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Contribution of on-site Coulomb repulsion energy to structural, electronic and magnetic properties of $SrCoO_3$ for different space groups: first-principles study

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We report structural, electronic, and magnetic properties of $SrCoO_3$ in $Pm\bar{3}m$ and P_4/mbm space groups, which are calculated by using generalized gradient approximation corrected with on-site Coulomb repulsion U and exchange energies J. The cubic lattice parameter a and local magnetic moments of Co (μ_{Co}) are optimized by varying U at Co 3d site. Employing ultrasoft pseudopotential, the values of U = 8 eV and J = 0.75 eV are the best choice for $Pm\bar{3}m$ space group. We found the value of $\mu_{Co} = 2.56\ \mu_B$, which is consistent with the previous results. It was also found that Co 3d, hybridized with O 2p, is the main contributor to ferromagnetic metallic properties. Besides, norm-conserving pseudopotential promotes a, which is in good agreement with experimental result. However, it is not suitable for P4/mbm space group. By using ultrasoft pseudopotential, the value of U = 3 eV (J = 0.75) is the most suitable for P4/mbm group. Ferromagnetic metallic properties, Jahn-Teller distortion, and reasonable lattice parameters have been obtained. This study shows that U has significant contribution to the calculated properties and also points out that P4/mbm space group with US-PP is suitable to describe experimental results.

Keywords: *structural properties; electronic properties; magnetic properties; $SrCoO_3$; on-site Coulomb repulsion energy*

1. Introduction

The oxide perovskite ABO_3 (A is the cation with larger size than that of B) of transition metal element has become an interesting system due to its diverse and rich physical properties, ranging from ferroelectric ($SrTiO_3$) [1], ferromagnetic (FM) ($SrCoO_3$) [2], giant magnetoelectric ($SrMnO_3$ and $SmFeO_3$) [3, 4]. In particular, for cobalt oxide materials, the valence state of Co ions strongly depends on the type and concentration of dopant, leading to non-stoichiometric value of oxygen content and variation in the valence state of Co^{2+} ($3d^7$), Co^{3+} ($3d^6$), Co^{4+} ($3d^5$) or fractional valence state as well as mixed valence states. Under crystal field potential with a certain symmetry from the surrounding oxygen ligand, the 5 degenerate d-orbitals split into 3-fold degenerated t_{2g} and 2-fold degenerated e_g orbitals. Furthermore, the proximity of crystal-field splitting energy (Δ_{cf}) of $t_{2g} - e_g$ and Hund rule intra-atomic exchange energy J result in the variation of Co spin sate, namely low-spin (LS) state ($t_{2g}^6 e_g^0$, S = 0), intermediate-spin (IS) state ($t_{2g}^5 e_g^1$, S = 1) or the high-spin (HS) state ($t_{2g}^6 e_g^2$, S = 2). All of these matters are responsible for more susceptible properties of cobalt oxide system as observed with the emergence of metal-insulator [5] and spin-state transitions [6] toward the external effects, such as temperature, pressure, or magnetic field.

In particular, perovskite cobalt oxide of $SrCoO_{3-\delta}$ is very interesting, since it can be used as a cathode material of solid oxide fuel cells [7] and active material in spintronic devices [8]. It has also been found that the structural and magnetic properties of $SrCoO_{3-\delta}$ sensitively depend on O_2 and applied pressure. The stoichiometric $SrCoO_3$ that crystallizes in $Pm\bar{3}m$ space group [9] can be obtained from orthorhombic brownmillerite $SrCoO_{2.5}$ with Pnma space group [10], at O_2 pressure and temperature of 6.5 GPa and 1023 K, respectively. Conversely, it has also been shown that

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$SrCoO_3$ can be transformed into $SrCoO_{2.5}$ in H_2 atmosphere by using the reduction process. Interestingly, the oxidation process provokes semi-reversible transformation of $SrCoO_{2.5}$ back into $SrCoO_3$ [11]. The previous experimental results [9] showed that $SrCoO_3$ is FM metallic with relatively high Currie temperature of about 305 K for $\delta = 0$. The most probable spin state, which is influenced by Δ_{cf} and J, is IS-state for Co^{4+} ion based on the saturation magnetic moment of 2.5 μ_B/f.u. at 7 K.

Regarding first-principles studies, suitable on-site Coulomb repulsion energy U, or so called Hubbard energy, and J, exchange energy, at Co 3d site are required to obtain an accurate description of $SrCoO_3$. Although the electronic-structure calculation of $SrCoO_3$ has shown the FM metallic properties of the compound [12], the values of U and J still vary significantly for different methods, as summarized in Table 1 for $Pm\bar{3}m$ and P4/mbm space groups. P4/mbm space group has been used by rotating $SrCoO_3$ primitive cell by the angle of 45° leading to $\sqrt{2} \times \sqrt{2} \times 1$ supercell [2].

