Electronic structures and magnetic properties of spinel $ZnMn_2O_4$ under high pressure

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Spinel $ZnMn_2O_4$, which has a Jahn-Teller active Mn^{3+} ion, was reported to exhibit a first order structural phase transition under high pressure. The c/a ratio in the tetragonal structure reduces drastically from 1.62 to 1.10 at the transition pressure of $P_c \sim 23$ GPa. The transition was attributed to the change in the electronic configuration of Mn ions. Employing the full-potential linearized augmented plane wave band method, we have investigated the change of the electronic structure with varying both the volume and c/a ratio. Under high pressure, we have demonstrated the structural and the spin-state transition from a high-spin to a low-spin configuration of Mn^{3+}.

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Spinel $ZnMn_2O_4$, which has a normal cation distribution, crystallizes in a body-centered-tetragonal structure with c/a ratio of 1.62. Octahedrally coordinated Mn^{3+} has a high-spin state with three t_{2g} and one e_g electrons. When one electron is in the e_g orbital, the structural transition is induced by the Jahn-Teller effect to lift the degeneracy of the e_g orbitals. High pressure experiment on $ZnMn_2O_4$ reveals an interesting first-order structural phase transition from the body-centered to the primitive tetragonal phase at $P_c \sim 23$ GPa.[1] The c/a ratio reduces drastically from 1.62 to 1.10 at the transition. It was conjectured that the pressure would not reduce the Jahn-Teller effect so that Mn^{3+} would still retain a high-spin state under high pressure.

To investigate electronic and magnetic properties of $ZnMn_2O_4$ under high pressure, we have performed band structure calculations using the full-potential linearized augmented plane wave (FLAPW) method[2] in the generalize gradient approximation (GGA).[3] At ambient pressure, $ZnMn_2O_4$ has a body-centered-tetragonal structure[1] (space group $I4_l/amd$) with the lattice constants of $a=5.720(1)$ Å, $c=9.245(2)$ Å and the volume $V=302.48(3)$ Å^3. As shown in Fig. 1, there are four formula units of $ZnMn_2O_4$ in the conventional unit cell, and two formula units in the primitive unit cell. Since $ZnMn_2O_4$ has a normal cation distribution, Zn ions are located at A sites of tetrahedral centers, while Mn ions at B sites of octahedral centers. Neighboring Zn and Mn ions are connected through O ions. Due to the crystal field of the six O ions at B sites, five d orbitals of a Mn atom are split into three t_{2g} and two e_g orbitals for each spin. Since Mn^{3+} in $ZnMn_2O_4$ has four d electrons and the exchange splitting is larger than the crystal field splitting, Mn^{3+} has a high-spin state at normal condition, and is influenced by the Jahn-Teller instability.

For the band structure calculations, we adopted the internal positions of the atoms from the experimental data. But, during the self-consistent iterations, the positions of O ions are relaxed as allowed by the symmetry in the space group until the Hellman-Feynman force at each atom reaches ~ 1 mRy/a.u. The muffin-tin (MT) radii R_{MT}'s employed in the FLAPW calculation are 1.71, 1.61, 1.48 a.u. for Zn, Mn, O, respectively. Rather small MT radii were chosen because the radii were adjusted for the high pressure phase of $V=220$ Å^3. We used the value of $R_{MT} \times K_{MAX}=6.97$ which produces about 2000 LAPW basis functions to describe valence states. On the magnetic configuration of $ZnMn_2O_4$, there is a controversy. One suggested a three collinear spin array of four Mn^{3+}'s forming a tetrahedron,[4] while the other suggested a helical spin arrangement of Mn ions.[5] Since the real magnetic configuration is still uncertain, we consider, in the present band calculation, the ferromagnetic phase of $ZnMn_2O_4$ assuming that the local electronic structures are more or less similar between the ferromagnetic and real magnetic spin configurations. This is plausible because the high pressure experiment[1] was done at room temperature that is much higher than the reported Néel temperature $T_N=21.5$ K.

