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Ab initio study on electronic states in
 $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ (A=Ca, Sr, La)

Keisuke Isoyama

March, 2015

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 $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ (A=Ca, Sr, La)

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Abstract

We investigate the effect of structural changes to the magnetic and charge order in $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ ($A = \text{Ca}, \text{Sr}, \text{La}$).

First, we study the effect of the lattice volume decrease on the electronic state and the magnetism in A-site ordered perovskite oxide $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ by means of *ab initio* calculation. It is consistent to experimental reports that the ground state is G-type antiferromagnetic (AFM) phase, in which Fe moments are AFM and Cu is nonmagnetic with the significant valence number 3+. In addition, we evaluate the half-metallic and ferrimagnetic (FiM) phase (Fe moments are ferromagnetic) in which the valence number of Cu is 2+ and the moment of Cu is antiparallel to Fe moments. The electronic configuration of cations ($\text{Fe}^{3+} : d^5 + \text{ligand hole } \underline{L}^{0.75}$, $\text{Cu}^{2+} : d^9$) in FiM phase is consistent to the phase at $P > 3.6$ GPa (HP phase) in the experiment. The phase stability is also changed by induction of pressure ; thus the HP phase is originated from FiM phase. In addition to the crystal structural data, the electronic configuration of cations in FiM phase is also close to the phase which has been reported at $T > 393$ K in experiments (HT phase).

Next, we study the change of magnetic order by the difference of A ion in $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ ($A = \text{Ca}, \text{Sr}$) under the same condition of calculation to $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$. In $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$, the stable phase (dispFe-P phase) is consistent to the experimental reports : the valence number of Fe are charge-disproportionated to Fe^{3+} (d^5) and Fe^{5+} ($d^5 + \underline{L}^2$) in rock-salt order ; the electronic state of Cu is Cu^{2+} which is qualitatively same to that in FiM phase in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$: the moments of Fe are ordered antiparallel ; the moments of Cu^{2+} are ordered anti parallel to them ; and it is insulating. By contrast, in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$, the phase (Fe-AP phase) in which Fe moments are ordered antiparallel and the valence number of Cu is 3+ and non-magnetic, has lower energy than the dispFe-P phase. This suggests that the stable antiferromagnetic order of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ is Fe-antiparallel and the temperature-induced second order phase transition in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ corresponds to the first order phase transition in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$.

In our calculations, the electronic states of Cu are unique in each phases and the valence number of Cu are shown to be strongly correlated to the magnetism of Fe moments in $ACu_3Fe_4O_{12}$ ($A=Ca, Sr, La$). Based on this result, we discuss each of the mechanism of the temperature-induced phase transition in $ACu_3Fe_4O_{12}$ ($A = Sr, La$) and of the stability change by pressure in $LaCu_3Fe_4O_{12}$ and by the difference of A ion ($A=Ca, Sr$), in terms of the electronic states of Cu.

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1 INTRODUCTION

Perovskite oxides have been investigated in many aspects, such as superconductivity[1], ferroelectricity[2], thermoelectricity[3] and magnetism[4]. The crystal structure of the standard perovskite oxide ABO_3 consists of a large ionic-radius cation A, like an alkaline metal, alkaline-earth metal or lanthanide ion; a transition-metal cation B; and O anions, which coordinates icosahedrally to the A cations and form corner-sharing octahedra BO_6 with the B cations (Fig. 1). It is also known that there is unique electronic state in some perovskite oxides. For example, $CaFeO_3$ indicates the “charge disproportionation” of Fe ($2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$) in rock-salt order under $T > 290$ K. This phase transition is accompanied with the metal-insulator transition and the structural transition which the crystal system changes from tetragonal to monoclinic[5, 6, 7, 8]. However, $SrFeO_3$, in which the valence number of A ion is 2+ and same to $CaFeO_3$, does not indicate the charge disproportionation of Fe like $CaFeO_3$ but has “anomalously high valence” Fe^{4+} in low temperature[9, 10]. Therefore the difference of A ions, even which have the same valence number, can change the whole electronic state in a perovskite oxide.

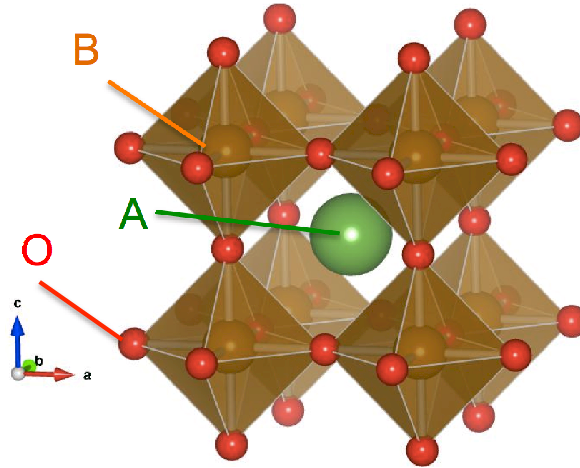


Figure 1: The structures of standard perovskite structure ABO_3

It is also known that introduction of an additional cation element to the perovskite oxides often induces structural change to superstructures. In most cases, they are B-site ordered superstructures[11, 12], whereas some of them are A-site ordered superstructures[13, 14]. It has been found that transition-metal cations A' such as Cu or Mn are introduced to the three quarters of the A sites in such a way that the oxygen coordination to the A' sites is changed from its original 12-fold coordination to square coordination accompanied with large tilt and rotation of the BO_6 octahedra, leading to a superstructure $\text{AA}'_3\text{B}_4\text{O}_{12}$ (Fig. 2) called as A-site ordered double perovskite[15, 16].

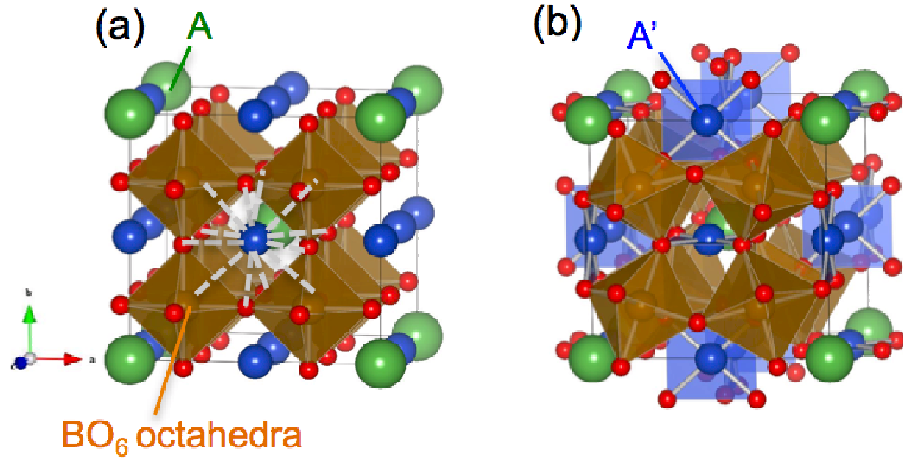


Figure 2: The structures of (a) standard perovskite structure ABO_3 indicated by double period and (b) A-site ordered double perovskite $\text{AA}'_3\text{B}_4\text{O}_{12}$. The standard perovskite structure ABO_3 is constructed with A ion (little blue and large green spheres) and BO_6 octahedra. In $\text{AA}'_3\text{B}_4\text{O}_{12}$, a transition-metal cation A' is introduced at the three quarters of A sites indicated by little blue spheres in ABO_3 , and change it's coordination from the original 12-fold (doted line) to square coordination accompanied with large tilt and rotation of the BO_6 octahedra.

The electronic state in A-site ordered perovskite oxides $\text{AA}'_3\text{B}_4\text{O}_{12}$ drastically changes from the one in ABO_3 by the induction of A' ion. For example,

$\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ crystalizes in $Im\bar{3}$ symmetry at $T > 210$ K where the valence number of Fe ions is 4+, and at $T = 210$ K, it shows charge disproportionation among Fe ions ($2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$) in rock-salt order, causing structural transition to $Pn\bar{3}$ symmetry along with metal-to-insulator [17], as same as CaFeO_3 . But this phase transition also accompanies the magnetic phase transition from paramagnetism to ferrimagnetism (FiM) in which Fe moments splitted the magnitude by the charge disproportionation order parallel and Cu moments orders antiparallel; this stable magnetic order in $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ is slightly different from the one of CaFeO_3 in which Fe moments order anti parallel.

$\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ shows another type of anomalously high valence. The average valence of Fe ions is considered to be 3.75+ (higher than usual 2+ or 3+) at $T < 393$ K by assuming formal valence of La^{3+} , Cu^{2+} , and O^{2-} . As temperature is increased, the phase transition occurs at $T = 393$ K with lattice shrink ($\sim 1.5\%$) preserving crystal symmetry $Im\bar{3}$, from paramagnetic metal to G-type antiferromagnetic (AFM) insulator. Based on these experimental results, it has been proposed that at the transition, inter-site charge transfer $3\text{Cu}^{2+} + 4\text{Fe}^{3.75+} \rightarrow 3\text{Cu}^{3+} + 4\text{Fe}^{3+}$ takes place[18, 19]. Since the same phase transition also happens by application of pressure at 3.6 GPa[20], the structural change, especially the lattice volume decrease might have large effect to the phase transition.

