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Magnetoelectric Multiferroicity and Magnetic Anisotropy in Guanidinium Copper(II) Formate Crystal

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Abstract: Hybrid metal-organic compounds as relatively new and prosperous magnetoelectric multiferroics provide opportunities to improve the polarization, magnetization and magneto-electric coupling at the same time, which usually have some limitations in the common type-I and type-II multiferroics. In this work we investigate the crystal of guanidinium copper(II) formate \([\text{C(NH}_2\text{)}_3]\text{Cu(HCOO)}_3\) and give novel insights concerning the structure, magnetic, electric and magneto-electric behaviour of this interesting material. Detailed analysis of crystal structure at 100 K is given. Magnetization points to the copper(II)-formate spin-chain phase that becomes ordered below 4.6 K into the canted antiferromagnetic (AFM) state, as a result of super-exchange interaction over different formate bridges. The performed \textit{ab-initio} colinear density functional theory (DFT) calculation confirm the AFM-like ground state as a first approximation and explain the coupling of spin-chains into the AFM ordered lattice. In versatile measurements of magnetization of a crystal, including transverse component besides the longitudinal one, very large anisotropy is found that might originate from canting of the coordination octahedra around copper(II) in cooperation with the canted AFM order. With cooling down in zero fields the generation of spontaneous polarization is found that might originate from canting of the coordination octahedra around copper(II) in cooperation with the canted AFM order. Measured polarization is somewhat smaller than the DFT value in the \(c\)-direction, possibly due to twin domains present in the crystal. The considerable magneto-electric coupling below the magnetic transition temperature is measured with different orientations of the crystal in magnetic field, giving altogether the new light onto the magneto-electric effect in this material.

Keywords: multiferroics; metal-organic perovskites; magneto-electric effect; magnetic anisotropy, canted antiferromagnet

1. Introduction

Multiferroics are materials with coexistence of more than one long-range order. Particularly interesting are magnetoelectric multiferroics, where a significant coupling between magnetic and ferroelectric orders is present, thereby allowing changes of magnetization with an electric field and changes of polarization with a magnetic field [1–3]. These materials are interesting because of the possibilities they offer in technological applications, such as in sensors, ferroelectric photovoltaics, spintronics and nanoelectronics [4–7]. In addition to technological applications, multiferroics are also
important for fundamental research of the interactions between electron charge, spin, orbital degrees of freedom, and crystal lattice [8].

It is very difficult to find magnetoelectric multiferroics with strong magnetoelectric coupling. The reason is mutually exclusive conditions for the existence of magnetic and electric order: magnetism requires partially filled $d$ orbitals, while ferroelectricity usually requires a configuration of filled $d$ orbitals [9]. According to the microscopic cause of ferroelectricity, multiferroics can be divided into two groups: type-I and type-II multiferroics. Type-I multiferroics are those materials in which the electrical and magnetic order have different origins and appear almost independently of each other. Phase transition temperatures are different and spontaneous polarization is of large value (order of magnitude of $10^{-100}$ $\mu$C/cm$^2$). The best known example of a type-I multiferroic is bismuth ferrite with phase transition temperatures 1100 K (ferroelectric) and 643 K (antiferromagnetic), and a polarization of $90 \mu$C/cm$^2$ [10], but with negligible magneto-electric coupling. Type-II multiferroics are the materials in which the origin of electric order is in magnetism. Usually, these are materials with a magnetic spiral order, and polarization occurs as a consequence of spin-orbit interactions. The coupling between the orders is large, but the polarization in such materials is much smaller ($10^{-2} \mu$C/cm$^2$). [2]

To avoid the problem of small coupling between the electric and magnetic orders in type-I multiferroics, and the problem of low magnetization and polarization in type-II multiferroics, composite multiferroics can be made where magnetic and ferroelectric materials are combined in the form of multilayered structures or self-organizing nanostructures [6]. Another way could be to use hybrid organic-inorganic materials. Most often, the inorganic part contains magnetic ions with a partially filled $d$ orbital and is responsible for magnetism and magnetic order, while polarization and electrical order occur as a consequence of the arrangement of organic blocks. By carefully selecting the organic groups, the desired physical properties can be obtained [11]. Hybrid organic-inorganic perovskites are one example of such materials. Perovskites are materials with a $ABX_3$ formula, where $A$ and $B$ are cations of different sizes, and $X$ anions form an octahedral coordination environment around the $B$ cation. Corner sharing octahedra form a 3D network with the cavities in which $A$ cations are located. A group of perovskites in which the $A$ cation and/or $X$ anion is replaced by organic cations and organic ligands, respectively, are called hybrid organic-inorganic perovskites. A large selection of organic groups of different structural and chemical properties provides the ability to adjust physical properties by simple chemical changes [12-14].

In already well known metal-formate perovskite, amine cations are located at the $A$ sites and HCOO$^-$ anions at the $X$ sites [15]. Formate anions, due to their size, allow only weak magnetic interaction of neighboring magnetic ions. As a consequence, a long range magnetic order in such materials usually occurs only below 50 K. The anti-anti configuration of the formate anion causes the tilting of adjacent octahedra, which provides the possibility of non-centro-symmetric bridging and appearance of anti-symmetric super-exchange, i.e. Dzyaloshinskii-Moriya interaction, which results in canted spins and weak ferromagnetism [12]. The ordering of organic cations at $A$ positions leads to the structural phase transitions. At higher temperatures, usually there are several equivalent ways in which organic cations couple through hydrogen bonds to formate bridges. By cooling, they order by bonding in the same way and as a result of ordering, spontaneous polarization can occur. The first found example with such a structural transition in metal-organic perovskite is $[\text{DMA}][\text{M(HCOO)}_3]$, where DMA is a dimethylammonium ion ($\text{CH}_3)_2\text{NH}_2^+$, and $M$ is a divalent metal ion [16,17].

