First-principles study of the spin-lattice coupling in spin frustrated DyMn$_2$O$_5$

Tianqi Shen, Kun Cao, Guang-Can Guo, and Lixin He

Key Laboratory of Quantum Information, University of Science and Technology of China, Hefei, 230026, People’s Republic of China

(Dated: October 12, 2008)

The lattice dynamic properties and spin-phonon coupling in DyMn$_2$O$_5$ are studied by using the density-functional theory. The calculated phonon frequencies are in very good agreement with experiments. We then compare the phonon modes calculated from different spin configurations. The results show that the phonon frequencies change substantially in different spin configurations, suggesting that the spin-phonon coupling in this material is very strong. Especially, the short range spin ordering has drastic effects on the highest Raman and IR phonon modes that might be responsible for the observed phonon anomalies near and above the magnetic phase transitions.

PACS numbers: 75.25.+z, 77.80.-e, 63.20.-e

I. INTRODUCTION

Manganese oxides including RMnO$_3$$_{1,2}$ and RMn$_2$O$_5$ (R=Tb, Dy, Ho, etc.) are a very special class of improper ferroelectrics that display strong magnetoelectric (ME) effects, such as the “colossal magnetoelectric” (CMD) effects and magneto-polarization-flop effects. These materials have attracted great attention, because in these materials, the electric properties of the materials via applied magnetic field, or vice versa, and therefore have great potential for future multifunctional device applications. The macroscopic ME effects have their microscopic origin from the interplay between the lattice degree of freedom and spin degree freedom. Neutron scattering has shown the microscopic origin from the interplay between the lattice degree of freedom and spin degree freedom. Neutron scattering shows as well as first-principles calculations shows that the improper ferroelectricity in TbMn$_2$O$_5$ is driven by the non-central symmetric magnetic ordering, which, by coupling to the lattice, lower the crystal symmetry. The spin-lattice coupling can also modify the lattice dynamic properties. Indeed, recent temperature dependent Raman measurements show anomalous phonon shift at $T^*\sim 1.5$ T$_N$ and near the magnetic phase transition temperature $T_N$ in DyMn$_2$O$_5$. Similar anomalies are also observed for the IR modes. Further B-field dependent measurements show that the IR modes are very sensitive to local magnetic structure which suggest that the spin-phonon coupling in this compound is very strong. However, the experiments give only the overall effects, and the detailed mechanism of the spin-phonon coupling is still lack.

First principles method has been applied successfully in studying spin-phonon coupling in geometrically frustrated spinel ZnCr$_2$O$_4$. It is a challenge problem to study the spin-phonon coupling in the spin frustrated systems, such as RMnO$_3$, because in these materials, the magnetic interactions are of different magnitudes (e.g., $|J_4|$, $|J_5|$ $\gg |J_3|$) and the spin frustration leads to complicated spin-spin correlations as functions of temperature and magnetic field. Therefore, the spin will develop different short range ordering at different temperature above the magnetic phase transition, and make it hard to identify the origin of the phonon anomalies. In this work, we study the spin-phonon coupling in DyMn$_2$O$_5$, to shed some light on the observed phonon anomalies. We show that the short range spin correlation and local spin structure have significant effects to the phonons frequencies in this material.

II. METHODOLOGY

The first-principles density-functional (DF) calculations are done by using the Vienna $ab$ initio Simulation Package (VASP) We use a spin-polarized generalized gradient approximation (GGA), with Perdew-Burke-Ernzerhof functional. A plane-wave basis and projector augmented-wave (PAW) pseudopotentials are used, with Mn 3$p^3d^4$s, and Dy 5$p^5d^6$s electrons treated self-consistently. A 500 eV plane-wave cutoff results in good convergence of the total energies. We relax the structure until the changes of total energy in the self-consistent calculations are less than $10^{-7}$ eV, and the remaining forces are less than 1 meV/Å. DyMn$_2$O$_5$ undergo several magnetic phase transitions at low temperature. We are interested in the phonon properties in the paramagnetic (PM) and anti-ferromagnetic (AFM) phase. To accommodate the magnetic structure, we use a 2$\times$1$\times$1 supercell. For the supercell we used, a 1$\times$2$\times$4 Monkhorst-Pack k-points mesh converges very well the results.