We have first calculated the total energy as a function of c/a for a given volume of 300 Å^3 which corresponds to the observed equilibrium volume of $ZnMn_2O_4$ at ambient pressure. The total energy curve in Fig. 2(a) shows that there are two minima, the global minimum at $c/a \approx 1.62$ and the local minimum at $c/a \approx 1.3$. This result is consistent with the observed body-centered-tetragonal structure of $ZnMn_2O_4$ with

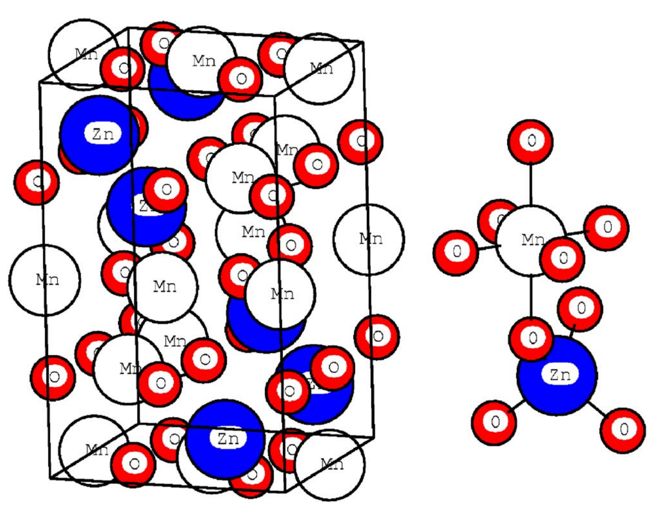

FIG. 1. (Color online) The body-centered-tetragonal unit cell of $ZnMn_2O_4$ and the neighboring Zn and Mn ions connected through O ions.

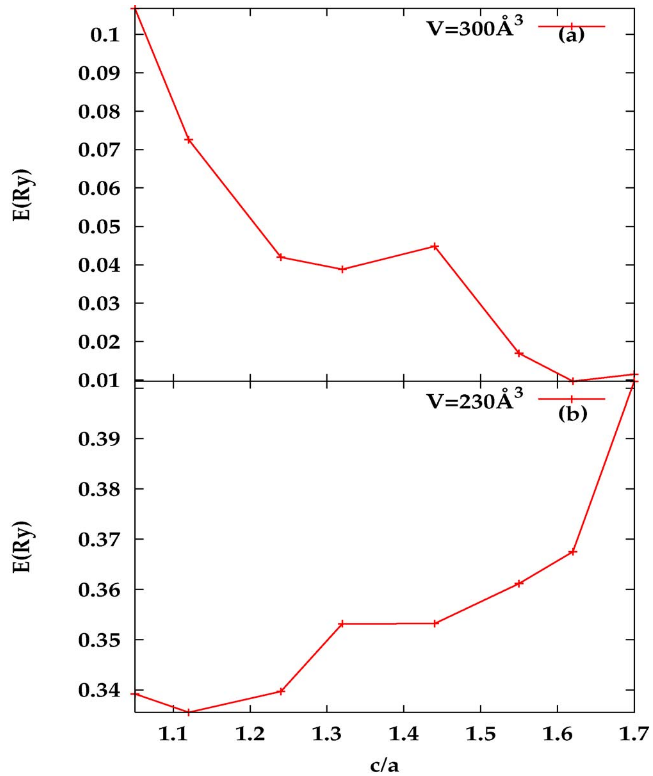

FIG. 2. (Color online) Total energies of $ZnMn_2O_4$ for given volumes. (a) $V=300$ Å^3 corresponding to the ambient pressure phase. (b) $V=230$ Å^3 corresponding to the high pressure phase. The reference energy is −17 658.277 657 Ry.

c/a ratio of 1.62. Then we have calculated the total energy as a function of c/a for a smaller volume of 230 Å^3 which corresponds to a high pressure phase. As shown in Fig. 2(b), there appear also two minima in the total energy curve, the global minimum at $c/a \approx 1.12$ and the local minimum at $c/a \approx 1.4$. Note that the global and local minima are interchanged with respect to the case of $V=300$ Å^3. This result indicates that the pressure makes a system more cubiclike.