In addition to these materials, Yamada reported that $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ has the crystal symmetry $Im\bar{3}$, not $Pn\bar{3}$, and some kind of antiferromagnetic order at $T < 180 \sim 207$ K, by reason that the total magnetization is close to 0 and Mössbauer spectroscopy indicates that the magnetic order of Fe moments exist [21]. And they also reported that at $170 \text{ K} < T < 270 \text{ K}$, it exhibits "negative thermal expansion" like volume dependance on temperature. This report suggests that the magnetism and charge order of the ground state in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ is remarkably different from $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$, despite Sr and Ca has the equal valence number 2+ and are considered to be less hybridized to other ions (Table 1).

These reports suggest that a structural change has some effect to the mag-

Table 1: Differences of the magnetic and charge orders in $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ (A=Ca, Sr) experimentally reported

	$\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ [17]	$\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ [21]
Magnetic order in low temperature	Fe : parallel Cu : antiparallel to Fe	some AFM order of Fe moments
Band structures	Insulating	No enrollment
Charge orders	Cu^{2+} , rock-salt ordered $\text{Fe}^{3+} + \text{Fe}^{5+}$. The crystal group changes from $Im\bar{3}$ to $Pn\bar{3}$ by the charge order of Fe.	In Mössbauer spectroscopy 2 types of Fe moments are observed. But the change of the crystal symmetry is not observed in $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ manner

netism and the charge order in $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ (A = Ca, Sr, La), but the mechanism is unknown. Then in the present paper, we investigate the effect of structural changes to the electronic states in $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ (A = Ca, Sr, La), especially to the valence number of cations and to the magnetic stability, by means of *ab initio* calculation; particularly we evaluate the effect of lattice volume change in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$. We also calculate the electronic state of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ and compare it to $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$, and investigate the mechanism of the change of magnetism and charge order induced by the difference of A site.

2 CALCULATION

2.1 Density Functional Theory

In density functional theory, the total energy of electrons is approximated by the energy functional $E[n]$ on only the function space of the density function $n(r)$; it has no other dependance on the wave function $\psi(r)$. The $E[n]$ is written concretely,

$$E[n] = T_0[n] + \int n(r)v(r)dV + \frac{1}{2} \iint \frac{e^2 n(r)n(r')}{|r - r'|} + E_{xc}[n] \quad (1)$$

In the right side of (1), the first term means a kinetic energy of the non-interacting system of electrons which density function is $n(r)$, the second term is a potential term; the third term is Hartree energy which means the electrostatic repulsion between electrons which density function is $n(r)$. These three terms are inducted by one-body approximation; however there is a gap between the sum of these terms and the “true” total energy of electrons as a many-body system. Therefore the forth term, called as exchange correlation term, is added to correct this gap. In general, this E_{xc} is treated as the local density approximation (LDA) which depends on only the density function $n(r)$; but in a strongly correlated system, LDA is not valid; then the generalized gradient approximation (GGA) which depends on not only $n(r)$, but also the gradient $\nabla n(r)$, is usually adopted in a strongly correlated system.

Next, to gain a ground state of electrons, we calculate $n(r)$ which minimize the total energy $E[n]$ in assumption that it has the minimum and varies continuously, functional differentiably on the function space of the density function $n(r)$. This is equivalent to calculate $n(r)$ that $\frac{\delta E}{\delta n}$ becomes zero at $n(r)$; then from (1), the $n(r)$ of the ground state suffices;

$$\frac{\delta T_0[n(r)]}{\delta n(r)} + v(r) + \frac{1}{2} \int \frac{e^2 n(r')}{|r - r'|} + \frac{\delta E_{xc}}{\delta n(r)} = 0 \quad (2)$$

Introducing one-electron wave functions $\{\varphi_i(r)\}$ ($i = 1 \dots N$, N is the number

of electrons) such that $n(r) = \sum_{i=1}^N |\varphi_i(r)|^2$, calculating $n(r)$ which suffices the equation of (2), is equivalent to calculating $\varphi_i(r)$ ($i = 1 \dots N$) which minimize the sum of eigenvalues ϵ_i below;

$$\begin{aligned} & \left(-\frac{\hbar}{2m}\nabla^2 + v_{eff}(r)\right)\varphi_i(r) = \epsilon_i\varphi_i(r) \\ & v_{eff}(r) = v(r) + \frac{1}{2} \int \frac{e^2 n(r')}{|r - r'|} + \frac{\delta E_{xc}}{\delta n(r)} \end{aligned} \quad (3)$$

The equation (3) is called as Kohn-Sham equation.

In *ab initio* calculation, we calculate the minimum value of the sum of $\{\epsilon_i\}$ and $\{\varphi_i(r)\}$ which minimize this, by numerical computation self-consistently between $n(r)$ in the left side of (3) and $\varphi_i(r)$ in the right side of (3). Calculations of electronic states are performed with the full-potential linearized augmented plane wave (FLAPW) method[23] in the HiLAPW code. In FLAPW method, Kohn-Sham equation for all electrons are calculated, and an one-electrons wave function are represented by a linear sum of the plane waves augmented by a product of a radial function which energy is equal to the plane wave, with a spherical harmonic function, in atomic core regions called Muffin-tin spheres. For numerical computations in our research, for the wave function in the interstitial region the plane wave cut-off energy is 20 Ry, while the charge density cut-off is 160 Ry in muffin-tin spheres. Muffin-tin sphere radii are taken to be 1.0 Å for all the cations and 0.8 Å for O sites. Thus, we treat a wave function as a linear sum of the electronic states parametrized by reciprocal vectors $\mathbf{k}$; then total energies are calculated by the numerical integration on the reciprocal space. The k point meshes in the Brillouin Zone of each structure for our calculation are fixed $6 \times 6 \times 6$.

2.2 +U method

In this research, we take a exchange correlation term E_{xc} into account within GGA using Perdew-Burke-Ernzerhof scheme[24] and +U method[25] to correct the strong electron correlation in 3d transition metal ions, Fe and Cu. In +U method, two terms, the interaction of localized orbitals E^U and the double counting term E^{dc} between $E_{xc,GGA}$ and E^U , are added to exchange correlation term by GGA (denoted by $E_{xc,GGA}$);

$$E_{xc} = E_{xc,GGA} + E^U(n_{(m,m'),\sigma}^d) - E^{dc}(n_{(m,m'),\sigma}^d) \quad (4)$$

$$E^U(n_{(m,m'),\sigma}^d) = \frac{1}{2} \sum_{\sigma, \{m\}} (U_{m_1, m_3, m_2, m_4} - U_{m_1, m_3, m_4, m_2}) n_{(m_1, m_2), \sigma}^d n_{(m_3, m_4), \sigma}^d + U_{m_1, m_3, m_2, m_4} n_{(m_1, m_2), \sigma}^d n_{(m_3, m_4), -\sigma}^d \quad (5)$$

$$E^{dc}(n_{(m,m'),\sigma}^d) = \frac{1}{2} U n(n-1) - \frac{1}{2} J \sum_{\sigma} n_{\sigma} (n_{\sigma} - 1) \quad (6)$$

where $n_{(m,m'),\sigma}^d$ means the occupation matrix of d electrons indexed by azimuthal m quantum numbers of the localized orbital $\{\phi_m^{\sigma}\}$ (σ is spin index); n and n_{σ} are the trace of occupation matrix and the partial trace given σ , of occupation matrix respectively; $U_{m_1, m_3, m_2, m_4} = \langle m_1, m_3 | \frac{1}{r} | m_2, m_4 \rangle$ are the electron-electron interactions, which can be linearly expanded by the complex spherical harmonics and effective Slater integrals[26]. In solids, the on-site coulomb repulsion U and the exchange integrals J are the prior terms in Slater integrals.

Additional terms in +U method shift an eigenvalue of a localized orbital. From (5) and (6), the variation of the eigenvalue $\Delta\epsilon_m$ with $\{\phi_m^{\sigma}\}$ can be written as follow;

$$\Delta\epsilon_m = \frac{\partial(E^U - E^{dc})}{\partial n_{(m,m),\sigma}^d}$$

$$\begin{aligned}
&= \frac{1}{2} \left\{ \sum_{(m_3, m_4)} (U_{m, m_3, m, m_4} - U_{m, m_3, m_4, m} + U_{m_3, m, m_4, m} - U_{m_3, m, m, m_4}) n_{(m_3, m_4), \sigma}^d \right. \\
&\quad \left. + U_{m, m_3, m, m_4} n_{(m_3, m_4), -\sigma}^d \right\} - U n_{(m, m), -\sigma}^d - (U - J)(n_{(m, m), \sigma}^d - \frac{1}{2}) \\
&= \frac{1}{2} \left\{ \sum_{(m_3, m_4)} (U_{m, m_3, m, m_4} - U_{m, m_3, m_4, m} + U_{m_3, m, m_4, m} - U_{m_3, m, m, m_4}) n_{(m_3, m_4), \sigma}^d \right. \\
&\quad \left. + \sum_{(m_3, m_4) \neq (m, m)} U_{m, m_3, m, m_4} n_{(m_3, m_4), -\sigma}^d \right\} - (U - J)(n_{(m, m), \sigma}^d - \frac{1}{2}) \quad (7)
\end{aligned}$$

While U is enough larger than J because $\{\phi_m^\sigma\}$ is localized, $U - J$ is positive. In (7), the only term which depends on U is $(U - J)(n_{(m, m), \sigma}^d - \frac{1}{2})$; then the main term in additional terms in $+U$ method is $(U - J)(n_{(m, m), \sigma}^d - \frac{1}{2})$. By this term, if $n_{(m, m), \sigma}^d > \frac{1}{2}$ ϵ_m is shifted lower, if not, shifted higher. In a band structure, an eigenvalue ϵ_k of a wave function $\Psi_{k, \sigma}$ is shifted priorly by $P_m^d (U - J)(n_{(m, m), \sigma}^d - \frac{1}{2})$ on each m ; where P_m^d is the component of $\{\phi_m^\sigma\}$ in $\Psi_{k, \sigma}$, so the variation of the eigenvalue ϵ_k shift is also scaled by P_m^d . Thereby if $\Psi_{k, \sigma}$ is localized and the component P_m^d is large, the variation of the shift becomes large. The dependence of ϵ_k on U and J is written by $U - J$ which is called as the effective Hubbard U_{eff} term. Then by the assignment of U_{eff} , the electronic state such as the band structure, can be tuned. In our calculation, J is fixed at 1 eV. Hereinafter, we will denote the effective Hubbard U_{eff} just as U for simplicity.

