
ORDER, DISORDER, AND PHASE TRANSITION
IN CONDENSED SYSTEM

Calculation and Comparison of Electronic, Vibrational, Polarization, and Magnetic Properties of Double Perovskites $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$

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Abstract—Vibrational, polarization, magnetic, and electronic properties of double perovskites $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$ with a rare type of “column” ordering of divalent metal cations have been calculated based on the density functional theory. Analysis of the crystal lattice dynamics for paraelectric phase $P4_2/nmc$ of both compounds has revealed that ferroelectric instability exists only in $\text{CaMnTi}_2\text{O}_6$. It is found that the structure distortion of the paraphrase of $\text{CaMnTi}_2\text{O}_6$ in the eigenvector of the unstable polar mode leads to a structure with the $P4_2/nmc$ space group. The calculated spontaneous polarization for the ferroelectric phase of $\text{CaMnTi}_2\text{O}_6$ is $P_s = 25 \mu\text{C}/\text{cm}^2$. The spin-polarization calculations have shown that the ground state is ferromagnetic in the $\text{CaFeTi}_2\text{O}_6$ crystal and antiferromagnetic in the $\text{CaMnTi}_2\text{O}_6$ crystal. The exchange interaction constants have been calculated using the Heisenberg model and the mean field approximation; the phase transition temperature for each compound has been estimated.

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1. INTRODUCTION

Advances in technologies of bulk crystal and thin film growth have provoked interest in the search and synthesis of new promising materials. One of the trends is the search for new materials with possible application of their magnetic, polarization, and magnetoelectric properties. The most promising materials with such properties are perovskite-like compounds, in particular, double perovskites $\text{AA}'\text{BB}'\text{O}_6$ containing ions of transition or rare-earth metals. These materials belong to the class of functional compounds due to the reach variety of physical properties determined by their composition and structure. Analysis of electronic, magnetic, ferroelectric, and magnetoelectric properties of such compounds is of considerable experimental and theoretical importance [1–5]. Different types of cation ordering determine different properties of such compounds. The ordering in the NaCl structure (staggered ordering) is the most common type of the B and B' cation ordering. As regards cations in the A and A' positions, “planar” ordering, in which one of lattice parameters of the perovskite structure is doubled, and A and A' cations alternate in this direction, is realized in most of the known compounds. In double perovskites $\text{CaMnTi}_2\text{O}_6$ and

$\text{CaFeTi}_2\text{O}_6$, a rare type of ordering of A and A' cations (namely, the “column” ordering in which A and A' cations alternate along two of three directions of the simple cubic perovskite lattice) is observed (Fig. 1). Both compounds are crystallized in the tetragonal structure with space group $P4_2/nmc$ with four molecules in the unit cell [6, 7]. This structure is distorted as a result of “rotation” of TiO_6 octahedrons ($a^+a^+c^-$) (in the Glazer notation [8]) in the “ideal” structure of the column ordering of the A and A' cations with space group $P4/mmm$ and with one molecule in the unit cell. Compounds $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$ differ significantly in that $\text{CaMnTi}_2\text{O}_6$ at $T = 630 \text{ K}$ experiences a ferroelectric phase transition with a high spontaneous polarization [7], while $\text{CaFeTi}_2\text{O}_6$ remains in the paraelectric state down to helium temperatures [9]. Magnetic properties of $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$ have been studied experimentally insufficiently. As follows from the results obtained in [7], $\text{CaMnTi}_2\text{O}_6$ at $T_N = 10 \text{ K}$ experiences a transition to the antiferromagnetic state, while $\text{CaFeTi}_2\text{O}_6$ does not exhibit magnetic order down to 4.2 K [10], although there are indications [9] that a transition to the ferromagnetic state can be observed below this temperature.

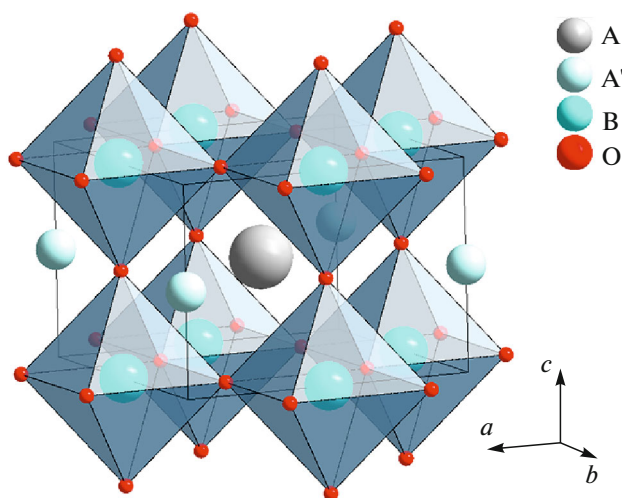


Fig. 1. (Color online) Double perovskite structure with column ordering for CaMTi_2O_6 ($M = \text{Fe}, \text{Mn}$).

