cm^{-1} at 34GPa [37]. In our case, net polarization along the crystallographic c axis might have appeared during the formation of the studied natural single crystal as a result of strain gradient related to the existence of a complex twin pattern. Indeed, the variations of the relative Raman intensities in spectra measured from different spatial areas indicate structural inhomogeneity and the existence of misaligned domains (**Figure 13**). The comparison of the intensity ratio I_{yy}/I_{xy} for a pair of A_g and B_g modes measured in different spatial spots with the angular dependence of $I_{yy}(A_g)/I_{xy}(B_g)$ shown in **Figure 13** reveals that the mismatch of the domain orientation within the plane perpendicular to the c axis is up to 20° . The high degree of structural inhomogeneity is also demonstrated by the Raman mapping in **Figure 14**, confirming the presence of microtwins.

Conclusion

The birefringence contrast over microtwins in a natural huebnerite crystal allowed accurate localization of measuring data points in synchrotron single crystal X-ray diffraction and Raman spectroscopy to show ferrodistorive domains in the PM state at RT. The most important finding from extended single crystal diffraction studies is the new polar space group symmetry $P2$ for the average nuclear structure of huebnerite while Raman data suggest triclinic distortion on the local scale. In spite of the small difference between two Mn sites refined independently in $P2$, the resulting weak polarity in the nuclear structure has two important consequences: (1) Formation of $\sim 180^\circ$ -in-plane domains at RT, as shown in the current study. The room-temperature net electrical polarization in the studied huebnerite single crystal might have been induced by strain inhomogeneities related to the microtwins, suggesting a possible way to tailor the properties of MnWO_4 by heavy doping and subsequent chemically-induced elastic-stress fields; (2) New magnetic modulations below T_N . All three AFM phases (AFM1, AFM2, and AFM3) have been thoroughly studied by neutron single-

crystal diffraction, revealing new magnetic structure models that will be reported elsewhere with results from magnetic susceptibility analyses.

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Table 1 Experimental conditions and agreement factors of refined structure model in *P2* obtained from single crystal neutron diffraction and synchrotron X-ray diffraction analyses.

Hubnerite (MnWO₄)	Neutron	X-ray
Crystal size [mm ³]	7.9 x 6.6 x 1.4	0.08 x 0.07 x 0.02
Calculated density [g/cm ³]	7.23	7.25
Temperature [K]	300	100
Lattice parameters	a = 4.831(15) Å b = 5.756(3) Å c = 4.998(3) Å β = 91.4(2)° V = 139.0(8) Å ³	a = 4.824(1) Å b = 5.754(1) Å c = 4.994(2) Å β = 91.09(2)° V = 138.60(1) Å ³
Wavelength [Å]	1.043(1)	0.5000(3)
Monochromator	Cu(422)	Si(111)
Absorption coefficient [μm ⁻¹]	0.026	18.382
Number of reflections	969	37927
Maximal sin(θ)/λ observed	0.712	1.429
2θ _{min} ; 2θ _{max}	5.19°; 47.93°	2.49°; 45.59°
Redundancy	1.9	7.78
R _{ini} after merging (Poisson)	0.04 for 405	0.039 for 4875
h k l range	-6 < h < 3; -8 < k < 8; -3 < l < 6	-13 < h < 13; -16 < k < 16; -11 < l < 10
Condition for unobserved reflections	I > 3σ(I);	I > 3σ(I);
Number of reflections used in the final refinement (F _o -F _c >5σ(F))	399	3654
Number of parameters	26	57
Absorption	none	Semi-empirical [14]
Extinction	none	none
R for against F	0.034	0.032
wR for against F ²	0.079	0.081
Goodness-of-Fit (S)	2.54	2.36
Shift/σ _{max} ; Shift/σ _{meam}	0.0016; 0.0007	0.0198; 0.0040
(Δ density) _{max}	0.51	1.41
(Δ density) _{min}	-0.64	-1.80
Volume ratio of Domain1: Domain2	0.84(4): 0.16 (4)*	0.95(2): 0.05(2)

$$R = [\sum |F_o| - |F_c|] / \sum |F_o|$$

$$wR = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_c^2]^{1/2}$$

$$\text{Weighting } w = 1 / (\sigma^2(I) + 0.0004 \cdot I^2)$$

$S = [\sum w(F_o^2 - F_c^2)^2 / (m - n)]^{1/2}$, where F_o and F_c are observed and calculated structure factors, respectively, m is number of reflections, and n is number of parameters.

