**Magnetic structures and phase transition of Ca2CoSi2O7**

Pham Thanh Cong1, Vuong Van Hiep2, Nguyen Anh Tuan2, Bui Dinh Tu3, Hoang Nam Nhat3,a)

1High Magnetic Field Laboratory, Helmholtz-Zentrum Dresden-Rossendorf, 01328 Dresden, Germany

2 Faculty of Physics, VNU-University of Science, 334 Nguyen Trai, Thanh Xuan, Ha Noi 10000, Viet Nam

3Faculty of Engineering and Nanotechnology, VNU-University of Engineering and Technology, 144 Xuan Thuy, Cau Giay,

Ha Noi 10000, Viet Nam

a) *Corresponding author:* [*namnhat@gmail.com*](mailto:namnhat@gmail.com)

**Abstract.** Recent advances in multiferroics, such as Ca2CoSi2O7, raise questions about their possible magnetic phases and transitions with temperature. In this article, we discuss all possible magnetic states and related structures of this compound on the basis of Density Functional Theory. The calculations were performed using different model supercells consisting of 1 to 4 unit cells. Different magnetic order states have been shown to transform into several basic structures whose population with temperature can clarify conflicting experimental data. The obtained probability of magnetic structures with temperature also explains the possible strong ferromagnetism, or weak paramagnetic response in the high field, and phase transition observed recently by acoustic phonon measurements. The competition between various magnetic ordering states shows why magnetization saturations were achieved only at high applied field and in low temperature region.

# INTRODUCTION

Complex oxides are often considered layered or clustered compounds in which planes or clusters consisting of oxygen and metal atoms are layered or bonded together to form strongly correlated electron systems. Many of these compounds are multiferroic, meaning there are multiple competing Ferron-like phases in the compound, so the properties of multiferroics often depend on temperature or other physical factors such as magnetic or electric fields1. As a typical multiferroic substance, Ca2CoSi2O7 exhibits different magnetic phases in both low and high temperature regions. These phases compete with each other and the intensity of ferromagnetic exchange determines the magnetic behavior of this compound in given temperature segment2. Therefore, this compound is ideal for application in modern spin electronics to create highly sensitive magnetic sensors and memory devices. Regarding its intrinsic properties, Ca2CoSi2O7 can exhibit both type I and type II multiferroic properties, i.e. magnetic phase transitions can occur with or without a change of the compound's crystal lattice3. However, Ca2CoSi2O7 mainly shows type II behavior with magnetic interactions originating from the Co2+ in the +3/2 high spin state4. It also shows large magneto-capacitance effects of 13% at 5.1 K5. Strong interactions between Co2+ spins can cause considerable large energy gaps among the magnetic ordering states. At room temperature, Ca2CoSi2O7 crystallizes in a tetragonal space group *P421m* with one Co at the origin (0,0,0) and the other at the center of *ab-*face (0.5, 0.5, 0).

But at low temperature (T < 10 K) it may occur in an orthorhombic P21212 structure with 3×3×1 supercell6. Due to the disorder of the Co spins, other less symmetric structures may also exist. Theoretically for supercells with P421*m* symmetry, spin disorder could reduce the symmetry of P421*c*, P4, P4, P21, P2 etc. As known experimentally, this compound undergoes structural transitions at around 200 and 500 K7, 8. At high field, antiferromagnetic order was observed at 5.7 K.

To elucidate the existence of different magnetic ordering of Ca2CoSi2O7 we performed an evaluation of the cell energy changes caused by different spin structures using Density Functional Theory (DFT) with the CASTEP code9, and discuss the probability of magnetic states at each temperature in the range from 0 to 2000 K.