The electronic and magnetic properties of compounds $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$ were investigated in [11, 12] using the density functional method. As regards the crystal lattice dynamics and structural instability, such investigations have not been performed for $\text{CaFeTi}_2\text{O}_6$ to our knowledge, while for $\text{CaMnTi}_2\text{O}_6$, only the results of calculation of unstable vibrational modes in the $P4/mmm$ phase are given in [13].

In this study, we report on the results of ab initio calculations and compare the structural, vibrational, electronic, polarization, and magnetic properties of double perovskites $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$, which are aimed at possible explanation of the reason for the difference in the ferroelectric properties of these compounds.

2. ANALYSIS

Calculations were performed using program package CRYSTAL in the molecular orbital approximation [14, 15]. We used hybrid exchange–correlation functional B3LYP including the combination of approaches of the density functional theory and the Hartree–Fock theory. For describing ions, we used complete-electron basic sets: Ca (86-511d3G), Ti (86411d31G), Fe (86-411d41G), Mn (86-411d41G), and O (8-411G). We specified the following high-spin state for magnetic ions: Fe^{2+} (4 unpaired electrons, $S = 2$) and Mn^{2+} (5 unpaired electrons, $S = 5/2$). In calculating the lattice dynamics and the dependences of the total energy on the amplitude of distortions in both compounds, we chose the ferromagnetic ordering of magnetic moments. The reciprocal space in our calculations was split by the Monkhorst–Pack grid into $8 \times 8 \times 8$ k -points of the Brillouin zone. In the calculations of the self-consistent field, the energy was

calculated to within 10^{-8} of the Hartree energy for structure relaxation and to 10^{-11} of the Hartree energy in the calculations of the crystal lattice dynamics.

3. RESULTS AND DISCUSSION

3.1. Structural, Vibrational, and Polarization Properties

In the case of column ordering of A and A' cations of $A_{1/2}A'_{1/2}\text{BO}_3$ compounds with the perovskite structure, the crystal symmetry is lowered to the tetragonal symmetry with space group $P4/mmm$; the unit cell volume is doubled upon an increase in the lattice parameters in the plane perpendicular to the axis in the direction of which “columns” of identical A or A' ions are formed (see Fig. 1).

As noted in Introduction, during distortion of the structure of the $P4/mmm$ phase in the $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$ crystals due to “rotations” of TiO_6 octahedrons ($a^+a^+c^-$), the experimentally observed $P4_2/nmc$ phase can be obtained in both compounds. To demonstrate the existence of corresponding unstable vibrations, we calculated the lattice dynamics for the $P4/mmm$ phase of compounds $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$.

Table 1 contains the calculated unit cell parameters and the coordinates of atoms of compounds $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$ in this structure. It should be noted that this structure has not been observed in experiments. Using the calculated unit cell parameters and coordinates of atoms in the $P4/mmm$ phase, we calculated the vibrational spectrum of the crystal lattice and Born dynamic charges. The results of calculations are given in Fig. 2 and Table 2. As can be seen from Fig. 2, both compounds in the $P4/mmm$ phase exhibit unstable modes of vibrations, which occupy the entire volume of the Brillouin zone. The most unstable modes with approximately the same imaginary frequency for $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$ belong to the center and boundary points A and Z of the Brillouin zone of the $P4/mmm$ tetragonal phase. At the center of the Brillouin zone, the “softest” polar mode of symmetry Γ_3^- is observed at frequencies of $266i \text{ cm}^{-1}$ and $242i \text{ cm}^{-1}$ for $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$, respectively. At boundary points A and Z, the softest modes are associated with rotations of the TiO_6 octahedron. At point A of the Brillouin zone of phase $P4/mmm$, the softest mode is a single mode of symmetry A_4^+ ; the eigenvector of this mode is the linear sum of eigenvectors of modes M_3 ($a^+a^0a^0$) and ($a^0a^+a^0$) of boundary points M of the Brillouin zone of perovskite structure $A_{1/2}A'_{1/2}\text{BO}_3$ (vectors $1/2(\mathbf{b}_2 + \mathbf{b}_3)$ and $1/2(\mathbf{b}_1 + \mathbf{b}_3)$ of the Brillouin zone of the perovskite pass to point A of the Brillouin zone of phase $P4/mmm$). The frequency of this mode has values of $289i \text{ cm}^{-1}$ and $300i \text{ cm}^{-1}$ for $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$, respectively. At point Z,

Table 1. Calculated cell parameters and atomic coordinates for $\text{CaFeTi}_2\text{O}_6$ ($a = 5.4360 \text{ \AA}$, $c = 3.8580 \text{ \AA}$) and $\text{CaMnTi}_2\text{O}_6$ ($a = 5.4505 \text{ \AA}$, $c = 3.8548 \text{ \AA}$) in the $P4/mmm$ phase