Caution is needed here to distinguish the c/a ratio of unit cell from the $d_{\parallel}/d_{\perp}$ ratio of an MnO_6 octahedron ($d_{\parallel}$, Mn-O bond length along the c axis; $d_{\perp}$, Mn-O bond length in the ab plane). The $d_{\parallel}/d_{\perp}$ ratio of the MnO_6 octahedron is determined by positions of the relaxed O ions surrounding a Mn ion. For a volume of 300 Å^3, the MnO_6 octahedron at the global minimum ($c/a \approx 1.62$) has an elongated structure with $d_{\parallel}/d_{\perp} \sim 1.17$, while the MnO_6 octahedron at the local minimum ($c/a \approx 1.3$) has a flattened structure with $d_{\parallel}/d_{\perp} \sim 0.92$. For the smaller volume of 230 Å^3, the $d_{\parallel}/d_{\perp}$ ratios are ~ 1 at both the global and local minima, due to the pressure effect. In this case, as the c/a ratio increases, the MnO_6 octahedra having nearly the same $d_{\parallel}/d_{\perp}$ ratio tend to align along the global z axis.

Figure 3 shows the total energies as a function of volume for given c/a ratios of 1.62 and 1.12. The calculated equilibrium volume for $c/a=1.62$ is ~ 310 Å^3, which is close to but a bit larger than the experimental equilibrium volume of 300 Å^3. Noteworthy in Fig. 3 are (i) the anomalous behavior in total energy curve near $V=270$ Å^3 for $c/a=1.62$, (ii) the

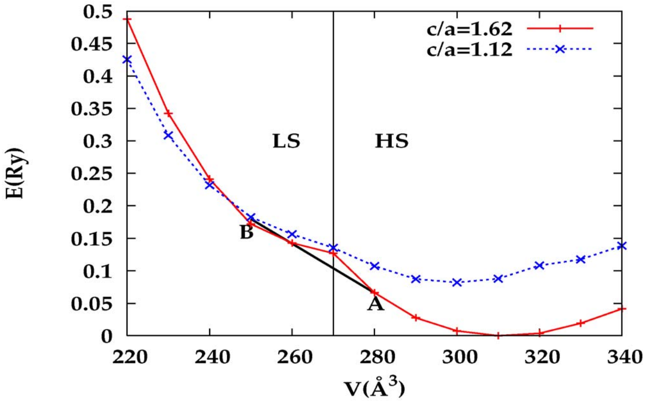

FIG. 3. (Color online) Total energies of $ZnMn_2O_4$ vs volume for given c/a ratios of 1.62 (solid line) and 1.12 (dotted line). HS and LS denote the high-spin and the low-spin state, respectively. The slope of the line connecting A to B yields the transition pressure in the framework of the Maxwell construction. The reference energy is −17 658.277 657 Ry.

crossing of total energy curves of $c/a=1.62$ and $c/a=1.12$ near $V=240$ Å^3. The former appears due to the spin-state transition from a high-spin to a low-spin state, as discussed below. The latter corresponds to the structural transition, as observed in the high pressure experiment.

We have analyzed the structural and spin-state transitions using the Murnaghan's formula of equation of state[6] that can be determined from the total energy curve. As shown in Fig. 3, we divide the region into two, the high-spin and the low-spin region, and employ the corresponding equilibrium total energy curve at each region to get the equation of state. That is, we consider the total energy curve of $c/a=1.62$ for the high-spin region, and that of $c/a=1.12$ for the low-spin region. Then, using the pressure obtained from the equation of state, as provided in Table I, the Gibbs free energy is determined as a function of the pressure.

Figure 4 presents the Gibbs free energies as a function pressure for $c/a=1.62$ with the high-spin state (solid line) and for $c/a=1.12$ with the low-spin state (dotted line). It is seen that the transition pressure amounts to be ~ 19 GPa, which is between 16.5 GPa (B) and 21.1 GPa (A). This value

TABLE I. The calculated pressure using the Murnaghan's equation of state.

