===== **DIELECTRICS** =====

Electronic Structure, Lattice Dynamics, and Magnetoelectric Properties of Double Perovskite La$_2$CuTiO$_6$

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Abstract—The results of ab initio calculations of the electronic structure, vibrational properties, and the magnetoelectric effect in the La$_2$CuTiO$_6$ crystal with double perovskite structure are presented. The lattice dynamics calculation shows the presence of unstable modes in the phonon spectrum of the high-symmetry cubic phase with space group $Fm\overline{3}m$. Condensation of two most unstable modes belonging to the center and the boundary point X of the Brillouin zone leads to the formation of a nonpolar stable phase with space group $P2_1/n$. The calculation taking into account spin polarization shows that the magnetic ground state is E^*-type antiferromagnetic with doubled magnetic cell and with the two spin-up and two spin-down configuration of magnetic moments of copper ions along the [010] crystallographic direction. Such ordering of magnetic moments leads to polar space group and polarization formation. The polarization magnitude is estimated as 71 μC/m^2.

1. INTRODUCTION

Double perovskites with the general formula $AA'BB'O_6$ have been studied for several decades due to the variety of their physical properties, which depend on both the chemical composition of A, A', B, B' cations and various types and the degree of cation ordering in the structure. Recently, there have been a large number of experimental and theoretical works devoted to the study of compounds belonging to double perovskites [1−5]. Compounds completely disordered by A, A' and B, B' cations have the perovskite structure and have space group $Pm\overline{3}m$ in the undistorted phase. $AA'BB'O_6$ and $A_2BB'O_6$ compounds cation-ordered in the [111] direction also have cubic symmetry with space groups $F\overline{4}3m$ and $Fm\overline{3}m$, respectively. Most double perovskites (with rare exception), independently of the degree of cation ordering in the cubic phase, exhibit instabilities associated with lattice vibrational modes whose eigenvectors correspond to BO_6 octahedron rotations. Recently, researchers' attention has been attracted by oxides with double perovskite structure, containing transition or rare-earth metal elements. Some of these compounds, along with lattice distortions caused by BO_6 octahedron "rotation," exhibit competing interactions between magnetic ions. Such interactions can result in ordered magnetic structures in which the inversion center is lost, hence, spontaneous polarization arises due to magnetic ordering.

The La$_2$CuTiO$_6$ (LCTO) compound has been known for more than twenty years [6, 7]; however, the data on its physical properties are few in number. Structural studies show that the crystal structure represents a distorted form of cubic double perovskite with space group $Pbnm$ and with two molecules in the unit cell [6−8]. In this case, sites B and B' are equiprobably occupied by Cu and Ti ions, i.e., according to the results of [6−8], the crystal remains cation-disordered to low temperatures. The study of the temperature dependence of the LCTO magnetic susceptibility [8] showed that the compound undergoes the antiferromagnetic transition with a paramagnetic Curie temperature of −38 K; however, the antiferromagnetic state type is not presented in this paper. We did not find the data on properties of Cu and Ti cation-ordered LCTO in the literature; although the study of the ordered crystal properties that can differ significantly from properties of the disordered crystal is of interest.

In this paper, we present the results of the ab initio calculation of the electronic structure, lattice dynamics, magnetic properties, and the magnetoelectric effect of the LCTO crystal ordered in the direction corresponding to the [111] direction in the perovskite structure.

2. CALCULATION METHOD

The calculations were performed within the density functional theory using the Perdew−Burke−Ernzerhof exchange-correlation interaction functionals with the generalized gradient approximation (PBE−GGA) implemented in the VASP ("The Vienna Ab initio Simulation Package") package [9, 10]. The GGA + U method was used in the Dudarev approximation [11] where U for copper and titanium ions were taken as 4 eV. The calculations were performed both without and with consideration of spin polarization. To calculate the magnetic ground state and exchange constants in the low-symmetry phase, supercells containing 40 atoms were used. The Monkhorst−Pack grid was taken as $6 \times 6 \times 6$. The lattice parameters and ion coordinates were optimized until the residual forces acting on ions became less than 0.02 eV/Å. Exchange constants of the Heisenberg Hamiltonian were calculated by the energy difference between ordered magnetic configurations.