Ion	Positions	$\text{CaFeTi}_2\text{O}_6$			$\text{CaMnTi}_2\text{O}_6$		
		x/a	y/b	z/c	x/a	y/b	z/c
Ca	$1d$	0.5	0.5	0.5	0.5	0.5	0.5
Fe/Mn	$1b$	0	0	0.5	0	0	0.5
Ti	$2f$	0	0.5	0	0	0.5	0
O_1	$4j$	0.2472	0.2472	0	0.2481	0.2481	0
O_2	$2e$	0	0	0.5	0	0	0.5

Table 2. Calculated diagonal components of the dynamic charge tensor in the units of electron charge

$\text{CaFeTi}_2\text{O}_6$				$\text{CaMnTi}_2\text{O}_6$			
ion	Z_{xx}	Z_{yy}	Z_{zz}	ion	Z_{xx}	Z_{yy}	Z_{zz}
Ca	2.41	2.41	2.42	Ca	2.38	2.38	2.36
Fe	2.65	2.65	2.89	Mn	2.69	2.69	2.68
Ti_1	6.53	6.91	6.56	Ti_1	6.54	6.87	6.63
Ti_2	6.91	6.53	6.56	Ti_2	6.87	6.54	6.63
O_1	-3.60	-2.89	-2.07	O_1	-3.60	-2.92	-2.02
O_2	-3.60	-2.89	-2.07	O_2	-3.60	-2.92	-2.02
O_3	-3.60	-2.89	-2.07	O_3	-3.60	-2.92	-2.02
O_4	-3.60	-2.89	-2.07	O_4	-3.60	-2.92	-2.02
O_5	-1.96	-2.16	-5.07	O_5	-1.94	-2.12	-5.11
O_6	-2.16	-1.96	-5.07	O_6	-2.12	-1.94	-5.11

the softest modes are also doubly degenerate modes of symmetry Z_5^+ ($(a^-a^0c^0)$, $(a^0a^-c^0)$) and a single mode of symmetry Z_2 ($a^0a^0c^-$) (“rotational” modes; in the perovskite structure, this is triply degenerate mode R_5 at boundary point $1/2(\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)$). The frequencies of these modes are $274i \text{ cm}^{-1}$ (2) and $272i \text{ cm}^{-1}$ for $\text{CaMnTi}_2\text{O}_6$ and $291i \text{ cm}^{-1}$ (2) and $258i \text{ cm}^{-1}$ for $\text{CaFeTi}_2\text{O}_6$. The distortion of the structure in eigenvector of mode A_4^+ leads to space group $I4/mmm$ with two molecules in the unit cell, while the distortion of the structure in the vector of mode Z_2 leads to space group $P4_2/mcm$ also with two molecules per unit cell. Figure 3 shows the dependences of the energies of crystals $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$ on the amplitude of displacement of ions in eigenvectors of modes A_4^+ and Z_2 (angles of “rotation” of the TiO_6 octahedron). As can be seen from the figure, there is a significant difference in the dependences of energies $\text{CaMnTi}_2\text{O}_6$

and $\text{CaFeTi}_2\text{O}_6$, which is associated with mode Z_2 ($a^0a^0c^-$). In the case of $\text{CaFeTi}_2\text{O}_6$, the energy minimum is much deeper as compared to $\text{CaMnTi}_2\text{O}_6$ and corresponds to stronger distortion.

The superposition of distortions of the structure in the eigenvectors of modes A_4^+ and Z_2 leads to space group $P4_2/nmc$ with four molecules in the unit cell. This structure is observed experimentally for $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$. Table 3 contains the lattice parameters and coordinates of atoms calculated in this study for $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$ in phase $P4_2/nmc$. It follows from Table 3 that the calculated and experimental values of the unit cell parameters and coordinates of atoms for $\text{CaMnTi}_2\text{O}_6$ coincide to within of fraction of percent, while for $\text{CaFeTi}_2\text{O}_6$, the largest difference on the order of 1% is observed between the calculated and experimental values only for parameter c . For the $P4_2/nmc$ phase, we calculated the frequencies of crystal lattice vibrations for the compounds in question. For the $\text{CaFeTi}_2\text{O}_6$ crystal, the calculations were performed for the experimental

