Solid State Communications 241 (2016) 43–55

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Phonons and stability of infinite-layer iron oxides $SrFeO_2$ and $CaFeO_2$

M.K. Gupta [a], R. Mittal [a], S.L. Chaplot [a], Cédric Tassel [b], Hiroshi Kageyama [b], K. Tomiyasu [c], Jon Taylor [d]

[a] Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India
[b] Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan
[c] Department of Physics, Tohoku University, Sendai 980-8578, Japan
[d] ISIS Facility, STFC, Rutherford Appleton Laboratory, Chilton, Oxfordshire OX11 OQX, United Kingdom

ARTICLE INFO

Article history:
Received 1 December 2015
Received in revised form
16 May 2016
Accepted 17 May 2016
Available online 19 May 2016

Keywords:
Magnetically ordered materials
Phonons
Phase transitions
Neutron scattering

ABSTRACT

We present detailed ab-initio lattice dynamical analysis of the Fe–O infinite-layer compounds $CaFeO_2$ and $SrFeO_2$ in various magnetic configurations. These indicate strong spin–phonon coupling in $SrFeO_2$ in contrast to that in case of $CaFeO_2$. From our ab-initio calculations in $SrFeO_2$ as a function of volume, we suggest that the distortion in $SrFeO_2$ above 300 K is similar to that in $CaFeO_2$ at ambient conditions. The distortion of the planer structure of $CaFeO_2$ involves doubling of the planer unit cell that may be usually expected to be due to a soft phonon mode at the M-point (1/2 1/2 0). However, our ab-initio calculations show quite unusually that all the M-point (1/2 1/2 0) phonons are stable, but two stable M_3^+ and M_2^- modes anharmonically couple with an unstable B_u mode at the zone center and lead to the cell doubling and the distorted structure. Magnetic exchange interactions in both the compounds have been computed on the basis of the ideal planar structure ($P4/mmm$ space group) and with increasing amplitude of the B_u phonon mode. These reveal that the magnetic exchange interactions reduce significantly with increasing distortion. We have extended the ab-initio phonon calculation to high pressures, which reveal that, above 20 GPa of pressure, the undistorted planer $CaFeO_2$ becomes dynamically stable. We also report computed phonon spectra in $SrFeO_3$ that has a cubic structure, which is useful to understand the role of the difference in geometry of oxygen atoms around the Fe atom with respect to planer $SrFeO_2$. Finally, powder neutron inelastic scattering experiments on $SrFeO_2$ have also been performed at temperatures from 5 K to 353 K in the antiferromagnetic phase. The 5-K data are compared to the ab-initio calculations.

1. Introduction

Low-dimensional magnetic systems have received much attention due to their exotic magnetic and electronic properties. Iron forms a large number of oxides with FeO_4 tetrahedral, FeO_5 pyramidal or FeO_6 octahedral configurations. The gillespite mineral $BaFeSi_4O_{10}$ was the first example with iron in square planar coordination [1], which is stabilized by four-member rings of SiO_4. The compounds $AFeO_y$ (A=Sr, Ca; $y\sim2.5$) adapt a brownmillerite structure consisting of tetrahedral and octahedral layers [2]. Later the synthesis of a metastable phase $SrFeO_2$ using a topochemical reaction of $SrFeO_y$ was reported [3]. $SrFeO_2$ is distinct (from $BaFeSi_4O_{10}$) in that square-planar FeO_4 units are connected with each other to form extended FeO_2 layers that are separated by strontium atoms (Fig. 1). The resultant structure is isostructural with the infinite-layer structure $SrCuO_2$ ($P4/mmm$). The Fe^{2+} ion is in a high spin state ($S=2$) with the electronic configurations of $(d_{z2})^2(d_{xz},d_{yz})^2(d_{xy})^1(d_{x2-y2})^1$ [4]. $SrFeO_2$ is an AFM insulator with a high ordering temperature T_N of 473 K, while at high pressure it undergoes a spin transition to $S=1$ accompanied by a transition to a ferromagnetic (FM) half-metallic state [5]. Magnetic properties of $SrFeO_2$ have been examined by density functional theory (DFT) band structure and total energy calculations [4,6]. Recently high pressure study [7] on $SrFeO_2$ based on first principles DFT simulation is performed to explain the antiferromagnetic to ferromagnetic phase transition at high pressure. In the last decade plenty of studies [7–20] have been reported on planer $AFeO_2$ (A=Ca, Sr) and their derivatives.

