Strain-induced phase transition in MnO$_2$
Strain-induced phase transition in \( \beta \)-MnO\(_2\)

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received 21 June 2012; accepted in final form 28 June 2012
published online 30 July 2012

PACS 75.25.-j – Spin arrangements in magnetically ordered materials (including neutron and spin-polarized electron studies, synchrotron-source X-rays scattering, etc.)
PACS 71.30.+h – Metal-insulator transitions and other electronic transitions
PACS 85.75.-d – Magnetoelectronics; spintronics: devices exploiting spin polarized transport or integrated magnetic fields

Abstract – The phase transition of \( \beta \)-MnO\(_2\) under negative pressure and external strain was investigated via the density function theory. During the expansion, the half-metallic phase appeared. Using the Heisenberg model, the variations in the exchange integrals between Mn\(^{4+}\) pairs were determined. A crossover between the dominate exchange integrals occurred, which resulted in the formation of the ferromagnetic phase. On the other hand, the double exchange mechanism and weakening of the crystal field were the two reasons for the formation of the majority of conduction bands.

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Introduction. – \( \beta \)-MnO\(_2\), which crystallizes in the same manner as the half-metallic (HM) material CrO\(_2\) [1], is known for its complex magnetic structure below \( T_N (\sim 92\, \text{K}) \) [2]. Neutron diffraction revealed that the magnetic unit cell of MnO\(_2\) is seven times larger than the chemical unit cell along the c-axis [3]. The following theoretical studies proposed that the local magnetic moments in MnO\(_2\) are helically arranged [3,4]. This helical magnetic order, together with the strong Coulomb correlation between Mn 3d, confers various electromagnetic properties to MnO\(_2\), which has gained increasing attention both theoretically and experimentally among researchers [5–8]. Thus far, MnO\(_2\) has been epitaxially grown on a TiO\(_2\) substrate by molecular beam epitaxy [5]. For the lattice mismatching, MnO\(_2\) is strained. Studies have shown that the epitaxial strain modifies the magnetic easy axis of the CrO\(_2\) film because lattice mismatching produces magnetoelastic anisotropy energy [6–9]. Moreover, the lattice expansion can determine the relative strength of two instabilities in the BaMnO\(_3\) bulk by inducing the second order John-Teller off-center distortion in the non-d\(^0\) magnetic cations [10]. However, little is known about the strain-dependent effect in MnO\(_2\). In this work, MnO\(_2\) under external strain was studied. We investigated the influence of volume expansion on the property of the MnO\(_2\) bulk and the expansion strain loaded on the (\( a, b \))-plane or c-axis to understand the behavior of MnO\(_2\) under tensile strain.

Calculation details. – The property of the MnO\(_2\) bulk was determined by the density functional theory (DFT) [11] using the VASP code [12,13]. A unit cell with a P42/mnm symmetry containing two Mn atoms and four O atoms was built (except for calculating the exchange parameter \( J_2 \) or \( J_3 \), \( 1 \times 1 \times 2 \) or \( 2 \times 1 \times 1 \) super-cells were used according to the magnetic structure, which will be discussed in detail in the last three paragraphs). The generalized gradient approximation (GGA) [14] was performed to determine the exchange-correlation effects, whereas the projector augmented wave [15] potential is used to describe the interaction between atoms and electrons. A \( 5 \times 5 \times 9 \) k-grid was sampled via the Monkhost-Pack scheme in the Brillouin zone, and a plane wave energy cutoff of 520 eV was chosen to fully converge the total energy. For the on-site Coulomb correlations in the Mn 3d orbitals, the Hubbard parameter \( U \) and exchange parameter \( J \) were taken into account using the fully localized

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Fig. 1: (Color online) Structures of the MnO$_2$ bulk. FM, AFM, AFM$^I$, and AFM$^{II}$ are the different magnetic structures considered in our calculations. Red spheres indicate oxygen atoms, whereas green and blue balls indicate spin-up and spin-down Mn atoms, respectively. The paths of exchange interactions are also shown.

limit (FFL) GGA+$U$ method [16,17]. The values of $U$ and $J$ were set at 4 eV and 0.9 eV according to previous studies, respectively [18–20]. During relaxation, all atoms are allowed to move until the Hellmann-Feynman forces acting on them become less than 0.01 eV/Å.

Our results are mainly based on a collinear magnetic arrangement, which is similar to the study by Franchini et al. on manganese oxides [18]. The antiferromagnetic (AFM) and ferromagnetic (FM) phases (as shown in fig. 1) were compared, and only the most stable phase is discussed. We also consider the non-collinear magnetic structure in the last part of our discussion to make our results more reliable.