3. RESULTS AND DISCUSSION

3.1. Structural and Vibrational Properties

The structural and vibrational properties were calculated without regard to spin polarization. The high-symmetry LCTO phase with staggered ordering of Cu and Ti cations has cubic symmetry with space group $Fm\overline{3}m$ and with one molecule in the unit cell (Fig. 1). The optimized values of the lattice parameter and atomic coordinates in the cubic phase are given in Table 1.

The calculated lattice vibration frequencies at the Brillouin zone center and their classification by irreducible representations are listed in Table 2. We can see two unstable F_{1u} and F_{1g} vibrational modes at the
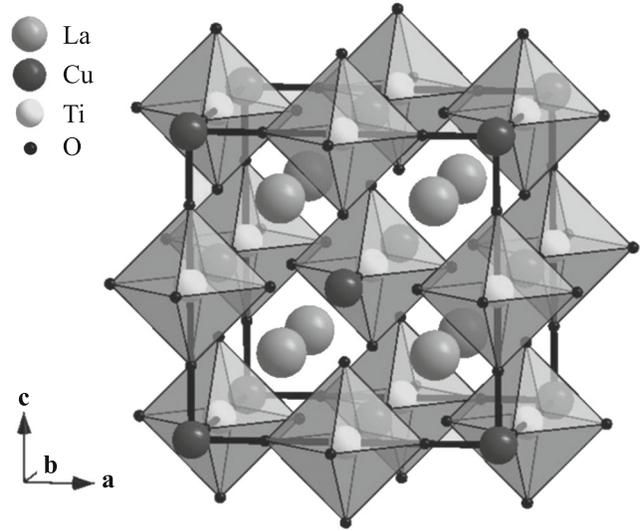

Fig. 1. LCTO structure with staggered ordering of Cu and Ti cations, space group $Fm\overline{3}m$.

Brillouin zone center of the compound under study. The F_{1g} triply degenerate mode is most unstable; only oxygen ions are displaced along its eigenvectors. These displacements correspond to TiO_6 octahedron "rotations" (a^-, b^-, c^- in Glazer notations [12]). The F_{1u} mode is a polar mode and is associated with ferroelectric instability of the cubic phase. It should be emphasized that along with instabilities at the Brillouin zones center, there are single-pass soft vibrational modes at the boundary points X, Y, and Z of type X_5, Y_5, and Z_5, respectively, in the crystal. The frequency of each such mode (225 cm^{-1}) is close in magnitude to the F_{1g} mode frequency, and their eigenvectors also correspond to

Table 1. Calculated lattice parameters and relative coordinates of LCTO atoms in the phases under consideration (experimental data for disordered LCTO in the phase with space group *Pbnm* [6] are parenthetical)

Space group	Atom	Wyckoff position	x/a	y/b	z/c	Lattice parameters
$Fm\overline{3}m$	La	8c	0.25000	0.25000	0.25000	$a = 7.86928$ Å
	Cu	4a	0	0	0	
	Ti	4b	0.50000	0.50000	0.50000	
	O	24e	0.25481	0	0	
$P2_1/n$	La	4e	−0.00909	−0.05429	0.24966	$a = 5.64082$ Å
			(−0.00970)	(−0.03870)	(0.25000)	($a = 5.5702$ Å)
	Cu	2c	0.50000	0	0.50000	$b = 5.85075$ Å
	Ti	2d	0.50000	0	0	($b = 5.6262$ Å)
	O1	4e	0.08474	0.52654	0.24737	$c = 7.70505$ Å
			(0.07593)	(0.51703)	(0.25000)	($c = 7.8396$ Å)
	O2	4e	0.68813	0.71408	0.04539	$\alpha = 90°$
			(0.71161)	(0.71088)	(0.04000)	$\beta = 90°$
	O3	4e	0.21442	0.81541	−0.04414	$\gamma = 90°$

TiO$_6$ octahedron "rotation" (a^+, b^+, c^+ in Glazer notations [12]). In most double perovskites $A_2BB'O_6$ with a trivalent ion at the site A, the low-symmetry phase with distortion (a^-, a^-, c^+) is most energetically favorable among possible phases with distortions associated with eigenvectors of F_{1g}, X_5, Y_5, and Z_5 modes. For BB' cation-unordered and -ordered compounds, such distortion leads to space groups *Pbnm* and $P2_1/n$, respectively. For the compound under study, small oxygen ion displacements along eigenvectors of F_{1g} and X_5 modes ($u = 0.01$) with respect to sites in the cubic phase were set, followed by structure relaxation.