# COMPUTATION DETAILS

*Model structures*. The models start from a tetragonal cell in P421*m* symmetry (*a = b  c*,  =  =  = 90o). This cell contains Co located at two symmetry-related positions (0,0,0) and (0.5, 0.5,0). So, preserving P421*m* symmetry it allows only one ferromagnetic (FM) configuration with net cell magnetic moment of 3B. Surprisingly, this cell is located in the energy scale by only 0.036 eV above the lowest antiferromagnetic (AF) state. It follows that the probability to observe this state is 5.9% at room temperature. If we consider two Co symmetry-related sites to occur in the low spin state, then the resulting probability should be 0 because of large energy gap (2.296 eV) above the lowest AF state. Another theoretically possible spin configuration in P421*m* symmetry is the total spin disorder state, where net cell magnetic moment is 0. This configuration is not probable at any physically meaningful temperature as it is 2.489 eV above the lowest AF state. Ignoring this initial cell, model cells are created and expressed according to the size of the corresponding supercell as 111 (*aac*), 112 (*aa2c*), 211 (*2aac*), 222 (*2a2a2c*) and 331 (*3a3ac*). Different magnetic orders are imposed on each supercell give rise to different final symmetries of P421*c*, P4, P4, P21212, P21, P2, and P1. Therefore, the modeled magnetic structures are denoted as 111P4A, 112P421*c*B etc., to indicate the cell size (111, 112…), symmetry (P4, P421*c* …) and type (A, B, C) of magnetic order. Some model structures relevant to this article are presented in Table 1 which includes illustrations to clarify the spin orientations. We briefly explain typical models as follows.

The 111 cell with P421*m* symmetry reduces its symmetry to P4 if two Co sites are spin-anti-parallel. Indeed, this 111P4A antiferromagnetic (AF) structure is the lowest energy state, resulting in a net cell magnetic moment of zero. The 23.7% probability of its associated macroscopic paramagnetic state at room temperature (calculated according to the Maxwell-Boltzmann statistics) is the highest in the entire range of temperature. Regarding the priority of high and low spin state, it can be confirmed that all low spin states were converged to the high spin ones when performing the geometry optimization with Co starting in a mixed high-low AF spin configuration (a model denoted 111P4B).

**TABLE 1.** Model structures of magnetic ordering statesin increase of supercell size

**Symmetry,**

**Supercell *abc*,**

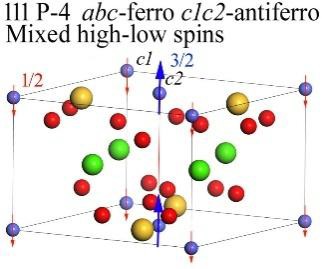
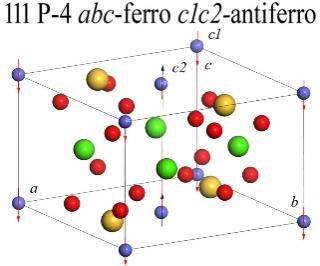
**Magnetic ordering states**

**No. of Co / all atoms**

**Cell maximum B**

***A B C***

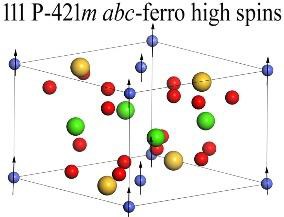
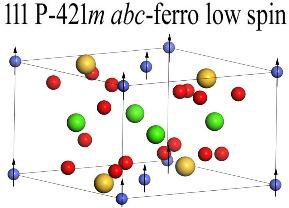
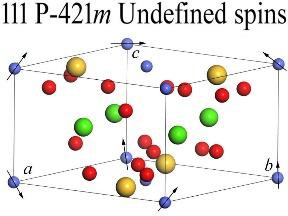
111-type A, net S = 0 111-type B, net S = 1 111-type C, net S = 3



P-4 111

2/12

3



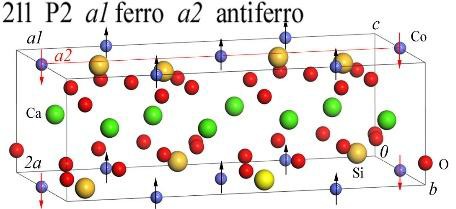
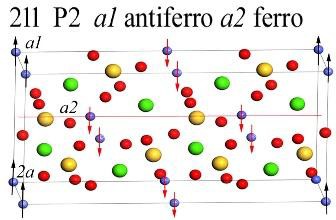
P-421*m* 111