In this paper, we report a first-principles study on the structural, electronic, and magnetic properties of perovskite $SrCoO_3$ for $Pm\bar{3}m$ and P_4/mbm space groups based on density-functional theory (DFT). Hohenberg-Kohn and Kohn-Sham scheme-based DFT [28, 29] have been used to calculate the properties of molecules [20–22] and solids [10, 14, 23–25]. The calculation in present study is performed by means of generalized gradient approximation (GGA) method, which has some advantages compared with local density approximation (LDA) in terms of better description of molecules and solids [26]. Besides, the magnetic and electrical properties obtained from spin-polarized projected density of states (PDOS), corresponding lattice parameters and local magnetic moment of Co ion (μ_{Co}) are also used to determine suitable values of U and J. The results are then compared with previous experimental and calculation results. The analysis is perfomed in three main frameworks. The first and second frameworks concern $Pm\bar{3}m$ and P4/mbm space groups, respectively. The third framework reveals the properties using norm-conserving pseudopotential (NC-PP), compared with that calculated using ultrasoft pseudopotential (US-PP). Hence, this study elucidates not only the suitable values of U and J for $SrCoO_3$ in different space groups but also the employed PP.

2. Computational

A plane-waves-based Quantum ESSPRESSO package [27] was used to perform spin-polarized density-functional calculation [28, 29]. The generalized gradient approximation (GGA) method was used alongside the Perdew-Burke-Ernzerhof exchange-correlation (XC) functional type [26]. The calculation was performed using Broyden mixing which employes quasi-Newton method [30]. The first calculation was performed to obtain electronic structures of 5-atom $SrCoO_3$ unit cell within $Pm\bar{3}m$ space group as the first model. The initial cubic lattice paramater a of 3.8289 Å based on the previous experimental result [9] and a k-point mesh of $8 \times 8 \times 8$ centered at Γ high-symmetry k-point, were employed. The $SrCoO_3$ supercell is shown in Fig. 1. A kinetic energy cutoff of 25 Hartree (~680 eV) was used. Rappe-Rabe-Kaxiras (RRK) and Vanderbilt scheme-based US-PP [31, 32] were used for all atoms of the first model. The cubic lattice parameters and all atomic positions were optimized by Broyden-Fletcher-Goldfarb-Shanno-minimization (BFGS) algorithm [33–36]. Besides, the nonlinear core [37] and/or semi-core correction [38] were employed for obtaining reliable description of US-PP. For realizing a Hubbard model, the cubic lattice parameter and local magnetic moments of Co μ_{Co}) and O (μ_O) ions were optimized as function of effective Hubbard potential energy values of $U_{eff} = U - J$. The Hubbard model (for GGA method) is described as [39]:

$$E_{GGA+U}[n] = E_{GGA}[n] + E_U\left[\left\{n^{i\sigma}_{mm'}\right\}\right] \quad (1)$$

$$E_U\left[\left\{n^{i\sigma}_{mm'}\right\}\right] = E_{Hub}\left[\left\{n^{i\sigma}_{m}\right\}\right] - E_{DC}\left[\left\{n^{i\sigma}\right\}\right] \quad (2)$$

where n(r) is the electron density at position r, $n^{i\sigma}_m$ is the spin-polarized occupation of atomic-orbital for the atom i on which the Hubbard is applied, and $n^{i\sigma}$ is expressed as:

$$n^{i\sigma} = \sum_m n^{i\sigma}_m \quad (3)$$

Table 1. Summary of previously reported results for $SrCoO_3$.

Space group	U [eV]	J [eV]	U_{eff} [eV]	Literature	Method	Electronic and magnetic properties
$Pm\bar{3}m$	10.83	0.76	10.07	[13]	LDA and DMFT[a]	FM metallic
$Pm\bar{3}m$	7.0	0.65	6.35	[10]	LDA	FM metallic
$Pm\bar{3}m$	8.0	–	–	[14]	GGA + U	FM metallic
$Pm\bar{3}m$	2.5	1.0	1.5	[5]	GGA + U	FM metallic
$Pm\bar{3}m$	–	–	2.75	[15]	GGA + U and GF[b]	FM metallic
$Pm\bar{3}m$	5.0	0.84	4.16	[16]	UHF[c]	FM half-metallic
$Pm\bar{3}m$, P4/mbm	6.0	–	6.0	[2]	GGA + U	FM metallic

[a]Dynamical mean-field theory [17].
[b]Green function [18].
[c]Unrestricted Hartree-Fock [19].

The term of E_{DC} is the double-counting term introduced to avoid double counting in E_{GGA} and E_{Hub} terms. The term E_U is the corresponding Hubbard term in the GGA + U method, which can be further expressed as [39, 40]:

$$E_U\left[\left\{n^{i\sigma}_{mm'}\right\}\right] = \frac{1}{2}\sum_{m,m',\sigma} U\left(n^{i\sigma}_{m} - n^{0}\right)\left(n^{i-\sigma}_{m'} - n^{0}\right) + \frac{1}{2}\sum_{\substack{m,m',\sigma \\ (m\neq m')}} U_{\text{eff}}\left(n^{i\sigma}_{m} - n^{0}\right)\left(n^{i\sigma}_{m'} - n^{0}\right) \quad (4)$$

In this study, we have introduced various values of U and J, each of them in a range of 0 eV to 10 eV and 0.60 eV to 0.75 eV, respectively.