$c/a=1.62$		$c/a=1.12$	
Volume (Å^3)	Pressure (GPa)	Volume (Å^3)	Pressure (GPa)
340	−11.226	270	5.385
330	−8.092	260	9.855
320	−4.337	250	16.514
310	0.3387	240	25.987
300	5.855	230	40.019
290	12.587	220	61.949
280	21.135		
270	31.435		

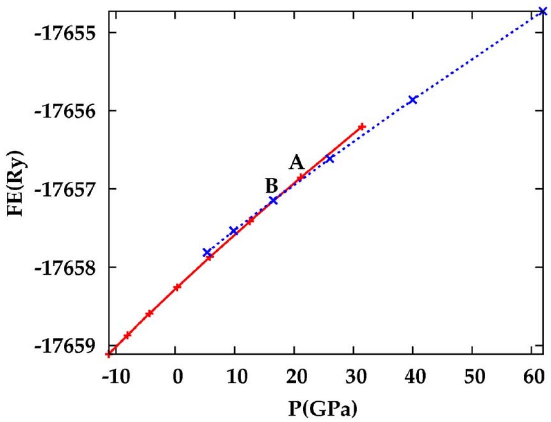

FIG. 4. (Color online) Gibbs free energies of $ZnMn_2O_4$ as a function of pressure for $c/a=1.62$ with the high-spin state (solid line) and for $c/a=1.12$ with the low-spin state (dotted line).

is close to the experimental $P_c=23$ GPa. Note that A and B in Fig. 4 are the same labels as marked in Fig. 3. In fact, the line connecting A to B in Fig. 3 also produces the transition pressure in the framework of the Maxwell construction. The slope of the line connecting A to B is estimated to be $\sim$19 GPa, as is consistent with the transition pressure obtained from the Gibbs free energy.

Figure 5 provides the Mn local density of states (DOS) of $ZnMn_2O_4$. The DOSs in Figs. 5(a) and 5(b) are, respectively, for $V=310$ Å^3 with $c/a=1.62$ corresponding to the calculated equilibrium state and for $V=280$ Å^3 with $c/a=1.62$ corresponding to the low pressure phase. It is evident that the spin state in both cases are in the high-spin state and the majority spin e_g orbitals near the Fermi energy are split due to the Jahn-Teller effect. The calculated magnetic moments per Mn are 3.22 and 3.17μ_B for Figs. 5(a) and 5(b), respectively. Indeed the local charge density plotted in Fig. 6, which is obtained by integrating the charge density over the energy range of -1.0–0.0 eV as marked in Fig. 5(b), reveals that the lower energy e_g orbital corresponds to the d_{z^2} orbital. This is expected considering the stable elongated MnO_6 octahedron for $c/a=1.62$. On the other hand, the DOS in Fig. 5(c), which is for the high pressure phase ($V=230$ Å^3), shows that the spin state is in the low-spin state. The calculated magnetic moment per Mn is 1.70μ_B. All the e_g states become empty and the minority spin t_{2g} states are partially occupied, and so the system becomes metallic. Interestingly the metallic phase in this case is half-metallic.

From the Mn local DOS in Fig. 5, one can obtain the crystal field splitting energy Δ_{CF}, the Jahn-Teller splitting energy Δ_{JT}, and the exchange splitting energy Δ_{EX}. For the calculated equilibrium phase of Fig. 5(a), it is estimated that $\Delta_{CF}^{\uparrow}\approx 2.56$, $\Delta_{CF}^{\downarrow}\approx 0.97$, $\Delta_{JT}\approx 1.58$, and $\Delta_{EX}\approx 4.0$ eV, respectively. Here $\uparrow$, $\downarrow$ represent the majority and minority spins. Hence the high spin state in $ZnMn_2O_4$ at ambient pressure results from $\Delta_{EX}>\Delta_{CF}$. Note that the Jahn-Teller splitting $\Delta_{JT}\approx 1.58$ eV is compatible with the experimentally determined parameter $\Delta_{JT}=1.6$ eV from the analysis of Mn $L_{2,3}$-edge x-ray absorption spectroscopy.[7] It is seen in Fig. 5 that, with applying the pressure, Δ_{CF} becomes enhanced from $\sim$2.5 to $\sim$3.1, whereas Δ_{EX} becomes reduced from $\sim$4.0 to $\sim$2.4. Accordingly Δ_{JT} becomes zero for the high pressure phase. This feature suggests that, as the Mn-O bond length gets shorter by the applied pressure, the electrons in the e_g states move to the t_{2g} states with the opposite spin, resulting in the low-spin state. Accordingly, the Jahn-Teller splitting is vanished to yield the insulator to metal transition under high pressure. Therefore the present finding rules out the experimental conjecture that the Jahn-Teller instability and the high-spin state would be retained even under high pressure.

