Electronic structure, linear, and nonlinear optical responses in magnetoelectric multiferroic material BiFeO₃

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BiFeO₃ has attracted great interest for its multiferroic property. The spontaneous electric polarization, multiferroism, and static magnetoelectric coupling have been widely studied both experimentally and theoretically. Here, in this paper, we report on the effects of magnetic ordering, spin fluctuation, and external magnetic field on the linear dielectric function and second-harmonic generation (SHG) in multiferroic BiFeO₃. First, our generalized gradient approximation plus Hubbard *U* calculations reproduce very well experimental data of linear dielectric function. In the mean time, it is revealed that SHG susceptibilities differ dramatically between antiferromagnetic configuration and ferromagnetic one, which is due to the enhanced contrast in the double-photon resonance absorption. Further Monte Carlo simulation of the coupling between electric order and spin-pair correlation function is presented for the spin fluctuation dependence of SHG. The significant nonlinear optical magnetoelectric effect around the Néel temperature provides novel route to enhancing magnetoelectric coupling in multiferroic materials. © 2009 American Institute of Physics. [DOI: 10.1063/1.3146796]

I. INTRODUCTION

Materials with strongly coupled magnetic and electronic degrees of freedom provide challenges for both fundamental many-body physics and advanced functional materials. Recently, multiferroics, where both electric and magnetic orders coexist in the same phase, have attracted great interest.^{1–8} However, such systems are rare in nature. Bi based multiferroics are one of such systems and have been studied extensively. Compared with the improper ferroelectrics, they show a much higher Curie temperature and stronger electric polarization. For example, BiFeO₃ is ferroelectric with the Curie temperature of 1123 K and electric polarization of 90–100 $\mu\text{C}/\text{cm}^2$.^{9–13} On the other hand, since the magnetic and ferroelectric orderings originate independently in these materials, it is generally believed that the magnetoelectric (ME) coupling in Bi based multiferroics is very weak.

Theoretically, the crystal structure, electronic structure, and spontaneous electric polarization were studied by Neaton *et al.*¹⁴ within the framework of the local spin-density approximation (LSDA) and LSDA+*U* methods. Based on Berry phase method, it is found that the spontaneous electric polarization is around 90–100 $\mu\text{C}/\text{cm}^2$, consistent with the large atomic displacements in ferroelectric phase and experimental results. On the other hand, chemical bonding in BiFeO₃ was analyzed by Ravindran *et al.*¹⁵ using partial density of states, charge density, charge transfer, electron localization function (ELF), Born effective charge tensor, and crystal orbital Hamiltonian population analysis. The ELF

shows that stereochemically active lone-pair electrons are present at Bi sites, which are responsible for the displacement of Bi atoms from the centrosymmetric position to polar structure, hence the ferroelectricity. Crystal structure, electronic structure, and magnetic properties were later reexamined by hybrid functional.¹⁶ On the other hand, ME coupling was investigated via considering the spin-orbit coupling.¹⁷ Recently, the finite-temperature properties of BiFeO₃ have been studied by Kornev *et al.*¹⁸ It is found that magnetodielectric (MD) effect is negligible in BiFeO₃, which is similar to the case of BiMnO₃,¹⁹ indicating weak ME coupling in this conventional multiferroic material.

Optical properties of BiFeO₃ polycrystal thin films and ceramics were studied experimentally.^{20–24} The optical gap is around 2.6 eV, which is much larger than previous LSDA, LSDA+*U* (with the effective *U* of up to 4 eV), but smaller than 3.1 eV from hybrid functional.^{14–16} Unlike the crystal structure and spontaneous electric polarization revealed in the abovementioned first principles studies,^{14,15} the optical responses depend strongly on the proper choice of Hubbard *U*. Therefore, it is important to make a further analysis of electronic structure as well as multiferroism in BiFeO₃ by using a more reasonable *U* from the fitting of the experimental optical response (linear dielectric function). In the meantime, in the optical frequency regime, significant change in the linear dielectric function, and second-harmonic generation (SHG) between different magnetic orderings have been observed in Co₃V₂O₈ (Ref. 25) and Bi₂FeCrO₆,²⁶ respectively. So, it is interesting to have the knowledge of the magnetic ordering dependence of linear and nonlinear optical responses in BiFeO₃.