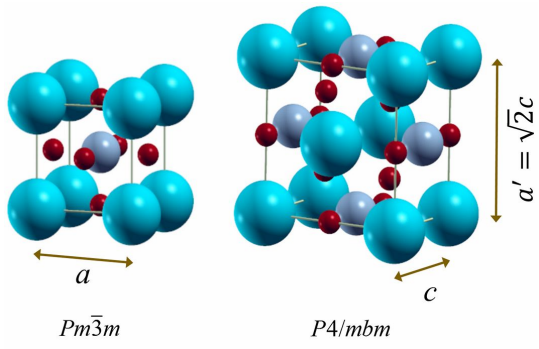

Fig. 1. Schematic diagram of $SrCoO_3$ in $Pm\bar{3}m$ and P4/mbm space groups. Grey, green, and red colors denote Co, Sr, and O atoms, respectively.

The second model is a 10-atom $\sqrt{2}\times\sqrt{2}\times 1$ $SrCoO_3$ supercell with P4/mbm space group. Initial tetragonal lattice parameters used for the supercell are c = 3.8289 Å, based on experimental report [9], and $a' = \sqrt{2}c = 5.414882309$ Å. The $SrCoO_3$ supercell is shown in Fig. 1. To avoid time-consuming calculation, we reduced the corresponding k-point mesh to 4 × 4 × 6, which is also centered at Γ high-symmetry k-point. A reduced kinetic energy cutoff of 20 Hartree (∼544 eV) was used. The structure was also optimized using BFGS scheme and US-PP is also used for this calculation. We changed U of 0 eV to 10 eV while J was set to be 0.75 eV. The reason of the using of the values of U and J will be discussed later. Our results obtained by using US-PP have been compared with those obtained by using norm-conserving pseudopotential (NC-PP) based on Troullier-Martins scheme [41–43].

3. Results and discussion

3.1. Bulk $SrCoO_3$ in $Pm\bar{3}m$ space group

The calculated cubic lattice parameter and its dependence on U for some values of J, i.e. J = 0.60 eV, 0.65 eV, 0.70 eV and 0.75 eV, are shown shown in Fig. 2. The lattice parameter a is not significantly affected by the J value, and it increases linearly with increasing of U. Unfortunately, the value of a = 4.08 Å for U = 10 eV is overestimated. The previous report presented U and J depencences of a for U = 0.0 eV, 6.5 eV, 7.0 eV, 7.5 eV and J = 0.00 eV, 0.60 eV, 0.65 eV,

0.70 eV. The resulted a values were in the range from 3.71 Å (U = 0, J = 0) to 3.92 Å (U = 6.5, J = 0.60) [10]. It is thus concluded that the calculated a for U < 10 eV is in a good agreement with the previously reported a, estimated experimentally and theoretically, as summarized in Table 2 and Table 3, respectively. The calculated value of a for U < 10 eV is close to that of the theoretically calculated by using LDA + U and GGA + U and also to the experimental a for small U. However, a calculated using hybrid calculation gives the overestimated value [2].

The analysis of U and J is then extended by using the calculated local magnetic moments of Co ions (μ_{Co}). As it is shown in Fig. 3, μ_{Co} increases linearly with increasing of U for U $\leqslant$ 6 eV and jumps up for U = 7 eV. For 7 eV < U < 9 eV, μ_{Co} does not change and jumps up for 9 eV < U $\leq$ 10 eV. The U-dependent behavior of μ_{Co} is consistent with that of previous report, in which μ_{Co} linearly increased until U = 7 eV and saturated for 7 eV < U < 9 eV [14]. Furthermore, the values of U of 8 eV and 9 eV, J = 0.75 eV provide very similarμ_{Co} values of 2.56 μ_B and 2.57 μ_B, which are in good agreement with the previous theoretical result of 3.19 μ_B (U = 8.0 eV) [14] and experimental result of 3.0 eV [44].

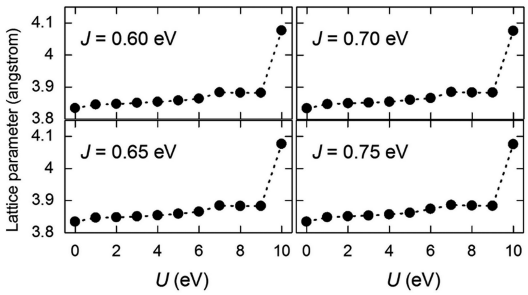

Fig. 2. Calculated cubic lattice parameter of $SrCoO_3$ as function of U for selected values of J from J = 0.60 eV to 0.75 eV in Pm$\bar{3}$m space group.

The value of μ_{Co} = 2.56 μ_B or μ_{Co} = 2.57 μ_B provides the number of unpaired electrons and corresponds to effective local magnetic moment μ_{eff} of 3.417 μ_B and 3.430 μ_B, respectively. We obtain μ_{eff} values by:

$$\mu_{\text{eff}} = 2\sqrt{S(S+1)} \tag{5}$$

where S is the spin which equals to ½ × unpaired electron. In this case, the value of μ_{Co} is in fair agreement with that of the IS state ($t_{2g}^4 e_g^1$, S = 3/2) at Co^{4+} ion in which there are three unpaired electrons. Each electron approximately gives 1 μ_B. It is, thus, suggested that there is a possibility of mixing between IS states and a small number of LS states, which produces lower μ_{Co} rather than the theoretically predicted μ_{Co}, as shown in Table 4. Table 4 presents the possible valence states of Co ion, i.e LS, IS, and HS.