Results and discussion. – After structure optimization, the lattice constants $a$ and $c$ are 4.46 and 2.91 Å, respectively. These values agree with the experimental findings ($a=4.40$ Å, $c=2.87$ Å). Figure 2(a) shows the density of states (DOS) of the unstrained bulk. The symmetrical DOS for the majority and minority spins reveals the AFM phase. The local magnetic moment of each Mn atom is $2.9\mu_B$, which corresponds to the +4 oxidation state of the element. As shown in fig. 2(a), a gap across the Fermi level ($E_F$) is observed, which can be traced to the splitting of Mn 3d. This splitting is driven by the O octahedron around Mn. According to the crystal field (CF) theory, the O CF would split the Mn 3d into a low-lying $t_{2g}$ triplet and a higher $e_g$ doublet. The $t_{2g}$ triplet shifts down below $E_F$, which corresponds to the three remaining 3d electrons of Mn$^{4+}$, whereas the $e_g$ doublet shifts above $E_F$. Thus, the gap is formed.

Volume expansion was also performed. The lattice expands to all directions by the same ratio, which is similar to previous findings [10,21,22]. The volume expansion can be considered a negative hydrostatic pressure. In practice, this condition is difficult to achieve, but the theoretical studies on the effect of negative pressures can help us understand the phenomenon in the strained MnO$_2$ films better [23]. Figure 2(b) shows the DOS when the cell volume is expanded to 105%. The majority states are spread across the $E_F$, whereas a gap larger than 1 eV splits the minority states. The total magnetic moment of the unit cell is 6.0$\mu_B$. The spin-down gap, together with the integral magnetic moment, strongly indicates that the HM phase exists. A value of 6.0$\mu_B$ per unit cell also implies that the FM magnetic moment arrangement between Mn$^{4+}$ retains its three 3d electrons after stretching.

When the volume further expands, the HM property is maintained, as shown in figs. 2(c)–(e). Moreover, the spin-down gap increases with volume expansion. The main conduction and magnetic properties of the strained bulk are listed in table 1. The strained bulk generally stabilizes in the HM phase if the volume is expanded beyond 105%. We also consider different $U$ ranging from 0.9 eV to 5 eV, and similar results are obtained.

The origin of the conduction bands across $E_F$ must be determined to understand the formation of the HM phase better. In fig. 3(a), we draw the local density of states (LDOS) for Mn 3d and O 2p when the cell volume was expanded by 110%. For the majority spin, the main part of $e_g$ is above $E_F$, whereas $t_{2g}$ is just below $E_F$. Unlike in the unstrained bulk, $t_{2g}$ and $e_g$ overlap each other. Thus, the DOS across $E_F$ becomes non-zero. Meanwhile, the minority 3d states are fully

![Fig. 2: (Color online) DOS of the MnO$_2$ bulks with different expansion rates. (a) DOS of the unstrained bulk; (b)–(e) the volume increased by 5%, 10%, 15%, and 20%, respectively.](image-url)
pushed up above \( E_F \) from the O 2\( p \) states because of the strong d-d exchange interaction, which leads to the spin-down gap. The distribution of the Mn 3\( d \) minority states becomes more local after being stretched (as shown in fig. 2). The overlap of the \( t_{2g}-e_g \) majority states are partly attributed to the weakening of the O CF. When the lattice expands, the O octahedron also expands. The interaction between the Mn 3\( d \) and the O octahedrons are also weakened, which reduces the \( t_{2g}-e_g \) splitting. This relatively smaller splitting is the first reason for the formation of the conduction bands, shown as reason I in fig. 3(c).

Another reason for the formation of the conduction band is the involvement of O 2\( p \) during \( t_{2g}-e_g \) overlapping. As shown in fig. 3(a), the O 2\( p \) states hybridize with the Mn \( e_g \) states near \( E_F \), which implies strong p-d hybridization. This hybridization can also be found in the HM phase of the BaMnO\(_3\) bulk [22]. The majority-spin band structure is given in fig. 3(b) to provide more details of the hybridization. The four bands above \( E_F \) are mainly produced by the \( e_g \) states. In some areas, these bands are quite flat, which indicates the pure 3\( d \) feature. Meanwhile, in other areas, these bands are dispersed. In such areas, the contributions of the O 2\( p \) states in the bands are greater. Some parts of these bands spread across \( E_F \) and overlap with the \( t_{2g} \) bands. This phenomenon produces the majority conduction channel. This phenomenon strongly indicates that a double exchange occurs. When the local spin positions are parallel to each other, the double exchange mechanism improves the localized \( e_g \) electron transfer from one Mn ion to another, which causes a decrease in energy. This behavior may be the key reason for the overlap of \( t_{2g}-e_g \). Through the participation of O 2\( p \), Mn \( e_g \) bands become more dispersed. For the decrease in the energy difference due to reason I, the strong dispersion finally leads to the overlap between the adjacent \( e_g \) and \( t_{2g} \) bands. This process is shown as reason II in fig. 3(c).

