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Magnetic and Electronic Properties of Double Perovskite Ba_2SmNbO_6 without Octahedral Tilting by First Principle Calculations

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The structural, magnetic and electronic properties of the double perovskite Ba_2SmNbO_6 (for the simple cubic structure where no octahedral tilting exists anymore) are studied using the density functional theory within the generalized gradient approximation as well as taking into account the on-site Coulomb repulsive interaction. The total energy, the spin magnetic moment, the band structure and the density of states are calculated. The optimization of the lattice constants is 8.5173 Å, which is in good agreement with the experimental value 8.5180 Å. The calculations reveal that Ba_2SmNbO_6 has a stable ferromagnetic ground state and the spin magnetic moment per molecule is 5.00 μB/f.u. which comes mostly from the Sm^{3+} ion only. By analysis of the band structure, the compound exhibits the direct band gap material and half-metallic ferromagnetic nature with 100% spin-up polarization, which implies potential applications of this new lanthanide compound in magneto-electronic and spintronic devices.

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The concept of half-metallic (HM) ferromagnets (FM) was first discovered by de Groot *et al.*[1] in 1983. Since the finding of the HM ferromagnetism, large tunneling magneto-resistance (TMR) in ordered Sr_2FeMoO_6[2] and Sr_2FeReO_6[3] by Kobayashi *et al.*, intensive research efforts have been devoted to understanding the magnetic and electronic properties of double perovskite with an $A_2B'B''O_6$ formula unit. HM materials are defined as those which are insulating for one spin direction, but metallic for the other spin channel. The electronic density of states is completely spin polarized on the Fermi level, and the conductivity is dominated by these metallic single-spin charge carriers. In fact, the HM property is considered to be closely related to the colossal magneto-resistance (CMR) phenomena observed in various materials.[4,5] What we are interested in this work is the compounds of the double perovskite families with the formula Ba_2LnNbO_6 (Ln=lanthanide), the presence of the Ln atom at the B octahedral position is expected to give rise to far more tunability and richness of the magnetic and electronic properties, and possibly be used in spintronic devices (sources for spin polarized electrons), spin filtering tunnel junctions, magneto-dielectric capacitors, electrode and electrolyte materials, photocatalysts for water splitting, solar cells components, low field magneto-resistive sensors, dielectrics or magnetic memory components, etc.[6] This series of double perovskites have been re-examined at room temperature by the Rietveld profile analysis of x-ray diffraction data,[7] to identify the exact symmetries and the associated space groups accurately. Depending on this experimental work, the structures of the double perovskites Ba_2LnNbO_6 (Ln=La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho and Y) can all be derived from the primitive cubic aristotype by ordering the LnO_6 and NbO_6 octahedra, and by tilting the octahedra around one of the principal axis of the cubic cell. For example in Ba_2LnNbO_6 compounds with (Ln=Sm) the octahedra is tilted around the twofold [110] axis (tilt system $(a^-a^-c^0)$), resulting in the monoclinic symmetry with the space group $I2/m$.[7–9] Under some external influences, the symmetry can be change from monoclinic $(I2/m)$ to tetragonal $(I4/m)$ then the simple double cubic $(Fm3m)$ for which the last one contains no octahedral tilting.[10] The tolerance factor for the double perovskite structure is defined as[11] $t = (r_{\rm Ba} + r_0)/\sqrt{2}(\bar{r}_{(B,B')} + r_0)$, where $\bar{r}_{(B,B')}$ is the averaged ionic radii of the B (Sm) and B' (Nb) cations. The double perovskite shows a cubic symmetry with space group $(Fm\bar{3}m)$ only for t close to unity ($t \cong 1$), which is investigated by Galasso[12] and Baran *et al.*[13] The oxidation state of (B, B') cations is representative of the second class $(Ba_2^{2+}Sm^{3+}Nb^{5+}O_6^{2-})$.[14] In this work, the study singled one compound Ba_2SmNbO_6 at cubic symmetry $(Fm\bar{3}m)$. The structural, magnetic and electronic properties of the double perovskite Ba_2SmNbO_6 have been studied using the all-electron full-potential linear augmented plane wave (FP-LAPW),[15] within the generalized gradient approximation (GGA) as well as taking into account the on-site Coulomb repulsive interaction (GGA+U).

