INORGANIC COMPOUNDS

Oxyhalides: A new class of high-T_C multiferroic materials

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Magnetoelectric multiferroics have attracted enormous attention in the past years because of their high potential for applications in electronic devices, which arises from the intrinsic coupling between magnetic and ferroelectric ordering parameters. The initial finding in TbMnO$_3$ has triggered the search for other multiferroics with higher ordering temperatures and strong magnetoelectric coupling for applications. To date, spin-driven multiferroicity is found mainly in oxides, as well as in a few halogenides. We report multiferroic properties for synthetic melanothallite Cu$_2$OCl$_2$, which is the first discovery of multiferroicity in a transition metal oxyhalide. Measurements of pyrocurrent and the dielectric constant in Cu$_2$OCl$_2$ reveal ferroelectricity below the Néel temperature of ~70 K. Thus, melanothallite belongs to a new class of multiferroic materials with an exceptionally high critical temperature. Powder neutron diffraction measurements reveal an incommensurate magnetic structure below T_N, and all magnetic reflections can be indexed with a propagation vector [0.827(7), 0, 0], thus discarding the claimed pyrochlore-like "all-in–all-out" spin structure for Cu$_2$OCl$_2$, and indicating that this transition metal oxyhalide is, indeed, a spin-induced multiferroic material.

INTRODUCTION

Magnetoelectric multiferroics with spiral magnetic structures are one of the central topics in contemporary condensed matter physics, inorganic chemistry, and materials science (1–8). These recently found multiferroics are expected to be the key ingredients for future magnetoelectrical or magneto-optic memory devices with enhanced efficiency. Generally, multiferroic materials simultaneously exhibit at least two ferroic ordering parameters. The simultaneous appearance of magnetic order and ferroelectricity is especially of interest for applications (9, 10). In multiferroics with a spiral magnetic structure, ferroelectricity is induced by the spin structure itself. Thus, large magnetoelectric effects can be expected for these novel multiferroics, which would allow for an efficient tuning of the ferroelectric polarization by applying an external magnetic field and, vice versa, the control of the magnetization with an applied electric field. These promising findings have triggered the search for new high-performance multiferroic materials in the past years. Besides a small induced electric polarization, the low transition temperatures (usually less than 40 K) especially hamper the use of multiferroics for applications.

A spiral magnetic structure appears when a competition of (next) nearest neighboring exchange interactions can be observed in the system. This effect is also called frustration. The lack of inversion symmetry of noncentrosymmetric spiral spin structures also alters the charge distribution via spin-orbit interactions. Thus, a ferroelectric polarization is created, which is proportional to $e_{i,j} \times (S_i \times S_j)$ in systems with a cycloidal magnetic structure according to the inverse Dzyaloshinskii-Moriya interaction mechanism (11–13) or proportional to $(S_i \cdot e_{i,j})S_i - (S_j \cdot e_{i,j})S_j$ in systems with a helical spin structure according to the Arima model (14, 15), with S_i being the spin at site i and $e_{i,j}$ being the vector between sites i and j.

Transition metal (TM) oxychlorides MOCl (M = Sc, Ti, V, Cr, Fe) are quasi–two-dimensional (2D) systems that exhibit interesting electronic and magnetic properties (16–22). Up to M = Fe, these 3d TM oxychlorides crystallize in the layered FeOCl structure with space group $Pmmn$. In the FeOCl structure, the trivalent TM ions are octahedrally coordinated by four oxygen atoms and two chlorine ions and arranged into bilayers that are separated by the large Cl ions. For M = Cu, on the other hand, the TM oxychlorides crystallize in a different melanothallite structure with space group $Fddd$ (see Fig. 1). As in the FeOCl structure, the copper ions are octahedrally coordinated by oxygen and chlorine ions. Yet, in the melanothallite structure, the TM ion is divalent and coordinated by four chlorine and two oxygen ions with two Cl ions located in the apical positions and with two Cl and two O ions in basal positions. Moreover, the structure is not quasi-2D anymore. Instead, edge-sharing CuO$_2$Cl$_2$ squares form chains running in the [1 1 0] and [±1 ∓1 0] directions that are interconnected via a common O ion in the c direction as well (see Fig. 1). Thus, the O ions are tetrahedrally coordinated by four Cu ions forming a corner-sharing 3D network, and the Cl ions are located in the free space between these OCu$_4$ tetrahedra.