In fact, linear MD effect is usually negligible in Bi based

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TABLE I. Calculated structure parameters for $R3c$ BiFeO₃ with $a = 0.571$ nm and $\alpha = 59.07^\circ$. The experimental data (Ref. 9) are shown in parentheses with $a = 0.563$ nm and $\alpha = 59.35^\circ$.

Site	Wyckoff position	x	y	z
Bi	$2a$	0 (0)	0 (0)	0 (0)
Fe	$2a$	0.221 (0.221)	0.221 (0.221)	0.221 (0.221)
O	$6a$	0.534 (0.528)	0.936 (0.933)	0.390 (0.395)

multiferroics. However, in the excited optical frequency region ($\hbar\omega$), the SHG, which is the unique feature of a polar structure, its strong dependence on the magnetic ordering, spin fluctuation, and external magnetic and electric fields are highly expected. In this paper, we explore the magnetic ordering dependence of SHG in BiFeO₃. Previous *ab initio* investigations as well as model calculations indicate that BiFeO₃ possesses very weak static ME effects.¹⁸ As revealed in the following, nonlinear optical ME (NOME) effect, on the other hand, is colossal. First, with fully relaxed crystal structure, the calculation is performed on the electronic structure, linear dielectric function, and SHG susceptibility. Antiferromagnetic (AFM) (G -type AFM) configuration with antiparallel and ferromagnetic (FM) configuration with parallel Fe³⁺ ($S=5/2$) spins are compared. A sizeable difference in low frequency SHG (98%) between AFM and FM configurations is found. Second, based on the first principles results and an effective model for the coupling between electric polarization and spin-pair correlation function, we study the effect of spin fluctuation on SHG via finite-temperature Monte Carlo simulation. In contrast to negligible MD effect, NOME effect is observable near the Néel temperature (T_N). The predicted NOME effect should be general in multiferroics and will open a novel direction in the study of multiferroic materials.

II. COMPUTATIONAL METHOD

Our *ab initio* calculations are performed using the accurate full-potential projector augmented wave (PAW) method,²⁷ as implemented in the VIENNA *AB INITIO* SIMULATION PACKAGE.^{28–31} They are based on the density functional theory with the generalized gradient approximation (GGA). The on-site Coulomb interaction is included in the GGA+ U approach with $U=7$ eV and $J=0.9$ eV for Fe 3d electrons.³² A large plane-wave cutoff of 500 eV is used throughout, and the convergence criteria for energy is 10^{-6} eV. PAW potentials are used to describe the electron-ion interaction, with 15 valence electrons for Bi ($5d^{10}6s^26p^3$), 14 for Fe ($3p^63d^64s^2$), and six for O ($2s^22p^4$). Brillouin zone integrations are performed with tetrahedron method in a $10 \times 10 \times 10$ Monkhorst-Pack k -point mesh centered at Γ .³³ The fully relaxed crystal structure (see Table I), which shows a $R3c$ rhombohedral symmetry, is in good agreement with experiment.⁹ In the mean time, AFM configuration is the ground state, with 0.1569 eV/f.u. lower than FM one.

The optical properties are calculated based on the independent-particle approximation, i.e., the excitonic effects and the local-field corrections are neglected.^{34,35} The imagi-

nary part of the dielectric function due to direct interband transitions is given by Fermi golden rule, i.e.,

$$\varepsilon''_{aa} = \frac{4\pi^2}{\Omega\omega^2} \sum_{i \in \text{VB}, j \in \text{CB}} \sum_{\mathbf{k}} w_{\mathbf{k}} |p_{ij}^a|^2 \delta(\varepsilon_{\mathbf{k}_j} - \varepsilon_{\mathbf{k}_i} - \omega), \quad (1)$$

where Ω is the unit-cell volume and ω is the photon energy. VB and CB denote the conduction and valence bands, respectively. The dipolar transition matrix elements $p_{ij}^a = \langle \mathbf{k}_j | p_a | \mathbf{k}_i \rangle$ are obtained from the self-consistent band structures within the PAW formalism. Here $|\mathbf{k}_n\rangle$ is the n th Bloch state wave function with crystal momentum $\mathbf{k}$, and a denotes the Cartesian component. The real part of the dielectric function is obtained from ε'' by a Kramers–Kronig transformation

$$\varepsilon'(\omega) = 1 + \frac{2}{\pi} \mathbf{P} \int_0^\infty d\omega' \frac{\omega' \varepsilon''(\omega')}{\omega'^2 - \omega^2}. \quad (2)$$