Here we study the metal-formate perovskite where the amine cation located at the $A$ sites is guanidinium (Gua) cation, with formula $\text{C(NH}_2)_3^+$, having six hydrogen atoms with which it can form three pairs of hydrogen bonds with the oxygen atoms in formate bridges. Properties of several guanidinium metal formates, $[\text{Gua}]\text{M(HCOO)}_3$ with divalent metal ions Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$ were investigated in [18]. They showed that compounds with magnetic ions Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Cu$^{2+}$ have long-range spin canted antiferromagnetic order with transition temperatures of 8.8 K, 10.0 K, 14.2 K, 34.2 K and 4.6 K, respectively. In the compound $[\text{C(NH}_2)_3]\text{Cu(HCOO)}_3$, abbreviated as GuaCuF, low-dimensional magnetism (AFM chains) is present...
at higher temperatures, which can be explained by the crystal structure in which the elongated
octahedra (Jahn-Teller effect) are arranged to form Cu-formate-Cu chains with a smaller distance of
copper ions than between copper ions from adjacent chains. Experimental and theoretical research has
shown that GuaCuF has a ferroelectric order that occurs due to Jahn-Teller distortion of octahedra in a
metal-formate network, which causes ferroelectric shifts of guanidinium cations through hydrogen
bonds [19,20]. Magnetolectric coupling was also observed. [20]

In this work, we discuss the crystal structure of GuaCuF at 100 K. The performed ab-initio DFT
calculation confirmed the nature of the magnetic ground state in agreement with the magnetization
of powder and with the previous reports. The magnetization of a GuaCuF crystal was thoroughly
measured, and very large anisotropy was found. The polarization was confirmed to be present
even in the crystals with twin domains, somewhat lower than value obtained in DFT, and the effect
of magnetic field on its value was observed even in the paramagnetic phase. The magnetolectric
coupling below the magnetic transition temperature was measured with different directions of electric
field and orientations of the crystal in the magnetic field, from which the new light onto the appearance
of magnetolectric effect in this material is given.

2. Materials and Methods

2.1. Synthesis

Guanidinium copper(II) formate \([\text{C(NH}_2\text{)}_3][\text{Cu(HCOO)}_3]\) was synthesized by a slight modification
of the previously reported procedure.[18] A fresh solution of formic acid (0.23 g, 6 mL water) was
mixed with \([\text{C(NH}_2\text{)}_3]_2\text{CO}_3\) (0.38 g, 2.1 mmol). To the above solution, a solution of copper(II) nitrate
(0.10 g \(\text{Cu(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O}\) dissolved in 2 mL of water) was added and the final mixture was allowed to
evaporate slowly at room temperature. After a few days large blue prismatic crystals formed and were
harvested by filtration. Yield: 77% based on \(\text{Cu(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O}\). Elemental analysis calculated (%) for
\(\text{C}_4\text{H}_9\text{N}_3\text{O}_6\text{Cu}:\) C 18.57, H 3.51, N 16.24; found: C 18.54, H 3.55, N 16.19.

The purity of bulk material was confirmed via powder X-ray diffraction (PXRD) experiment
performed on Panalytical Aeris diffractometer in Bragg-Brentano geometry (Figure A1).

2.2. Single-Crystal X-ray Diffraction

A crystal of suitable diffraction quality was chosen and mounted on a glass needle. The data
were collected at 100 K on an Oxford Xcalibur diffractometer with 4-circle kappa geometry goniometer,
CCD Sapphire 3 detector and graphite-monochromated Mo \(\text{K}\alpha\) radiation (\(\lambda = 0.71073\)Å) using
\(\omega\)-scans. The data reduction and the analytical absorption correction were performed with the CrysAlis
software package.[21,22] The structure was solved by direct methods and refined against \(F^2\) by the
weighted full-matrix least-squares method by using programs SHELXS (Version 2013/1)[23] and
SHELXL-2018/3[24] working under the WinGX system[25]. Selected crystallographic and refinement
data for the title compound are summarized in Table A1. The structure was solved in \(Pn\text{a}_2_1\) space
group, while the Flack parameter refined to 0.45(2). The structure of the compound, previous to this
report, was investigated via single-crystal X-ray diffraction in the temperature range 120-300 K (see
[18,20,26]) and by neutron diffraction (on a deuterated analogue) in the temperature range 30-300 K (see
[27–31]). The studies unveiled that the system does not suffer from symmetry related transitions in the
low temperature region (30-300 K; see [27–31]). While the systematic absences allow the choice of the
centrosymmetric \(P\text{nna}\) and non-centrosymmetric \(P\text{na}_2_1\) space groups, based on the previous structural
studies, extensive DFT calculations and the ferroelectric behaviour of the compound, the polar \(P\text{na}_2_1\)
space group was chosen. The value of the Flack parameter, in this particular case, was interpreted in
the context of (racemic) twinning. Finally, it should be noted that the \(P\text{nna}\) (or \(P\text{nna}\)) is considered to be
a spacegroup of the paraelectric phase for this compound. All non-hydrogen atoms were refined
anisotropically. Hydrogens attached to carbon atoms were placed in geometrically idealized positions
and refined using the riding model. Hydrogen atoms bonded to nitrogen atoms of guanidinium cation
were found in the difference Fourier maps at final steps of the refinement. Their coordinates were refined freely, but N–H distances were restrained to 0.88 Å. The structural analyses and geometrical calculations were done with PLATON[32,33], while the drawings were made with Mercury[34], POV-Ray[35] and Diamond[36]. Selected bond distances and angles are presented in Table A2, whereas hydrogen bond geometry is given in Table A3. CCDC 2058552 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