Cu$_2$OCl$_2$ exhibits long-range antiferromagnetic order below T_N ~70 K, as observed in muon spin rotation/relaxation (μSR) experiments (23). Recently, a nuclear magnetic resonance (NMR) study claimed that melanothallite is a pyrochlore-like antiferromagnet with the so-called "all-in–all-out" spin structure (24). Above room temperature, an anomalous negative thermal expansion of the b lattice constant, has been reported (25). This anomalous thermal expansion above room temperature is induced by a change of the angle between the chains of edge-sharing CuO$_2$Cl$_2$ squares running in the [1 1 0] and [−1 1 0] directions. At room temperature, this angle amounts to 76°, and upon heating, it increases towards 90° (25).

RESULTS

Magnetism and magnetoelastic coupling

Figure 2A shows the magnetic susceptibility of our synthetic melanothallite single crystals. As can be seen, the magnetic ordering temperature T_N amounts to ~70 K in our Cu$_2$OCl$_2$ samples, which is in

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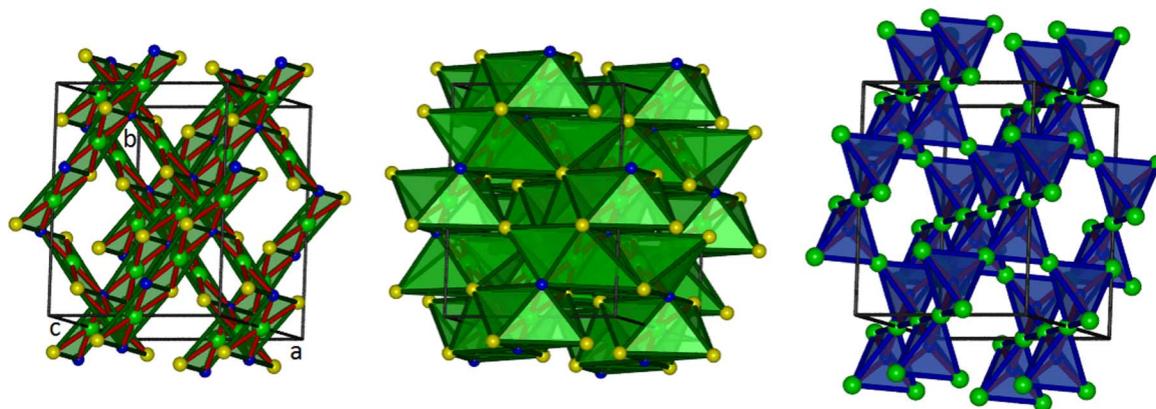*Corresponding author. Email: Alexander.Komarek@cpfs.mpg.de