However, as discussed by Sato et al., the double exchange cannot determine the magnetic structure in the unstrained MnO\(_2\) bulk [2]. Other exchange interactions, such as superexchange, exist. Therefore, the effective exchange integrals between Mn\(^{4+}\) ions can be considered as the total effect of all these exchange interactions. The variations in the exchange integrals need to be determined to interpret the AFM-FM transition. Thus far, the Heisenberg model has been used to determine various kinds of magnetic coupling in transition metal complexes [3,24–28]. In the present study, we use the classical Heisenberg model to estimate the exchange integral between the Mn pairs. In the classical Heisenberg model, the quantum fluctuation is negligible, and the local spins are treated as classical vectors. In MnO\(_2\), the exchange coupling energy induced by the Mn pairs can be expressed as \( H_{ij} = -J_{ij}\mu_i\cdot\mu_j \), where \( \mu_i \) and \( \mu_j \) are the local magnetic moments of the neighboring Mn\(_i\) and Mn\(_j\), respectively, whereas \( J_{ij} \) stands for the exchange integral between the Mn\(_i\) and Mn\(_j\). We can substitute \( |\mu_i| \) and \( |\mu_j| \) into J and treat the local spins as unit vectors because \( |\mu_i| = |\mu_j| = 3\mu_B \) remains unchanged during the expansion [24]. Three exchange integrals mainly exist in the MnO\(_2\) bulk [3]. As shown in fig. 1, \( J_1 \) is between the neighboring Mn\(^{4+}\) pairs along (111), whereas \( J_2 \) is along (001), and \( J_3 \) is along (100). Thus, the total energy per unit cell can be expressed as

\[
E = E_0 - \sum_{ij} J_n \cos \theta_{ij},
\]

where \( \theta_{ij} \) is the angle between the localized spins \( \mu_i \) and \( \mu_j \), and \( i \) and \( j \) are dependent on \( n (n = 1,2 \text{ or } 3) \) in \( J_n \). \( E_0 \) is the energy independent of the magnetic structure.

For the FM phase, \( \theta_{ij} = 0 \). Therefore, the total energy per unit cell is expressed as

\[
E_{FM} = E_0 - 16J_1 - 4J_2 - 8J_3.
\]

Correspondingly, for the AFM phase (marked as MnF\(_2\)-type antiferromagnetic structure in Yoshimori’s work [3]), the total energy can be expressed as

\[
E_{AFM} = E_0 + 16J_1 - 4J_2 - 8J_3.
\]
Fig. 3: (Color online) (a) LDOS of Mn $3d$ and O $2p$ for the MnO$_2$ bulk when the cell volume was expanded to 110%. Green curves stand for Mn $t_{2g}$ states, whereas cyan curves stand for $e_g$ states. Blue curves represent O $2p$ states. (b) Band structure of the strained bulk, for majority spin. (c) The two reasons for the $t_{2g}$-$e_g$ majority overlap, marked by reason I and reason II. $e_g$ and $t_{2g}$ are the majority-spin states of Mn $3d$. $\Delta$ and $\Delta'$ are the splitting energies between the $t_{2g}$ and $e_g$ centers. $\Delta$ represents the case in the unstrained bulk where CF is much stronger, whereas $\Delta'$ is the splitting energy in the weakened CF. According to the CF theory, $\Delta > \Delta'$.

Comparing the two equations above, we can find that $J_1$ determines the competition between the FM and AFM phases. We can obtain $J_1$ using

$$J_1 = (E_{AFM} - E_{FM})/32.$$

Using the equation above, $E_{FM}$ and $E_{AFM}$ can be obtained. The calculated $J_1$ for different cell volumes are listed in table 1. $J_1$ is positive in the unstrained bulk, which implies that the AFM phase is more stable than the FM phase. However, when the cell volume size expands by 5%, $J_1$ becomes negative, which indicates that the bulk shifts to the FM phase. When the cell volume further expands, $J_1$ becomes more negative (except for an expansion of 120%, where $J_1$ nearly becomes zero due to the excessively long distance between two Mn$^{4+}$). This trend is consistent with Néel and Slater’s deduction, which states that when the distance between the cations becomes larger, the localized spins become arranged in an FM order [29,30]. Thus, we can conclude that the lattice expansion causes the exchange integral $J_1$ to become negative, which transfers the bulk to the FM phase. As soon as the FM phase is formed, the double exchange closes the majority gap. Thus, the bulk HM property is formed.