2.3 $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$

We calculate electronic states not under the symmetry of the crystal structure $Im\bar{3}$, but under the crystal symmetry $Pn\bar{3}$ in order to take into account the arrangement of Fe moments in the G-type antiferromagnetic (AFM) order reported in the experiments. Under the crystal symmetry $Pn\bar{3}$, there are two crystallographic sites of Fe ordered in a rock-salt manner and one site of Cu. Then the rock-salt type charge disproportion of Fe is also permitted. In terms of the magnetic order of Cu, only ferromagnetism and non-magnetism are permitted. It is reasonable because the moments of Fe are regarded sufficiently larger ($4.03 \mu_B$ from Chen's neutron diffraction data [19]) than Cu and the nearest distance between Cu and Fe is closer than that between Cu ions; thus the magnetic interaction between the Fe and Cu sites is larger, and the moments of Cu are considered to be ordered ferromagnetically by the Fe moments in evaluated magnetic phases.

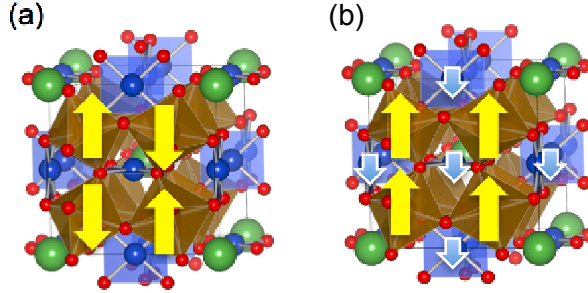


Figure 3: The magnetic orders which we evaluate in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$. (a) is the order in which the moments of the nearest neighbor Fe are antiparallel and Cu has no magnetic moment (AFM). (b) is the order in which the moments of Fe are parallel and the moments of Cu are antiparallel to them (FiM)

We start our calculations from the following two types of magnetic order; (i) the AFM phase which moments of Fe is ordered with G-type AFM, and (ii) the ferrimagnetic (FiM) phase in which Fe moments are ordered ferromagnetically and the Cu moment is opposite to them, corresponding to the magnetic order of

the ground state in $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ (Fig. 3). The crystal structure of each phase is optimized and the total energies are converged. Then we compare the total energies of the magnetic phases while changing the lattice volume.

2.4 $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ ($\text{A} = \text{Ca, Sr}$)

We also calculate electronic states under the crystal symmetry $Pn\bar{3}$ in order to take into account the arrangement of rock-salt type order of the valence number of Fe in $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$. Under the crystal symmetry $Pn\bar{3}$, there are two sites of Fe ordered by rock-salt type and one site of Cu. Then the G-type AFM order of Fe moments is also permitted, but the magnetic order of Cu is forbidden except for the ferromagnetism and non-magnetism. It is reasonable because the moments of Fe are regarded sufficiently larger than Cu and the nearest distance between Cu and Fe is closer than that between Cu ions; thus the magnetic correlation is larger, and the moments of Cu are considered to be ordered ferromagnetically by the Fe moments in the magnetic phases which we evaluate.

We start calculation from the following three types of magnetic order; (i) the moments of Fe, not charge disproportionated, is ordered antiparallel (Fe-AP phase), corresponding to G-type AFM which is stable in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$, (ii) the ferromagnetic phase in which Fe moments, not charge disproportionated, are ordered ferromagnetically and the Cu moment is opposite to them (Fe-P phase), and (iii) the orientation of magnetic moments are same to Fe-P but Fe is charge disproportionated by the difference of Fe-O bond length (dispFe-P phase), corresponding to the magnetic order of the ground state in $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$. The crystal structure of each phases are optimized and the total energies are to be converged. Then we compare the total energies of the magnetic phases while changing the lattice volume.

3 RESULTS and DISCUSSION

3.1 $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$

3.1.1 The U parameter

The U parameters are chosen to reproduce the experimental results[18, 19], i. e. the structural and magnetic phase stabilities, the band structure, and the magnetic order of the ground state in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$. In Table 2, we list calculated energy difference between AFM and FiM phases with optimized structures (lattice parameters and atomic coordinations), and energy gaps in AFM phase for several sets of U values. In the bare GGA ($U_{\text{Cu}} = U_{\text{Fe}} = 0$ eV), FiM phase is stable and AFM phase is not insulating, being inconsistent with the experiment[18, 19]. When U_{Cu} is larger than U_{Fe} , the magnetic stability is inconsistent with the experiment, so the reasonable U parameters in unit of eV is $(U_{\text{Cu}}, U_{\text{Fe}}) = (3,4)$. Around $(U_{\text{Cu}}, U_{\text{Fe}}) = (3,4)$, the ground state is also consistent with the experiments and the density of states in both magnetic phases are little variant enough for qualitative discussion. Therefore, we fix $(U_{\text{Cu}}, U_{\text{Fe}}) = (3,4)$ and discuss the electronic states of $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ below.

Table 2: Dependence of the magnetic stability and band gaps in AFM phase on the parameters U_{Cu} and U_{Fe}

$(U_{\text{Cu}}, U_{\text{Fe}})$ eV	$\Delta E = E_{\text{FiM}} - E_{\text{AFM}}$ (eV/f.u.)	Band gap of AFM phase (eV)
(0,0)	-1.01	metal
(3,4)	0.43	0.71
(5,3)	-0.44	0.5

3.1.2 Optimization of crystal structure

Optimized crystal structural data of each magnetic phase are listed in Table 3. Each magnetic phase does not represent the charge disproportionation of Fe. The lattice constants of AFM phase in this calculation are slightly larger by approximately 1% than those of the low-temperature (LT) structure in experiments[18]. The atomic coordinates of O in AFM phase are remarkably closer to LT structure. The optimized lattice constant is calculated to be smaller in FiM phase than in AFM phase; yet the bond angle of Fe-O-Fe becomes larger, and then the Cu-O bond length becomes larger in FiM phase than in AFM phase. It corresponds the fact that the lattice constant is smaller in HT structure than in LT structure in experiments. In addition to that, the coordinations of cations in FiM phase, bond length and angle, well coincide with those in HT structure. This suggests that the electronic structure of the HT phase is closer to that of FiM phase rather than of AFM phase. But, on the other hand, the crystal structure of HP phase does not become close to neither of the optimized structures. HP phase will be discussed later with respect to the dependence of the phase stability on lattice volume.

Table 3: Optimized crystal structure in AFM and FiM phase in our calculation and Long's experimental report of low-temperature (LT) at 150 K, high-temperature (HT) at 450 K and high-pressure (HP) phase at room temperature, 4.2 GPa[18, 20]. The atomic position ($x, y, 0$) of O is indicated.

	AFM	FiM	LT[18]	HT[18]	HP[20]
a (Å)	7.510	7.461	7.42246	7.41420	7.34281
V (Å ³)	423.49	415.38	409.27	407.56	395.91
x	0.3119	0.3054	0.3112	0.3070	0.3133
y	0.1683	0.1777	0.1705	0.1744	0.1764
Fe-O (Å)	2.029	1.985	2.000	1.9778	1.973
Fe-O-Fe angle (°)	135.41	139.95	136.3	139.2	136.95
Cu-O (Å)	1.895	1.966	1.889	1.937	1.876

3.1.3 Electronic state in optimized structure

The electronic density of states (DOS) of $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ in G-type AFM and FiM phase are shown in Figs. 4 and 5, respectively. In AFM phase, the band structure is insulating. From lower to higher energy, the electronic states consist of comparatively sharp Fe 3*d* state at ~ -6 eV, strongly hybridized Cu 3*d* + O 2*p* state spreading over $-5 \sim 0$ eV, empty Cu 3*d* state and empty Fe 3*d* state. There is no component of La in the energy range of the figure. As for the spin polarization of Fe, the majority spin state of Fe is fully occupied, whereas the minority spin state is empty, indicating that the valence number of Fe in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ is 3+ and the electronic configuration is half-filled 3*d* state. The magnetization of Fe in our calculation result, $3.95 \mu_B$ (integrated inside the Fe muffin-tin sphere) is also consistent with Chen's neutron diffraction data $4.03 \mu_B$ [19]. On the other hand, the Cu states are spin-degenerated. The lowest empty band is constructed with only Cu $3d_{x^2-y^2}$ orbitals (oriented to O and shown by filled area in the figure) and the other orbitals are occupied (Fig.4 (b)). The occupied Cu 3*d* orbitals are strongly hybridized with O and among themselves, and form the broad band, indicating that they are delocalized. Compared to them, the band of empty Cu $3d_{x^2-y^2}$ orbitals is remarkably sharper; the electronic states are localized mainly around Cu ions. So the Cu state is considered to be nonmagnetic Cu^{3+} where the spatial distribution of the empty Cu $3d_{x^2-y^2}$ orbitals and the occupied others are significantly different.