2.3. Density Functional Theory (DFT) calculations

For all DFT calculations we used a plane-wave code Quantum ESPRESSO [37,38] with GBRV pseudopotentials [39] and PBE exchange-correlation functional [40]. The energy cut-off for the plane wave basis set is set to 680 eV. Relaxation of ionic positions starting from experimental structure was performed until forces on all atoms were smaller than 0.01 eV Å^{-1} and change in energy of two consecutive steps was smaller than 0.5 meV. The Brillouin zone is sampled with a Monkhorst-Pack mesh with density of k-points of at least 2.5 Å. Magnetic interaction parameters \( J \) are calculated by fitting total energies of different spin configurations to Heisenberg Hamiltonian. Polarization was calculated within so-called modern theory of polarization [41] as implemented in Quantum Espresso.

2.4. Magnetic measurements

Magnetic properties were investigated on the polycrystalline powder sample and on the single crystals of guanidinium copper(II) formate using a MPMS 5 commercial superconducting quantum interferometer device (SQUID) magnetometer (Quantum Design, San Diego, CA, USA). MPMS 5 magnetometer enables the measurements of magnetization in the temperature range of 2-400 K, and in fields up to 55 kOe. For the powder sample, the ampule filled with powder was inserted into the measuring straw as a sample-holder, while the crystals were attached on a small piece of circular paper support so that the crystal is placed in the centre of the straw which is important for the measurement of transverse component of magnetization. The temperature dependence of magnetization \( M(T) \), was measured from 2 to 330 K, and higher temperatures were not used in order to avoid the grease melting and decentering or reorientation of the sample, as well as to stay far from the thermal instability of the sample which appears somewhat above 400 K. For several applied fields, \( M(T) \) was measured two times, first the sample was cooled in zero field and then measured in applied magnetic field while heating (the zero field cooled - ZFC curve), and the second time also while heating but after the sample was cooled down in the same applied field as the measuring one (the field cooled - FC curve). The field dependence of magnetization \( M(H) \) was measured at several stable temperatures in magnetic field up to 50 kOe. Besides the usually measured longitudinal magnetization in the direction of vertically applied magnetic field, the transverse component of magnetization which is in horizontal plane, \( i.e. \) the component that is perpendicular to the applied field, was also measured. The horizontal sample rotator enabled the sample rotation in the horizontal plane and maximal magnetization during this rotation corresponds to the horizontal component of the magnetization vector. In such a way, the complete vector of magnetization is determined, consisting of the longitudinal (vertical) and transverse (somewhere in horizontal plane) components.

2.5. Magneto-electric measurements

Magneto-electric measurements were performed on the homemade modified sample-rod with wires going down to the sample within MPMS 5 magnetometer. The wires are made from the low thermal conductivity electric conductor in order to keep the lowest possible heat transmission and to ensure thermal stability of the sample-space down to 1.8 K.
For making the electric contacts to the crystal sample, the silver paste was used. The contacts were applied in such a way that the electric field goes parallel with the crystallographic c-axis. Namely, in this direction spontaneous polarization develops and can be measured most appropriately.

The polarization was calculated from the measurements of the pyroelectric current by integrating it with time. Pyroelectric current flows due to the charges generated on the surface of crystal during the establishing of the electric polarization. Current was measured with Keithley 6517B electrometer (precise femtoampermeter) while cooling, in zero electric and magnetic field, from 330K with constant rate of 2 K/min. The measurement was repeated for 50 kOe magnetic field applied in a-direction.

The magneto-electric effect was measured as an effect of electric field on the temperature dependence of magnetization. The electric field was applied using a high voltage source SRS-PS350. Maximum used value of applied voltage was 250 V resulting in the field of around 2.5 kV/cm. Magnetization was measured two times in zero magnetic field, first the sample was cooled down in zero electric field and measured while heating, then above the magnetic order temperature the electric field was applied, and the sample cooled down to 2 K and measured again while heating.

3. Results and Discussion

3.1. Molecular and Crystal Structure

At 100 K the title compound crystallizes in an orthorhombic system in a Pna2₁ space group. As established previously by neutron diffraction studies on a deuterated analogue (30-300 K) and by single-crystal X-ray diffraction in the temperature interval 120-300 K, [20] the compound does not experience symmetry-related transitions in this low-temperature region.[27–31] It was recognized that in the 120-300 K temperature range all three cell axes expand with increasing temperature, although the crystallographic b-axis changes only slightly.[20] Additionally, it was shown that around 120 K unit cell b-axis exhibits a crossover from negative to positive thermal expansion.[30] Our results, as evident from the data presented in Table A1, in general support such conclusions.

**Figure 1.** Mercury-ORTEP[34] POV-Ray[35] rendered view of a) Jahn-Teller distorted octahedral environment of Cu²⁺ cation in GuaCuF; b) The guanidinium cation residing in the pseudo-cubic cavity whose size is determined by positions of eight bridged copper(II) ions. Guanidinium cation is anchored in the cavity by six hydrogen bonds. Ellipsoids are drawn at the 50% probability level while H-atoms are shown as spheres of arbitrary size. In b) hydrogen bonds are presented by an array of yellow cylinders.