III. RESULTS AND DISCUSSION

The fully relaxed DyMn$_2$O$_5$ is an AFM insulator, and has same lattice structure to that of TbMn$_2$O$_5$, both are of $P6_3/m$ symmetry, as Tb and Dy are isovalent. The lattice structure is distorted from a $Pbam$ high ($H$) symmetry structure, due to the spin-lattice coupling. The

*corresponding author, Email address: helx@ustc.edu.cn
calculated lattice constants are \(a=7.270 \, \text{Å}, b=8.518 \, \text{Å}\) and \(c=5.600 \, \text{Å}\, \text{respectively, and are in very good agreement}

in experimental values (7.285, 8.487 and 5.668 Å respectively). The lattice constants are somewhat smaller than those of TbMn\(_2\)O\(_5\), DyMn\(_2\)O\(_5\). Like TbMn\(_2\)O\(_5\), DyMn\(_2\)O\(_5\) has two energetically degenerate lattice (and magnetic) structures, \(L\) and \(R\), in which Mn\(^{4+}\) form an AFM square lattice in the \(ab\) plane, whereas Mn\(^{3+}\) couples to Mn\(^{4+}\) either antiferromagnetically via \(J_3\) along \(a\) axis or with alternating sign via \(J_5\) along \(b\) axis. Mn\(^{3+}\) ions in two connected pyramids also couple antiferromagnetically through \(J_2\). Here, we adopt the notations \(J_3\), \(J_4\) and \(J_5\) from Ref. 4, and define the \(J_3\) to be the Mn\(^{4+}\)-Mn\(^{3+}\) superexchange interaction through pyramidal base corners, and \(J_5\) the superexchange interaction through the pyramidal apex.

We first calculate all zone-center optical phonon frequencies of the fully relaxed structure (\(L\) or \(R\)) via a frozen-phonon technique and the results are listed in Table I. Symmetry analysis shows that for the high symmetry (\(Pbam\)) structure \(H\), phonons belong to 8 irreducible representations (irreps), among them \(B_{1u}\), \(B_{2u}\) and \(B_{3u}\) are IR active, where \(B_{1g}\), \(B_{2g}\), \(B_{3g}\) and \(A_g\) are Raman active and \(A_u\) is silent. However, in the low symmetry (\(Pb21m\)) structure (\(L\) or \(R\)), the Raman and IR modes couple to each other, and regroup to 4 irreps, i.e.,

\[
A_1 = B_{2u} \oplus A_g; A_2 = B_{2g} \oplus A_u; B_2 = B_{3u} \oplus B_{1g}; B_3 = B_{1u} \oplus B_{3g}.
\]

The couplings between irreps. are very small, therefore the results are given by their major symmetry characters. As we see from Table I, the results are in excellent agreement with experiments. The calculated phonon frequencies are very close to those of TbMn\(_2\)O\(_5\), because Tb and Dy are isovalent and the two materials have very similar lattice structures. The inner products between the corresponding phonon modes of the two compounds are close to unity, suggesting that they have very similar mode patterns.

Experimentally, there are several anomalies found for both Raman modes in the magnetic phase transitions. For example, anomalous phonon shift for the Raman modes had been observed at \(T^* \sim 60-65\, \text{K}\), and near the Neel temperature \(T_N\). The highest \(A_g\) mode show a steep hardening upon cooling between \(T^*\) and \(T_N\). For the IR modes, it has been found near 60K, the infrared active modes soften and several modes soften substantially. The phonon modes are also found to be very sensitive to the magnetic field. The observed phonon anomaly phonon shift strongly suggest that the spin-phonon coupling in this material is very strong.