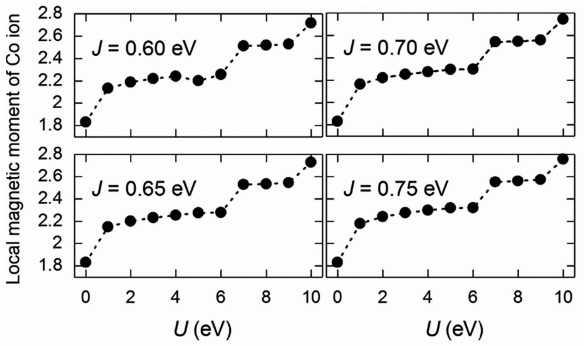

Fig. 3. Calculated local magnetic moments of Co ion as function of U for selected values of J in Pm$\bar{3}$m space group.

It is concluded that the values of U = 8 eV or 9 eV (J = 0.75 eV) are suitable. They are consistent with that of the previously suggested values of (U, J) = (10.0 eV, 0.76 eV) [10]. However, the value of U = 8 eV is in a very good agreement with that of previous reported values of U = 7.8 eV [40] and 8.0 eV [14]. The J-dependence of a, and μ_{Co} does not cause any significant change. According to these results, we then applied the value of J = 0.75 eV, which is close to the previously reported J [13, 14, 40]. The analysis of both U values is further conducted by considering electronic and magnetic properties of the $SrCoO_3$.

Regarding electronic and magnetic properties of $SrCoO_3$, calculated projected-density of states (PDOS) of Co 3d orbitals, i.e. three-fold degenerate t_{2g} and two-fold degenerate e_g and O 2p states, for U = 0 eV to 10 eV and J = 0.75 eV, are shown in Fig. 4. However, Sr 5s orbital provides almost no contribution to chemical bondings and

Table 2. Experimental results for lattice parameter, total and local magnetic moments, with corresponding measurement method and material type of $SrCoO_3$.

a [Å]	μ [μ_B/f.u]	T [K]	μ_{Co} [μ_B]	Measurement method	Material type	Literature
3.8289	2.5	2	–	SQUID magnetometer	Single crystal	[9]
3.8292	2.5	1.8	–	SQUID magnetometer	Polycrystalline	[45]
3.835	2.1	0 K	–	Foner-type magnetometer	Polycrystalline	[46]
3.836			3.0	Automatic recording balance	Crystal	[44]

Table 3. The values of lattice parameters, total and local magnetic moments, of $SrCoO_3$ obtained using theoretical studies.

Space group	a [Å]	c [Å]	μ [μ_B/f.u]	μ_{Co} [μ_B]	Temp. [K]	Literature
$Pm\bar{3}m$	–		–	3.19	300 K	[14]
$Pm\bar{3}m$	3.84		–	1.30	300 K	[10]
$Pm\bar{3}m$	3.833		2.281	–	–	[15]
$Pm\bar{3}m$	3.842		2.6	–	–	[5]
$Pm\bar{3}m$	–		–	2.96 (IS)	–	[16]
$Pm\bar{3}m$	–		–	2.70	232 K	[13]
P4/mbm (GGA + U)	3.943	5.502	–	2.84	0 K	[2]
P4/mbm (LDA + U)	3.811	5.313	–	2.86	0 K	[2]
P4/mbm (HSE06)*	3.912	5.429	–	2.53	0 K	[2]

*Hybrid-functional method: Heyd-Scuseria-Ernzerhof [47, 48].

phenomena around E_F. This is confirmed by the absence of electron in the outer shell of Sr^{2+} ion, described as $[Kr]5s^0$ configuration. The ferromagnetic behavior is reflected by PDOS for all U values and it is mainly contributed by Co 3d states hybridized with O 2p states. We also suggest that the $SrCoO_3$ has metallic character, as reported in the previous reports [9, 15], which is summarized in Table 2 and Table 3. We thus propose that the values of U = 8 eV and J = 0.75 eV are the best values for $SrCoO_3$ with $Pm\bar{3}m$ space group. The calculated total energy per Co is −243.138 Ry (−3308 eV). Yet, IS state is also proposed in half-metallic $SrCoO_3$ studied by using the unrestricted Hartree-Fock (UHF) approximation, as shown in Table 3 [16].

Fig. 4 shows crystal-field effect in cubic symmetry, which produces three-degenerate Co 3d-t_{2g} and two-degenerate Co 3d-e_g states. The spin-up Co 3d-t_{2g} and Co 3d-e_g states are shifted to the lower energy and the spin-down states are shifted to the higher energy by increasing U. These shifts are suggested to be the result of suppression by the high U.

However, the Co 3d-t_{2g} states are much more sensitive to the change in U in the range of 6 eV $\leqslant$ U $\leqslant$ 7 eV. The enhanced sensitivity was described by the previous report showing similar sensitivities of Co 3d-t_{2g} and Co 3d-e_g states in the whole U range [14]. The spin-down t_{2g} states generally overlap the spin-down Co 3d-e_g states above E_F. On the other hand, for U $\leqslant$ 9 eV, smeared Co 3d-e_g and spin-up Co 3d-t_{2g} states are below E_F due to the hybridization with O 2p states. These results are similar to those of previous results [13, 15] but are different from the picture of IS-state t_{2g} [49]. However, the configuration of $t_{2g}^4 e_g^1$ in IS-state is reproduced by our calculations.