The structure of the title compound, GuaCuF, consists of the anionic framework [Cu(HCOO)₃]⁻ whose pseudo-cubic cavities are populated by guanidinium cations. The Cu²⁺ is found in the Jahn-Teller distorted octahedral environment, resulting in 4+2 geometry (Figure 1). The Cu²⁺ cations are mutually connected through formate bridges. A useful description of the structure of GuaCuF, especially given its magnetism, is the one that considers the square-planar CuO₄ units, defined by the shorter Cu—O bonds, i.e. two short and two medium-length bonds. Accordingly, the structure can
be perceived as composed of the chains containing CuO\(_4\) units, which run along the crystallographic c-axis (Figure 2a). The Cu\(^{2+}\) ions within the chains are connected through anti-anti formate bridges, which include medium-length Cu—O bonds, while the intrachain Cu ··· Cu distance is 5.643(3) Å. The neighbouring chains are linked via long and short Cu—O bonds, and the interchain Cu ··· Cu distances are 6.1617(5) Å and 6.1838(5) Å. The main geometrical parameters of GuaCuF structure at 100 K roughly resembles the scenario observed at room temperature.[18]

Figure 2. a) The chains of CuO\(_4\) units (defined by two short and two medium Cu—O bond lengths). The chains, which run along the crystallographic c-axis are formed via two medium Cu—O bonds of the formate anions. The chains further associate through long and short Cu—O distances, which involve formate anions. Guanidinium cations are not shown for clarity reasons. b) Hydrogen bonds and the related graph-set notations formed by guanidinium cation. Hydrogen bonds are presented by yellow dashed lines.

As mentioned previously, guanidinium cations are anchored within the pseudo-cubic framework cavities via strong hydrogen bonds (Figure 1b) and Figure 2b) and Table A3). More precisely, each guanidinium cation participates in six fairly strong N—H···O hydrogen bonds in total (there are three non-equivalent R\(_2^2\)(8) rings).

3.2. Magnetic Susceptibility

Susceptibility obtained from the temperature dependence of magnetization M(T) in 1000 Oe is shown in Figure 3. The broad peak, with the maximum at 45 K, points to the existence of antiferromagnetic (AFM) chains with relatively strong intra-chain coupling. The strength of the AFM interaction was obtained by fitting the data with the Bonner-Fisher formula for antiferromagnetic (AFM) spin 1/2 chains[42]:

\[
\chi_{\text{chain}} = \frac{N_A \beta^2 g^2}{k_B T} \frac{0.25 + 0.074975x + 0.075235x^2}{1 + 0.9931x + 0.172135x^2 + 0.757825x^3},
\]

where \(x = |J|/k_B T\) and \(J\) is the super-exchange interaction between the neighbouring copper ions inside the chain, defined by the Hamiltonian \(H = -J \sum S_i \cdot S_{i+1}\). The values of \(J = (-65.5 \pm 0.1)\) K and \(g = (2.18 \pm 0.02)\) were obtained, with the RMSE (Root Mean Squared Error) of 1.37 \(\cdot\) 10\(^{-5}\). If we take into account the secondary bonds (super-exchange between the chains) as a mean field correction, the susceptibility becomes:

\[
\chi = \frac{\chi_{\text{chain}}}{1 - \frac{2j}{N_A g^2 \chi_{\text{chain}}}},
\]

where \(j\) is the inter-chain interaction and \(z = 4\) is number of the nearest chains. The obtained values are following: \(J = (-66.5 \pm 0.3)\) K, \(g = (2.17 \pm 0.02)\) and \(j = (8.3 \pm 2.6)\) K, with reduced RMSE = 1.23 \(\cdot\) 10\(^{-5}\). From these results we can describe the basic magnetic structure as an A-type AFM, where antiferromagnetic chains are mutually weakly coupled by ferromagnetic interaction. This
is consistent with the magnetic ground state given by DFT calculations, (Figure 4) where the obtained super-exchange interactions were $J_c = -886$ K, and $J_{ab} = 296$ K. The reason for such large values is the use of PBE exchange-correlation functional that tends to delocalize $d$ electrons and, thus, overestimate super-exchange. However, the ground state is correctly predicted and better agreement would be obtained by using DFT corrected by Hubbard term [43] or DFT functional containing part of exact exchange [44]. Such calculations were performed in Ref. [19] with resulting $J_c = -63.3$ K and $J_{ab}=12$ K.

Figure 3. Temperature dependence of molar susceptibility of the powder sample of GuaCuF, measured in 1 kOe. Red line represents the Bonner-Fisher spin-chain fit with mean field correction for the inter-chain interactions.

The magnetic ground state of an A-type AFM can be explained by looking at the orbitals. The antiferro-orbital ordering within the $ab$ plane and ferro-orbital ordering along the chain, along with the Goodenough-Kanamori-Anderson rules points to ferromagnetic coupling within the $ab$ plane and antiferromagnetic coupling along the chain in $c$ direction. The detailed explanation can be found in [19].

Figure 4. Spin polarization density (difference of electronic density of spin up and spin down) of ground state. Spin up polarization is shown with blue isosurfaces and spin down polarization is shown with green isosurfaces.

The previous work on the GuaCuF powder reported magnetic structure of antiferromagnetic chains with the intra-chain interaction of $J_{\text{intra}} = -68.1$ K and weak ferromagnetism resulting from
3.3. Magnetic Anisotropy

If we look at the magnetization of the single crystals (Figures 5 and 6), we can see a large difference in magnetization, both in \( M(T) \) and in \( M(H) \), along different crystallographic axis, which indicates a large magnetic anisotropy of the compound.