For the double perovskite Ba_2SmNbO_6 within the $(Fm\bar{3}m)$ space group, the experimental lattice constant $a = 8.5180$ Å was used,[16] and the refined atomic

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positions was taken to be similar to Ba_2YNbO_6,[17] but the internal parameter is calculated at (x = 0.26616) by the min-position program. Its crystal structure is shown in Fig. 1. The six oxygen atoms surrounding the Sm and Nb sites provide an octahedral environment, which can be described as a chain of order (SmO_6/NbO_6) oxygen octahedral, the Sm ions are in the same planes as the Nb ions (parallel to the a and b axes), the Ba ions also form parallel layers in the space between the (Sm, Nb) planes. We can see four formula-units Ba_2SmNbO_6 ($Z = 4$), and the Wyckoff positions are Ba at 8(c), Sm at 4(a), Nb at 4(b) and O at 24(e).

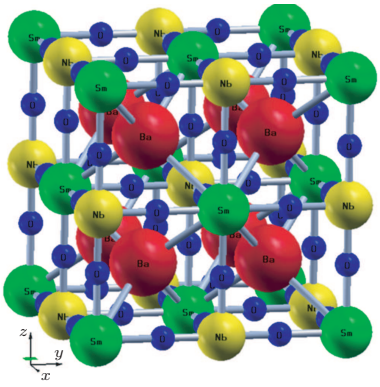

Fig. 1. Crystal structure of simple double cubic Ba_2SmNbO_6 at the experimental lattice constant a_{exp} = 8.518 Å for FM, without octahedral tilting.

Density functional theory (DFT) calculations were performed using the all-electron full-potential linear augmented plane wave (FP-LAPW)[18] method as implemented in the WIEN2K code. For the exchange correlation potential, it is known that the pure generalized gradient approximation GGA–(Wu and Cohen),[19] could give an incorrect result for 4f atoms systems (lanthanide elements), because the electron correlations were assumed to be insufficiently described. However, GGA calculations can be corrected using a strong-correlation called the GGA+U method.[20] In this approximation, U and J stand for Coulomb and exchange parameters, respectively, based on the formulation by Dudarev *et al.* which combines the two parameters U and J to produce an effective Coulomb repulsion $U_{eff} = U - J$, which we call U in the following.[21,22] For the Ba_2SmNbO_6 compound we explore the behavior of the system for U varying from 4 to 7 eV. The calculation shows that the value U = 4.75 eV agrees very well with the experimental lattice constant. The spin polarization has been considered and the relativistic effect is taken into account in the scalar style because of the heavy atom of Sm.

We define the muffin-tin spheres radii (r_{Ba}, r_{Sm}, r_{Nb}, r_O) are (2.78 ua, 1.83 ua, 1.43 ua, 1.25 ua) and (2.55 ua, 2.30 ua, 2.00 ua, 1.32 ua) for FM and AFM, respectively. The density plane-wave cut-off $R\,K_{max}$ parameter is set at 5.6 and 6.6 for FM and AFM respectively. We used 56 k-points for FM and 47 k-points for AFM in the first irreducible Brillouin zone. For all electronic structure calculations we reduplicate the Monkhorst-Pack k-point grid in the first irreducible Brillouin zone at 84. The electronic valence configurations for each atomic species are Ba ($5s^25p^66s^2$), Sm ($5s^25p^64f^66s^2$), Nb ($4s^24p^64d^45s^1$), and O ($2s^22p^4$). The self-consistent calculations are considered to be converged only when the integration of absolute charge and spin density difference per formula unit between the successive loops is less than $0.0001|e|$, where e is the electron charge. Also the stability is better than 0.01 mRy for the total energy per cell.

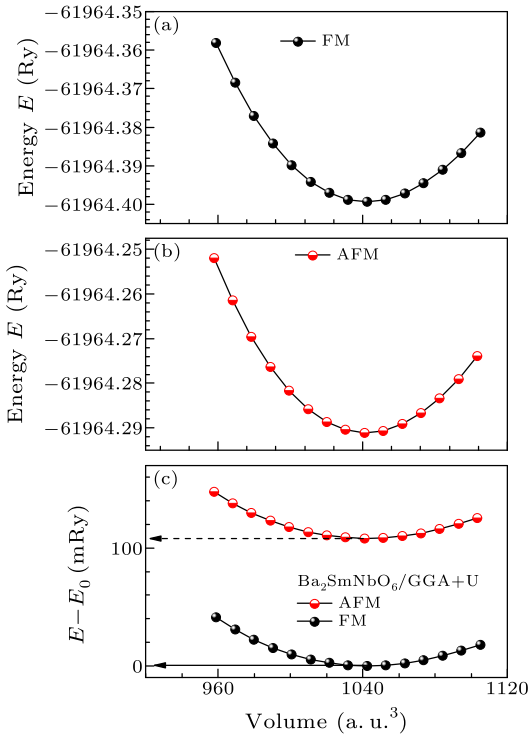

Fig. 2. The total energies as a function of the volume, obtained by using GGA+U for FM and AFM configurations. Also we show a comparison curve where the minimum energy in the graph is chosen as the reference energy and it is set to zero. The curve is the result fitted to Murnaghan's equation of state.