Theoretically, the spin-lattice coupling in this compound can be described via an effect Hamiltonian.

\[
E(\{u_\lambda\}) = (E_0 - \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j) - \sum_{ij} \sum_\lambda \frac{\partial J_{ij}}{\partial u_\lambda} u_\lambda \mathbf{S}_i \cdot \mathbf{S}_j + \left( \frac{1}{2} \sum_{\lambda} m_\lambda \omega_\lambda^2 u_\lambda^2 - \sum_{ij} \sum_\lambda \frac{\partial^2 J_{ij}}{\partial u_\lambda \partial u_\rho} u_\lambda u_\rho \mathbf{S}_i \cdot \mathbf{S}_j \right),
\]

where \(u_\lambda\) is the \(\lambda\)-th zone-center phonon, and \(\mathbf{S}_i\) is the magnetic moment of the \(i\)-th atom. Here, we consider only the magnetic moments of the Mn\(^{3+}\) and Mn\(^{4+}\) ions. \(J_{ij}\) is the exchange interaction between two adjacent Mn

| \(B_{2u}\) GGA Exp. | \(A_g\) GGA Exp. | \(B_{2g}\) GGA Exp. | \(A_u\) GGA Exp. | \(B_{3u}\) GGA Exp. | \(B_{1g}\) GGA Exp. | \(B_{1u}\) GGA Exp. | \(B_{3g}\) GGA Exp. |
|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| 671.8                | 680.0                | 679.2                | 693.0                | 687.7                | 675.0                | 697.2                | 557.2                | 585.0                |
| 628.4                | 617.6                | 625.0                | 598.0                | 610.1                | 647.0                | 530.0                | 507.9                | 495.0                |
| 553.4                | 615.0                | 470.8                | 499.5                | 597.1                | 588.3                | 497.9                | 471.7                | 460.5                |
| 535.8                | 531.5                | 545.0                | 452.3                | 460.0                | 429.1                | 512.7                | 519.0                | 547.5                | 540.0                | 437.2                | 450.4                | 440.0                |
| 473.8                | 491.7                | 500.0                | 444.7                | 402.3                | 475.6                | 521.2                | 410.6                | 403.0                | 430.5                |
| 438.0                | 444.2                | 460.0                | 336.5                | 287.5                | 465.5                | 470.1                | 485.0                | 296.7                | 290.0                | 324.7                | 320.0                |
| 412.1                | 407.2                | 420.0                | 293.0                | 305.0                | 225.7                | 378.3                | 411.0                | 420.0                | 249.3                | 289.8                |
| 351.0                | 336.9                | 350.0                | 273.6                | 132.5                | 351.5                | 371.3                | 330.0                | 142.5                | 264.5                |
| 314.4                | 311.1                | 230.7                | 220.0                | 110.8                | 317.0                | 299.6                | -2.0                 | 241.5                |
| 267.8                | 267.0                | 235.4                | 209.6                | 265.4                | 242.6                | 235.0                | 189.8                |
| 223.0                | 224.2                | 215.0                | 96.6                 | 216.3                | 217.0                | 220.2                | 205.0                | 103.6                |
| 163.2                | 136.4                | 108.4                | 151.5                | 146.1                | 145.0                | 111.6                |

TABLE I: Calculated phonon frequencies of ground state structure \(L\). The experimental values for Raman phonons are extracted from Ref. 14, whereas the IR phonons frequencies are extracted from Ref. 16.
ions. $E_0$ is the total energy of high symmetry structure $H$ without spin-spin interactions, where the ground state spin configuration is determined by the first term. $\omega_\lambda$ is the frequencies of the $\lambda$-th phonon, calculated in the high symmetry PM state. The spin-lattice coupling have two effects: (i) The second term, which is linear in $u$, breaks the inversion symmetry of the system, and drive the structure to a low symmetry polarized state leading to coexistence of AFM and ferroelectricity. The spin-lattice coupling strength is proportional to $\partial J_i / \partial u_\lambda$. However, this term would not change the phonon frequencies (at least to the first order approximation). (ii) The phonon modes $\omega_\lambda$ (including frequencies and eigenvectors) are modified in the presence of spin-phonon interaction, due to the third term of Eq. (1), where the spin-phonon coupling strength is $\partial^2 J_{ij} / \partial u_{\lambda'} \partial u_\lambda$. Different spin configuration (SC) $\{S_i\}$ would therefore have different phonon frequencies.