![Figure 5](image-url)  
**Figure 5.** Temperature dependence of magnetization of single crystal GuaCuF in different fields. The magnetization was measured along the applied field. Red rectangles represent magnetization measured along the \( a \)-axis, blue triangles along the \( b \)-axis, and green diamonds along the \( c \)-axis. Empty/filled symbols stand for ZFC/FC curves respectively.

On Figure 5, the low temperature magnetization along different crystal axes is shown. On the left side, magnetization measured in 10 and 100 Oe of applied field is shown. From the magnetization in the field of 10 Oe (upper left figure) we have found the critical temperature, the temperature below which the weak ferromagnetic long range order (LRO) is established, to be \( T_N = 4.6 \) K (in agreement with the value found in [18]). The irreversibility, by means of difference between the ZFC and FC curves, is noticeable only in the lowest field of 10 Oe for the \( b \) and \( c \) direction, while for \( a \) direction it is still around 25% in the field of 100 Oe. The large difference between the values of magnetization in different directions, below the transition temperature \( T_N \), indicates large anisotropy with easy axis being in \( c \) direction and hard axis in \( a \) direction, concerning at least the macroscopic magnetization. The easy axis in canted weak ferromagnets indicates the direction in which the uncompensated magnetic moment of canted AFM ordered spins is oriented most favourably, so that the same magnetic field applied in directions different from the direction of the easy axis, will produce much lower value of magnetization. However, in this material, higher fields change the direction in which the spins are...
most favourably canted. On the right side of the Figure 5, the $M(T)$ in fields 1 kOe and 10 kOe are shown. Increasing the field the sample becomes more magnetized in $a$ direction. For the field of 1 kOe, it is still easiest to magnetize the sample in $c$ direction, but it is easier to cant the spins in $a$ direction than in $b$ direction. Finally the field of 10 kOe (lower right part of Figure 5) changes the easy axis to $a$ direction, while the hard axis stays in $b$ direction. It has to be noted, that this discussion covers only the main crystallographic directions due to simplicity, while more detailed research of anisotropy will be continued with other appropriate techniques for magnetic anisotropy.

The field dependence of magnetization of single crystals at 2 K, (Figure 6) clearly shows the anisotropic behaviour discussed above. At the lowest fields, till around 20 Oe, the magnetization in $b$ and $c$ direction increases rapidly and achieves the values $M_c = 0.012 \mu_B$ and $M_b = 0.003 \mu_B$ per Cu$^{2+}$ ion. After this initial rapid increase, they continue with slow linear increase with the same slope. The magnetization in $a$ direction starts to increase with the field with much smaller rate, achieving only $M_a = 0.00006 \mu_B$ f.u. (one formula unit - f.u. contains one Cu$^{2+}$ ion) at 20 Oe. After 20 Oe it continues with the same slope, and at the field of 80 Oe attains larger value of magnetization than in $b$ direction, while at fields larger than 2300 Oe it becomes larger than $M_c$. After 3000 Oe, it becomes harder to increase the magnetization further, the change of the magnetization stays linear, and the rate at which it changes with field becomes equal to the slopes of $M_b$ and $M_c$.

**Figure 6.** Field dependence of magnetization of the powder and single crystal samples of GuaCuF. Black dots represent powder data, red rectangles the magnetization of single crystal in the direction of the applied field, parallel to $a$-axis, blue diamonds parallel to $b$-axis, and green triangles parallel to $c$-axis.

Besides anisotropy, from the $M(H)$ it could also be seen that the saturation is not achieved even in fields of 50 kOe, where the value of magnetisation is only 0.04 $\mu_B$ f.u. (for $S = 1/2$ of copper, the saturation value should be around 1 $\mu_B$ f.u.). This confirms our claim of canted spins and weak ferromagnetism. Higher magnetic fields for studying the possible spin flip/flop processes are unreachable in this setup.

**Figure 7** shows the field dependence of magnetization at 3K, measured simultaneously along the field applied in $a$ direction (longitudinal magnetization, $M_L$) and perpendicular to the field (transverse magnetization, $M_T$). With horizontal rotator the crystal is firstly rotated in such a direction, so that the detector coil measures $M_T$ in the direction of maximum value of magnetization in the plane perpendicular to the applied field (here that is along $c$-axis, as it is the easy axis). It can be seen that even though the field is applied in $a$ direction, the magnetization in the $bc$ plane is larger than in $a$
direction. Only the fields higher than 3 kOe manage to overcome the anisotropy of the crystal and magnetize the sample in the direction of vertically applied field, \textit{i.e.} the longitudinal direction. If we look at the total magnetization as a vector, we can calculate its value and angle of direction and observe how do they change with the applied field. The value of total magnetization is shown on the Figure 7 with the green diamonds. For the small fields the vector of total magnetization lies in \( c \) direction and \( M_{\text{tot}} \) is almost equal to the \( M_T \). Increasing the field the direction changes almost linearly towards the \( a \) direction till around 2.5 kOe, where it is almost parallel to the \( a \) axis.

\[ M_{\text{tot}} = \sqrt{M_L^2 + M_T^2}. \]

Possible reason for anisotropy can be found in the crystal structure. The elongated octahedra, which are alternately canted one from another, influence the local anisotropy around \( \text{Cu}^{2+} \) ions. More detailed analysis will be made using the techniques more appropriate for the investigation of magnetic anisotropy, as well as for microscopic origins of it, successfully contributing in oxides having similar magnetic complexity.[45,46]