Compared to AFM phase, the occupied Fe 3*d* states and Cu+O band becomes hybridized, and they form a wide spreading band in FiM phase. This makes the band structure metallic where the Fermi level crosses the valence band in the majority-spin side whose main components are O 2*p* and Fe 3*d* state. Then the holes consist of the hybridized O 2*p* + Fe 3*d* state which is a part of the wide band, and thus are not localized around the Fe ions. Therefore the electronic state of Fe can be regarded as half-filled $d^5\bar{L}^{0.75}$ ($\bar{L}$ means ligand hole that is delocalized between Fe and O), in FiM phase. The Cu orbitals except for $3d_{x^2-y^2}$ are quali-

tatively invariant from AFM phase, but the Cu $3d_{x^2-y^2}$ orbital drastically changes. In majority-spin side, the Cu $3d_{x^2-y^2}$ orbital is located above the Fermi level as in the case of the AFM phase. But in minority-spin side, it shifts down to the bottom of the Cu $3d + O 2p$ band. It is hybridized with them, and then broadened. The large split of majority-spin and minority-spin sides in Cu $3d_{x^2-y^2}$ orbital is almost 8 eV; therefore the electronic state of Cu corresponds to Cu^{2+} in FiM phase. Considering that the majority-spin side of Cu $3d_{x^2-y^2}$ is well localized, the split is caused by the on-site Coulomb repulsion of Cu $3d_{x^2-y^2}$ state. As the result, Cu has the magnetic moment $0.60 \mu_B$ (integrated inside the Cu muffin-tin sphere) that is coupled antiparallel to the Fe moments.

In both phase, the electronic states of Fe stands deeply from the Fermi level, and the wide band of Cu and O lies between Fe states and the Fermi level. So as aspect of the Fe $3d$ state in $LaCu_3Fe_4O_{12}$, the Fe $3d$ state is well localized, and the hopping of electrons between these states induced by the effect of the kinetic energy had better to be represented as intermediated by O rather than direct hopping between Fe. And following this aspect, the electronic configuration of Fe is $d^5 \underline{L}^{0.75}$ in metallic FiM phase.

The density of states are consistent to a previous work using *ab initio* calculations[27]. It also shows the correspondence between the FiM phase in our calculation and HT, HP phases in experiments[18, 19]; the metallic band and electronic configuration of Fe and Cu ($d^5 \underline{L}^{0.75}$, Cu^{2+}) in FiM phase corresponds to the experimental reports which evaluate the valence number of cations empirically from the bond length in paramagnetic HP and HT phase.

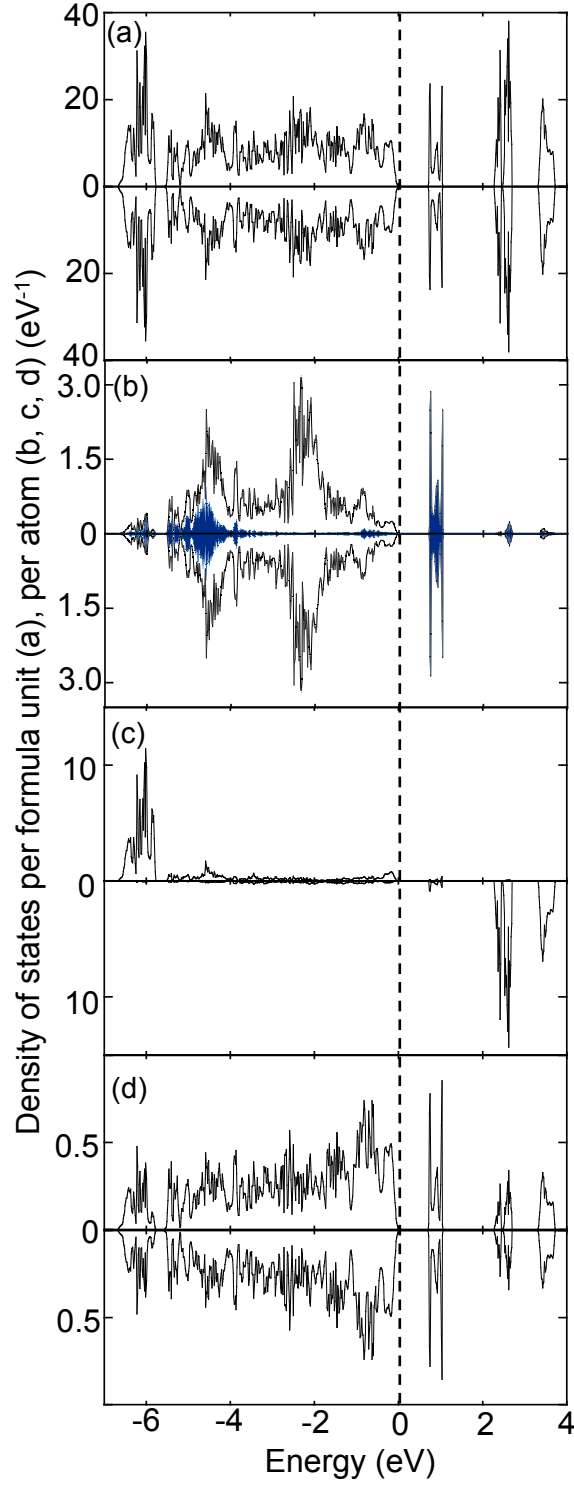


Figure 4: DOS of $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ in AFM phase. Total DOS (a) and partial DOS of Cu (b), Fe (c), and O (d) are plotted. The range and unit of the vertical axis are different for each panel [per formula unit for panel (a) and per atom for the others]. The origin means the top of the valence band (dashed line). The filled section in (b) indicates the orbital component of Cu $3d_{x^2-y^2}$.

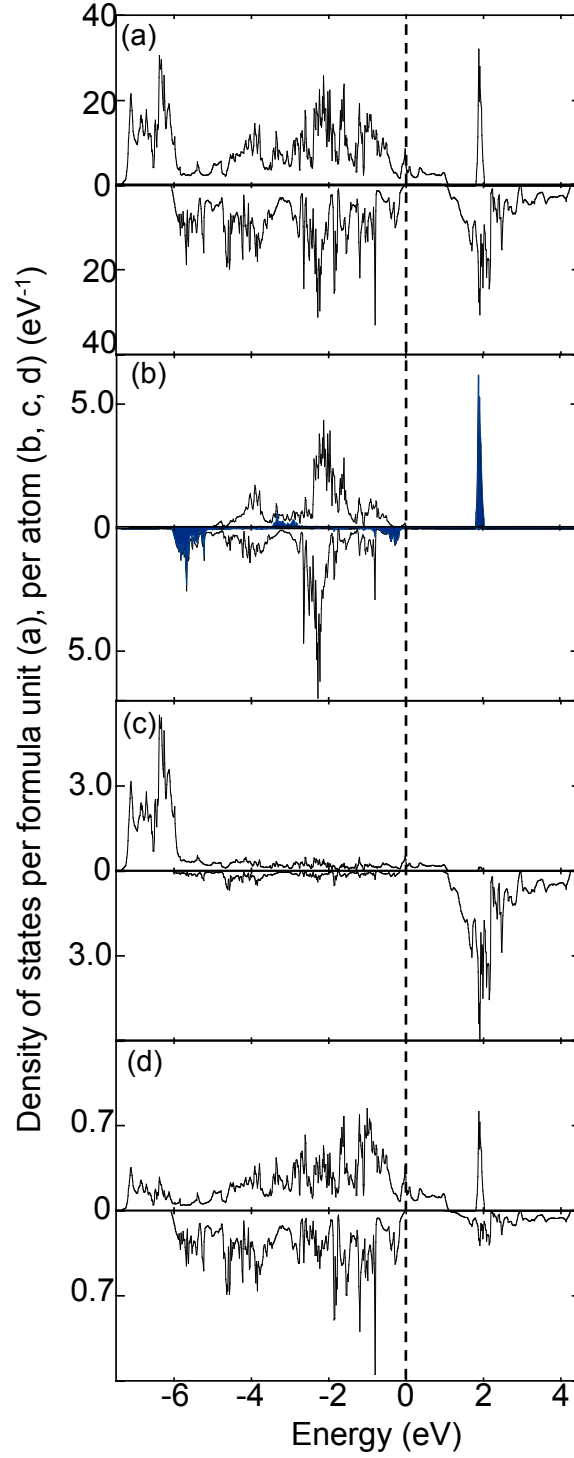


Figure 5: DOS of $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ in FiM phase. Total DOS (a) and partial DOS of Cu (b), Fe (c), and O (d) are plotted. The range and unit of the vertical axis are different for each panel [per formula unit for panel (a) and per atom for the others]. The origin means Fermi energy (dashed line). The filled section in (b) indicates the orbital component of Cu $3d_{x^2-y^2}$.