*Twin matrix = (-0.9925, -0.1453, 0.0414; 0.1022, -0.9926, -0.0021; 0 0 1)

Table 2 Relative strong $h0l$ ($l = \text{odd}$: forbidden to $P2/c$) reflections obtained from neutron single crystal diffraction at 293 K are given on the left side with intensity (I), counting error of intensity ($\sigma(I)$), and respective ratios ($I/\sigma(I)$). On the right side, such forbidden reflections collected by synchrotron X-ray diffraction at 293 and 100 K are compared with their $I/\sigma(I)$ values.

Neutron single crystal diffraction at 293K				Synchrotron X-ray diffraction						
h	k	l	I	$\sigma(I)$	I/ $\sigma(I)$	h	k	l	I/ $\sigma(I)$, 293K	I/ $\sigma(I)$, 100K
1	0	1	458.8	85.4	5.4	1	0	1	4.8	8.9
-1	0	1	497.7	71.0	7.0	2	0	1	4.5	7.2
-2	0	1	421.4	90.4	4.7	3	0	1	2.9	2.0
2	0	1	245.6	74.0	3.3	4	0	1	2.0	4.3
1	0	3	830.8	96.2	8.6	-1	0	1	2.9	3.8
1	0	5	975.1	157.1	6.2	-2	0	1	13.3	10.1
2	0	3	544.4	92.6	5.9	-3	0	1	3.3	3.2
3	0	3	444.8	106.4	4.2	-4	0	1	2.7	1.8

Table 3 Structure model obtained from Patterson synthesis in $P2$ using synchrotron X-ray single crystal diffraction data of hubnerite at 100K

Atom site	x	y	z
Mn _a	0.5	0.3118	0
Mn _b	0.5	0.6882	0.5
W _a	0	0.8198	0
W _b	0	0.1802	0.5
O1 _a	-0.2532	0.6221	-0.1464
O1 _b	0.2514	0.3779	-0.3531
O2 _a	0.2094	0.10086	-0.8125
O2 _b	-0.2112	0.8991	0.3130

Table 4 Atomic parameters refined in the space group *P2* and its supergroup *P2/c* (neutron single crystal data, 293 K).

P 2/c				P2				
Atom site	x	y	z	Atom site	x	y	z	0.001 x U_{iso} [$\text{\AA}^2$]
Mn	0.5	0.8152(3)	0.25	Mn _a	0.5	0.8160(5)	0.25	7.0(7)
				Mn _b	0.5	-0.8128(6)	0.75	8.5(7)
W	0	0.3197(2)	0.25	W _a	0	0.3185(4)	0.25	5.5(6)
				W _b	0	-0.3215(5)	0.75	6.0(6)
O1	-0.2516(2)	0.1257(1)	0.1080(2)	O1 _a	-0.2426(4)	0.1241(4)	0.1023(4)	8.3(3)
				O1 _b	-0.2568(3)	-0.1268(4)	0.6136(4)	8.5(3)
O2	-0.2111(2)	0.6017(1)	0.0554(2)	O2 _a	-0.2163(4)	0.5979(3)	0.0517(4)	10.8(4)
				O2 _b	-0.2063(3)	-0.6052(3)	0.5601(4)	5.8(3)

Table 5 Comparison of atomic shifts from atom positions of the hubnerite structure in *P2/c* to the respective equivalent sites in *P2* along with relative shifts of atom pairs (neutron single crystal data, 293K).

Atom site	Shift in x	Shift in y	Shift in z	Relative shift of atom pair	Δx	Δy	Δz
Mn _a	0	0.0008	0	Mn _a -Mn _b	0	0.0016	0
Mn _b	0	0.0024	0				
W _a	0	-0.0012	0	W _a -W _b	0	0.0006	0
W _b	0	-0.0018	0				
O1 _a	0.0090	-0.0016	-0.0057	O1 _a -O1 _b	0.0142	0.0005	0.0113
O1 _b	-0.0052	-0.0011	-0.0056				
O2 _a	-0.0052	-0.0038	-0.0037	O2 _a -O2 _b	0.0100	0.0003	0.0084
O2 _b	0.0048	-0.0035	0.0047				

Table 6 Atomic parameters refined for the space group *P2* and its super group *P2/c* (synchrotron X-ray single crystal data, 100K).