3.4. Magneto-electric study

Polarization of the GuaCuF crystal measured in the fields of 0 and 50 kOe is shown on Figure 8. The black dots show spontaneous polarization in zero magnetic field, while the blue rectangles show spontaneous polarization measured in the magnetic field of 50 kOe. The polarization is measured and magnetic field applied in \( c \) direction. Even though we applied no electric field \( E \), just as a consequence of cooling the sample, measurable current was generated at the electrical contacts made on the \( ab \) planes of the crystal and integrated with time it gave the polarization of the sample. Because the measurement was done in \( E = 0 \) while cooling, the gradual formation of the ferroelectric order toward the maximal polarization of the sample is observed. From the Figure 8 can be seen that the value of polarization depends on the value of applied magnetic field. The polarization in 0 Oe is 0.072 \( \mu \text{C/cm}^2 \), while the field of 50 kOe suppresses the polarization to the value of 0.053 \( \mu \text{C/cm}^2 \). The ordering of dipole moments happen in two main parts. As we cool down the sample, the polarization starts to rise at around 270 K, and rises to the value of 0.019 \( \mu \text{C/cm}^2 \) at 245 K. After this initial rise, the ordering of the dipoles abates and the polarization stays almost constant till 210 K, where again the rapid increase of polarization happens. The final value of polarization is achieved at 110 K and amounts 0.072 \( \mu \text{C/cm}^2 \). Similar behaviour is also seen from the measurements in applied magnetic field. Magnetic
field suppresses the ordering of electric dipoles, so that the transitions happen at somewhat lower temperatures and the final value is around 75% of the value in zero magnetic field. Similar effect was also observed in [20], where the polarization was measured in magnetic fields 0, 70 and 110 kOe, applied in $ab$-plane. There the pyroelectric current was measured with poled samples, and the obtained values were $0.11 \mu C/cm^2$, $0.023 \mu C/cm^2$ and $0.011 \mu C/cm^2$, respectively. The transition temperature was found as an onset of ferroelectric ordering, $T_C = 277K$. The difference in behaviour of polarization with temperature and the higher value at which the polarization starts to develop can be understood if we notice the fact that the samples were poled. [20] The electric field enabled easier ordering of the dipoles and thereby enabled full ordering at the higher temperatures. Theses measurements show that the magnetic field can influence polarization even in the paramagnetic state (paramagnetoelectric effect - PME effect). It was suggested that the PME effect appears due to the nonlinear ME coupling via magnetostriction and ferroleastic effects.[20]

Figure 8. Polarisation of GuaCuF. Measured in c direction while cooling. The black circles represent measurement in zero magnetic field and blue rectangles in 50 kOe magnetic field.

From the previous theoretical considerations of the mechanism of polarization it was concluded that the main contribution to the polarization comes from the dipole moments induced by the displacements of NH$_2$ groups of Gua cation, which couple through the hydrogen bonds with Jahn-Teller distortions and enable the formation of ferroelectric order. More details can be found in [19,20].

From the DFT calculations, the polarization of $0.19 \mu C/cm^2$ was obtained (previous reports gave the value of $0.37 \mu C/cm^2$ due to different computational setup [19]). To compare it with the experimental value, we have to take into account the twinned nature of our crystal. The size-ratio of two twin components being around $40:60$, means that only around $20\%$ of total polarization will not cancel out. The experimental value, $P = 0.072 \mu C/cm^2$ is around $19\%$ of the value obtained in [19], and $38\%$ of the here calculated $0.19 \mu C/cm^2$, showing relatively good agreement with the amount of twinned domains whose contributions do not cancel out.

The influence of the electric field $E$ on magnetization was observed as a change in the value of magnetization $M$ at the temperatures below $T_N$. On Figure 9, measurements of magnetization with (empty symbols) and without (filled symbols) the electric field applied in c direction is shown. Five figures represent five different measurement setups where the magnetization was measured along a (Fig. 9a and 9c), b (Fig. 9b and 9d) and c crystal axis (Fig. 9e). Measurements were done in different remanent fields and different attempts of orienting the crystal. The measurements on Fig. 9a and 9b
were done when the superconducting magnet was first time cooled, before turning on the magnet so that there was no remanent magnetic field present, while 9c, 9d and 9e measurements were done after the magnet was used, thereby having some remanent field which was not possible to quantify or remove completely. For each setup, the transverse component of magnetization (the maximum value of magnetization in the plane perpendicular to the magnetic field direction) was measured at the same time as the longitudinal component. Black circles represent longitudinal, while red rectangles transverse component of magnetization. Obviously, the vector of magnetization is changed solely by electric field, since we did not apply any magnetic field. For measurements on Figs. 9a and 9b the magnetometers superconducting magnet in a fresh state is used having no remanent magnetic field and the crystal was magnetized only by the Earths magnetic field, while for measurements on Figs. 9c, 9d and 9e there is some unknown remanent field. This still makes complications in interpretation since crystal is oriented differently with respect to the Earths magnetic field and remanent field, making it hard to compare the measurements and deduce precise conclusions about the exact change of the vector of magnetization. In that sense our experiment is complementary to the findings in [20] where they have applied relatively large magnetic field (1kOe) during magnetoelectric measurement and obtained relative change of magnetization of 7%. Our experiment is different and has different results, since we changed the almost spontaneous magnetic state using the electric field alone.