3.1.4 Discussion about the electronic states of HT phase

Since the ground state of $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ is G-type AFM, it is usual to consider the paramagnetic HT phase as being magnetically disordered from AFM phase. But in the previous section, we see that the electronic configuration in FiM phase corresponds to the experimental reports in HT phase. In addition to this, the crystal structure of HT phase are similar to FiM phase, as discussed in Sec. 3.2. These results suggest that HT phase is magnetically disordered from the FiM phase; however this hypothesis is not firmed without the existence of the driving force of the phase transition exceeding the original energy difference at 0 K between AFM and FiM phase.

In LaFeO_3 , the magnetic transition from G-type AFM to paramagnetism occurs at $T=750$ K[28], but it has not been reported that the lattice volume shrinks and insulator-to-metal transition of first order follow the magnetic transition as $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$. Therefore the high temperature phase in LaFeO_3 is considered to be magnetically disordered from the AFM phase, and thereby the existence of Cu is considered to be the main factor of the temperature-induced phase transition in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$, by at least either suppressing the energy distance between AFM and FiM phase, or contributing to entropy increase. Both in LaFeO_3 and $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$, the electronic states of Fe is half-filled d^5 ; then the energy distance between antiparallel and parallel order of Fe moments is regarded large (the Néel temperature 750 K of LaFeO_3 is comparatively high). However, in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$, the change of Fe moments order invokes the charge transfer between Fe and Cu ($3d^8+4d^5 \longrightarrow 3d^9+4d^5 \underline{L}^{0.75}$), and it drops the electron at the top of the valence band in AFM phase to the minority-spin side Cu $3d_{x^2-y^2}$ state which is located as deep as $\sim 6\text{eV}$. Thus the energy loss caused by Fe parallel order is cancelled by the energy benefit from the charge transfer; therefore the energy distance between AFM and FiM phases is suppressed in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$.

Not only the suppression of the energy distance, but there is also entropic benefit in FiM phase. FiM phase has magnetic moment of Cu (Cu^{2+}) whose majority-

and minority-spin sides of Cu $3d_{x^2-y^2}$ splits sufficiently large such that the electronic state can be regarded as that minority-spin side is occupied and majority-spin side is empty. So the entropy of Cu moment can be considered as $k_B \ln 2$. This value is slightly high as one electron has. Compared to this, AFM phase does not have magnetic moment of Cu (nonmagnetic Cu^{3+}), and the paramagnetic phase disordered from AFM phase has no benefit with respect to the entropy of Cu moments. Therefore it is regarded that in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$, G-type AFM phase transits to paramagnetic phase magnetically disordered from the FiM phase by raising temperature with the entropic benefit of Cu^{2+} moments.

3.1.5 Dependence of magnetic stability on lattice volume

The volume dependence of the energy difference between the FiM and AFM phases is depicted in Fig. 6. The energy curves are fitted to the Murnaghan equation of state. At each volume, the atomic coordinations do not change so much under the structural optimization, and then only bond lengths are changed, while bond angles are merely preserved. The equilibrium volume is smaller in the FiM phase by 2.2% than in AFM phase. The energy difference decreases as the lattice volume decreases. By considering enthalpy from this energy curve, the lattice volume shrinks by 2.7% at $P \sim 9.1$ GPa (calculated from common tangent of the curves in Fig. 6), and FiM phase becomes more stable than AFM phase. Since the phase transition occurs at 3.6 GPa and the lattice shrinks $\sim 1.7\%$ in the experiment[20], our values reasonably reproduce the experimental results. At the same time, the band structure changes from insulating to metallic. This suggests that only a small change such as $\sim 2\%$ compression of lattice volume (corresponds to the bond length change) preserving crystal symmetry $Pn\bar{3}$ destabilize the magnetic and valence order (G-type AFM, Fe^{3+} , Cu^{3+}) at the ground state in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$, and so the high pressure phase paramagnetic at room temperature in the experiment[20] originates from the FiM phase, whose electronic configuration also corresponds, as discussed in Sec. 3.3. The bulk modulus B_0 at equilibrium volume and the first order differential by pressure B' fitted by the Murnaghan equation in each phase, $B_0 \sim 185$ GPa in AFM phase and ~ 170 GPa in FiM phase where B' is around 4 in each phase, correspond to the experimental value in AFM and paramagnetic phase respectively, $B_0 = 133$ GPa in AFM phase and 118 GPa in paramagnetic phase under fixed $B' = 4$.

In the perovskite oxide SrFeO_2 , it has been reported that pressure invokes the similar phase transition at room temperature, around 33 GPa, from G-type AFM to ferromagnetism, and from insulator to half-metal[29]. But, there are many differences between SrFeO_2 and $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$; in SrFeO_2 , the d^6 electronic configuration of Fe^{2+} is drastically changed by the phase transition, from the high-spin state

to the low-spin state, but in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$, the d^5 electronic configuration of Fe^{3+} is not changed. Moreover, in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$, the similar phase transition is invoked by changing temperature, but, in SrFeO_2 , the phase transition has not been reported by changing temperature. So the mechanisms of SrFeO_2 and $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ are different.

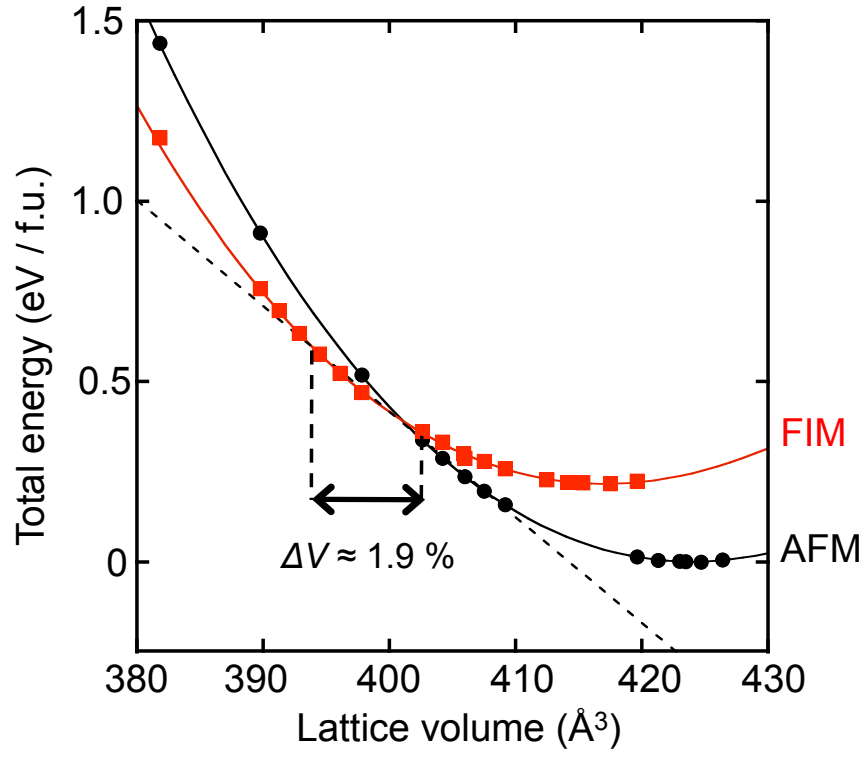


Figure 6: Total energy of $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ as a function of volume in AFM (circles) and FIM (squares) phases. The energy zero is set at the AFM lowest energy.

3.1.6 The mechanism of the pressure-induced phase transition

Next, we consider the reason why the total energy of FiM phase becomes lower than that of AFM phase. In that Figs. 7 and 8, we show the electronic states of AFM and FiM phase at which lattice volume FiM phase becomes stable. As lattice volume decrease, in FiM phase the band structure changes from metallic to half-metallic because the mixed states of Cu $3d_{x^2-y^2}$ and O $2p$ moved below the Fermi level, and, in AFM phase, the gap between deep and localized Fe states and the strongly hybridized Cu $3d$ + O $2p$ states is closed. But if these small change of the electronic states has much effect in the magnetic stability of $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$, the curve in Fig. 6 should change drastically at the lattice volume which these changes happen. So these small change of the electronic states is not the cause of the change in the magnetic stability.

Remarkably, AFM phase is still insulating at the lowest volume that we evaluate in Fig. 6. Then at least under 10% lattice volume compression, this confirms the claim by Allub and Alascio[30] that the AFM phase is insulating at any volume. So, as discussed by them, the compression of the lattice volume decreases the kinetic energy of electrons around Fe ions in FiM phase as that the hybridization between Fe and O states increases, more than in AFM phase which remains insulating. Then lattice volume decreases, the increase of the total energy is suppressed in FiM phase compared to AFM phase, and then the FiM phase become stable at lower volume. This is also reflected to the difference of bulk modulus B_0 at equilibrium volume between AFM and FiM phase ($\sim 8\%$ smaller in FiM phase). This mechanism is based on the result that AFM phase keeps insulating where the empty Cu $3d_{x^2-y^2}$ states are localized and are not hybridized with occupied and wide Cu+O band (Allub and Alascio assumed this at any volume, in addition to Cu^{2+} states in FiM phase.). Therefore the fixity of the electronic state of Cu^{3+} in AFM phase is regarded as the reason why FiM phase becomes stable at smaller lattice volume.