To investigate how the SCs change the phonons in DyMn$_2$O$_5$, we calculate the phonons frequencies of different SCs including the high temperature PM state, the AFM state, and the ferromagnetic (FM) state. The spin-lattice coupling strength $J''$ can be extracted by comparing the force-constant matrices calculated from these different spin states $^{12}$ [see Eq. (1)]. In this work, we focus on the $B_{2u}$ and $A_g$ modes, whereas other modes can be studied in similar way. To simplify the discussion, all following calculations are done in the high symmetry structure $H$, constructed via symmetrizing structures $L$ and $R$ according to the $Pbam$ symmetry. $^{12}$ In reality, the lattice constants would be somewhat different at different SCs. In the present calculations, this effect is ignored and the lattice constants are fixed in the calculations.

The phonon frequencies of PM, AFM (SC G in Fig. H) and FM (SC H in Fig. H) states are compared in Table III for the $A_g$ modes and in Table III for the $B_{2u}$ modes. One may attempt to calculate the phonon frequencies of the PM state using spin unpolarized GGA, which is listed in the column under $u$-GGA. A quick look reveals that the phonon frequencies in this column are significantly lower than those of AFM and FM state. Especially, as shown in Table II the $A_g$ irrep has a soft mode, causing a Jahn-Teller distortion. $^{24}$ The phonon frequencies calculated from $u$-GGA is not a good approximation for the PM state, because the Mn ions have local magnetic moments even in the PM phase, although their directions are distributed randomly. Alternatively, we calculate $\langle \omega \rangle_{dis}$, which are the averaged phonon frequencies of several fully disordered SCs ($A$, $B$, $C$ in Fig. H) so all exchange interactions are canceled out. The averaged phonon frequencies $\langle \omega \rangle_{dis}$ are close to those of the AFM and FM states without soft phonons.

However, the spins are fully disordered only at very high temperature. At lower temperature, especially close to the magnetic phase transition, the spins are somehow correlated, and develop short range ordering. Since $J_4$ is the largest among all the exchange interactions $^{13}$ to compare with experiments, we consider the ordering of $J_4$ interactions. We calculate $\langle \omega \rangle_{dis}$, which are the averaged phonon frequencies of three SCs ($D$, $E$, $F$ in Fig. H) in which $J_4$ are fixed in the AFM configuration, whereas all other exchange interactions are canceled out. As we see from Table II and Table III the frequencies of most modes in different SCs differ by about 3 - 5 cm$^{-1}$, which are of similar magnitude to the phonon shifts in the magnetic field experiment. $^{26}$ However, the high frequency $B_{2u}$ (671 cm$^{-1}$) and $A_g$ (679 cm$^{-1}$) modes change dramatically ($\sim$ 20 cm$^{-1}$) for different SCs. Especially, $\langle \omega \rangle_{dis}$ and $\langle \omega \rangle_{dis}$ for the $A_g$ and $B_{2u}$ modes, respectively, though both belong to the PM phase. Interestingly, the two modes frequencies $\langle \omega \rangle_{dis}$ have the mean values of those of AFM and FM states. It is usually believed that GGA overestimates the exchange interactions, whereas including the on-site Coulomb correlation may improve this problem. To see how including the on-site Coulomb correlation will change the spin-phonon coupling in DyMn$_2$O$_5$, we have carried out GGA + U calculations of the phonons in different SCs. The on-site Coulomb $U$ of Mn ion has been taken to be a reasonable value 4.0 eV, whereas the exchange parameter $j = 0.8$ eV is used. The results are also listed in Table II and Table III for the $A_g$ and $B_{2u}$ modes respectively. As we see, GGA + U significantly overestimates the frequencies of the high frequency modes when compared to experi-