The magnetic stability is derived from a comparison of the total energies, therefore the total energies for FM and AFM(001) configurations are fitted by means of Murnaghan's equation of state.[23,24] The optimization structure of double perovskite Ba_2SmNbO_6 for FM and AFM(001) are illustrated in Fig. 2. The order of energies is found such that a system FM spin order with a space group of ($Fm\bar{3}m$) symmetry possesses a lower energy (FM ground state), than the AFM(001) spin order with a space group of $I4/mmm$ symmetry. The energy necessary to reverse the magnetic coiling from FM to AFM(001) spin configura-

tions ($E_{\rm FM} - E_{\rm AFM}$) by about -108.27 mRy. The optimized lattice constant is about $a = 8.5173$ Å, which is in good agreement with the experimental value 8.518 Å by about 0.008%. For the simple cubic order double perovskite Ba_2SmNbO_6 where no octahedral tilting exists anymore, there are three bond lengths ((Sm–O), (Nb–O) and (Ba–O)), as listed in Table 1. The derived bulk modulus $B_0(V\partial^2 E/\partial V^2)_{V_0}$ is about 156 GPa, while the pressure derivative of bulk modulus $B' = \partial B/\partial P$ is about 4.6 GPa. Also we can see that Ba_2SmNbO_6 is a strong condensation structure by a large value of about 6.6 g/cm^3.

Table 1. The values of total energy (Ry/f.u.), total energy difference between FM and AFM $\Delta E = (E_{\rm FM} - E_{\rm AFM})$ (mRy/f.u.), lattice constant a (Å), bonds lengths d (Å), density ρ (g·cm^{-3}), the derived bulk modulus B_0 (GPa), the pressure derivative of bulk modulus B', the local moments ($m_{\rm Ba}, m_{\rm Sm}, m_{\rm Nb}, m_{\rm O}$) ($\mu_{\rm B}$), the total magnetic $M_{\rm tot}$ ($\mu_{\rm B}$/f.u.), and the band gap (eV).

Method Calculation	GGA+U	Experiment
$E_{\rm tot(FM)}$ (Ry/f.u.)	−61964.4	
$\Delta E_{\rm tot} = (E_{\rm FM} - E_{\rm AFM})$ (mRy/f.u.)	−108.27	
a_0 (Å)	8.5173	8.518[16]
$d_{\rm Sm-O}$ (Å)	2.26715	
$d_{\rm Nb-O}$ (Å)	1.99185	
$d_{\rm Ba-O}$ (Å)	3.0147	
ρ (g·cm^{-3})	6.6	
B_0 (GPa)	156	
B'	4.6	
$m_{\rm Ba}$ (Å)	0.003	
$m_{\rm Sm}$ (Å)	4.825	
$m_{\rm Nb}$ (Å)	0.007	
$m_{\rm O}$ (Å)	−0.023	
$M_{\rm tot}$ ($\mu_{\rm B}$/f.u.)	5	
Nature (Magn/elec)	FM/Half metallic	
Band gap (eV)	3.334 ↓	

The (GGA+U) calculation at $U = 4.75$ eV shows that the values of total and partial moments are 5.00 $\mu_{\rm B}$/f.u. and 4.825 $\mu_{\rm B}$/f.u. for Ba_2SmNbO_6 and Sm, respectively. Note that there is notable disagreement between the local partial magnetic moment within the muffin-tin sphere for B site (Sm) 4.825 $\mu_{\rm B}$ and the ideal ionic value of local magnetic moment 5.00 $\mu_{\rm B}$ corresponding to fully localized spin (5/2). The explanation of this disagreement may be due to the strong spin-orbit coupling (antiparallel effects between orbital moment and spin moment for $4f$ electrons) where the main contribution of magnetization comes from the Sm ion. In addition, the hybridization induces a small spin moment on the Ba, Nb and O sites of Ba_2SmNbO_6, which are 0.003 $\mu_{\rm B}$, 0.007 $\mu_{\rm B}$ and -0.023 $\mu_{\rm B}$, respectively. The results also indicate that such a hybridization induces two antiferromagnetic couplings between (Sm, O) and (Nb, O) in alternative SmO_6 and NbO_6 octahedron along the three cubic axes (see Table 1).