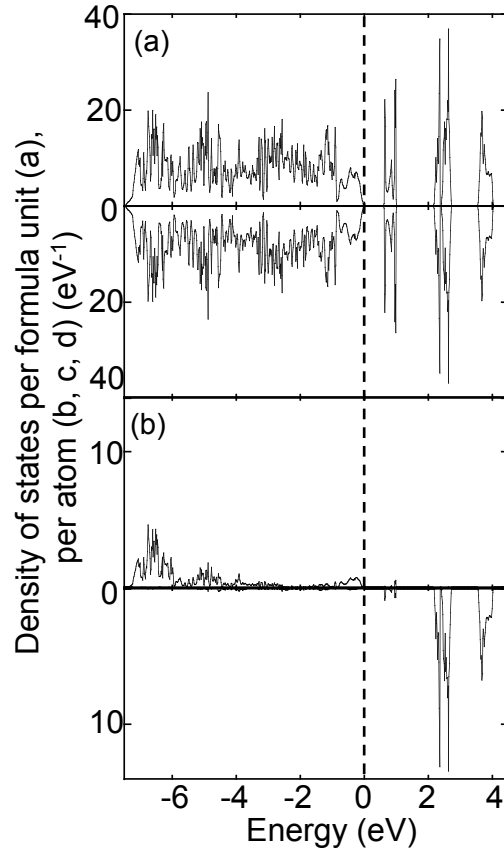


Figure 7: The total DOS (a) and PDOS of Fe (b) in metastable AFM phase at the lowest volume ($381.82 \text{ \AA}^3$) in our calculation. We show majority-spin side DOS at upper panel, and minority-spin side at lower panel.

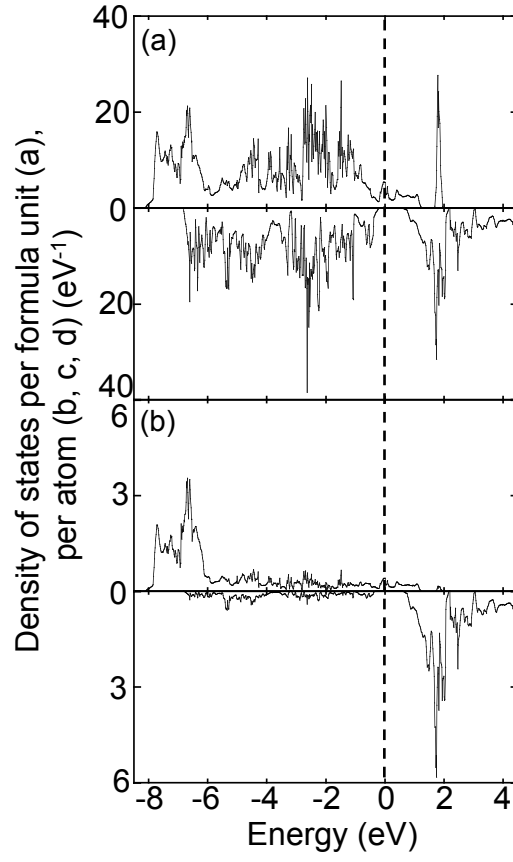


Figure 8: The total DOS (a) and PDOS of Fe (b) in stable FiM phase at the lowest volume ($381.82 \text{ \AA}^3$) in our calculation. We show up-spin side DOS at upper panel, and down-spin side at lower panel

3.2 $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ ($\text{A}=\text{Ca},\text{Sr}$)

3.2.1 Magnetic stability and electronic state in $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$

In $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$, the total energy of dispFe-P phase is 78.4 meV / formula unit (f. u.) lower than Fe-AP phase; thereby dispFe-P phase is stable in consistent to the experiments. In dispFe-P phase, Fe ions have different magnetic amplitude in two sites under the crystal symmetry $Pn\bar{3}$. The higher spin Fe has $3.82 \mu_B$, and the lower spin Fe has $3.17 \mu_B$ (integrated within the muffin-tin sphere). We show the density of states (DOS) of stable dispFe-P phase of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ in Fig. 9. As previously reported[31], from lower to higher energy, the electronic states consist of comparatively sharp Fe 3d state at ~ -6 eV, strongly hybridized Cu 3d + O 2p state spreading over $-5 \sim 0$ eV, lower-spin Fe 3d empty state and Cu 3d state in majority spin-side and empty Fe 3d state in minority spin-side. The higher-spin Fe state is half-filled d^5 , which the occupied majority spin states are located at ~ -6 eV and the empty minority spin states are at $1 \sim 4$ eV; the majority and minority spin states split sufficiently large ~ 8 eV.

Compared to this, the component of the lower-spin Fe state decreases at ~ -6 eV, and the empty band in majority spin which Fe and O states hybridize, occurs in. These difference of magnetic amplitudes and DOS between Fe ions in each sites indicates the charge disproportionation of Fe which is experimentally reported in $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$. It is also consistent to the experiments that dispFe-P phase is insulating.

Next, we see the electronic state of Cu. The Cu orbitals except for $3d_{x^2-y^2}$ are spin-degenerated and occupied in the wide band formed with Cu 3d + O 2p state, but the Cu $3d_{x^2-y^2}$ orbital drastically changes. In majority-spin side, the Cu $3d_{x^2-y^2}$ orbital forms sharp band and is located above the Fermi level. But in minority-spin side, it shifts down to the bottom of the Cu 3d + O 2p band. It is hybridized with them, and then broadened. The large split of up-spin and down-spin sides of Cu $3d_{x^2-y^2}$ orbital is almost 8 eV; therefore the electronic state of Cu corresponds

to Cu^{2+} , which has magnetic moment $0.60 \mu_{\text{B}}$. Then the valence number of Cu is 2+ as reported in the experiments, and the electronic states of Cu is almost same to that in ferrimagnetic phase in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$.

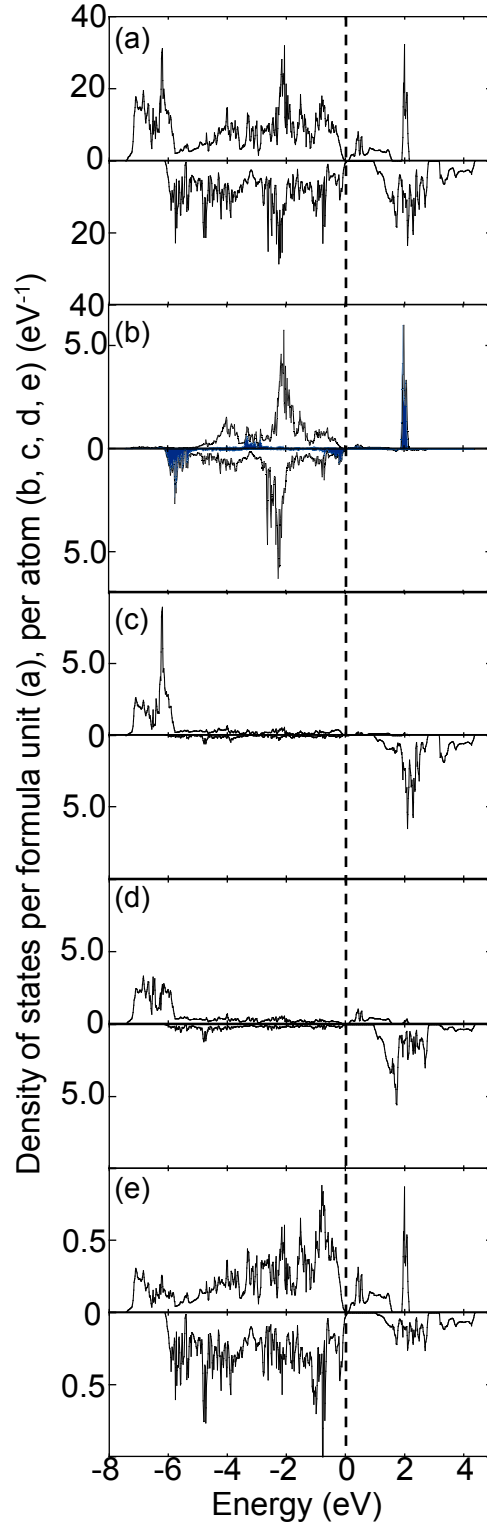


Figure 9: DOS of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ in dispFe-P phase. Total DOS (a) and partial DOS of Cu (b), higher-spin Fe (c), lower-spin Fe (d), and O (e) are plotted. The range and unit of the vertical axis are different for each panel [per formula unit for panel (a) and per atom for the others]. The origin means the top of the valence band (dashed line). The filled section in (b) indicates the orbital component of Cu $3d_{x^2-y^2}$.

In the previous paper, Ueda *et. al.* calculated the electronic states of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ in the crystal structure experimentally reported, using the comparatively high $+U$ term of Cu, 7 eV[31]. It is because the phase in the experimentally reported crystal structure is not insulating, which is inconsistent to the experiment, when U_{Cu} is less than 7 eV. But in our calculation, by the optimization of crystal structure, the electronic state is still insulating (band gap is 0.082 eV in major-spin side, 0.85 eV in minor-spin side.) using reasonable $U_{\text{Cu}} = 3$ eV. Our band structure is almost same to that of Ueda, except for Cu $3d_{x^2-y^2}$ orbital that in Ueda's report, by using high U_{Cu} , the occupied majority-spin side state of Cu $3d_{x^2-y^2}$ orbital is splitted from the wide Cu $3d + \text{O } 2p$ band and localized as narrow as the empty minority-spin state of Cu $3d_{x^2-y^2}$ orbital.

The DOS of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ in Fe-AP phase is almost same to that of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ which is shown in next section.