The resulting optimized cell parameters and atomic coordinates for LCTO in the phase $P2_1/n$ are presented in Table 1. Distortions in the structure are mostly associated with TiO$_6$ octahedron "rotations" by approximately equal "rotation" angles (~11°) for a^- and c^+. We note that this "rotation angle" is in quite good agreement with the "rotation" angle (~9°) calculated from experimentally determined LCTO atomic coordinates in the *Pbnm* phase with complete disordering of copper and titanium ions (Table 1). The calculated frequencies of limiting LCTO lattice vibrations in the $P2_1/n$ phase are listed in Table 2. We can see that all bound vibrational modes are stable in the monoclinic phase, i.e., ferroelectric instability existing at the cubic phase is significantly suppressed by antiferrodistorsion lattice distortions (the frequency of the lowest in magnitude polar mode in the $P2_1/n$ phase is 86 cm^{-1}).

3.2. Electronic Structure

The electronic structure of La$_2$CuTiO$_6$ was calculated both with and without consideration of spin polarization. The results are shown in Figs. 2–5. Figure 2 shows the band structure calculated without regard to spin polarization along symmetric directions of the Brillouin zone of the cubic $Fm\overline{3}m$ phase. There the total electron density of states is also shown. Figure 3 shows the expansion of the partial densities of states for La, Cu, Ti, and O in orbital momenta. We can see that two bands formed by p-electrons of oxygen and d-electrons of titanium and copper in the valence band are near the Fermi level and partially occupy it.

The result of calculation of the band structure in the monoclinic phase with doubled unit cell without regard to spin polarization qualitatively does not differ from that shown in Fig. 2 and is not presented here. Figure 4 shows the result of calculations of the LCTO band structure taking into account spin polarization in the monoclinic $P2_1/n$ phase for a cell containing four LCTO molecules (such a cell corresponds to the magnetic ground state of the compound under consideration with two-by-two ordering of copper ion magnetic moments; see below). This figure also shows the total electron density of states; the expansion of the

Table 2. Calculated vibration frequencies (cm^{-1}) of the LCTO lattice at the Brillouin zone center in the phases under study (the expansion of the complete vibrational representation has the form $\Gamma = A_{1g} + E_g + F_{1g} + 2F_{2g} + 5F_{1u} + F_{2u}$, which includes acoustic vibrations F_{1u} for the cubic phase; $\Gamma = 12A_g + 12B_g + 18A_u + 18B_u$, which includes acoustic vibrations $A_u + 2B_u$ for the monoclinic phase)

Cubic phase ($Fm\overline{3}m$)						Monoclinic phase ($P2_1/n$)			
A_{1g}	E_g	F_{1g}	F_{2g}	F_{1u}	F_{2u}	A_g	B_g	A_u	B_u
772	404	235i	360	643	131	635	617	514	518
			57	363		458	479	495	508
				237		411	454	469	460
				70i		401	406	456	428
						322	344	406	384
						320	331	356	352
						292	275	330	349
						244	202	309	309
						194	177	271	283
						140	167	249	259
						120	134	200	211
						98	99	189	177
								174	159
								153	149
								150	132
								91	99
								86	

partial densities of states for La, Cu, Ti, and O in orbital momenta in the monoclinic phase is shown in Fig. 5. These figures show that LCTO in the structure ordered by copper magnetic moments is a dielectric with a band gap of ~1.5 eV. The valence band near the Fermi level is mostly occupied by d-electrons of copper and titanium and p-electrons of oxygen. Large peaks in the conduction band are attributed to unoccupied f-states of lanthanum and d-states of titanium.

3.3. Magnetic Structure and Magnetoelectric Effect

The divalent copper ion is magnetic with spin $s = 1/2$. To determine the magnetic ground state and exchange interaction parameters in LCTO, the total crystal energies were calculated taking into account spin polarization for various magnetic ordered structures. The exchange coupling interaction constants were estimated within the classical Heisenberg model