When Sr is replaced by Ca with a smaller ionic radius, the infinite-layer structure becomes corrugated [21]. In $CaFeO_2$ ($P\text{-}42_1m$), oxygen atoms move along the z direction to distort FeO_4 square planar unit toward a tetrahedral shape. This distortion affects the exchange interaction and leads to a reduction in T_N (420 K). The origin of this distortion in $CaFeO_2$ is discussed in terms of phonons. Ab-initio density functional perturbation theory (DFPT) calculation of the phonon modes at a few selected points in

http://dx.doi.org/10.1016/j.ssc.2016.05.010
0038-1098/

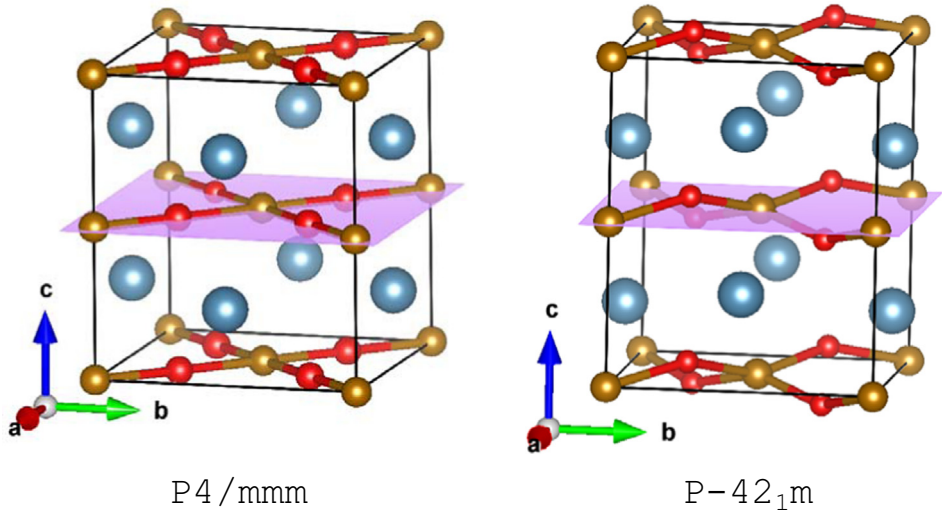

Fig. 1. (Color online) Structures of planer $CaFeO_2$ ($P4/mmm$) and distorted $CaFeO_2$($P\text{-}42_1m$). The *ab* plane in these structure are depicted by violate sheet. Supercell's compatible to the magnetic unit cell are shown, i.e. a $\sqrt{2}\times\sqrt{2}\times 2$ supercell of the P4/mmm structure and $1\times1\times2$ supercell of P-42_1m structure. The oxygen atoms in the distorted structure are shifted along *z* axis by $\pm\delta$. Key: Ca, blue spheres; Fe, golden spheres; O, red spheres.

the Brillouin zone has also been reported [6,21]. For $CaFeO_2$ assuming the $P4/mmm$ space group, two unstable phonon modes are indicated, one of which involves out-of-plane translation motion of the oxygen atoms along *z*-axis, while the other zone boundary mode shows in-plane rotation of the FeO_4 squares. Recently, a high-resolution neutron diffraction study at various temperatures [22] has demonstrated that even in $SrFeO_2$ the ideal infinite-layer structure is destabilized upon approaching to the Neel temperature (473 K). The analysis shows a local transverse mode creates buckling in the FeO_4 planes, resulting in lowering the tetragonal symmetry. Such transverse distortion created by local structural instability significantly weakens the exchange interactions.