Fig. 1. The crystal structure of Cu$_2$OCl$_2$. Green, yellow, and blue atoms denote Cu, Cl, and O ions, respectively. The structure consists of CuO$_2$Cl$_2$ square chains running in the [1 1 0] and [±1 ∓1 0] directions (*left*). The squares are the basal planes of strongly distorted CuO$_2$Cl$_4$ octahedra (green) with apical Cl ions that are farther away from the Cu ions (*middle*). Alternatively, the structure can be described as a network of OCu$_4$ tetrahedra (*right*).
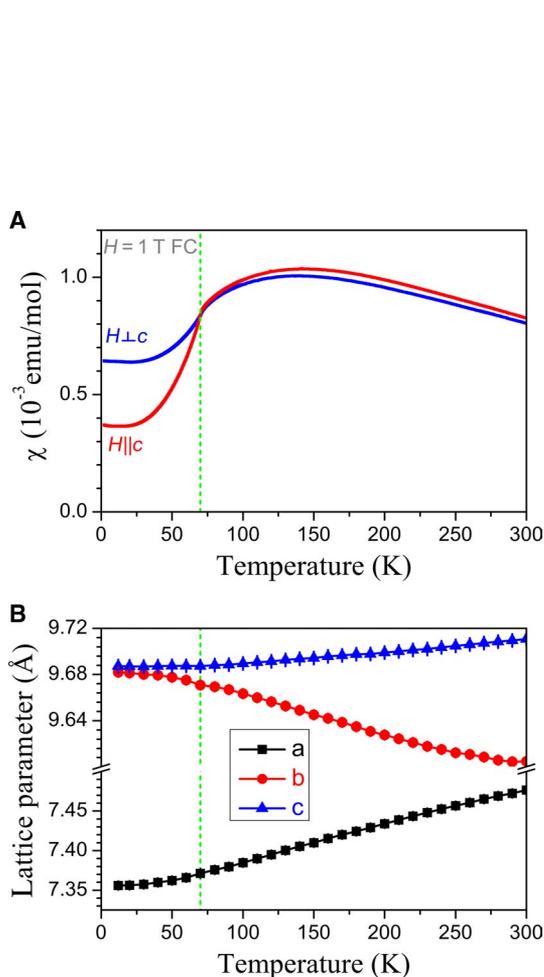
Fig. 2. Magnetism and magnetoelastic coupling in Cu$_2$OCl$_2$. (**A**) Magnetic susceptibility of Cu$_2$OCl$_2$ with T_N ~70 K. A field of 1 T was applied perpendicular to the *c* direction (blue) and parallel to the *c* direction. (**B**) Temperature dependence of the lattice parameters of Cu$_2$OCl$_2$.
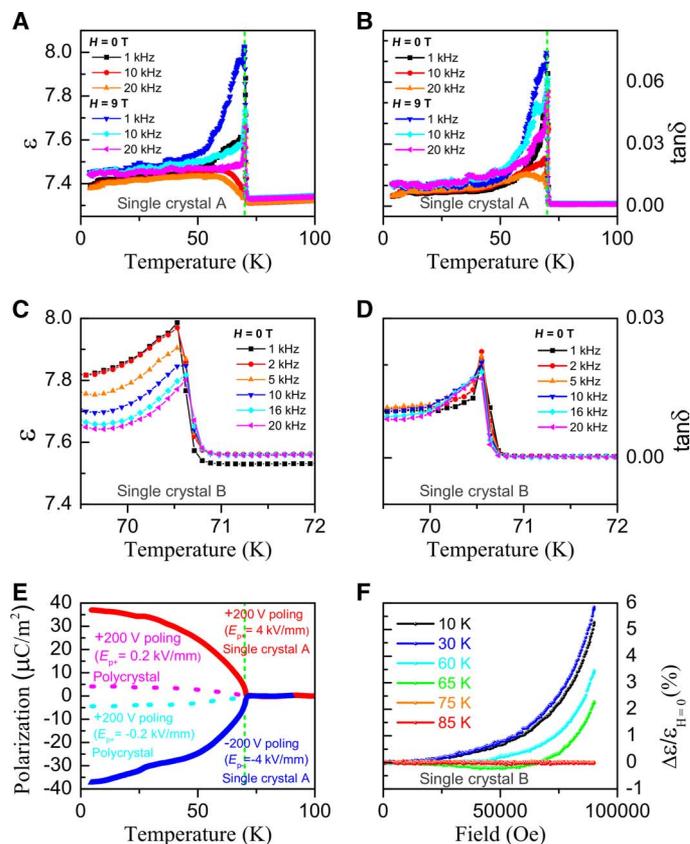

Fig. 3. Evidence of multiferroicity in Cu$_2$OCl$_2$. (**A** to **D**) Dielectric constant ε(T) and dielectric loss tanδ(T) of Cu$_2$OCl$_2$ single crystals measured in the *c* direction at different frequencies in zero field and also at 9 T. (**E**) The temperature dependence of the zero-field electric polarization in Cu$_2$OCl$_2$, measured with applied positive and negative poling electric fields. The dotted curves are the corresponding values for a polycrystalline (pellet) sample. (**F**) The coefficient (ε(H) − ε(H = 0))/ε(H = 0) as a function of magnetic field shows the magnetodielectric effect in Cu$_2$OCl$_2$ for different temperatures (measured with 10 kHz).

agreement with previous studies (26). The derivative of χ is shown in the Supplementary Materials. Figure 2B shows the lattice parameters of Cu_2OCl_2 as a function of temperature. At the lowest temperatures, the b and c lattice parameters become identical (within the error bars). This indicates that the OCu_4 tetrahedra become more symmetric roughly below T_N. Either this could be caused by magnetoelastic coupling or the system could start to order magnetically once the OCu_4 tetrahedra are more symmetric.

Dielectric properties and magnetodielectric effect

The temperature dependence of the zero-field dielectric constant ε and the dielectric loss $\tan\delta$ measured in the c direction are shown in Fig. 3 (A to D). For all measurement frequencies (1 to 20 kHz), an anomalous λ-like peak can be observed in ε and $\tan\delta$ at T_N, which is indicative of a ferroelectric transition. Artificial signals can be excluded as a result of the frequency invariance in our observations (see Fig. 3, C and D). These findings were also reproducible for several different single crystals that we measured as well as for our polycrystalline pellets. Furthermore, our pyrocurrent measurements on Cu_2OCl_2 single crystals reveal a ferroelectric polarization P in the c direction that appears below T_N (see Fig. 3E), which amounts to roughly $40~\mu C/m^2$ at the lowest temperature. A measurement on polycrystalline pellets yields values that are one order of magnitude smaller, which confirms the ferroelectric polarization in the c direction. Moreover, P can be inverted by opposite poling, thus unambiguously confirming the ferroelectric nature of Cu_2OCl_2. Therefore, the TM oxyhalide Cu_2OCl_2 is multiferroic, and oxyhalides with a melanothallite structure turn out to be a new class of multiferroic materials.