On the other hand, the spin-up O 2p states are quite strongly affected by increased U. Spin-up and spin-down O 2p peaks at around −2 eV (for U $\geqslant$ 7 eV) and −4 eV are O $2p_\sigma$ peaks

Table 4. Possible valence states and spin states with corresponding electron configurations and effective magnetic moment values calculated from equation 5.

Co valence state	LS		IS		HS	
	unpaired electron	μ_{eff} [μ_B]	unpaired electron	μ_{eff}[μ_B]	unpaired electron	μ_{eff} [μ_B]
2+	1 ($t_{2g}^6 e_g^1$)	1.732	–	–	3 ($t_{2g}^5 e_g^2$)	3.872
3+	0 ($t_{2g}^6 e_g^0$)	0	2 ($t_{2g}^5 e_g^1$)	2.828	4 ($t_{2g}^4 e_g^2$)	4.899
4+	1 ($t_{2g}^5 e_g^0$)	1.732	3 ($t_{2g}^4 e_g^1$)	3.872	5 ($t_{2g}^3 e_g^2$)	5.916

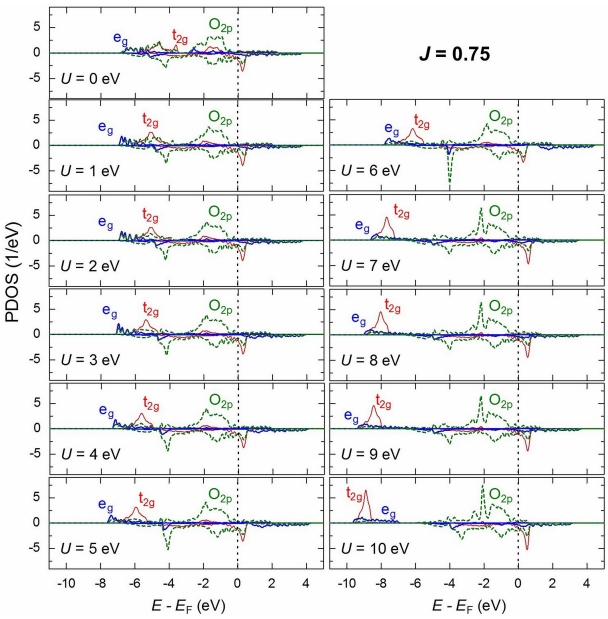

Fig. 4. Calculated projected-density of states of $SrCoO_3$ in $Pm\bar{3}m$ space group for U = 0 eV to 10 eV with J = 0.75 eV. The Fermi level is set to be zero as reference.

based on previously calculated PDOS by dynamical mean-field theory (DMFT) [13]. However, O $2p_\pi$ states are not significantly changed. It is thus clear that U widens the separation between spin-up O $2p_\sigma$ and O $2p_\pi$ states. In addition, the hybridization of Co 3d-t_{2g} and O 2p states is weakened by the increasing of U, while U-dependence of hybridization of Co 3d-e_g and O 2p states is small. In spite of the presence of crystal-field effect in d orbitals, Jahn-Teller (JT) distortion has not been found for all U and J values. The spin-up and spin-down Co 3d-t_{2g} states are evidently higher than the Co 3d-e_g states for U = 8 eV and J = 0.75 eV. Looking back, the proposed IS-LS states for both values of U and J as well as the local magnetic moment of Co ion are mainly contributed by spin-up t_{2g} states at around −8.02 eV and spin-down t_{2g} states at around 0.54 eV as shown in Fig. 4.

3.2. Bulk $SrCoO_3$ in P4/mbm space group

In this space group, J is not varied because J would not significantly change lattice parameters and local magnetic moment of Co ion as it has been found for the previous space group. Although U = 10 eV results in an overestimated value for the cubic symmetry, we used U = 0 eV to U = 10 eV to study the properties of $SrCoO_3$ in P4/mbm space group. The calculated tetragonal lattice parameters and their dependence on U for J = 0.75 eV are shown in Fig. 5. It is seen that the optimized a′ ($= \sqrt{2}c$) and c are generally increased with increasing value of U. However, a′ is minimum at U = 4 eV (5.4480 Å) and maximum at U = 10 eV (5.4809 Å). On the other hand, c is minimum at U = 3 eV (3.8489 Å) and maximum at U = 9 eV (3.9209 Å).