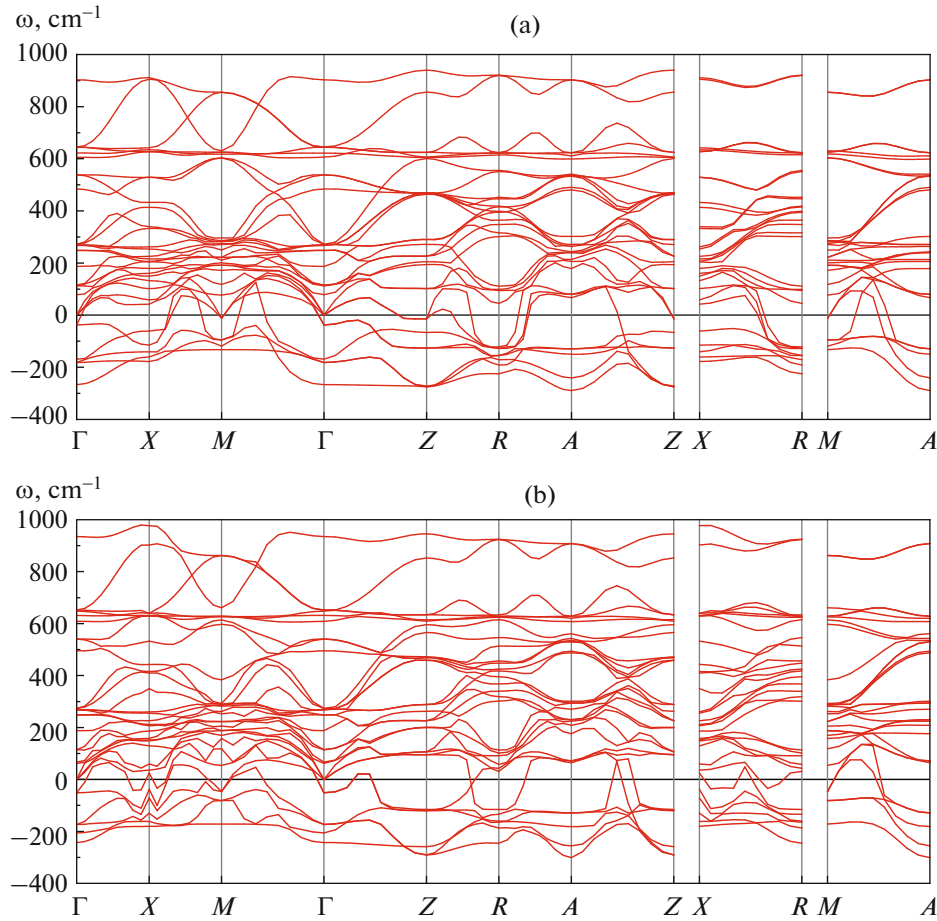


Fig. 2. (Color online) Phonon spectrum in the $P4/mmm$ phase: (a) $\text{CaMnTi}_2\text{O}_6$; (b) $\text{CaFeTi}_2\text{O}_6$.

value of lattice parameter c . The results of calculations for the center of the Brillouin zone together with available experimental data are given in Table 4. As follows from this table, all vibrational modes in the $\text{CaFeTi}_2\text{O}_6$ crystal, including the polar mode (although the frequency for this mode is anomalously low) are hard, while for the $\text{CaMnTi}_2\text{O}_6$ crystal in the $P4_2/nmc$ phase, polar mode A_{2u} remains soft with a quite high value of the imaginary frequency. It is well known that in compounds with the perovskite structure, the ferroelectric instability in the cubic phase is suppressed partly or completely in the distorted phase associated with the rotation of the octahedron. In the case of compounds considered here, the polar mode for and $\text{CaMnTi}_2\text{O}_6$ is stabilized partly (the value of frequency of the Γ_3^- mode in the undistorted phase $P4/mmm$ is $266i \text{ cm}^{-1}$, while in the $P4_2/nmc$ phase, the value of frequency of the A_{2u} mode is $75i \text{ cm}^{-1}$), while for $\text{CaFeTi}_2\text{O}_6$, the polar mode is stabilized completely (the value of frequency of mode Γ_3^- in undistorted phase $P4/mmm$ is $242i \text{ cm}^{-1}$, while the value of frequency of mode A_{2u} in phase $P4_2/nmc$ is 21 cm^{-1}). The

stabilization of the polar mode in $\text{CaFeTi}_2\text{O}_6$ is associated, as noted above, with the energetically more advantageous and stronger distortion ($a^0a^0c^-$). The distortion of the $\text{CaMnTi}_2\text{O}_6$ structure in phase $P4_2/nmc$ in the eigenvector of polar mode A_{2u} leads to space group $P4_2/nmc$ with four molecules in the unit cell. It is this structure that is observed experimentally in the $\text{CaMnTi}_2\text{O}_6$ crystal below the ferroelectric phase transition at $T = 630 \text{ K}$. Figure 4 shows the dependence of the change in energy in $\text{CaMnTi}_2\text{O}_6$ on the amplitude of the ion displacement along the eigenvector of polar mode A_{2u} .

Using the value of the of atomic displacement amplitude corresponding to the energy minimum and the values of dynamic Born charges Z from Table 2, we calculated spontaneous polarization

$$P_s = \frac{1}{V} \sum_i Z_{zz}^i u_z^i$$

(V_0 is the unit cell volume), which turned out to be $25 \mu\text{C}/\text{cm}^2$, which is in very good agreement with experimental value ($24 \mu\text{C}/\text{cm}^2$) [7].