P 2/c				P2				
Atom site	x	y	z	Atom site	x	y	z	U_{iso} [$10^{-3} \text{\AA}^2$]
Mn	0.5	0.81471(6)	0.25	Mn _a	0.5	0.8149(1)	0.25	5.9(1)
				Mn _b	0.5	-0.8151(1)	0.75	6.0(1)
W	0	0.31974(1)	0.25	W _a	0	0.31974*	0.25	4.73(3)
				W _b	0	-0.31993(2)	0.75	3.93(3)
O1	-0.2519(3)	0.1253(2)	0.1079(4)	O1 _a	-0.2511(6)	0.1257(4)	0.1065(9)	8.8(6)
				O1 _b	-0.2507(5)	-0.1257(4)	0.6071(7)	5.1(5)
O2	-0.2101(3)	0.6017(2)	0.0610(4)	O2 _a	-0.2121(6)	0.6010(5)	0.0570(8)	5.8(5)
				O2 _b	-0.2081(6)	-0.6044(4)	0.5580(7)	7.7(5)

* fixed due to high correlation (> 0.9) with y coordinates of oxygens

Table 7 Anisotropic harmonic atomic displacements (ADPs), refined in *P2* (synchrotron X-ray single crystal data, 100 K).

Atom site in <i>P2</i>	Harmonic ADPs [$10^{-3}\text{\AA}^2$]					
	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Mn _a	6.2(1)	5.9(1)	5.5(4)	0	-0.01(2)	0
Mn _b	4.7(1)	7.4(2)	6.0(3)	0	0.08(2)	0
W _a	5.33(4)	3.13(3)	5.74(9)	0	0.25(5)	0
W _b	3.31(3)	5.99(4)	2.55(7)	0	0.07(4)	0
O1 _a	7.1(6)	5.8(5)	13.6 (1.7)	-2.0(4)	0.0(8)	2.1(6)
O1 _b	5.1(4)	7.4(5)	2.7(1.2)	0.2(4)	-1.5(6)	1.3(5)
O2 _a	6.1(5)	8.8(5)	2.5(1.2)	0.9(5)	-0.9(6)	-0.8(6)
O2 _b	6.4(5)	5.0(4)	11.7(1.3)	-0.6(4)	3.1(7)	-1.5(6)

Table 8 Comparison of atomic shifts from atom positions of the hubnerite structure in *P2/c* to the respective equivalent sites in *P2* along with relative shifts of atom pairs (X-ray single crystal data, 100 K).

Atom site	Shift in x	Shift in y	Shift in z	Relative shift of atom pair	Δx	Δy	Δz
Mn _a	0	0.0002	0	Mn _a -Mn _b	0	0.0006	0
Mn _b	0	-0.0004	0				
W _a	0	0	0	W _a -W _b	0	0.0002	0
W _b	0	-0.0002	0				
O1 _a	0.0008	0.0004	-0.0014	O1 _a -O1 _b	0.0004	0.0008	0.0006
O1 _b	0.0012	-0.0004	-0.0008				
O2 _a	-0.0020	-0.0007	-0.0040	O2 _a -O2 _b	0.0040	0.0020	0.0010
O2 _b	0.0028	-0.0027	-0.0030				

Figure captions

Figure 1 Nuclear structure of huebnerite in $P2/c$.

Figure 2 Birefringence contrast between micro twins is visible within a single huebnerite crystal under polarisation microscope. This allows for accurately localizing the probed data points in single crystal X-ray diffraction.

Figure 3 Sketch of the scattering geometries (in Porto's notation) of collected polarized Raman spectra; a , b , and c are the monoclinic crystallographic axes (unique axis b), a^* is perpendicular to the (b,c) plane. $\mathbf{E}_i$ and $\mathbf{E}_s$ denote the directions of the polarization of incident and scattered light, X , Y , and Z are along a^* , b , and c , respectively.

Figure 4 Reconstructed reciprocal $hk0$ planes obtained X-ray single crystal diffraction from a single domain region (left) and from the domain boundary (right). The former one shows typical single crystal pattern while the latter case corresponds to two reciprocal lattices superimposed about c^* with a misfit of 173° .