In order to obtain further insight into structural instability of $SrFeO_2$ and $CaFeO_2$ as well as its effect on exchange parameters, we have performed the *ab-initio* phonon calculations for planar $SrFeO_2$ ($P4/mmm$) and both planar and distorted $CaFeO_2$ ($P4/mmm$ and $P\text{-}42_1m$), termed here after by p-$CaFeO_2$ and d-$CaFeO_2$, respectively, in various magnetic configurations in the entire Brillouin zone. The longitudinal and transverse optic (LO–TO) splitting has been taken into account in the calculations of phonon frequencies. These calculations are useful to interpret the measured spectrum and able to explain the origin of distortion in $CaFeO_2$ as well as high-pressure stability of $CaFeO_2$. Our calculations show that $SrFeO_2$ ($P4/mmm$) and d-$CaFeO_2$ ($P\text{-}42_1m$) are dynamically stable with the G-type AFM structure, while p-$CaFeO_2$ ($P4/mmm$) is dynamically unstable at ambient pressure. The calculated phonon density of states of $SrFeO_2$ has been compared with the powder inelastic neutron scattering result.

Here we have also performed the lattice dynamical calculation in $SrFeO_3$ system and compared it with the $SrFeO_2$ spectra. The calculations highlight the role of difference in the geometry of oxygen atoms around Fe atom in both the compounds, which leads to the difference in the phonon spectra in these compounds. The paper is organized as follows. In Sections 2 and 3, we describe experimental and calculation methods. In Section 4.1, we discuss the result of neutron inelastic scattering experiments of $SrFeO_2$. Section 4.2 gives detailed lattice dynamical calculations of $CaFeO_2$ and $SrFeO_2$. In Section 4.3, dynamical instabilities in planer $CaFeO_2$ and stabilization of distorted $CaFeO_2$ at ambient pressure has been discussed. Phase transition from distorted to planer $CaFeO_2$ at high pressure is discussed in Section 4.4. The work on Spin phonon coupling and magnetic exchange interaction Parameters in planar $SrFeO_2$ and $CaFeO_2$ is given in Section 4.5. In Section 4.6, we discuss the comparison of the phonon spectra of $SrFeO_2$ and $SrFeO_3$ followed by conclusions in Section 5.

Table 1
Comparison of the calculated structural parameters of $SrFeO_2$ and $CaFeO_2$ with the experimental data. The experimental data [6,10] of lattice parameters is at 293 K, while the calculated values are given at 0 K. For isotropic temperature factors experimental data [14] and calculations are given at 293 K.

	$SrFeO_2$, $P4/mmm$ Expt. [3]	$SrFeO_2$ $P4/mmm$ Calc.	$CaFeO_2$, $P\text{-}42_1m$ Expt [6]	$CaFeO_2$ $P\text{-}42_1m$ Calc.
a (Å)	3.991	4.042	5.507	5.550
c (Å)	3.474	3.497	3.355	3.443
B_{iso}(Sr/Ca) (Å^2)	0.470	0.440	0.485	0.580
B_{iso}(Fe) (Å^2)	0.470	0.380	0.590	0.490
B_{iso}(O) (Å^2)	0.790	0.610	0.909	0.660
Volume/atom	13.83	14.28	12.72	13.26

2. Experimental

The polycrystalline sample of $SrFeO_2$ was prepared by a topochemical reduction of $SrFeO_{2.875}$ with CaH_2 (2 molar excess) at 300 °C for 48 h in an evacuated tube [3]. After this reaction, the residual CaH_2 and the byproduct were eliminated by methanol. The inelastic neutron scattering experiments were performed using the MARI time of flight spectrometers at ISIS, UK. The measurements were done in the neutron-energy-loss mode using incident neutron energy of 120 meV at several temperatures from 5 to 353 K. The incoherent approximation [23–25] was used for extracting neutron weighted phonon density of states from the measured scattering function $S(Q,E)$.

3. Computational details

The Vienna *ab initio* simulation package (VASP) [26,27] was used for calculations. The plane wave pseudo-potential with plane wave kinetic energy cutoff of 400 eV was used for both compounds. The