

# Theoretical modeling of high spin to low spin transition and structural stability under pressure in $\text{CaFeO}_3$

A. O. Shorikov<sup>1)</sup>

*M. N. Mikheev Institute of Metal Physics of Ural Branch of the Russian Academy of Sciences, 620108 Yekaterinburg, Russia*

*Department of Theoretical Physics and Applied Mathematics, Ural Federal University, 620002 Yekaterinburg, Russia*

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Compounds with a perovskite structure have been intensively investigated during the last decades due to the variety of electronic and magnetic properties and the great interest in their practical applications [1–7].  $\text{CaFeO}_3$  is of a special interest due to unusual valence of iron ions  $\text{Fe}^{4+}$  which is in a high spin (HS) state at ambient pressure with electronic configuration  $t_{2g}^3 e_g^1$ . Since the double degenerate  $e_g$  subshell is occupied by one electron, the instability known as the Jahn–Teller effect could arise. It is energetically favorable to lift the degeneracy by distorting the octahedron around the transition metal. Another way for lifting the degeneracy and minimizing the total energy is charge ordering or charge disproportionation (CD) which is observed in the  $\text{CaFeO}_3$  in the low temperature phase.

$\text{CaFeO}_3$  has a perovskite-like structure consisting of corners-shared octahedrons  $\text{FeO}_6$  and Ca ions in the spaces of this 3D structure. The structure of  $\text{CaFeO}_3$  is distorted by the tilt of the octahedrons, leading to orthorhombic or monoclinic symmetry. Takeda et al. showed that at room temperature  $\text{CaFeO}_3$  has  $Pnma$  space group with the average Fe–O bond length 1.91870(6) Å. With decreasing temperature the CD state occurs at  $T_{CD} \approx 290$  K, that leads to a phase transition to the monoclinic structure with  $P2_1/n$  space group and with two inequivalent  $\text{FeO}_6$  octahedrons [1]. The average Fe–O bond length for the small octahedron is 1.87244(6) Å, and 1.97317(6) Å for the larger one.

At ambient pressure and temperature above 290 K  $\text{CaFeO}_3$  is paramagnetic without CD and all iron ions are equivalent and have  $\text{Fe}^{4+}$  valence. With decreasing temperature the CD state with  $\text{Fe}^{3+}$  and  $\text{Fe}^{5+}$  ions is observed below 290 K, but  $\text{CaFeO}_3$  remains paramagnetic until the CD AFM phase occurs at  $T_N = 115$  K.

The GGA +  $U$  calculations were performed using the pseudopotential method implemented in the Quan-

tum ESPRESSO package [8]. We use the exchange-correlation potential in the form proposed by Perdew, Burke, and Ernzerhof [9]. A similar approach was previously successfully applied for modeling structural transition and for description of the evolution of magnetic properties in correlated materials under pressure [10]. To take into account the correlation effects,  $U = 4.5$  eV and  $J = 0.95$  eV were applied to the Fe  $d$ -shell.

We consider three magnetic orders, namely AFM-A, AFM-C, and AFM-G for both structures:  $Pnma$  and  $P2_1/n$ . For each magnetic order full structure optimization was performed. The AFM-A ordering has the lowest total energy for both structures, which agrees with experimental data for the monoclinic structure. One can see that the AFM-A ordering is persistent against the structural transition and its traces could be observed in the  $Pnma$  structure at high pressure. Optimization of the crystal structures in the framework of the GGA +  $U$  method shows that both structures are stable at ambient pressure. The monoclinic structure  $P2_1/n$  has a total energy 0.029 eV lower than the orthorhombic  $Pnma$  structure in agreement with the experimental phase diagram.

A series of calculations with full relaxation of the crystal structure was performed for various external pressures (cell volumes). The unit cell parameters obtained in the GGA +  $U$  calculation are in a good agreement with the experimental data [1]. If the shape of the unit cell was not preserved during relaxation of the crystal structure, the orthorhombic phase keeps the symmetry below 30 GPa only. At higher pressures  $\text{FeO}_6$  octahedrons become non-equivalent indicating that the monoclinic structure might be favorable. The length of the Fe–O bonds at various pressures obtained in GGA +  $U$  is shown in Fig. 1. One can see that the bond length is tending to the values obtained for monoclinic phase, which gives two metastable structures with non-equivalent octahedrons. However, high pres-

<sup>1)</sup>e-mail: shorikov@imp.uran.ru

sure XRD shows that orthorhombic structure is stable above 30 GPa at room temperature [2]. This result can indicate that the transition is entropy driven and proper accounting of phonon entropy and temperature is necessary. Similar results were obtained for transition under pressure in FeS [11]. It was shown recently, that transition from  $P2_1/n$  to  $Pnma$  structure under pressure could be reproduced in the framework of DFT + DMFT method [12] at finite temperature without full relaxation of atomic positions but with accurate accounting for many body correlation effects, which underscores the importance of the temperature effects.

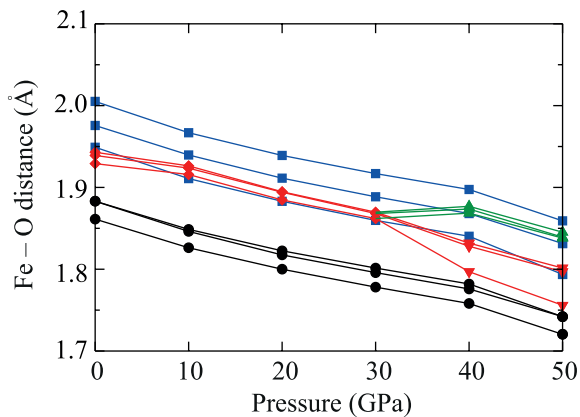


Fig. 1. (Color online) Dependence of Fe-O bond length from pressure for orthorhombic (red and green lines) and monoclinic (black and blue lines) structures obtained in GGA +  $U$  calculations

Spin transition pressure  $\approx 35$  GPa obtained in GGA +  $U$  is close to the experimental value of 30 GPa at room temperature. At pressures lower than 30 GPa, the LS solution was unstable and only HS was obtained. In the pressure range 30–40 GPa the value of magnetic moment decreases from  $3.18\mu_B$  to  $1.6\mu_B$  which indicates the spin transition. This agrees well with the experimentally observed HS state in  $\text{CaFeO}_3$  at ambient pressure [2]. Calculations made for  $P2_1/n$  show similar magnetic collapse with decreasing magnetic moments from  $3.55\mu_B$  for Fe(1) and  $2.7\mu_B$  for Fe(2) to  $1.52\mu_B$  and  $1.47\mu_B$ , correspondingly.

In the present work, magnetic and spectral properties of  $\text{CaFeO}_3$   $Pnma$  and  $P2_1/n$  phases under pressure were investigated in framework of GGA +  $U$  method. A-type AFM was found energetically favorable for both structures that agrees with experimental data for monoclinic phase below 127 K [13]. With increasing pressure and decreasing Fe-O distance, hybridization increases,

leading to the HS-to-LS transition at  $\approx 35$  GPa. However, the structural phase transition cannot be reproduced in the framework of the GGA +  $U$  method. The explanation of this could be the following: the ground state energy calculated in DFT +  $U$  assumes  $T = 0$  K, whereas the impact of temperature and vibrational entropy [11] could be important for a proper description of the phase transition under pressure in  $\text{CaFeO}_3$ .

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