Figure 9. Magnetoelectric effect. Five different measurement setups, a) and b) measurements in H = 0 Oe, directly after cooling the superconducting magnet (no remanent fields). c), d) and e) after using the magnet (unknown remanent field). Black circles represents longitudinal magnetization, while red rectangles transverse magnetization. Filled symbols represent the magnetization measured in zero electric field, while empty symbols magnetization measured in electric field (E ≈ 2.5 keV/cm) applied in c direction.

The biggest ME effect was observed when the magnetization was measured in a direction (Fig. 9a and 9c), with the relative change in magnetization of 17% and 21%, respectively. Slightly lower relative change, 16%, was observed in component transverse to a direction on the Fig. 9a, while on the Fig. 9c, the relative change in transverse direction was 36%. The measurements in b direction showed the relative change of 10% in longitudinal and 12% in transverse component of magnetization for the setup in Fig. 9b, while there was no change of magnetization neither in longitudinal nor in transverse
direction for the measurement shown on Fig. 9d. The electric field had no influence on magnetization when it was measured in $c$ direction. From the observed behaviour we could conclude that the electric field has an influence on the magnetization mostly in $a$ direction (or the direction near $a$ direction), and all the observed changes in other directions happened because of the non perfect orientation of the crystal on the sample holder (it was easiest to orient the crystal in $c$ direction, therefore we measured only $M_L$ in longitudinal direction and $M_b$ in transverse direction - $a$ being the hard axis). If the sample was not positioned ideally, meaning that there was a small component of $M_a$ in transverse direction, the change in $M_T$ could be explained. It is possible that the remanent field hinders the effect that electric field has on magnetization in the longitudinal direction, therefore enabling the change in $M_T$ to be larger than in $M_L$ (no remanent field in transverse direction), (Fig. 9c). Better orientation of the crystal in the setups on 9d and 9e figures, and higher remanent field caused no visible ME effect in $b$ and $c$ directions. Electric field applied in the other main crystallographic directions showed no measurable ME effect. Both longitudinal and transverse component of magnetization change with the application of the electric field, therefore we conclude that the electric field changes the vector of magnetization.

Additionally it is important to remark that the change in magnetization which occurred from applying the electric field, was not returned to its original value with turning off the field or even with reversing the field. Only by heating the sample above the ferroelectric transition and then cooling it in zero electric field, were we able to obtain the initial magnetization, the same one as prior to application of the electric field. Origin of the magneto-electric effect could be found in the detailed explanations of electric polarization mechanism [19]. Electric field or electric ordering induced rotations of guanidinium ions produce some slight distortions of formate bridges, that changes the amounts of the symmetric and anti-symmetric super-exchange interactions as well as eventual local anisotropy around Cu. All of this can change the vector of magnetization coming from canted magnetic moments, and provide the reasons for magneto-electric effect. This mechanism is still not know completely and motivates for further research of the microscopic origins of this relatively strong magneto-electric effect.

4. Conclusions

In this work we investigate a single crystal of guanidinium copper(II) formate [C(NH$_2$)$_3$]Cu(HCOO)$_3$ and give some novel insights concerning the structural, magnetic, electric and magneto-electric properties of this interesting magnetoelectric multiferroic material. Magnetic susceptibility points to the existence of antiferromagnetic spin-chains of Cu(II) and their much weaker ferromagnetic interaction with neighbouring chains. The performed ab-initio colinear DFT calculation confirms in first approximation the magnetic ground state determined with super-exchange interactions over the formate bridges and explains the ferromagnetic coupling of the antiferromagnetic spin-chains running along the $c$ direction into an overall antiferromagnetic-like ordered lattice below 4.6 K.

More thorough analysis of magnetization measured on a single crystal shows that system in ground state is actually a canted antiferromagnet and that magnetization coming from the canted magnetic moments has a very large anisotropy, with easy axis in $c$ direction and $a$ as a hard direction (small fields produce almost no magnetic moment along $a$). Special benefits come from the measurements using the transverse moment, besides the longitudinal which is standard in the magnetometers. Origins of canted magnetic moments and anisotropy of magnetization could be found in the canting of the coordination octahedra around copper(II) ions throughout the crystal lattice.

With cooling down in zero electric field the generation of spontaneous polarization is found below 270 K and 210 K even in this twinned crystal, and the effect of magnetic field on its value is observed also in the paramagnetic phase. Polarization is measured in $c$ direction since DFT calculations predicted this vector. Measured value is somewhat smaller than the DFT value and smaller than it should be in a non-twinned crystal.
The considerable magnetoelectric coupling below the magnetic transition temperature was measured with different directions of electric field and orientations of the crystal in magnetic field, giving altogether the new light onto the magnetoelectric effect in this material. Although the polar and magnetic order establish at very different temperatures, coupling between these two orders is considerably high.

Along with these novel results about magnetic anisotropy and magnetoelectric effect in guanidinium copper(II) formate, their further research is needed to fully understand the microscopic origins of these interesting phenomena in this hybrid metal-organic magnetoelectric multiferroic.

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Appendix A Structural features

From the X-ray diffraction analysis (Figure A1), many different parameters can be extracted. Selected crystallographic and refinement data is given in Table A1. For discussions of the physical properties and comparison to other known systems, a bond lengths and bond angles are useful, therefore their values are given in table A2 for selected bonds. Also, the hydrogen bonds play an important role in forming and stabilization of the crystal lattice, therefore their geometry is described with parameters given in table A3.