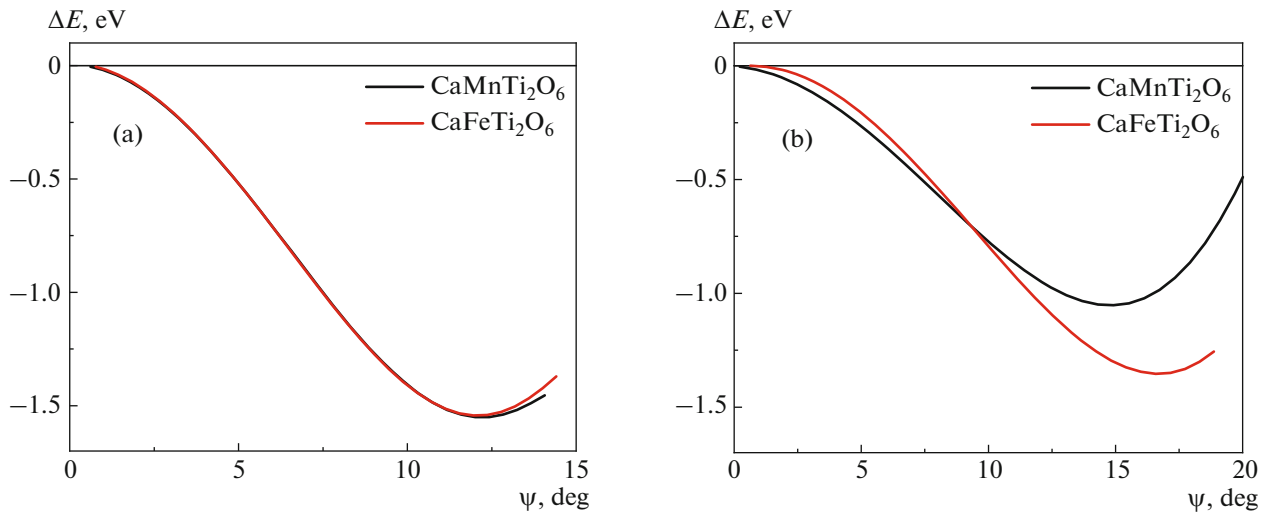


Fig. 3. (Color online) Dependence of the change in the total energy on the rotation angles of octahedrons for $\text{CaFeTi}_2\text{O}_6$ and $\text{CaMnTi}_2\text{O}_6$ for distortions: (a) $\psi = (a^+ a^0 c^0) + (a^0 a^+ c^0)$; (b) $\phi = (a^0 a^0 c^-)$.

It was found from calculations that the mean length of bond Ti–O between titanium and oxygen ions in phase $P4_2/nmc$ phase is 1.976 Å in $\text{CaMnTi}_2\text{O}_6$ crystal and 1.978 Å in the $\text{CaFeTi}_2\text{O}_6$ crystal. In the $P4_2mc$ in the $\text{CaMnTi}_2\text{O}_6$ crystal the minimal and maximal values of the Ti–O bond length are 1.897 and 2.084 Å,

respectively. In [16], it is reported that the mean length of the Ti–O bond in the $P4_2/nmc$ phase is 1.964 Å, while the minimal and maximal lengths of the Ti–O bond in the polar $P4_2mc$ phase are 1.836 and 2.107 Å, respectively. It can be seen that the results of calculations are in good agreement with experimental data.

Table 3. Calculated unit cell parameters and coordinates of atoms for $\text{CaFeTi}_2\text{O}_6$ ($a = 7.5449$ Å, $c = 7.6196$ Å) and $\text{CaMnTi}_2\text{O}_6$ ($a = 7.5921$ Å, $c = 7.6175$ Å) in the $P4_2/nmc$ phase

Ion	Positions		$\text{CaFeTi}_2\text{O}_6$			$\text{CaMnTi}_2\text{O}_6$		
			x/a	y/b	z/c	x/a	y/b	z/c
Ca	4d	Calc.	0.25	0.25	0.2750	0.25	0.25	0.27417
		Exp. [6, 7]	0.25	0.25	0.2754	0.25	0.25	0.27212
Fe_1/Mn_1	2b	Calc.	0.75	0.25	0.25	0.75	0.25	0.25
		Exp. [6, 7]	0.75	0.25	0.25	0.75	0.25	(0.25)*
Fe_2/Mn_2	2a	Calc.	0.75	0.25	0.75	0.75	0.25	0.75
		Exp. [6, 7]	0.75	0.25	0.75	0.75	0.25	0.75
Ti	8e	Calc.	0	0	0	0	0	0
		Exp. [6, 7]	0	0	0	0	0	0
O_1	8g	Calc.	0.25	0.5431	0.4293	0.25	0.543	0.4361
		Exp. [6, 7]	0.25	0.5437	0.4343	0.25	0.538	0.4442
O_2	8g	Calc.	0.25	0.0554	0.0346	0.25	0.0538	0.0336
		Exp. [6, 7]	0.25	0.0543	0.0362	0.25	0.0549	0.0344
O_3	8f	Calc.	0.5561	0.4439	0.25	0.5513	0.4487	0.25
		Exp. [6, 7]	0.5527	0.4473	0.25	0.5479	0.4521	0.25