1/12

3

111P-4-type A, net S = 0 111P-4-type B, net S = 1

211P2-type A, net S = 3 211P2-type B, net S = 3

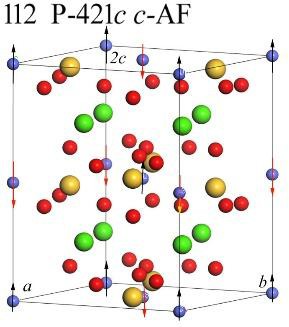
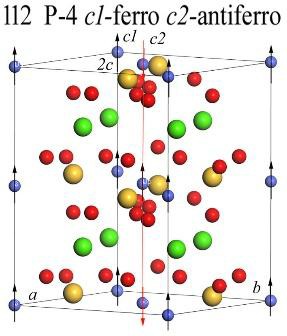


P2 211

4/24

6

112P-4-type A, net S = 3 112P-421c-type B, net S = 0



P-4, P-421*c* 112

4/24

6

P1

222

16/96

24

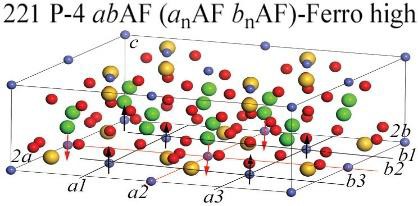
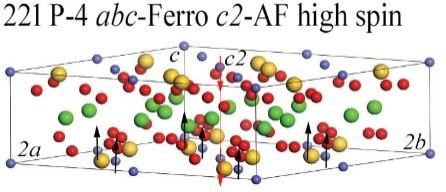
P21212 331

18/108

27

221P-4-type A, net S = 9 221 P-4-type B, net S = 6

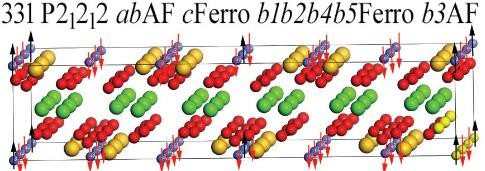
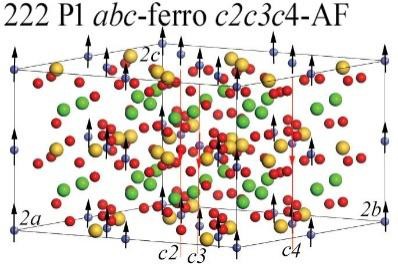
331P21212-type A, net S = 21



P-4 221

8/48

12



222P1-type A, net S = 18

By doubling the size of supercell along *a*, two spin configurations can be obtained in P2 symmetry and denoted accordingly as 211P2- A and 211P2- B. Both these structures have ferromagnetic axes (*a, b, c, c1*) in anti-parallel configuration. Since there are 4 Co atoms in the supercell, the spin alignment can be denoted () resulting in a net cell magnetic moment of 3B. Similarly, by doubling the *c* axis the 2-fold supercells 112P-4A and 112P-4B can be found. The net cell magnetic moment is either 3 or 0 depending on how the spin of the Co at (0,0,0.5) is aligned. The larger supercells i.e. 221 (4-fold supercell), 222 (8-fold supercell) and 331 (9-fold supercell) are also modeled: 221P-4A (all axes in FM up but *c2* in FM down configuration), 221P-4B (*a,b*axes in AF, all other in FM up except *a2b2* in FM down configuration), 222P1A (all axes in FM up, *c2c3c4* in AF configuration), 331P21212A (*ab* axes in AF, *c, b1, b2, b4, b5* in FM, *b3* in AF configuration). Because of positive net cell magnetic moments (S = 6, 9, 18, and 21 B for 221P-4B, 221P-4A, 222P1A and 331P21212A structure correspondingly), these model supercells are ferromagnetic.