3.2.2 Magnetic stability and electronic state in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$

First, we see the magnetic stability of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$. The energy distances of Fe-P phase and dispFe-P phase, from Fe-AP phase, are +34.5 and +14.8 meV per f. u. respectively, It indicates that the charge-disproportionation of Fe has energy benefit in ferromagnetic-Fe-ordered phase, and the stable magnetic order of Fe in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ is antiparallel. The DOS of dispFe-P phase in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ is qualitatively same except for that the band gap is broken in majority-spin side and it becomes half-metallic.

We show the DOS of Fe-AP phase in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ in Fig. 10. There is no component of Sr in the energy range of the figure, and thus the valence number of Sr is 2+, not 3.23+ empirically estimated from the bond length in the experiment[21]. Compared to dispFe-P phase, occupied Fe 3d states in both spin side are splitted from the wide Cu 3d+O 2p band and become sharp. In addition to this, strongly hybridized Cu 3d + O 2p state spreading over -5~0 eV, empty Cu 3d state and empty Fe 3d state. As for the spin polarization of Fe, the majority spin state of Fe is fully occupied, whereas the minority spin state is empty, indicating that the valence number of Fe in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ is 3+ and the electronic configuration is half-filled 3d state. The magnetization of Fe in our calculation splits a little into two values , 3.82 and 3.94 μ_B (integrated inside the Fe muffin-tin sphere).

On the other hand, Cu states are spin-degenerated. The lowest empty band is constructed with only Cu $3d_{x^2-y^2}$ orbitals (oriented to O and shown by filled area in the figure) and the other orbitals are occupied (Fig.10 (b)). The occupied Cu 3d orbitals are strongly hybridized with O and themselves, and form the broad band, indicating that they are delocalized. Compared to them, the band of empty Cu $3d_{x^2-y^2}$ orbitals is remarkably sharper; the electronic states are localized mainly around Cu ions. So the Cu state is considered to be nonmagnetic Cu^{3+} where the spatial dispersions of the empty Cu $3d_{x^2-y^2}$ orbitals and the occupied others are significantly different.

The DOS of the Fe-AP phase is remarkably similar to that in G-type anti-

ferromagnetic (AFM) phase in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$, except for metallicity and charge disproportionation of Fe ions. Since the valence number of A ion changes from 3+ of La to 2+ of Ca, Sr, holes are doped to the spatially-spreaded Cu + O states and the existence rate on Fe ions splits slightly. That invokes charge disproportionation of Fe in the Fe-AP phase.

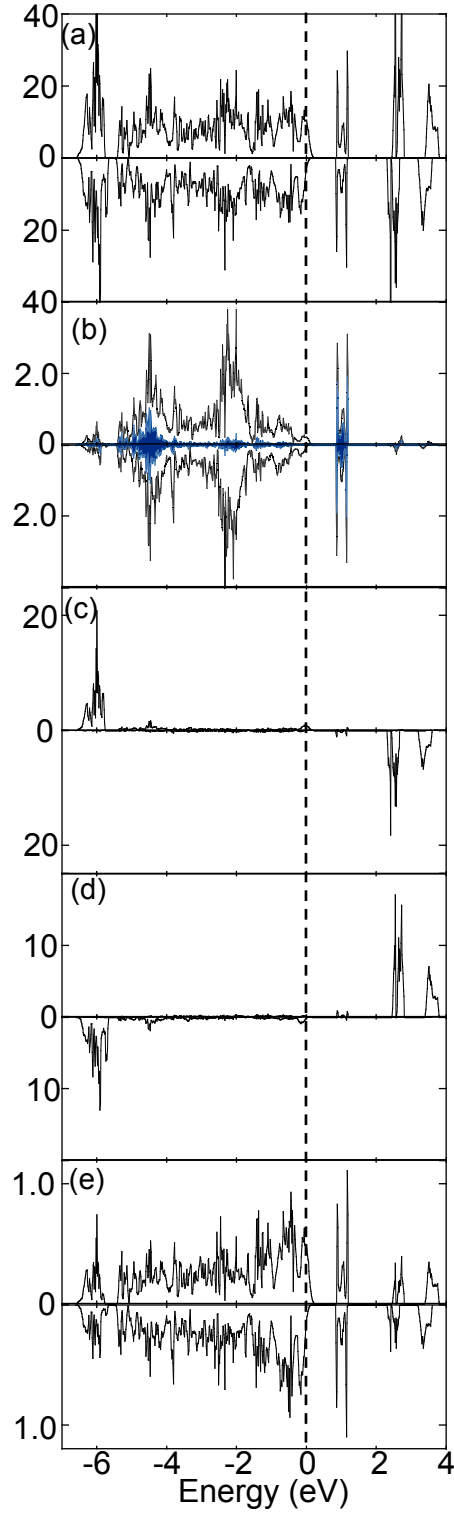


Figure 10: DOS of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ in the Fe-AP phase. Total DOS (a) and partial DOS of Cu (b), lower-spin Fe (c), higher-spin Fe (d), and O (e) are plotted. The range and unit of the vertical axis are different for each panel [per formula unit for panel (a) and per atom for the others]. The origin means the Fermi Level. The filled section in (b) indicates the orbital component of Cu $3d_{x^2-y^2}$.

3.2.3 Charge disproportionation of Fe in dispFe-P phase

Next, we study in detail the charge-disproportionated Fe states observed in the dispFe-P phase. In Fig.10, the lowest empty band in majority-spin is mainly constructed with lower-spin Fe and O, though the component of higher-spin Fe consist little in the band. We show DOS of lower-spin Fe orbitals in Fig. 11. The main component in this band is lower-spin Fe $3d_{3z^2-r^2}$ orbital which intensity is at least two times larger than other Fe $3d$ orbitals and O states per electron. Thus, it can be regarded as crystal-field splitting owing to octahedral environment. However, the Fe $3d$ states is originally located deeply from the Fermi level (~ -7 eV) and the splitting needs much hybridization to O which makes Fe states broaden. Then, the existence of anomalously high Fe^{5+} state is regarded as energy loss for the Fe state. Though by half of Fe ions in $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ being Fe^{5+} , another half of Fe states are permitted to be Fe^{3+} which is half-filled and localized d^5 state. Without charge disproportionation, the valence number of Fe ions is $3.75+$ and each Fe states has to be hybridized with O to some extent; however the existence of Fe^{5+} allows another half of Fe states to be Fe^{3+} which be less hybridized to O and suppress the energy loss. Therefore it makes the charge disproportionation of Fe to have the total energy benefits rather than not charge disproportionated.

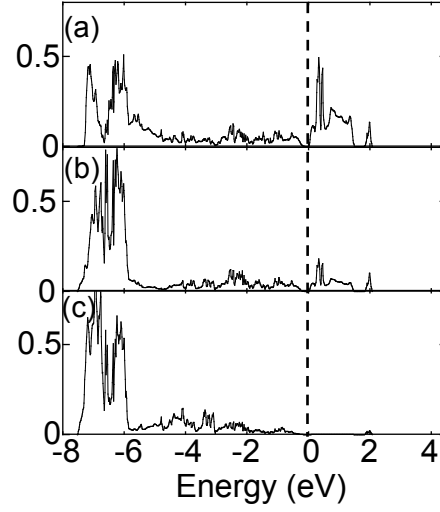


Figure 11: DOS of lower-spin Fe orbitals in the dispFe-P phase of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$. The electronic state of $3d_{3z^2-r^2}$ (a) and $3d_{x^2-y^2}$ (b), $3d_{xz}$ orbitals (c) are plotted. The range and unit of the vertical axis are per atom. The origin means the top of the conduction band.

3.2.4 The temperature-induced phase transition in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$

In addition to the correspondence between the DOS of Fe-AP phase in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ and of G-type AFM phase in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$, the DOS of the dispFe-P phase in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ is almost same to that of the FiM phase in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$, except for whether Fe states are charge disproportionated or not (In $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$, the total energy of FiM phase is a little lower than the phase in which Fe moments are parallel and charge disproportionated).

In the previous section, we discussed the temperature-induced phase transition in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ such that by raising temperature, the G-type AFM insulating phase transits to the paramagnetic and metallic phase magnetically disordered from FiM phase. The mechanism of this phase transition was explained with the entropy benefit of the magnetic moment of Cu; in AFM phase, the valence number of Cu is 3+ and nonmagnetic, but on the other hand in FiM phase the valence number of Cu is 2+ and it has magnetic moment originated from the sufficiently splitted Cu $3d_{x^2-y^2}$ orbitals; thereby FiM phase has the entropy benefit $k_B \ln 2$ per Cu atom. Since in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ the similar phase transition occurs, from Fe antiparallel ordered phase to paramagnetic phase accompanied with the cell volume contradiction but without insulator-metal transition, it is natural to consider that the mechanism of the phase transition in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ is similar to that in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$. Thus, in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$, by raising temperature it transits from the Fe-AP phase (corresponds to the AFM phase in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$) to dispFe-P phase (corresponds to the FiM phase in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$) in order to the entropy benefit of Cu moments.