Experimental values of the unit cell parameters for $\text{CaFeTi}_2\text{O}_6$ at 300 K: $a = 7.5157$ Å, $c = 7.5548$ Å [6]. For $\text{CaMnTi}_2\text{O}_6$ at 700 K, $a = 7.5827$ Å, $c = 7.5922$ Å [7]. Asterisk marks the mean value of coordinate of Mn1, while in [7], Mn1 was in position 4c with coordinate $z/c = 0.2072$ and with an occupancy of 0.5.

Table 4. Frequencies of vibrational modes at the center of the Brillouin zone in the $P4_2/nmc$ phase classified in irreducible representation. Mn_{calc} corresponds to calculated frequencies in $CaMnTi_2O_6$; Mn_{exp} are experimental data on Raman scattering for $CaMnTi_2O_6$ [13]; Fe_{calc} are calculated frequencies in $CaFeTi_2O_6$

Symmetry	Mn_{calc}	Mn_{exp}	Fe_{calc}	Symmetry	Mn_{calc}	Fe_{calc}
A_{1g}	222	—	236	A_{1u}	155	145
	246	—	276		178	185
	347	344	365		242	252
	399	395	427		415	404
	545	—	565		442	444
	563	595	578		507	503
A_{2g}	290		289	A_{2u}	75i	0
	487		491		0	21
	505		514		174	178
	800		800		196	217
					249	271
					274	283
					332	349
					360	370
					420	441
					486	475
			546	553		
			620	629		
B_{1g}	49	—	97	B_{1u}	122	124
	177	—	182		146	138
	233	—	250		157	161
	272	279	284		206	214
	286	—	302		435	438
	383	—	400		445	446
	498	—	508		490	494
	521	529	530			
	732	—	730			
B_{2g}	369	—	372	B_{2u}	191	200
	500	—	510		281	303
	777	—	777		299	312
					351	364
					364	378
					449	471
					545	552
			612	625		
			627	368		
E_g	129	—	142	E_u	0	0
	166	—	170		82	81
	202	—	211		115	119
	232	228	243		150	160
	260	—	282		156	160

Table 4. (Contd.)

Symmetry	Mn _{calc}	Mn _{exp}	Fe _{calc}	Symmetry	Mn _{calc}	Fe _{calc}
	313	—	320		180	193
	351	—	360		185	201
	390	—	410		215	224
	417	432	420		231	248
	490	483	498		248	262
	513	—	524		308	319
	734	—	729		343	357
	778	818	781		373	390
					434	440
					488	487
					492	495
					508	513
					539	544
					550	554

3.2. Electronic and Magnetic Properties

To determine the ground magnetic state, the constants of magnetic interaction and the temperatures of phase transition from the paramagnetic and magnetically ordered state, we performed the spin-polarized collinear calculation of four magnetic configurations [11] in the $P4_2/nmc$ phase for $\text{CaFeTi}_2\text{O}_6$ and in the $P4_2mc$ phase for $\text{CaMnTi}_2\text{O}_6$. These four magnetic configurations are shown schematically in Fig. 5. The

magnetic moments for iron and manganese ions were $3.7\mu_B$ and $4.7\mu_B$, respectively. The differences in the energies for four magnetic configurations per formula unit of the compounds under investigation are given in Table 5. As follows from the table, the ground state in $\text{CaMnTi}_2\text{O}_6$ corresponds to the C -type antiferromagnetic ordering. The polar structure with $P4_2mc$ with such a magnetic configuration corresponds to magnetic symmetry group $P4_2m'c$, which is in conformity with the results obtained in [16].

The exchange interaction constants J_1 , J_2 , and J_3 (between the nearest, second, and third neighbors, respectively, as shown in Fig. 5) were calculated using the classical Heisenberg Hamiltonian in form

$$\mathcal{H} = -\frac{1}{2} \sum_{ij} J_{ij} S_i S_j,$$

where J_{ij} is the constant of the exchange interaction between the i th and j th sites, and S_i and S_j are the