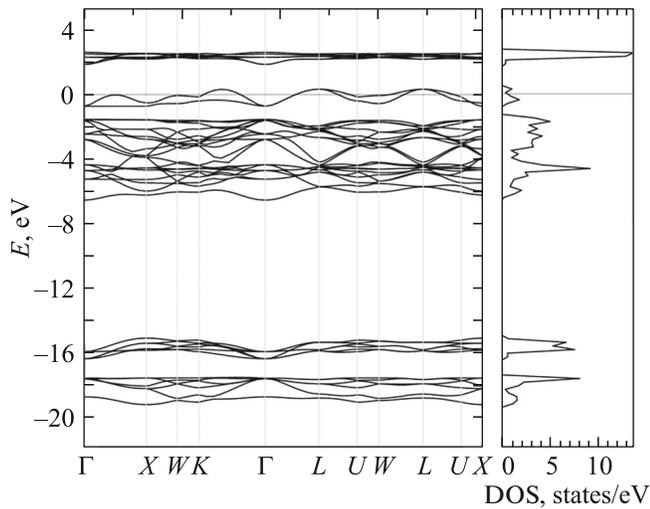$$\mathscr{H} = -\frac{1}{2}\sum_{i,j} J_{ij}\hat{S}_i\hat{S}_j, \tag{1}$$

Fig. 2. Electronic band structure and the density of states (DOS) of the LCTO crystal in the cubic phase with space group $Fm\bar{3}m$.
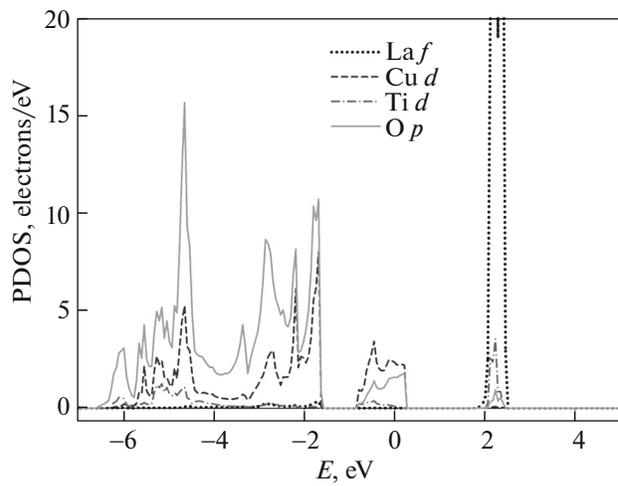

Fig. 3. Expansion of the partial densities of states (PDOS) for La, Cu, Ti, and O in orbital momenta in the $Fm\bar{3}m$ phase of LCTO.
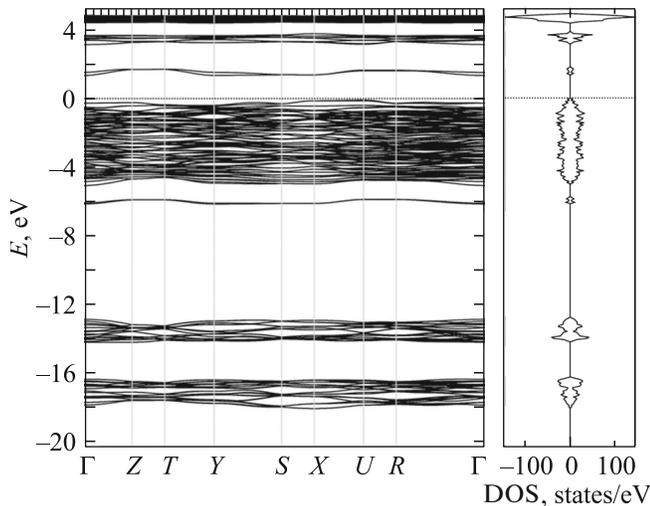

Fig. 4. Electronic band structure and the density of states of the LCTO crystal in the magnetically ordered state with doubled monoclinic cell.
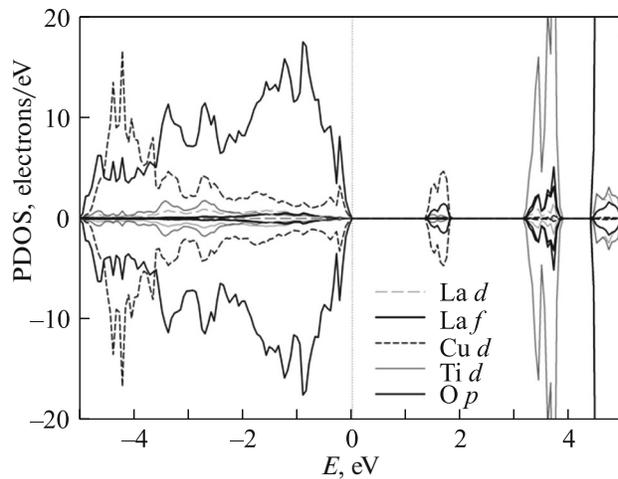