*DFT setting.* Calculations were performed using CASTEP code9 with GGA/PBE functional and ultra-soft potential and spin polarized plane wave basis of energy cut-off 350 eV. The Self-Consistent-Field (SCF) tolerance was 10-6 eV/atom; energy convergence 10-5 eV/atom; maximum force 0.03 eV/Å, maximum stress 0.05 GPa, maximum displacement 0.001 Å. The *k-*point grid was 3×3×3 for the original unit cell (i.e. 27 *k-*points) and reduced to 1×1×3 (preserving 27 *k-*points for original unit cell) for the larger supercells, such as 331 supercell. All spin values were taken as the starting values only, the final spin densities were obtained with Mulliken population analysis. Geometry optimizations were converged well after a few refinement cycles. These materials are considered

to be insulators and in most cases the band gap is found to be in good agreement with experimental data10 when DFT+*U* is considered.

# RESULTS AND DISCUSSION

The magnetic order with lowest ground state energy is 111P-4A where two Co2+ spin are aligned parallel in ferromagnetic configuration. The final obtained energy per cell is -12658.396 eV for a volume of 296.07 Å, which

42.9

**Energy density (eV/Å)**

42.8

42.7

1.930

1.925



1.924

1.922

**<Co-O> (Å)**

**Average <Co-O> (Å)**

1.920

1.0

0.5



**V /V(%)**

42.6

1.920

1.918

0.0

0 2 4 6 8

**Cell magnetic moment (B)**

0.00 0.01 0.02 0.03 0.04 0.05

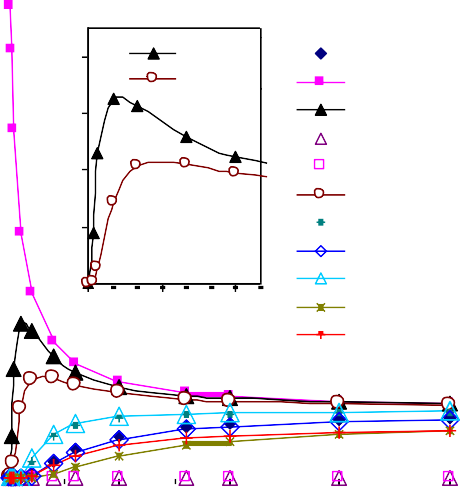
**Ground state E (eV)**

FIG. 1. (Left) The change of energy density and average <Co-O> bond distance according to the strength of ferromagnetic interaction; (Right) Average Co-O bond distance and relative volume increase V/V (%) according to the increase of ground state energy of models.

results at a density 42.75 eV/Å3. This energy density is not the highest one, which belongs to 112P-4A structure (42.86 eV/Å3). The lowest density (42.69 eV/Å3) corresponds to 211P2B structure which has Co atoms at the edge of supercell pointing down in a ferromagnetic coupling whereas the atoms inside the supercell point up also in ferromagnetic coupling.

The small difference in energy density, 0.17 eV/Å3 among the spin configurations should attribute to the ferromagnetic interaction between Co2+ sites in the lattice as depicted in Fig. 1. Higher density corresponds to higher cell magnetic moment, as well as shorter average <Co-O> bond length. However, the fluctuation of <Co-O> bond length is quite small, only in the range of 0.003 Å3 and is typical for the known rigid coordinating sphere of Co. It is worth noting that, for the structure of undefined spins, the Co-O bond is 1.878 Å3, much shorter than that of structures considering spin interactions. Therefore, the stress imposed on unit cellhas to originate from spin interaction. Another interesting observation is that the band-gap is detected for all spin related structures (from 0.404 to 0.696 eV) but not for the spin undefined one. When the cell magnetic moment is 0 (full antiferromagnetic structures), there band-gap is highest (0.686, 0.696 eV for 111P-4A and 111P-4B respectively). The band-gap is shown to decrease with increasing cell magnetic moment. This observation is in good agreement with the larger energy density, cell volume as the cell magnetic moment increases.