![FIG. 1: (Color online) The spin configurations used in calculating phonon frequencies of different spin states.](image-url)
TABLE II: The $A_g$ modes calculated in high symmetry structure $H$ of different spin configurations using GGA and GGA + U methods.

| $u$ | GGA | GGA + U |
|-----|-----|---------|
|     | $\langle \omega \rangle_{\text{dis}}$ | $\langle \omega \rangle_{\text{j4}}$ | AFM | FM | $\langle \omega \rangle_{\text{dis}}$ | $\langle \omega \rangle_{\text{j4}}$ | AFM | FM |
| 571.1 | 667.7 | 671.6 | 679.0 | 662.8 | 746.1 | 759.9 | 759.0 | 723.2 |
| 569.2 | 621.5 | 625.8 | 618.6 | 629.7 | 658.8 | 661.3 | 659.4 | 653.4 |
| 539.7 | 617.7 | 618.4 | 613.5 | 617.3 | 634.2 | 635.3 | 631.0 | 638.3 |
| 463.3 | 537.2 | 540.9 | 531.1 | 547.0 | 559.3 | 561.1 | 556.6 | 562.2 |
| 432.9 | 490.6 | 492.2 | 491.3 | 494.1 | 505.4 | 506.3 | 506.0 | 506.4 |
| 369.6 | 414.3 | 407.9 | 407.0 | 429.8 | 438.2 | 436.6 | 436.0 | 440.3 |
| 024.6 | 340.0 | 337.6 | 337.6 | 340.3 | 342.6 | 342.3 | 341.6 | 343.0 |
| 078.8 | 321.9 | 329.2 | 311.0 | 331.7 | 328.9 | 331.9 | 323.2 | 334.8 |
| 527.2 | 238.7 | 237.2 | 236.2 | 243.9 | 248.3 | 248.0 | 247.5 | 249.2 |
| 072.9 | 222.3 | 229.2 | 219.6 | 225.9 | 217.7 | 216.9 | 216.6 | 220.1 |
| 66.1 | 136.8 | 137.5 | 136.0 | 137.6 | 141.1 | 141.6 | 140.9 | 141.0 |
| -174.2 | 110.0 | 110.0 | 109.3 | 111.2 | 113.2 | 113.4 | 113.1 | 113.5 |

TABLE III: The $B_{2u}$ modes calculated in high symmetry structure $H$ of different spin configurations using GGA and GGA + U methods.

| $u$ | GGA | GGA + U |
|-----|-----|---------|
|     | $\langle \omega \rangle_{\text{dis}}$ | $\langle \omega \rangle_{\text{j4}}$ | AFM | FM | $\langle \omega \rangle_{\text{dis}}$ | $\langle \omega \rangle_{\text{j4}}$ | AFM | FM |
| 586.4 | 660.2 | 673.3 | 671.7 | 649.6 | 723.7 | 736.6 | 735.9 | 705.8 |
| 512.8 | 627.2 | 625.5 | 626.1 | 623.8 | 659.1 | 659.4 | 659.1 | 657.9 |
| 507.2 | 551.6 | 552.2 | 553.4 | 552.3 | 578.5 | 578.7 | 579.4 | 577.9 |
| 488.7 | 534.0 | 530.9 | 535.3 | 534.1 | 566.6 | 567.0 | 568.3 | 564.6 |
| 431.2 | 474.5 | 473.5 | 475.7 | 476.4 | 495.5 | 494.5 | 495.6 | 498.1 |
| 391.0 | 439.5 | 437.2 | 439.2 | 438.1 | 461.8 | 462.0 | 462.2 | 459.4 |
| 381.3 | 409.7 | 410.0 | 411.7 | 406.0 | 419.9 | 420.2 | 420.9 | 418.0 |
| 310.0 | 353.6 | 350.2 | 350.8 | 357.6 | 365.7 | 364.9 | 365.2 | 366.1 |
| 274.3 | 315.0 | 314.3 | 315.2 | 314.6 | 316.2 | 315.8 | 316.3 | 316.6 |
| 257.7 | 272.7 | 266.0 | 267.9 | 280.1 | 283.8 | 282.5 | 282.5 | 285.5 |
| 211.1 | 222.2 | 221.8 | 223.4 | 220.8 | 211.7 | 212.0 | 212.5 | 212.7 |
| 142.6 | 162.0 | 162.2 | 162.0 | 161.4 | 165.6 | 165.7 | 165.5 | 165.7 |
| 139.2 | 156.8 | 156.9 | 157.0 | 157.3 | 163.3 | 163.5 | 163.7 | 162.7 |
| 93.9 | 98.4 | 98.6 | 99.2 | 96.8 | 94.0 | 94.3 | 94.6 | 93.4 |