Fig. 5. Expansion of partial densities of states for La, Cu, Ti, and O in orbital momenta in the magnetically ordered state with doubled monoclinic cell.

where the summation is over all pairs of various magnetic lattice sites, J_{ij} are exchange interaction constants, $\hat{S}_i$ and $\hat{S}_j$ are spin operators at sites i and j, respectively. Magnetic copper cations in the cubic phase are ordered on the fcc lattice, hence, each atom has twelve nearest neighbors. In the monoclinic phase, these twelve neighbors are divided into three groups. In this case, each atom has two neighbors along minor axes **a** and **b** of the monoclinic cell and eight neighbors arranged at the midpoints of body diagonals of unit cells. Therefore, to determine the exchange constants, the copper ion system was divided

into four sublattices. Within the calculation taking into account spin polarization, the energies of four magnetic structures were calculated: the ferromagnetic structure energy F; the energy AF1 of the structure with ferromagnetic ordering in the (**a**, **b**) and antiferromagnetic ordering between planes perpendicular to the major axis of the monoclinic cell; the energy AF2 of the structure with ferromagnetic ordering of copper magnetic moments in the (**b**, **c**) plane and antiferromagnetic ordering such as two spins up and two spins downs ($\uparrow\uparrow\downarrow\downarrow$) in planes along the **a** axis with unit cell doubling along this axis; and the energy AF3 of the structure with ferromagnetic ordering of copper mag-
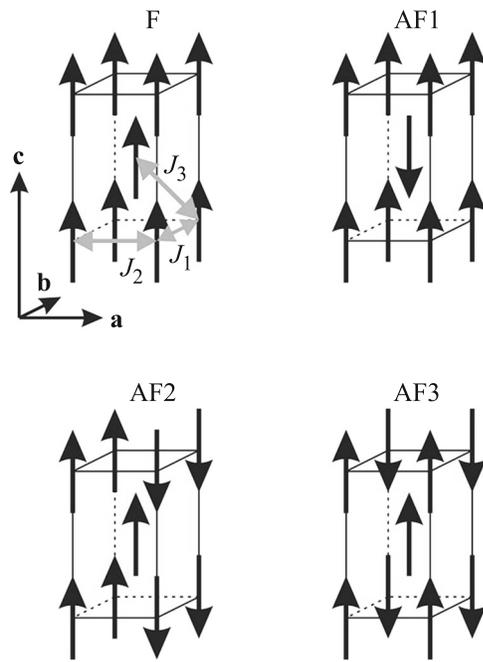
Fig. 6. Schematic representation of LCTO crystal magnetic structures under study.

netic moments in the (**a**, **c**) plane and antiferromagnetic ordering such as ↑↑↓↓ along the **b** axis with unit cell doubling along this axis. These magnetic structures are schematically shown in Fig. 6.

Table 3 lists the expressions for the energies of considered magnetic configurations in terms of exchange constants of Hamiltonian (1) and the energies of these configurations relative to the ferromagnetic state energy. We can see that the AF3 state is most energetically favorable in LCTO. The calculated exchange constants were $J_1 = -1.8$ meV, $J_2 = -0.55$ meV, and $J_3 = 0.175$ meV. The paramagnetic Curie temperature was estimated using these exchange constants as -27.2 K, which is in quite good agreement with the experimental value of -38 K obtained for LCTO disordered by titanium and copper cations [8].

Table 3. Expressions for energies of the considered magnetic structures in terms of the exchange constants of the Heisenberg Hamiltonian and the energies of these configurations relative to the ferromagnetic state energy

Structure	Expression for the energy	$\Delta E = E_i - E_F$, meV
F	$-J_1 - J_2 - 4J_3$	0
AF1	$-J_1 - J_2 + 4J_3$	1.4
AF2	$-J_1 + J_2$	-0.4
AF3	$J_1 - J_2$	-2.9

The calculated copper magnetic moment is 0.7 μ_B, which is also in satisfactory agreement with the experimental value of 0.9 μ_B [7].