We also consider a more realistic case, in which the lattice is stretched along one or two directions. This phenomenon can be achieved by applying epitaxial strain to the lattice. We first fixed the lattice constant $a$, $b$ with a given expansion ratio, which correspond to an in-plane tensile stress. The proper length of $c$ was then obtained to make the strained bulk reach the minimal total energy. We then drew the DOS for each case to determine if the AFM-FM transition happens. As shown in fig. 4, the red curve displays the changes in $c$ when $a$ and $b$ are stretched. $c$ decreases from 100% to 95% during the expansion process. The energy differences ($E_{AFM} - E_{FM}$) when $a$, $b$, and $c$ are all sampled are shown in fig. 4. The lower left area is the AFM-dominant area, whereas the top right area is the FM-dominant area. The white belt represents the FM-AFM boundary. The red curve intersects the white belt when $a$ and $b$ are expanded by 6%, which imply that an AFM-FM transition occurs. We then examine the conduction property of these FM phases. The HM property appears when the FM phase appears, which is similar to the aforementioned results. We also
consider the case when only $c$ is extended, as shown by the pink curve in fig. 4. The FM phase appears when the length of $c$ is expanded beyond 8%. This relative larger expansion ratio needed for the AFM-FM phase transition may be attributed to the smaller original length of lattice parameter $c$ compared with those of $a$ and $b$. The FM phase also exhibits the HM property, as shown in table 1.

In summary, when properly expanded along the $a$ and $b$ (>106%) or $c$ (>108%) axes, the strained bulk favors the HM phase, which is similar to the all-direction expansion.

As mentioned before, all results above were obtained by considering only the collinear magnetic structure. However, as pointed out by Yoshimori, the screw-type spin arrangement is more stable in the unstrained bulk compared with the AFM phase [3]. Hence, the helical spin states and other magnetic structures need to be considered to examine the stability of the HM phase. The magnetic structure is dependent on the values of $J_1$, $J_2$, and $J_3$. For example, if $J_1 < 0$ and $J_2 > 0$, the MnF$_2$-type magnetic structure would be dominant. Similarly, when the helical magnetic structure appears, $J_2$ or $J_1 > 1$ and $J_1$ and $J_2 > 0$ must be fulfilled. We already obtained the value of $J_1$, but $J_2$ and $J_3$ are still unknown. Thus, we consider two other kinds of magnetic structures (marked by AFM$^1$, AFM$^2$, and AFM in fig. 1) to obtain $J_2$ and $J_3$. These two magnetic phases are more complex than the FM or AFM phase mentioned before. Therefore, the supercell containing two super cells was used in the calculation. The total energy per unit cell for the two magnetic structures can be expressed as

$$E_{AFM^1} = E_0 + 4J_2 - 8J_3,$$
$$E_{AFM^2} = E_0 - 4J_2.$$

With the two additional equations above, $J_2$ and $J_3$ can be obtained as follows:

$$J_2 = (2E_{AFM^1} - E_{FM} - E_{AFM})/16,$$
$$J_3 = (2E_{AFM^2} - E_{FM} - E_{AFM})/16.$$

Table 1 lists the values of $J_1$, $J_2$, and $J_3$ when $a$, $b$, or $c$ is expanded and fixed. In the unstrained bulk, $J_1$, $J_2$, and $J_3$ are negative. When $J_2 > J_1$ the helical magnetic structure can exist. However, as the cell volume increases, a crossover corresponding to the AFM-FM transition between $J_1$ occurs (see table 1). Meanwhile, $J_2$ and $J_3$ also become positive. When $J_1$, $J_2$, and $J_3 > 0$, the helical magnetic structure, as well as the other AFM phases, become unstable. As a result, the HM phase remains in the strained bulk.

**Conclusion.** In summary, using the DFT+ $U$ scheme, the magnetic and conduction properties of MnO$_2$ under negative pressure and tensile strain are investigated. Under specific strain values, the FM phase is more dominant than AFM. The formation of the FM phase may be driven by the lattice expansion, which converts the exchange integrals $J_1$, $J_2$, and $J_3$ into positive values.

As soon as the FM phase appears, the HM property can be obtained synchronously, which is induced both by the weakening of O CF and by the O 2p-mediated double exchange between Mn 3d orbitals. Our results may provide a reference for the epitaxial growth of HM MnO$_2$ on specific substrates for spintronic applications.

### REFERENCES