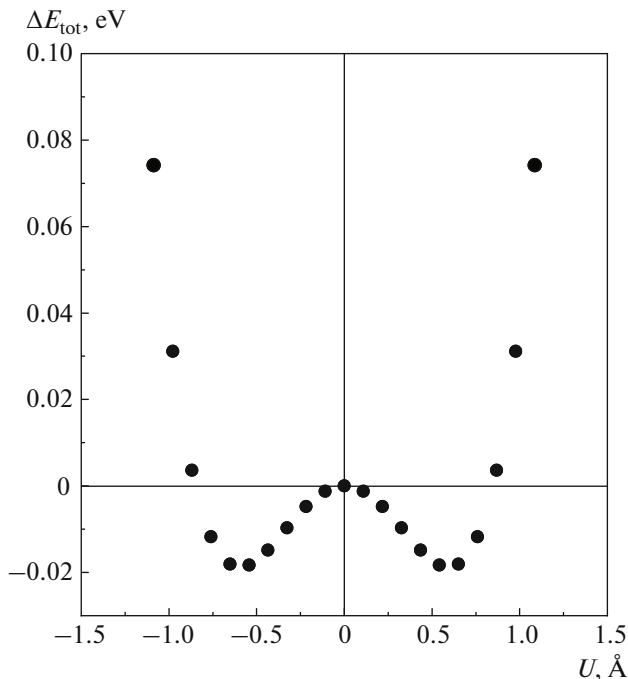


Fig. 4. Dependence of the change in the total energy on polar distortion amplitude U in $\text{CaMnTi}_2\text{O}_6$.

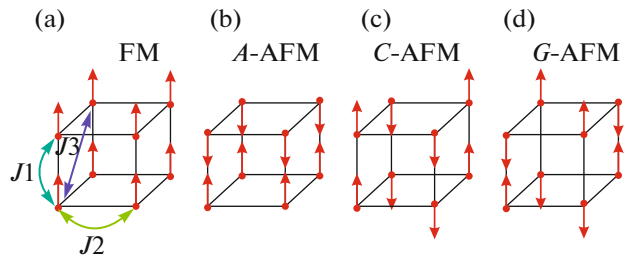


Fig. 5. (Color online) Magnetic configurations under study with included exchange interactions: (a) ferromagnetic ordering; (b) A -type antiferromagnetic ordering; (c) C -type antiferromagnetic ordering; (d) G -type antiferromagnetic ordering.

effective values of spin at the i th and j th sites, respectively. The exchange interaction constants for $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$ are given in Table 6. The temperature of the phase transition to the magnetically ordered state was estimated in the mean field approximation. With allowance for the interaction up to the third nearest neighbors, the magnetic system is divided into the four sublattices; in this case, the ordering temperature is determined from the system of four equations [17]

$$\begin{aligned} T_1 &= \frac{2(S+1)S}{3K}(2J_1 + 4J_2 + 8J_3), \\ T_2 &= \frac{2(S+1)S}{3K}(-2J_1 + 4J_2 - 8J_3), \\ T_3 &= \frac{2(S+1)S}{3K}(2J_1 - 4J_2 - 8J_3), \\ T_4 &= \frac{2(S+1)S}{3K}(-2J_1 - 4J_2 - 8J_3). \end{aligned} \quad (1)$$

Using the exchange interaction constants from Table 6 and the spin values ($S = 5/2$ for Mn and $S = 2$ for Fe), we obtained temperatures $T_N = 33$ K for the antiferromagnetic phase transition (of the C type) for $\text{CaMnTi}_2\text{O}_6$ and $T_C = 10$ K of the ferromagnetic phase transition in $\text{CaFeTi}_2\text{O}_6$. The Curie temperature obtained for the $\text{CaMnTi}_2\text{O}_6$ crystal is $T_C = -18$ K. The calculated values of the phase transition temperature are approximately thrice as high as experimental value $T_N = 10$ K for $\text{CaMnTi}_2\text{O}_6$ [7] and $T_C = 3$ K for $\text{CaFeTi}_2\text{O}_6$ [9], which is not surprising when the mean field approximation is used for systems with competing interactions.

The calculated and partial densities of electronic states for $\text{CaFeTi}_2\text{O}_6$ in the ferromagnetic phase and $\text{CaMnTi}_2\text{O}_6$ in the antiferromagnetic phase of the C type are shown in Fig. 6. Both compounds are dielectrics with a bandgap of 3 eV for $\text{CaMnTi}_2\text{O}_6$ and 2.4 eV for $\text{CaFeTi}_2\text{O}_6$. A peculiar feature of the electronic structure of both compounds is the existence of a narrow band separated by approximately 0.3 eV from the main part of the valence band at its edge near the Fermi level (insets to Fig. 6). In the case of $\text{CaFeTi}_2\text{O}_6$, this narrow band represents strongly hybridized states of d electrons of iron Fe1 and Fe2 and p electrons of oxygen with a small fraction of d electrons of titanium. In such a hybridized state, d electrons of iron have the magnetic moment direction opposite to that of the ground state. In the case of $\text{CaMnTi}_2\text{O}_6$, the narrow band in the vicinity of the Fermi level also represents a strongly hybridized state. However, in contrast to $\text{CaFeTi}_2\text{O}_6$, d electrons in $\text{CaMnTi}_2\text{O}_6$ are hybridized in this state with both positive and negative magnetic moments of only one species of manganese atoms: d electrons of titanium and p electrons of oxygen are also hybridized with positive and negative magnetic