The values of U = 0 eV and U = 3 eV provide a good agreement with the results of the previous reports, presented in Table 2. The lattice parameters are however overestimated for U $\geqslant$ 4 eV. The inset in Fig. 5 presents U-dependence of μ_{Co}. There is an increase in μ_{Co} from U = 0 eV to U = 1 eV and until U = 8 eV μ_{Co} remains nearly constant from 2.2431 μ_B to 2.3146 μ_B, which is close to the picture of IS states mixed with a few LS states for Co^{4+}. The values of μ_{Co} are consistent with that obtained by using HSE06 method [2]. The values

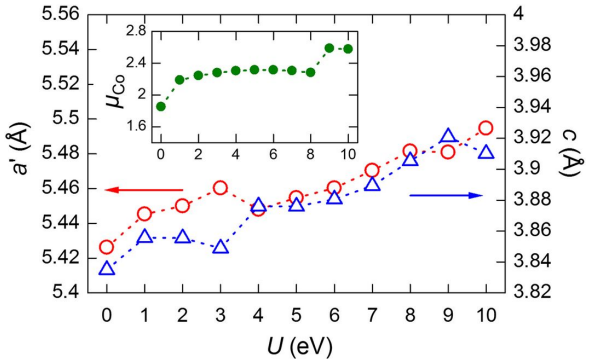

Fig. 5. Calculated tetragonal lattice parameters and local magnetic moments (μ_{Co}) of Co ion as function of U (J = 0.75 eV) in P4/mbm space group.

of U = 9 eV and 10 eV, respectively, give higher μ_{Co} values of 2.5871 eV and 2.5767 eV, which are close to the picture of IS states mixed with a few LS sates for Co^{4+} as well. However, the overestimated tetragonal lattice parameters do not fit with the presented experimental reports, as shown in Table 2 and Table 3, although HSE06 also promotes the overestimated results [2]. Considering these results, we propose that U = 3 eV (J = 0.75 eV) is the most suitable for $SrCoO_3$ in P4/mbm space group. The calculated total energy per Co is −243.385 Ry (−3311 eV). It means P4/mbm space group results in more stable ground state rather than that of $Pm\bar{3}m$ after choosing the suitable U. Further analysis has been extended by the calculated electronic and magnetic properties.

The calculated PDOS of Co 3d orbitals, i.e., t_{2g} and e_g, and O 2p states for U = 0 eV to 10 eV at J = 0.75 eV for P4/mbm space group are shown in Fig. 6. As results for $SrCoO_3$ in $Pm\bar{3}m$ space group, PDOS of Sr^{2+} ion provides negligable contribution near E_F. Also, FM metallic behavior is found for this system in P4/mbm space group for all U values. Crystal-field effect is also found in this symmetry. The spin-up Co 3d states are shifted to the lower energy and the spin-down states are shifted to the higher energy with increasing U but the increase is not as significant as that of the system in $Pm\bar{3}m$ space group. Hence, it is suggested that the suppression of U to Co 3d binding energy levels is not as strong as in $Pm\bar{3}m$ space group. Until U = 8 eV, Co 3d-t_{2g} states are sensitive to

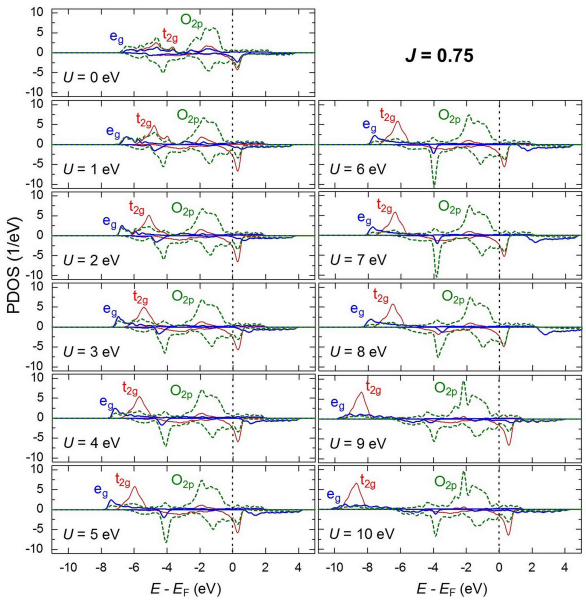

Fig. 6. Calculated projected-density of states of $SrCoO_3$ in P4/mbm space group for U = 0 eV to 10 eV with J = 0.75 eV. The Fermi level is set to be zero as reference.

changing of U in 5 eV $\leqslant$ U $\leqslant$ 6 eV range, while Co 3d-e_g states are not sensitive. For U = 9 eV and 10 eV, the profile of Co 3d states changes significantly and corresponds to high μ_{Co}. As also seen for $Pm\bar{3}m$ space group, the spin-down Co 3d-t_{2g} states overlap the spin-down Co 3d-e_g states above E_F. These results are also similar to the previously reported [13, 15] but are different from the picture of IS-state Co 3d-t_{2g} [49]. Interestingly, $t_{2g}^4 e_g^1$ configuration is also reproduced with P4/mbm space group. The spin-up O 2p states are strongly affected by the increasing U, especially in the range of 6 eV $\leqslant$ U $\leqslant$ 7 eV. Spin-up and spin-down O 2p peaks at around −2 eV (U = 9 eV and 10 eV) and −4 eV are O $2p_\sigma$ peaks, which are strongly affected by U, based on previously calculated PDOS by DMFT [13]. It is also suggested that U widens the separation between spin-up O $2p_\sigma$ and O $2p_\pi$ states.