To study the magnetoelectric coupling in Cu_2OCl_2, we measured the magnetodielectric effect. In Fig. 3F, the coefficient $(\varepsilon(H) - \varepsilon(H=0))/\varepsilon(H=0)$ is shown as a function of external magnetic field for different temperatures. As can be seen, a sizeable magnetodielectric effect is only found in the multiferroic phase below T_N. The field dependence observable in the magnetically ordered phase is also indicative of a magnetic origin for ferroelectricity in Cu_2OCl_2.

Spin structure

For an understanding of the origin of the magnetoelectric coupling and multiferroicity in Cu_2OCl_2, knowledge of its magnetic structure is required. To date, only μSR studies report long-range magnetic orders below T_N with first indications for frustration effects in the system (23). Furthermore, an NMR study suggested an all-in–all-out spin structure for Cu_2OCl_2 (24). Here, we studied the magnetic structure of synthetic melanothallite by means of powder neutron diffraction measurements using the D1B diffractometer. Below T_N, three incommensurate magnetic reflections appear (see Fig. 4A). These reflections can all be indexed with the propagation vector [0.827(7), 0, 0]. Hence, we can exclude the claimed pyrochlore-like $k = 0$ all-in–all-out spin structure (24). According to the symmetry analysis performed with the FullProf program package, there are four possible irreducible representations $Irep_1$-$Irep_4$. A successful magnetic structure refinement of our powder neutron diffraction data is possible with a spin structure based on the irreducible representation $Irep_2$ and moments within the ac plane (see Fig. 4B). The ordered magnetic moment amounts to $1.0(2)~\mu_B$ and points in the direction of Cu-O-Cu chains formed by the OCu_4 tetrahedra running in the $[\pm1~0~1]$ direction (see also Fig. 1, right). Also, our susceptibility measurements on oriented single crystals, shown in Fig. 2A, would be in agreement with the $Irep_2$ spin structure shown

in Fig. 4 (right). Considering the fact that we are dealing with a local moment magnetic Mott insulator, our neutron results point toward the presence of a spiral magnetic structure in synthetic melanothallite rather than a spin structure where the moment sizes are modulated. These observations, together with the coincidence of the magnetic and ferroelectric transition temperatures in Cu_2OCl_2, indicates spin-driven ferroelectricity in melanothallite—either via the Arima model or via the inverse Dzyaloshinskii-Moriya interaction mechanism.

DISCUSSION

To date, multiferroic properties have been observed in binary copper oxide CuO, also known as tenorite (27), as well as in binary copper halogenides such as $CuBr_2$ (28). Multiferroicity occurs below 73.5 K in $CuBr_2$ (28), whereas it occurs only within a very narrow temperature range of ~17 K in CuO (27), where noncollinear spiral spin order occurs. The size of the ferroelectric polarization amounts to about $8~\mu C/m^2$ in $CuBr_2$ (28) and $160~\mu C/m^2$ in CuO (27).

In TM oxyhalides, no observation of multiferroicity has been reported before. Here, we find multiferroic properties in Cu_2OCl_2 below ~70 K with a polarization that amounts to roughly $40~\mu C/m^2$. The coincidence of magnetic and ferroelectric transition temperatures in Cu_2OCl_2 and the presence of incommensurate magnetism indicate a magnetic origin of ferroelectricity in Cu_2OCl_2. Thus, TM oxyhalides with a melanothallite structure are a new class of multiferroic materials with potentially promising properties because of the emergence of spin-induced ferroelectricity.