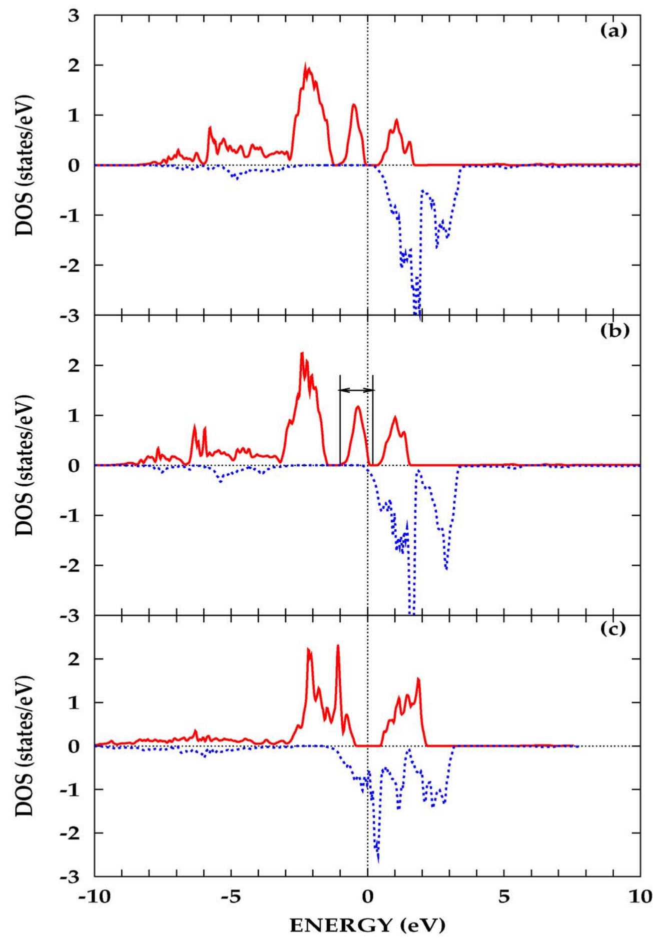

FIG. 5. (Color online) The Mn local DOS of $ZnMn_2O_4$ for given volume. (a) $V=310$ Å^3 with $c/a=1.62$. (b) $V=280$ Å^3 with $c/a=1.62$. (c) $V=230$ Å^3 with $c/a=1.12$.

In conclusion, using the first principles band method, we have demonstrated that the c/a ratio of tetragonal $ZnMn_2O_4$

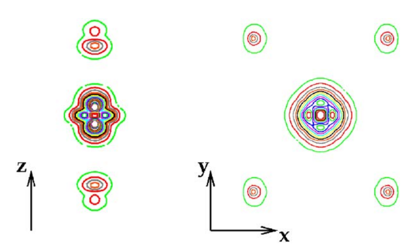

FIG. 6. (Color online) Local charge density in the local coordinate of MnO_6 octahedron, that is obtained by integrating the charge density over the energy range from -1.0 eV to 0.0 eV, as marked in Fig. 5(b).

is transformed from 1.62 to 1.12 under high pressure. The spin-state under pressure is also transformed from the high-spin state with the Jahn-Teller distortion into the low-spin state without the Jahn-Teller distortion.

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