3.3. Norm-conserving pseudopotential for $SrCoO_3$

PDOS of $SrCoO_3$ obtained by using NC-PP, are shown in Fig. 7a. We found that the optimized a of

3.83 Å is in good agreement with experimental result [9] but the calculated μ_{Co} of 2.5267 μ_B is lower than that of the picture of IS-state. The calculated total energy per Co is −151.965 Ry (−2680 eV), which is too high compared with that of US-PP. Furthermore, we found a sharp spin-down O 2p peak at −4.4 eV which is similar to the peak at −4.0 eV for U = 6 eV (J = 0.75 eV) as shown in Fig. 7b. On the other hand, the separated spin-up O $2p_\sigma$ and O $2p_\pi$ peaks at −2.1 eV and around −1.2 eV for NC-PP are similiar to the separated peaks at −2.18 and around −1.5 eV for U = 8 eV (J = 0.75 eV) shown in Fig. 7c. The Co 3d-e_g and spin-up Co 3d-t_{2g} states for NC-PP also spread below E_F, while spin-down Co 3d-t_{2g} states lie above E_F and are hybridized with some spin-down O 2p states. Consequently, the employed NC-PP and US-PP with suitable U can be used to describe the electronic and magnetic properties of $SrCoO_3$ in Pm$\bar{3}$m space group.

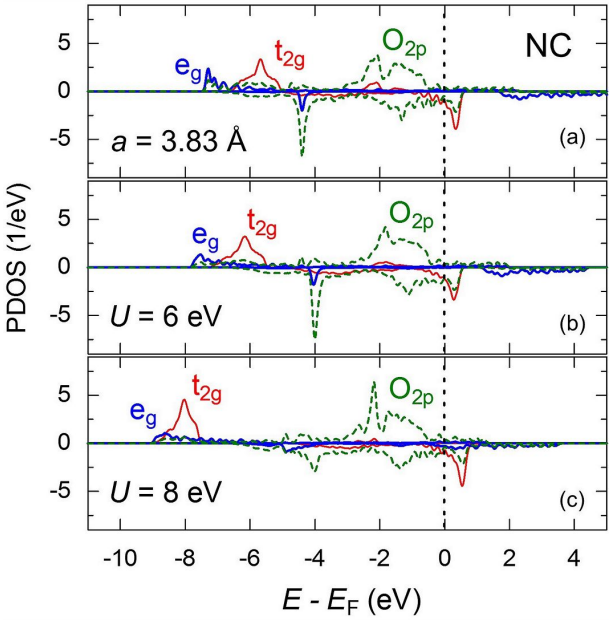

Fig. 7. Calculated projected-density of states of d and O 2p orbitals in $SrCoO_3$ in Pm$\bar{3}$m space group (a) for norm-conserving pseudopotential, (b) U = 6 eV, (c) U = 8 eV.

PDOS of $SrCoO_3$ in P4/mbm space group obtained by using NC-PP is shown in Fig. 8a. We found that c of 3.884 Å is overestimated relative to the experiments (Table 2). The calculated μ_{Co} of 2.5953 μ_B is lower than that of the picture of IS-state.

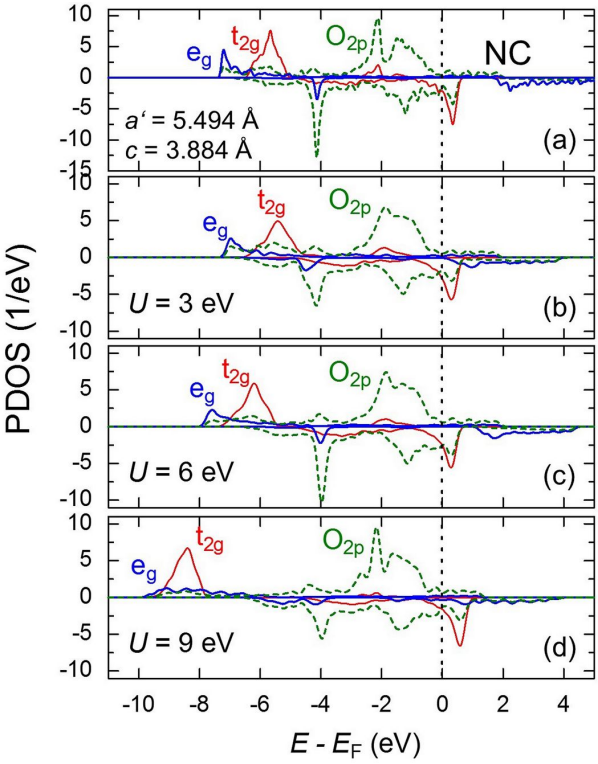

Fig. 8. Calculated projected-density of states of d and O 2p orbitals in $SrCoO_3$ in P4/mbm space group (a) for norm-conserving pseudopotential, (b) U = 3 eV, (c) U = 6 eV.

Calculated total energy per Co is −303.930 Ry (−4135 eV), which is lower than that of US-PP. We have also found a sharp spin-down O 2p peak at −4.2 eV which is similar to the peak at −4.0 eV for U = 6 eV (J = 0.75 eV) as shown in Fig. 8c. On the other hand, separated spin-up O $2p_\sigma$ and O $2p_\pi$ peaks at −2.1 eV and around −1.3 eV for NC-PP are close to the separated peaks at −2.18 and around −1.5 eV for U = 9 eV (J = 0.75 eV) shown in Fig. 8d. The Co 3d-e_g and spin-up Co 3d-t_{2g} states for NC-PP also spread below the E_F, while spin-down Co 3d-t_{2g} states lie above E_F and are hybridized with some spin-down O 2p states. However, the PDOS profile for NC-PP is different from that for U = 3 eV, as shown in Fig. 8b. We can conclude that US-PP with GGA + U method is

more suitable for $SrCoO_3$ in P4/mbm space group rather than NC-PP with GGA method, in spite of the lower ground-state total energy.