Our finding gives rise to the search for new high-performance multiferroic materials because various substitutions are possible in this ternary melanothallite system, which is an advantage compared to binary copper oxide CuO and binary copper halogenides. For example, the substitution of Cl ions by other halogen ions, such as Br, seems promising with regard to the change of the critical temperature from 23.9 K in $CuCl_2$ (29, 30) to 73.5 K in $CuBr_2$ (28). Note that the physical properties do not change qualitatively when transitioning from $CuCl_2$ to $CuBr_2$ (28–30); the same is true for other oxychlorides, such as TiOCl and TiOBr (31). In Cu_2OCl_2, the TM ion could be substituted as well, for example, by Ni or Co, thus altering the magnetoelectric properties like in the series $MTeO_6$, with M = Mn, Co, and Ni (32–39). Thus, our findings open new ways of discovering materials with potentially interesting magnetoelectric properties and of investigating the systematics of multiferroics.

Furthermore, our finding of multiferroicity in Cu_2OCl_2 shows that divalent copper compounds have the potential to be high-T_C multiferroic materials. This systematic observation of high-T_C multiferroicity in divalent copper compounds might arise from the presence of comparably large exchange interactions J in these materials. The importance of exchange interactions for multiferroicity in CuO has been pointed out by theoretical calculations (40, 41). A high J value is responsible for a high magnetic ordering temperature despite the presence of frustration in these systems, but this frustration is the prerequisite for incommensurate magnetism, which is responsible for spin-induced ferroelectricity and, thus, for the desirable magnetoelectric properties. This might also be a common phenomenon in high-T_C multiferroics and high-T_C superconductors, which are based on copper compounds (42–44), thus linking some of the most active research fields in contemporary condensed matter physics.
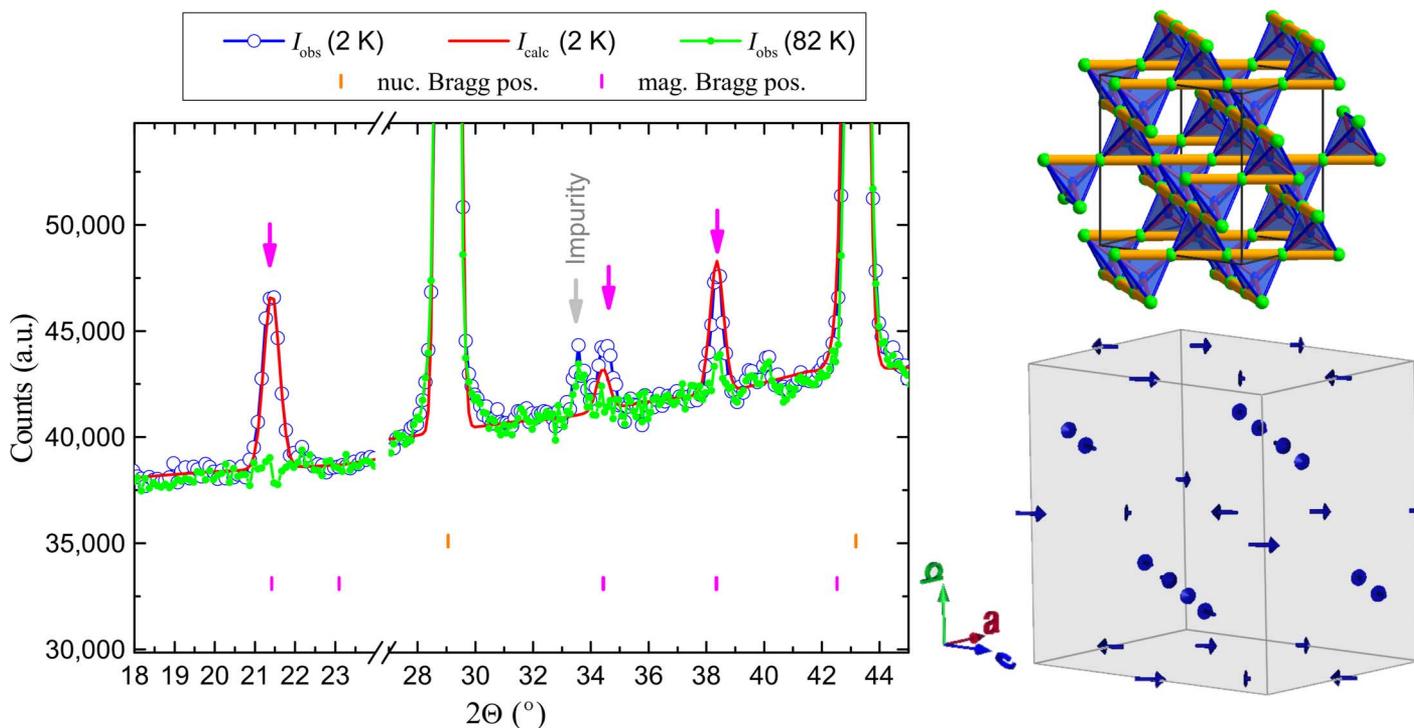
Fig. 4. Incommensurate magnetic structure of Cu₂OCl₂. Powder neutron diffraction measurements of Cu_2OCl_2. Below T_N, three magnetic peaks appear (magenta arrows). The red line represents the refinement with a spin structure according to the irreducible representation $Irep_2$. The right bottom panel depicts the spin structure. For clarity, we show the corresponding OCu_4 tetrahedral chains (orange) in the upper right panel. Within each OCu_4 tetrahedral chain, the magnetic moments point in the chain direction. a.u., arbitrary units.