It should be noted that ↑↑↓↓ antiferromagnetic structures were detected both experimentally and by ab initio calculations in some compounds with distorted perovskite structures (e.g., $HoMnO_3$ [13]) and double perovskite (e.g., Lu_2CoMnO_6 [14]) containing transition and/or rare-earth ions. A feature of ↑↑↓↓ ordering in distorted perovskite structures (with space group *Pbnm*) and double perovskite (with space group $P2_1/n$) is the fact that the inversion center is lost on such magnetic ordering, hence, spontaneous polarization arises.

In the LCTO compound under study, ↑↑↓↓ ordering of copper magnetic moments along the lattice vector **b** of the monoclinic cell leads to polar space group *Pn* and the appearance of spontaneous polarization in the (**b**, **c**) plane. To estimate spontaneous polarization in the LCTO crystal in the *Pn* phase, a set of equilibrium coordinates obtained upon structure relaxation without regard to spin polarization and a set of equilibrium coordinates obtained upon structure relaxation taking into account ↑↑↓↓ ordering of copper magnetic moments were used (the unit cell parameters in both calculations corresponded to equilibrium parameters of the monoclinic cell doubled in the parameter **b** in the calculation taking into account spin polarization). The spontaneous polarization was calculated by the formula

$$P_i = \frac{1}{V} \sum_{j=1}^{N} Z_j u_j^i, \qquad (2)$$

where $i = x, y, z$; V is the cell volume; N is the number of atoms in the cell; Z_j is the nominal charge of the ion with number j; and u_j^i is the displacement of the ion with number j. The obtained ion displacements and polarization components are given in Table 4.

4. CONCLUSIONS

Electronic, dynamic, and magnetoelectric properties of double perovskite La_2CuTiO_6 with staggered ordering of copper and titanium cations were studied within the density functional theory implemented in the VASP package. The results of calculations of the electronic structure taking into account spin polarization suggest that this compound is a dielectric. The vibrational spectrum of the high-symmetry cubic phase lattice contains unstable polar and antiferrodistorsion vibrational modes. Condensation of the most unstable antiferrodistorsion modes leads to the formation of a nonpolar monoclinic phase with space group $P2_1/n$. The calculation of the energies of various magnetic configurations in the low-symmetry phase showed that copper magnetic moments in the mag-

Table 4. Changes in relative coordinates of crystal ions, nominal ion charges (e is the electron charge), and spontaneous polarization of the LCTO crystal with space group *Pn* on antiferromagnetic ordering such as AF3

Atom	Wyckoff position	Charge, e	$\Delta x \times 10^4/a$	$\Delta y \times 10^4/b$	$\Delta z \times 10^4/c$	P_x, μC/m²	P_y, μC/m²	P_z, μC/m²
La1	2*a*	+3	−0.1701	1.4533	0.1773			
La2	2*a*	+3	−0.1761	1.4535	0.1788			
La3	2*a*	+3	0.1861	1.0989	−0.1540			
La4	2*a*	+3	0.1809	1.0985	−0.1539			
Cu1	2*a*	+2	−0.0097	0.3553	−0.0702			
Cu2	2*a*	+2	−0.0094	0.3559	−0.0701			
Ti1	2*a*	+4	−0.0667	−0.1579	−0.0951			
Ti2	2*a*	+4	−0.0736	−0.1584	−0.0963			
O1	2*a*	−2	0.4038	−0.2185	−1.2983			
O2	2*a*	−2	0.4076	−0.2190	−1.2971	−29	0	−71
O3	2*a*	−2	−0.3663	−0.0848	1.3025			
O4	2*a*	−2	−0.3718	−0.0840	1.3022			
O5	2*a*	−2	−1.0273	1.2317	0.2593			
O6	2*a*	−2	−1.0352	1.2309	0.2588			
O7	2*a*	−2	−0.7425	−2.0209	−0.1130			
O8	2*a*	−2	−0.7506	−2.0204	−0.1132			
O9	2*a*	−2	1.1089	−1.2447	−0.0566			
O10	2*a*	−2	1.0992	−1.2457	−0.0572			
O11	2*a*	−2	0.7108	1.8896	0.0488			
O12	2*a*	−2	0.7021	1.8907	0.0476			

netic ground state have ↑↑↓↓ antiferromagnetic ordering with doubled parameter **b** of the monoclinic cell. In the case of such ordering, the crystal symmetry decreases and spontaneous polarization arises. The spontaneous polarization was estimated as 71 μC/m².

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