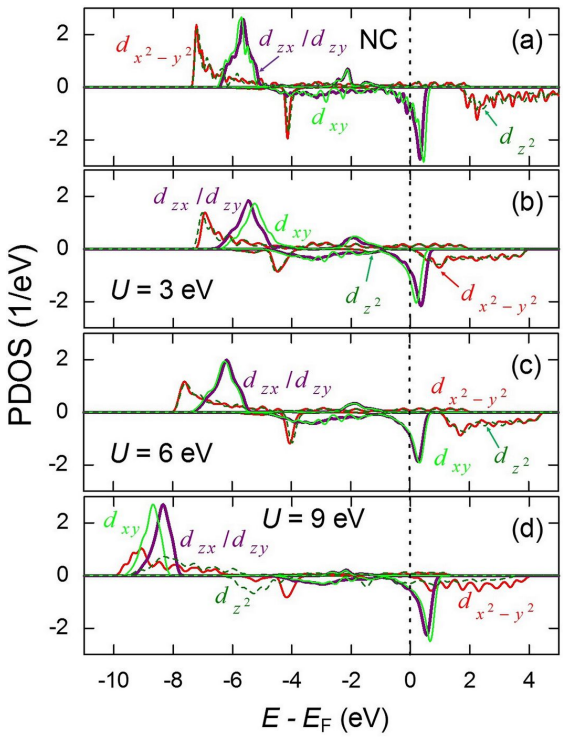

Fig. 9. Calculated projected-density of states of d in $SrCoO_3$ in P4/mbm space group (a) for norm-conserving pseudopotential, (b) U = 3 eV, (c) U = 6 eV, and (c) U = 9 eV.

Interestingly, JT distortion is found in P4/mbm space group. Fig. 9a shows JT distortion in Co 3d orbital obtained by using NC-PP. It is found that the spin-up Co $3d_{xy}$ level is below Co $3d_{zx}$/Co $3d_{zy}$ levels, while the spin-down Co $3d_{xy}$ level is at the highest level. The spin-up and spin-down Co $3d_{z^2}$ levels are close to Co $3d_{x^2-y^2}$ level. This profile is very similar to that for U = 6 eV, as shown in Fig. 9c. For U = 3 eV, this profile is different from that calculated using NC-PP. The spin-up Co $3d_{xy}$ level is above Co $3d_{zx}$/Co $3d_{zy}$ levels, while the spin-down Co $3d_{xy}$ level is at the lowest level, as shown in Fig. 9b. Interestingly, a large JT distortion is found for U = 9 eV in which the spin-up Co $3d_{xy}$ level is below Co $3d_{zx}$/Co $3d_{zy}$ levels and the spin-down Co $3d_{xy}$ level is at the highest level, as shown in Fig. 9d. This also applies to Co 3d-e_g in which spin-up Co $3d_{z^2}$ level is higher than Co $3d_{x^2-y^2}$ level and spin-down Co $3d_{z^2}$ level is approximately the same as Co $3d_{x^2-y^2}$ level, especially above E_F. This result remarkably shows the significance of U contribution to JT distortion in Co 3d in P4/mbm space group, in contrast with that in Pm$\bar{3}$m space group. The increasing of U strongly flips each d orbital in t_{2g}.

4. Conclusions

Based on the analysis, the values of U = 8 eV and J = 0.75 eV are the best choice for the $SrCoO_3$ description in terms of the local magnetic moment of Co ion and electronic structure for Pm$\bar{3}$m space group. We found that the Co ion has a local magnetic moment of 2.56 μ_B, which is in good agreement with the previous results obtained by theoretical (3.19 μ_B) and experimental (3.0 μ_B) studies. The resulted PDOS shows that the Co 3d states are the main contributor to FM metallic properties of $SrCoO_3$, alongside with their hybridization with O 2p states. Otherwise, the Sr 5s states do not play almost any role. In general, increasing of U causes the shift of spin-up and spin-down Co 3d states to lower energy and higher energy, respectively. We also confirm that NC-PP calculation gives the lattice parameter which is in good agreement with experimental result, while Co ion local magnetic moment is still too low compared with the picture of IS-state. However, NC-PP is not suitable to be used for P4/mbm space group. The value of U = 3 eV (J = 0.75) is the most suitable choice for this space group. For this U value, FM metallic properties and good agreement of tetragonal lattice parameters with experimental results are also obtained but the local magnetic moment of Co ion is much lower than the picture of IS state. This indicates that LS states for P4/mbm space group have larger contribution to Co 3d orbital rather than that for Pm$\bar{3}$m space group. Interestingly, the result also shows the significance of U contribution to JT distortion in Co 3d for P4/mbm space group even though the shifts of each orbitals are consistent with that for Pm$\bar{3}$m space group. This study generally shows the significant contribution of U and space group in calculating

structural, electronic, and magnetic properties of $SrCoO_3$. Based on the more stable ground state, it also shows that P4/mbm space group with US-PP is more suitable for connecting the theoretical and observed experimental properties after choosing the suitable U value.

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