To give a better description of the electronic structure of double perovskite Ba_2SmNbO_6 in FM ground states, we have performed the GGA+U calculation, which includes the electron correlation between Sm($4f$) electrons only. Figure 3 shows the calculated band structure along the high-symmetry directions in the Brillouin zone. It is clear that the majority-spin electrons in Fig. 3(a) are metallic due to strong overlap close to the Fermi level, whereas there is a direct band gap type material of about $E_{\rm g} = 3.334$ eV at the X point around the Fermi level in the bands for the minority-spin electrons in Fig. 3(b). The bottom of the minority-spin conduction bands locates at +1.562 eV and the top of the minority-spin valence bands at −1.772 eV. Hence, the minimal energy gap for a spin–flip excitation is 1.772 eV. This non-zero spin–flip gap illustrates that Ba_2SmNbO_6 is a ferromagnetic half metallic (FM-HM).

The calculated total and partial density of states (TDOS and PDOS) projected onto O ($2p$), Sm ($5p, 4f$), Nb ($4d$) and Ba ($4p$) orbitals are summarized in Figs. 4 and 5. In all the DOS figures, the energy is counted from the Fermi energy. We can see that the Sm ($5p$) state is dominated at the lowest energy at −20.02 eV and −15.5 eV, where the band from −12.93 eV to −12.27 eV is contributed mainly by the Ba ($4p$) states. The band extending from −5.54 eV to −1.72 eV is composed mainly of O ($2p$) states hybridized with much less numbers of the dominant Nb ($4d$) and Sm ($4f$) electrons.

It is interesting to note that the ground state of the Ba_2SmNbO_6 has an FM-HM nature, because the TDOS (black lines) of the up-spin channel overlaps strongly with the Fermi level in Fig. 4 while the down-spin channel forms a gap of about 3.334 eV around the Fermi level, see Fig. 6, resulting in a complete (100%) spin-up polarization of the charge carriers, usable in magneto-electronic and spin tronic-devices.

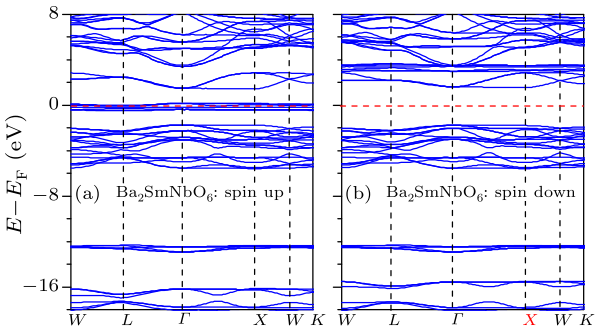

Fig. 3. Band structures of double perovskite Ba_2SmNbO_6, calculated by GGA+U for the ferromagnetic ground state at $U = 4.75$ eV (a) for spin-up channel and (b) for spin-down channel. The horizontal dashed line indicates that the Fermi energy E_F is set to zero.

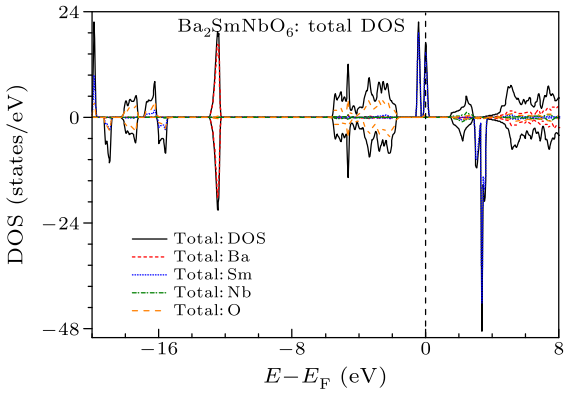

Fig. 4. Spin-resolved density of states (DOS, in states/eV per formula unit) of double perovskite Ba_2SmNbO_6, calculated by GGA+U for the ferromagnetic ground state at $U = 4.75$ eV. The black line is the TDOS, and color lines refer to the TDOS projected in the atomic spheres of Ba, Sm, Nb and O.