To understand the results, we analyze the vibrational pattern of the two modes, shown in Fig. 2. For the high-frequency $A_g$ mode, about 90% of the vibration is associated with O$_3$ (the oxygens that connect Mn$^{3+}$ and Mn$^{4+}$ along the a axis, and convey $J_4$ interaction). The O$_3$ atoms vibrate in the $ab$ plane, with an angle of 21.4° to a axis. This mode also has small components of Mn$^{3+}$ vibrating in the $a$-axis, and Mn$^{4+}$ motion in the $c$-axis. Therefore $J_5$ may also affect the $A_g$ mode (but considerably smaller than $J_4$). In the high-frequency $B_{2u}$ mode, more than 70% of the contribution comes from O$_3$, which also vibrate in the $ab$ plane, with an angle of 19.9° to a axis. The rest contribution includes the motion of Mn$^{4+}$ along $a$ axis. If the spin exchange interaction is local, the motion the O$_3$ atoms would only tune the $J_4$ interactions. Therefore the $J_4$ interaction plays an essential role of the spin-phonon coupling in these two modes. Now it is easy to understand the phonon shifts of the two modes in different SCs. According to Eq. 11, the frequency shifts of the highest $A_g$ and $B_{2u}$ modes are $(S_3 \cdot S_4) \partial^2 J_4 / \partial u_{\text{dis}}^2$, where $S_3$, $S_4$ are the spin vectors of Mn$^{3+}$ and Mn$^{4+}$ ions associated with $J_4$, respectively. For the fully disordered SC, $(S_3 \cdot S_4)=0$. In the $J_4$ short range orderd state and in AFM state $(S_3 \cdot S_4)=-S_3 S_4$, whereas in FM state, $(S_3 \cdot S_4)=S_3 S_4$. $S_3=2.3 \mu_B$ and $S_4=1.64 \mu_B$, are the local magnetic moments. By comparing the force-constant matrices of different SCs, we estimate $\partial^2 J_4 / \partial u_{\text{dis}}^2 \sim 0.12$ meV/($\bar{A} \cdot \mu_B$)$^2$ for the two high frequency modes. As discussed in previous section, this value remain unchanged when including the on-site Coulomb interactions.
maximum value when temperature lower from 1.5 \( T_N \) to 25 \( J \) the temperature dependent measurement\[4\] for two reasons. First, the \( J_4 \) ordering develop gradually with decreasing of the Néel temperature and it is hard to isolate the anharmonic effects and spin-ordering is accompanied by the anharmonic effects\[13\]. Second, the phonon frequencies hardening due to \( J_4 \) ordering is accompanied by the anharmonic effects\[13\] and it is hard to isolate the anharmonic effects and spin-phonon effects in experiments. The lower frequencies modes involve collective motion of many atoms. Therefore, the phonon frequency shifts due to spin-phonon coupling are a consequence of the competition of many \( J'' \)'s, and are much smaller than the high frequency modes.

Below Néel temperature, \( T_N \), the material is in the long range ordered AFM state. We then compare the phonon frequencies of short range ordered state \( \langle \omega \rangle_{J_4} \) to those of AFM state. As we see, while the highest \( A_g \) mode hardens by 2 cm\(^{-1}\), and the highest \( B_{2u} \) mode softs by 2 cm\(^{-1}\), consistent with experiments\[14,15\]. The frequencies difference between \( \langle \omega \rangle_{J_4} \) and AFM might come from the \( J_5 \) interactions.

\[\text{IV. SUMMARY}\]

To summarize, we have investigated the spin-phonon coupling in a spin frustrated DyMn\(_2\)O\(_5\) system via first-principles calculations. We compare the phonon modes calculated from different spin configurations. The results show that the short range spin ordering can dramatically change the phonon frequencies in this compound, and might be responsible for the observed phonon anomalies near and above the magnetic phase transitions.