Table 5. Calculated total energies of various magnetic configurations per formula unit. Zero energy is the energy of the ferromagnetic state

Configuration	$\text{CaFeTi}_2\text{O}_6$, $E - E_{FM}$, meV	$\text{CaMnTi}_2\text{O}_6$, $E - E_{FM}$, meV
FM	0.000	0.000
A -AFM	1.062	0.831
C -AFM	0.235	-4.746
G -AFM	2.447	-2.618

Table 6. Calculated exchange interaction constants

	$\text{CaFeTi}_2\text{O}_6$	$\text{CaMnTi}_2\text{O}_6$
J_1 , meV	0.102	0.059
J_2 , meV	0.025	-0.082
J_3 , meV	-0.009	-0.006

moments. It should be noted that for simple titanium oxides with the perovskite structure (BaTiO_3 and PbTiO_3), strong hybridization of d electrons of tita-

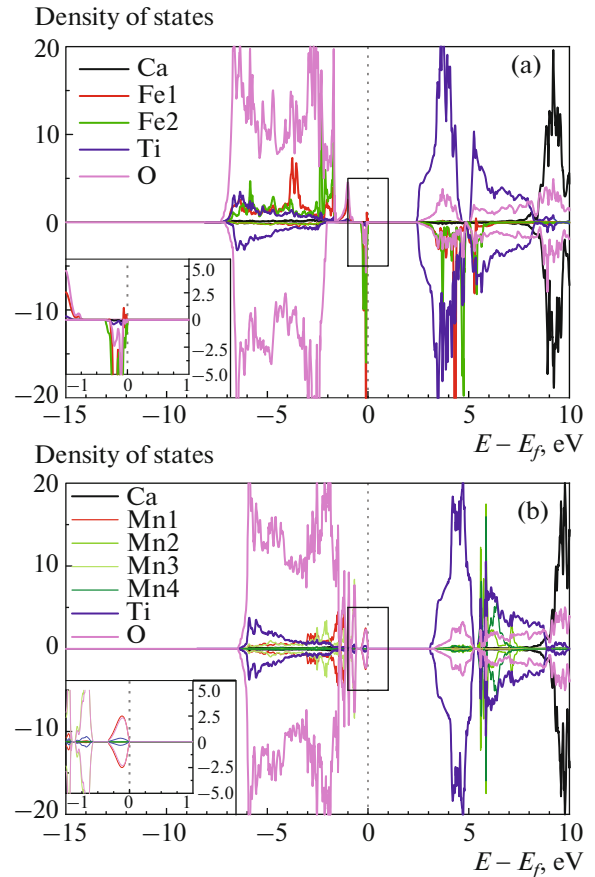


Fig. 6. Partial electron density of states (per unit cell): (a) $\text{CaFeTi}_2\text{O}_6$; (b) $\text{CaMnTi}_2\text{O}_6$. The insets show the region near the Fermi energy on magnified scale.

mium with p electrons of oxygen facilitates the emergence of ferroelectric instability in the cubic phase [18]. It can be seen from Fig. 6 that the main contribution to the conduction band in both compounds comes from empty $3d$ states of titanium with small contributions from empty states of the remaining atoms.

4. CONCLUSIONS

Ab initio calculations of the vibrational, polarization, magnetic, and electronic properties of double perovskites $\text{CaMnTi}_2\text{O}_6$ and $\text{CaFeTi}_2\text{O}_6$ with a rare type of column ordering of cations of divalent metals have been performed based on the density functional theory realized in the CRYSTAL package. The vibrational spectrum of the lattice in the ordered phase with space group $P4/mmm$ showed the presence of unstable vibrational modes occupying the entire volume of the Brillouin zone. Distortion of the structure in the eigenvectors of the most unstable modes leads to space group $P4_2/nmc$ with four molecules in the unit cell, which is observed in experiments with both compounds. As follows from the results of calculation of lattice vibrational frequencies in $\text{CaFeTi}_2\text{O}_6$ in this phase, all vibrational frequencies are real-valued; i.e., the unstable polar mode is suppressed by distortions associated with rotation of the TiO_6 octahedron. In the $\text{CaMnTi}_2\text{O}_6$ crystal in the $P4_2/nmc$ phase, the polar mode remains unstable, and distortion in the eigenvector of this mode leads to space group $P4_2mc$, which is observed in experiments. The calculated value of spontaneous polarization $P_s = 25 \mu\text{C}/\text{cm}^2$ for $\text{CaMnTi}_2\text{O}_6$ is in good agreement with experimentally observed value of $P_s = 24 \mu\text{C}/\text{cm}^2$. It was found from the results of spin-polarization calculations that the ground state is ferromagnetic in the $\text{CaFeTi}_2\text{O}_6$ crystal and antiferromagnetic in the $\text{CaMnTi}_2\text{O}_6$ crystal. The exchange interaction constants have been calculated using the Heisenberg model and in the mean field approximation, and phase-transition temperatures have been estimated.

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