Figure 5 Reciprocal $h0l$ plane reconstructed from synchrotron single crystal X-ray diffraction data collected at 293 K (a) and 100 K (b). There are numbers of weak $h0l$ ($l = \text{odd}$) reflections which are forbidden to $P2/c$.

Figure 6 Renninger scans of the reflection 301 of huebnerite at 3, 10, and 13 K on the neutron single crystal diffractometer RESI at FRMII.

Figure 7 Variable temperature Renninger scans of the reflection 301 between 3 and 88 K using neutron single crystal diffraction predict the presence of this reflection still at 300 K.

Figure 8 Local configurations of independent atomic sites in the huebnerite structure in $P2$ from different points of view.

Figure 9 Atomic shifts in y (a), x (b), and z (c) in the polar space group $P2$ with respect to their equivalent positions in $P2/c$, resulted from structure refinements using neutron single crystal data at 293 K.

Figure 10 Schematic presentation of polar atomic shifts (arrows) from the respective equivalent sites (spheres) in $P2/c$ at the boundary of two 180° -in-plane micro twins.

Figure 11 Room-temperature polarized Raman spectra of MnWO_4 . The symmetry of the phonon modes is given in $P2/c$. The peak positions were obtained by fitting the spectra with Lorentzians and taking the average over all measured scattering geometries, excluding $\bar{Z}(YY)Z$ that showed a subtle peak shift towards higher wavenumbers for all A_g modes. The standard deviations for all peak positions were less than 0.4 cm^{-1} . The arrows mark two additional Raman signals seen in $\bar{Z}(XY)Z$ as shoulders of the neighbouring peaks.

Figure 12 Raman peak near 884.8 cm^{-1} arising from fully symmetrical irreducible representation: A_g in $P2/c$, A in $P2$, or A' in Pc . The peak position should remain the same in all scattering geometries if the structure symmetry is $P2/c$ but may shift in the case of non-centrosymmetric structure due to LO-TO phenomena.

Figure 13 Angular dependence of the intensity ratio I_{yy}/I_{xy} for two A_g/B_g pairs of Raman peaks: $A_g(129.6 \text{ cm}^{-1})/B_g(90.5 \text{ cm}^{-1})$ and $A_g(698.2 \text{ cm}^{-1})/B_g(674.1 \text{ cm}^{-1})$. The solid black symbols represent data collected from the same spatial area with initial scattering geometry $\bar{Z}(XX)Z$ for $\phi = 0$ (see Fig.4a) and rotating the sample about the c axis at angle ϕ . Open red symbols represent experimental data collected from different spatial areas, keeping the sample in the same orientation ($\phi = 0$) with respect to the polarization of incident and scattering light and plotted versus ϕ in a way to match the intensity ratio values of the data set collected on rotation. The lines represent the theoretical angular dependence of the intensity ratio for a monoclinic system $\frac{I_{yy}}{I_{xy}} \propto \frac{(\alpha_{xx} \sin^2 \phi + \alpha_{yy} \cos^2 \phi)^2 + \alpha_{xy}^2 \sin^2 2\phi}{(\alpha_{yy} - \alpha_{xx})^2 \sin^2 2\phi / 4 + \alpha_{xy}^2 \cos^2 2\phi}$, where α_{ij} are the Raman polarizability tensor components in a Cartesian system with X , Y , and Z , parallel to a^* , b , and c , respectively (see **Figure 3**).

Figure 14 Optical reflectance image of the area probed by Raman spectroscopy, Raman mapping on the ratio $I(698.2)/I(674.1)$ measured in $\bar{Z}(YX)Z$ scattering geometry, and example Raman scattering in the spectral range used for mapping. The use of other intensity ratios $I(A_g)/I(B_g)$ generate the same Raman map.

Highlights

- Neutron and X-ray diffraction analyses reveal the polar symmetry $P2$ for MnWO_4
- Raman mapping shows ferrodistorive domains in its RT paramagnetic state
- These observations are explained by the hidden polar site C_2 for Mn atoms

Figure

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5a

Huebnerite 293K
Scale: 0.2% I_{max}

Figure 5b

Huebnerite 100K
Res: 0.0484 Scale: 0.20% I_{max}

Figure 6

Figure 7

Figure 8

Figure 9a

Figure 9b

Figure 9c

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Schematic presentation of polar atomic shifts (arrows) in $P2$ from the respective equivalent sites (spheres) in $P2/c$ at the boundary of two 180° -in-plane micro twins