100



40

111P- 4B

211P2A

30

20

10

0

0 150 300

111P-421mC

111P-4A

111P-4B

111P-421mA

111P-421mB

211P2A

211P2B

112P-4A

112P-421cB

221P-4A

221P-4B

80

**Probability of state (%)**

60

40

20

0

0 500 1000 1500 2000

**Temperature (K)**

FIG. 2. The probability of state for various magnetic orders of Ca2CoSi2O7 as a function of temperature from 0 to 2000K. The inset magnifies the curves for spin configuration 111P-4B (fully antiferromagnetic with mix high-low spins) and 211P2A (two ferromagnetic axes in anti-parallel directions).

As the supercell size increases, the maximum magnetic moment per supercell also increases but its final value depends on spin configuration. For Ca2CoSi2O7 the lowest value is 0 for full antiferromagnetic spin configurations and 3×*n* for *n-*fold ferromagnetic supercell. A typical Co spin after optimization is ±1.28(1) B, using the given PBE functional and plane wave basis as discussed previously.

Fig. 2 illustrates the probability of state as a function of temperature. Assuming the population *pi* of a state *i* is

given in the proportion to that of the lowest energy state as *pi*  *p e i B* , it follows directly *p0*(*E0* = 0) = 1 and

*E* / *k T*

0

*n*

the probability of a state *i*is given by *P*  *e**Ei* / *kBT* / *e**Ei* / *kBT* . From our calculation results, the lowest energy

*i*0

*i*

state is 111P-4A with AF spin setting, and just 0.006 eV above it is 211P2A (two FM axes in opposite directions). The ground state energy increases by 0.02 eV (211P2B, and 112P-421c) to 0.04 eV (111P-421mC, 112P-4A, 221P-4B), and 0.06 eV (221P-4A). The energy increase gives rise to the following state probabilities (%) at room temperature, listed in the increase order: 2.1 (221P-4A), 4.6 (221P-4B), 4.9 (112P-4A), 5.6 (111P-421mC), 10.2 (211P2B), 10.6 (112P-421cB), 18.3

(211P2A), 20.9 (111P-4B) and 22.6 (111P-4A).

As seen from Fig. 2, although paramagnetic behavior is fundamental for Ca2CoSi2O7, the occurrence of ferromagnetic states cannot be ruled out. The probability of those states is equivalent to the probability of the paramagnetic state. Two main conclusions can be drawn: first, ferromagnetism is due to the remaining magnetic moment of the FM-AF network after cancellation, so it cannot be strong and is difficult to saturate in a weak applied field; second, paramagnetism itself also results from full cancellation of the FM and AF lattices, so this paramagnetic state can change to an AF or FM state depending on the specific direction of the applied field. This is why the magnetic phase transitions in Ca2CoSi2O7 often take place in strong applied field and are direction dependent.

Another important factor that can be depicted from Fig. 2, and its inset, is the bell-like evolution of the probabilities of the 111P-4B and 211P2A spin lattices. The 111P-4B is a mixed high and low Co spin configuration, it is fully antiferromagnetic with zeroed total net magnetic moment, and its energy is higher than that of 111P-4A only by a very small amount of 0.002 eV. The 211P2A is formed by parallel FM axes with the two axes pointing in opposite directions, resulting in a net magnetic moment of 2.57 per supercell, and is 0.006 eV higher in energy. These two structures show high probabilities (> 20%), equivalent to that of the lowest state, in the low temperature region below 100 K. Although at high temperatures all spin configurations can be considered equally likely, the favored states in the low temperature region are either absent or have a small magnetic moment.

# CONCLUSIONS

We show that Ca2CoSi2O7 can theoretically exhibit many different magnetic phases and structures depending on the internal spin configuration. Overall, since these spin configurations are most likely to occur at low and high temperatures, they may ultimately imply a paramagnetic behavior whose transition phase can be either ferromagnetic or antiferromagnetic, depending on the direction of the applied magnetic or electric field. Ca2CoSi2O7 prefers an antiferromagnetic arrangement of spin, but there are many low-energy structures with nonzero net magnetic moments, so that both paramagnetic and ferromagnetic behaviors are macroscopically possible. This is the key point for multiferroics, compounds that have competing properties within a single structural framework.

# ACKNOWLEDGMENTS

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