The other difference between the phase transition in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ and in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ is the order of the phase transitions, second-ordered in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ contrastively to first-ordered in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$. In $\text{LaCu}_3\text{Fe}_{4-x}\text{Mn}_x\text{O}_{12}$ which is substituted B site with Mn, It is experimentally reported that the first-ordered phase transition with temperature in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ is broadened by doping of Mn[32]. By increasing the composition ratio x of Mn, the negative thermal expan-

sion becomes broadened and at $x = 1.0$ the zero thermal expansion is exhibited in a wide temperature range (240 - 360 K), simultaneously with the transition of the magnetism in the ground state from Fe-antiparallel to Fe-parallel. It is regarded that by the substitution of Fe^{3+} by Mn^{2+} , holes are doped and the Fe-antiparallel order is destabilized. In our research, holes are doped in the Fe-AP phase in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ by the change of A ions from La^{3+} to Sr^{2+} and the magnetism also changes to Fe-parallel. Then this experimental report supports that these lattice volume contraction in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ and in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ is the phase transition from the Fe-antiparallel magnetic ordered and Cu^{3+} charge ordered phase to the Cu^{2+} charge ordered phase which corresponds to the Fe-parallel phase. It is also suggested that doped holes make the charge order of Cu fragile and the charge disorder of Cu occurs continuously in lower temperature than the temperature which Fe-magnetic order is broken.

3.2.5 The change of the magnetic order caused by the difference between A = Sr and Ca

In previous section, we found that the stable magnetic order is changed by the difference of A ion in $ACu_3Fe_4O_{12}$ such that in $SrCu_3Fe_4O_{12}$ the magnetic moments of Fe ions are ordered antiparallel and the Cu state is non-magnetic, but on the other hand in $CaCu_3Fe_4O_{12}$ the magnetic moments of Fe ions are ordered parallel and Cu has magnetic moment which are ordered antiparallel to Fe moments. In addition that, the valence number of Cu is 3+ in $SrCu_3Fe_4O_{12}$ and 2+ in $CaCu_3Fe_4O_{12}$. The Cu^{2+} states of Cu^{2+} in $CaCu_3Fe_4O_{12}$ and Cu^{3+} in $SrCu_3Fe_4O_{12}$ are almost same to the Cu^{2+} state of FiM phase and the Cu^{3+} state of G-type AFM phase in $LaCu_3Fe_4O_{12}$. These charge and magnetic orders are consistent to the experiments.

The DOS of the Fe-AP and the dispFe-P phase does not have large differences by the change of A ion between Ca and Sr. Since both of Ca and Sr states has little component in the energy range shown Figs. 9, 10 and can be regarded as ionic Ca^{2+} and Sr^{2+} , the effect of the difference of A ions is considered mainly as the structural change of the coordination of the other cation, Fe and Cu. Optimized crystal structural data of each magnetic phase and A ions are listed in Table 4. With both A ions, the lattice parameter of Fe-AP phase is larger than that of dispFe-P phase. It corresponds the difference of lattice parameters between G-type AFM and FiM phase in $LaCu_3Fe_4O_{12}$ and this suggests that also in $SrCu_3Fe_4O_{12}$, the lattice shrink second-ordered by raising temperature, corresponds to the phase transition from the Fe-AP phase to the paramagnetic phase magnetically disordered from Fe-P phase.

By the change of A ion from Sr to Ca, the lattice parameter decreases naturally. But Fe-O-Fe angle changes little in each magnetic phase by the difference of A ions, so the structural change by the difference of A ions induces mainly the change of bond length, Fe-O and Cu-O. These bond length changes of Cu-O in each magnetic phase is slightly larger than that of Fe-O. in addition that,

Table 4: Optimized crystal structure of Fe-AP and dispFe-P phase in $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ ($A = \text{Ca}, \text{Sr}$) with our calculation. Parentheses in lattice parameters and bond length means rate of change from the same magnetic phase in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$. The atomic position (x, y, z) of O is indicated.

	Fe-AP A = Sr	Fe-AP A = Ca	dispFe-P A = Sr	dispFe-P A = Ca
a (Å)	7.500	7.440 (-0.80 %)	7.419	7.371 (-0.65 %)
V (Å ³)	421.84	411.76	408.37	400.42
x	0.3137	0.3115	0.3062	0.3033
y	0.1697	0.1686	0.1810	0.1790
z	0.0010	0.0024	0.0051	0.0053
Higher spin Fe-O (Å)	2.033	2.025 (-0.39 %)	2.005	1.992 (-0.65 %)
Lower spin Fe-O (Å)	2.020	1.992 (-1.40 %)	1.934	1.919 (-0.75 %)
Fe-O-Fe angle (deg.)	135.41	135.61	140.69	140.89
Cu-O (Å)	1.890	1.882 (-0.42 %)	1.966	1.961 (-0.25 %)

The Cu-O bond length of Cu^{3+} in Fe-AP phase and of Cu^{2+} in disp-FeP phase are close to that of Cu^{3+} (1.895 Å) in G-type AFM phase of $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ and that of Cu^{2+} (1.966 Å) in FiM phase of $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ respectively. These suggest that the change of 4-square coordination of Cu increases the total energy and the equilibrium volumes of each magnetic phases in $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ ($A = \text{Ca}, \text{Sr}$) are determined in order to stabilize the local environment around Cu. In partial DOS of Cu, since the Cu $3d_{x^2-y^2}$ state is slightly sharp and then localize, a little change of the coordination of Cu is able to have large effect to the stability of Cu $3d_{x^2-y^2}$ state. In terms of the change of the magnetic stability by the difference of A ions, the energy distance between each magnetic order is small in both of Sr and Ca and the electronic state and coordination of Cu is not changed so much. Although the Fe-O bond length mainly changes; it is supposed that the change of the mag-

netic stability by the difference of A ions is caused by the small difference of the coordination of Fe.

4 CONCLUSION

We investigate the effect of structural changes to the magnetic and charge order in $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ ($\text{A} = \text{Ca}, \text{Sr}, \text{La}$). We found that the valence state of Cu in AFM phase of $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ is $3+$ and has no magnetic moment, showing good agreement with the LT phase in experimental report[18]. In terms of the charge order of cations ($\text{Fe}^{3+} : d^5 \underline{L}^{0.75}$, $\text{Cu}^{2+} : d^9$) and the crystal structure, the electronic structure of the HT phase is similar to that of FiM phase where magnetic order of Fe is ferromagnetic and moments of Cu order opposite to Fe. FiM phase has magnetic moment of Cu originated from Cu $3d_{x^2-y^2}$ orbital whose occupied and empty states split by ~ 8 eV, but AFM phase does not have. Then it suggests that the paramagnetic phase magnetically disordered from FiM phase has entropic benefit from Cu moments, $k_B \ln 2$ per Cu atom, and is stabilized at higher temperature. We also investigate the dependence on the lattice volume, of the total energies of each magnetic ordered phase, and found that even $\sim 2\%$ decrease of lattice volume preserving crystal symmetry $Pn\bar{3}$ can invoke the change of magnetic stability of $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$, from AFM to FiM. Thereby the magnetic order of the ground state in HP phase is also supposed to be FiM, and so it is regarded that both of HT and HP phases are originated from FiM phase. Remarkably, the AFM phase compressed by 10% of the lattice volume from its equilibrium volume is still insulating and the electronic state of Cu remains Cu^{3+} . Therefore the fixity of Cu^{3+} in AFM phase keeps the band structure insulating, contributes to increase total energy of AFM phase at lower volume, and so is the cause of the change of magnetic stability by a small structural change. In conclusion, based on the existence of “anomalously high” Cu^{3+} state, the temperature-induced and pressure-induced phase transition in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ can be explained.

Next, we investigate the change of magnetic order by the difference of A ion in $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ ($\text{A} = \text{Ca}, \text{Sr}$) under the same calculational condition to $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$. In $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$, the stable phase (dispFe-P phase) is consistent to the experi-

mental reports : the valence number of Fe are charge-disproportionated to Fe^{3+} (d^5) and Fe^{5+} ($d^5 + \underline{L}^2$) in rock-salt order ; the electronic state of Cu is $\text{Cu}^{(2+)}$ which is qualitatively same to that in FiM phase in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$: the moments of Fe are ordered antiparallel ; the moments of $\text{Cu}^{(2+)}$ are ordered anti parallel to them ; and it is insulating. By contrast, in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$, the phase (Fe-AP phase) in which Fe moments are ordered antiparallel and the valence number of Cu is 3+ and non-magnetic, has lower energy than the dispFe-P phase. This suggests that the stable antiferromagnetic order of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ is G-type and the temperature-induced second order phase transition in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ corresponds to the first order phase transition in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$. Also in our calculation, the magnetic order is changed by the difference of A ion ($A = \text{Ca}, \text{Sr}$); nevertheless the electronic states in each evaluated magnetic phase is not changed. In the optimized structure of each magnetic phase in $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ ($A = \text{Ca}^{2+}, \text{Sr}^{2+}$, and even La^{3+}) the bond length of Cu-O changes less on each valence number. Thus it is supposed that the magnetic order change is originated from the small difference of the coordination of Fe induced by the difference of A ion and the valence number of Cu is sensitive to the small structural change of the local environment by the localized Cu $3d_{x^2-y^2}$ state sensitive to it.

In conclusion, the electronic states of Cu are unique in each magnetic ordered phases, and qualitatively invariant by structural changes; that invokes the pressure-induced phase transition in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ and the change of the magnetic order in the ground state by the change of A ion ($A = \text{Ca}, \text{Sr}$). In addition that, the mechanism of the lattice volume contraction in $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ ($A = \text{La}, \text{Sr}$) can be explained by the change of the valence number of Cu.

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7 PUBLICATION LIST

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