We would like to thank J. L. Musfeldt and J. Cao for communicating results prior to publication. L.H. acknowledges the support from the Chinese National Fundamental Research Program 2006CB921900, the Innovation funds and “Hundreds of Talents” program from Chinese Academy of Sciences, and National Natural Science Foundation of China.

1. T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature(London) 426, 55 (2003).
2. T. Goto, T. Kimura, G. Lawes, A. P. Ramirez, and Y. Tokura, Phys. Rev. Lett. 92, 257201 (2004).
3. N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, and S.-W. Cheong, Nature (London) 429, 392 (2004).
4. L. C. Chapon, G. R. Blake, M. J. Gutmann, S. Park, N. Hur, P. G. Radaelli, and S. W. Cheong, Phys. Rev. Lett. 93, 177402 (2004).
5. G. R. Blake, L. C. Chapon, P. G. Radaelli, S. Park, N. Hur, S.-W. Cheong, and J. Rodriguez-Carvajal, Phys. Rev. B 71, 214402 (2005).
6. N. Hur, S. Park, P. A. Sharma, S. Guha, and S.-W. Cheong, Phys. Rev. Lett. 93, 107207 (2004).
7. R. ValdesAguilar, A. B. Sushkov, S. Park, S. W. Cheong, and H. D. Drew, Phys. Rev. B 74, 184404 (2006).
8. S.-W. Cheong and M. Mostovoy, Nature Materials 6, 13 (2007).
9. H. Katsura, N. Nagaosa, and A. V. Balatsky, Phys. Rev. Lett. 95, 057205 (2005).
10. I. A. Sergienko and E. Dagotto, Phys. Rev. B 73, 094434 (2006).
11. L. C. Chapon, P. G. Radaelli, G. R. Blake, S. Park, and S.-W. Cheong, Phys. Rev. Lett. 96, 097001 (2006).
12. C. Wang, G.-C. Guo, and L. He, Phys. Rev. Lett. 99, 177202 (2007).
13. C. Wang, G.-C. Guo, and L. He, Phys. Rev. B 77, 134113 (2008).
14. A. F. García-Flores, E. Granado, H. Martínho, R. R. Urbano, C. Rettori, E. I. Golovenchits, V. A. Sanina, , S. B. Oseroff, S. Park, et al., Phys. Rev. B 73, 104411 (2006).
15. J. Cao, L. I. Vergara, J. L. Musfeldt, A. P. L uk, Y. J. Wang, S. Park, and S.-W. Cheong, Phys. Rev. B 78, 064307 (2008).
16. J. Cao, L. I. Vergara, J. L. Musfeldt, A. P. Litvinchuk, Y. J. Wang, S. Park, and S.-W. Cheong, Phys. Rev. Lett. 100, 177205 (2008).
17. C. J. Fennie and K. M. Rabe, Phys. Rev. Lett. 96, 205505 (2006).
18. G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
19. G. Kresse and J. Furthmuller, Phys. Rev. B 54, 11169 (1996).
20. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
21. P. E. Blochl, Phys. Rev. B 50, 17953 (1994).
22. J. A. Alonso, M. T. Casais, M. J. Martinez-Lope, J. L. Martinez, and M. T. Fernandez-Diaz, J. Phys.: Condens. Matter 9, 8515 (1997).
23. L. He, J. B. Neaton, D. Vanderbilt, and M. H. Cohen, Phys. Rev. B 67, 012103 (2003).
24. C. Kittel, Introduction to Solid State Physics, 7th edition (John Wiley & Sons, 1996).
25. K. Cao and L. He, (unpublished).