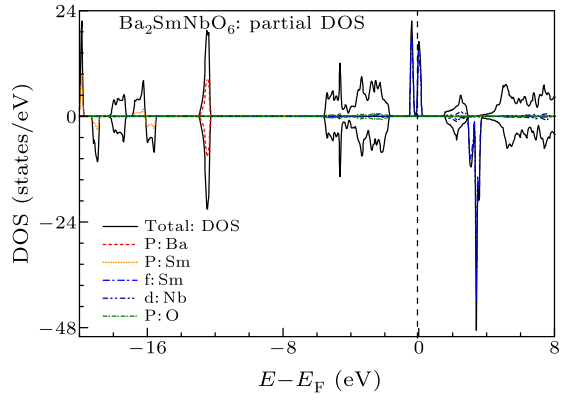

Fig. 5. Spin-resolved density of states (DOS, in states/eV per formula unit) of double perovskite Ba_2SmNbO_6, calculated by GGA+U for the ferromagnetic ground state at $U = 4.75$ eV. The black line is the TDOS, and color lines refer to the PDOS projected in the atomic spheres of Ba, Sm, Nb and O.

As displayed in Figs. 5 and 6 we find that the GGA+U separates 6 occupied Sm ($4f$) states and 8 unoccupied states of about 2.67 eV. The occupied f states form two narrow peaks in the up-spin band at the Fermi level, which range from −0.56 eV to 0.25 eV. The spin-orbits coupling contributes significantly to the splitting of the states of about 0.4 eV. The two peaks in the vicinity of the Fermi level are dominated by the $f_{5/2}$ states, which are completely occupied by 5 electrons, whereas the unoccupied f states are formed by narrow $f_{7/2}$ states in the range of 0.83 eV above the Fermi level in the deep conduction band (CB), and the magnetic moment of 5 μ_B (comes mostly from Sm^{3+} ion only) due to the half-filled $4f$ shell. The corresponding ionic valence states of Sm in Ba_2SmNbO_6 compound become Sm^{3+} ($4f^{5\uparrow}$), where the lower lying energy level is ${}^6H_(5/2)$.[25] This result implies that the partially filled Sm ($4f^5$) here is responsible for the half metals. The molecular formula of Ba_2SmNbO_6 in the ground state is $Ba_2^{2+}Sm^{3+}Nb^{5+}O_6^{2-}$.

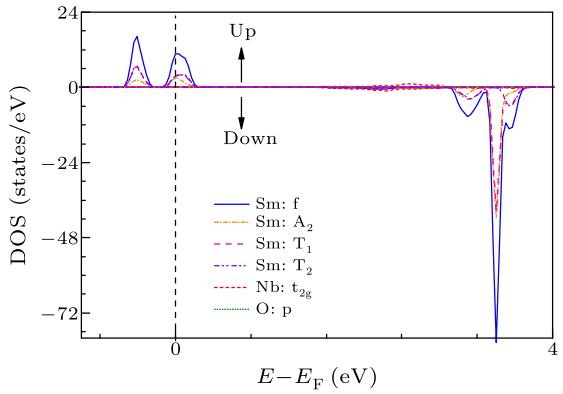

Fig. 6. Partial density of state projected in the atomic spheres of Sm ($4f$), Nb (t_{2g}) and O (p) at the vicinity of Fermi level E_F, which corresponds to the zero energy. Calculated by the QTL program where the spectral decomposition appears.

In summary, we have clarified the ferromagnetic ground state and half metallic nature of ordered double perovskite Ba_2SmNbO_6 in the ideal cubic structure where no octahedral tilting exists anymore. The DFT calculations are performed within semi-empirical approximation GGA+U. As well as taking into account the on-site Coulomb repulsive interaction for the B-site (Sm) only, we can obtain the optimization structure of ideal cubic double perovskite Ba_2SmNbO_6 and find that a system is in FM spin order, which possesses the lowest energy, and the lattice constant is in good agreement with the experimental value. The calculations show that the total spin magnetic moment is 5 μ_B, which comes mostly from the Sm ion only, corresponding to fully localized spin (5/2). The band structure calculations show a direct band gap type material at the X point around the Fermi level by non-zero spin-flip gap. The TDOS shows that Ba_2SmNbO_6 has an FM-HM nature in a complete (100%) spin-up polarization, which is usable in magneto-electronic and

spin-tronic devices. The ionic valence states of Sm in Ba_2SmNbO_6 compound is Sm^{3+} $(4f^{5\uparrow})$, corresponding to the lower lying energy level ${}^6H_{(5/2)}$, and the molecular formula of Ba_2SmNbO_6 in the ground state is $Ba_2^{2+}Sm^{3+}Nb^{5+}O_6^{2-}$.

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