MATERIALS AND METHODS

Cu_2OCl_2 single crystals were synthesized by chemical vapor transport techniques using copper(II) chloride and oxide as starting materials in stoichiometric ratios ($CuCl_2/CuO$ = 1:1). The starting materials were pressed to pellets and sealed in quartz ampoules. Afterward, the pellets were sintered at 350°C for 24 hours. These polycrystalline starting materials were sealed together with a tiny excess of 20 mg of $CuCl_2$ in quartz ampoules and heated at 455°C for 14 days in the hot zone (T_{source}) of a two-zone furnace. Single crystals with a plate-like shape crystallized in the cold zone at 355°C (T_{sink}). Single-crystal x-ray diffraction measurements performed with a Bruker D8 VENTURE single-crystal x-ray diffractometer (Mo Kα) indicate that all our tested single crystals (including larger pieces with a size of several millimeters) are free from any impurity phase and are twinned with two twin domains marked as A and B. The twinning occurs in the ab plane, which is also the plane of the plate-like grown single crystals. At room temperature, the b axis of twin domain B is rotated by about 75.5° away from the corresponding axis of twin domain A. This angle is identical to the angle between the chains of edge-sharing CuO_2Cl_2 squares running in the $[1 1 0]_A$ and $[−1 1 0]_A$ directions and, thus, explains the origin of twin formation with the underlying twin law matrix (−1/4 −5/4 0, −1/4 3/4 0, 0 0 −1): in twin domain B, the direction of one of the edge-sharing CuO_2Cl_2 square chains is mirrored (or rotated by 180°) across the other square chain. Details of the crystal structure can be obtained from the cif file in the Supplementary Materials. For the powder neutron diffraction measurements, Cu_2OCl_2 powder samples were synthesized in a similar way in sealed quartz glass ampoules. Because Cu_2OCl_2 is hygroscopic and any exposure to air should be avoided, a minor impurity phase appears in our powder samples. Magnetic properties were measured in a SQUID (superconducting quantum interference device) magnetometer (MPMS, Quantum Design) (see the Supplementary Materials). The magnetic ordering temperature T_N amounts to ~70 K in our Cu_2OCl_2 samples, which is in agreement with previous studies (26). The plate-like single crystals were coated on both sides with silver paint as electrodes to measure the dielectric properties of Cu_2OCl_2. Thus, the dielectric properties of Cu_2OCl_2 could be measured in the c direction, where twinning plays no role. The dielectric constant was measured within a Quantum Design PPMS (Physical Property Measurement System) using a homemade sample holder and an Andeen-Hagerling capacitance bridge. For pyroelectric current measurements, we polarized the samples upon cooling with a static electric field of roughly 500 kV/m. The pyroelectric current was, then, measured upon heating. Powder neutron diffraction measurements were performed using the D1B and D2B diffractometers at the Institut Laue-Langevin in Grenoble, France. The incident neutron wavelength amounts to 2.52 Å (D1B) and 1.59 Å (D2B). Powder x-ray diffraction measurements were performed with a Bruker D8 Discover A25 powder x-ray diffractometer using Cu Kα₁ radiation (Johansson monochromator) and an Oxford PheniX helium cryostat.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/2/5/e1600353/DC1
Powder x-ray diffraction

Magnetization measurements
Single crystal x-ray diffraction
Pyroelectric coefficient measurements
fig. S1. Powder x-ray diffraction pattern of Cu_2OCl_2.
fig. S2. Magnetic susceptibility of our polycrystalline Cu_2OCl_2 samples.
fig. S3. First temperature derivative of the magnetic susceptibility of Cu_2OCl_2 single crystals indicating T_N.
fig. S4. Specific heat of a Cu_2OCl_2 single crystal indicating a value of T_N that is consistent with our magnetization.
CIF-file: Cu2OCL2_Fddd_v3_s.cif

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