![Figure A1](image.png)

**Figure A1.** Comparison of the powder pattern for the synthesized material and the pattern simulated from the single crystal data (CSD Refcode: YUKVOQ). [18]
Table A1. Crystallographic data for compound 1

| Property                                      | Value                              |
|-----------------------------------------------|------------------------------------|
| Complex                                       | 1                                  |
| Chemical formula                              | C₄H₄CuN₃O₆                         |
| Mr                                            | 258.69                             |
| Crystal system, colour and habit              | orthorhombic, blue, prism          |
| Crystal dimensions / mm³                       | 0.06 x 0.08 x 0.21                 |
| Space group                                   | Pna₂₂₁ (No. 33)                    |
| Z                                             | 4                                  |
| Unit cell parameters:                         |                                    |
| a /Å                                          | 8.4350(2)                          |
| b /Å                                          | 9.0145(2)                          |
| c /Å                                          | 11.2820(4)                         |
| α /°                                          | 90                                 |
| β /°                                          | 90                                 |
| γ /°                                          | 90                                 |
| V /Å³                                         | 857.85(4)                          |
| D<sub>calc</sub>/ g cm<sup>-3</sup>            | 2.003                              |
| µ / mm<sup>–1</sup>                           | 2.558                              |
| F(000)                                        | 524                                |
| No. refined parameters, N<sub>p</sub> / restraints | 146/6                             |
| Reflections collected, unique (R₁), observed | 8136, 2072 (0.016), 1996            |
| R₁<sup>a</sup> [I ≥ 2σ(I)]                   | 0.0202                             |
| S₁, S₂ in w<sup>b</sup>                       | 0.0326, 0.2077                     |
| wR<sup>c</sup> (all data)                    | 0.0354                             |
| Goodness of fit on F<sup>2</sup>, S<sup>d</sup> | 1.08                               |

<sup>a</sup> R = Σ ||F<sub>o</sub>|| – ||F<sub>c</sub>|| / Σ ||F<sub>o</sub>||
<sup>b</sup> w = 1/[σ<sup>2</sup>(F<sub>o</sub>)<sup>2</sup> + (g₁P)<sup>2</sup> + g₂P]
<sup>c</sup> wR = [Σ[w(F<sub>o</sub>–F<sub>c</sub>)<sup>2</sup>]/Σ[w(F<sub>o</sub>)<sup>2</sup>]<sup>1/2</sup>
<sup>d</sup> S = [Σ[w(F<sub>o</sub>–F<sub>c</sub>)<sup>2</sup>]/(N<sub>r</sub>–N<sub>p</sub>)]<sup>1/2</sup>

where N<sub>r</sub> = number of independent reflections, N<sub>p</sub> = number of refined parameters.
Table A2. Selected bond lengths and angles for [C(NH$_2$)$_3$][Cu(HCOO)$_3$].

| Bond lengths | \( d(A - B)/\text{Å} \) |
|--------------|----------------------|
| Cu1–O1       | 1.992(3)             |
| Cu1–O2       | 1.991(3)             |
| Cu1–O3       | 1.953(2)             |
| Cu1–O4       | 2.3597(19)           |
| Cu1–O5       | 1.9674(19)           |
| Cu1–O6       | 2.331(2)             |
| O5–C3$^1$    | 1.272(3)             |
| O4–C2$^2$    | 1.238(3)             |
| O2–C1$^3$    | 1.251(6)             |
| O6–C3$^3$    | 1.235(3)             |
| N3–C4        | 1.321(2)             |
| N2–C4        | 1.306(12)            |
| C4–N1        | 1.352(13)            |

| Bond angles | \( \angle(A - B - C) \) |
|-------------|------------------------|
| O1–Cu1–O2   | 179.36(8)              |
| O1–Cu1–O3   | 89.54(9)               |
| O1–Cu1–O4   | 89.91(8)               |
| O1–Cu1–O5   | 89.57(12)              |
| O1–Cu1–O6   | 90.70(12)              |
| O2–Cu1–O3   | 121.3(2)               |
| O2–Cu1–O4   | 120.6(2)               |
| O2–Cu1–O5   | 128.22(18)             |
| O2–Cu1–O6   | 119.87(19)             |
| O3–Cu1–O4   | 124.1(3)               |
| O3–Cu1–O5   | 129.3(2)               |
| O3–Cu1–O6   | 118.3(11)              |
| O4–Cu1–O5   | 124.1(3)               |
| O4–Cu1–O6   | 124.2(2)               |
| O5–Cu1–O6   | 118.9(7)               |

Symmetry codes: $^1$-1/2+x,1/2-y,z; $^2$-1/2+x,3/2-y,z; $^3$-1-x,1-y,1/2+z; $^4$1/2+x,3/2-y,z; $^5$-1-x,1-y,1/2+z; $^6$1/2+x,1/2-y,z

Table A3. The geometry of hydrogen bonds (Å, °) for [C(NH$_2$)$_3$][Cu(HCOO)$_3$].

| D–H  | A      | D–H...A  | Symmetry code |
|------|--------|----------|---------------|
| N1–H1A–O5 | 0.84(3) | 2.15(3) | -x,1-y,1/2+z |
| N1–H1B–O1 | 0.820(19) | 2.12(2) | 1/2-x,1/2+y,1/2+z |
| N2–H2A–O4 | 0.87(3) | 2.07(3) | -x,1-y,1/2+z |
| N2–H2B–O2 | 0.818(18) | 2.18(2) | 1/2-x,1/2+y,1/2+z |
| N3–H3A–O6 | 0.84(3) | 2.10(3) | 1/2-x,1/2+y,1/2+z |
| N3–H3B–O3 | 0.83(3) | 2.17(3) | 1/2-x,1/2+y,1/2+z |

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