Here $\mathbf{P}$ is the principle value of the integral. Given the complex dielectric function $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$, all the other linear optical properties can be calculated, e.g., linear refractive index $n(\omega) = ((\sqrt{\varepsilon'^2(\omega) + \varepsilon''^2(\omega)} + \varepsilon'(\omega))/2)^{1/2}$, and the linear absorption coefficient is related to ε'' by $\alpha = \varepsilon''\omega/(nc)$, where c is the velocity of light in the vacuum. The electron energy loss function is given by $\text{Im}(-1/\varepsilon)$.

The imaginary part of the second-order optical susceptibility due to direct interband transitions is given by^{34,35}

$$\chi_{abc}^{(2)}(-2\omega, \omega, \omega) = \chi_{abc, \text{VE}}^{(2)}(-2\omega, \omega, \omega) + \chi_{abc, \text{VH}}^{(2)}(-2\omega, \omega, \omega), \quad (3)$$

where the contribution due to the so-called virtual-electron (VE) process is^{34,35}

$$\begin{aligned} \chi_{abc, \text{VE}}^{(2)}(-2\omega, \omega, \omega) &= -\frac{\pi}{2\Omega} \sum_{i \in \text{VB}} \sum_{j, l \in \text{CB}} \sum_{\mathbf{k}} w_{\mathbf{k}} \left\{ \frac{\text{Im}[p_{ji}^a \langle p_{li}^b p_{ij}^c \rangle]}{\varepsilon_{li}^3 (\varepsilon_{li} + \varepsilon_{ji})} \times \delta(\varepsilon_{li} - \omega) \right. \\ &\quad - \frac{\text{Im}[p_{ii}^a \langle p_{jl}^b p_{li}^c \rangle]}{\varepsilon_{li}^3 (2\varepsilon_{li} - \varepsilon_{ji})} \delta(\varepsilon_{li} - \omega) \\ &\quad \left. + \frac{16 \text{Im}[p_{ij}^a \langle p_{jl}^b p_{li}^c \rangle]}{\varepsilon_{ji}^3 (2\varepsilon_{li}^3 - \varepsilon_{ji}^3)} \delta(\varepsilon_{ji} - 2\omega) \right\}, \end{aligned} \quad (4)$$

and that due to the virtual-hole (VH) process is^{34,35}

$$\begin{aligned} \chi_{abc, \text{VH}}^{(2)}(-2\omega, \omega, \omega) &= -\frac{\pi}{2\Omega} \sum_{i \in \text{VB}} \sum_{j, l \in \text{CB}} \sum_{\mathbf{k}} w_{\mathbf{k}} \left\{ \frac{\text{Im}[p_{ji}^a \langle p_{li}^b p_{ij}^c \rangle]}{\varepsilon_{li}^3 (\varepsilon_{li} + \varepsilon_{ji})} \times \delta(\varepsilon_{li} - \omega) \right. \\ &\quad - \frac{\text{Im}[p_{ii}^a \langle p_{jl}^b p_{li}^c \rangle]}{\varepsilon_{li}^3 (2\varepsilon_{li} - \varepsilon_{ji})} \delta(\varepsilon_{li} - \omega) \\ &\quad \left. + \frac{16 \text{Im}[p_{ij}^a \langle p_{jl}^b p_{li}^c \rangle]}{\varepsilon_{ji}^3 (2\varepsilon_{li}^3 - \varepsilon_{ji}^3)} \delta(\varepsilon_{ji} - 2\omega) \right\}. \end{aligned} \quad (5)$$

Here $\varepsilon_{ji} = \varepsilon_{\mathbf{k}_i} - \varepsilon_{\mathbf{k}_j}$ and $\langle p_{jl}^b p_{li}^c \rangle = \frac{1}{2} (p_{jl}^b p_{li}^c + p_{li}^b p_{jl}^c)$. The real part of the second-order optical susceptibility is then obtained from the imaginary part by a Kramers–Kronig transformation

FIG. 1. (Color online) Crystal structure of BiFeO₃. FIG. 2. (Color online) ELF in BiFeO₃.

$$\chi'^{(2)}(-2\omega, \omega, \omega) = \frac{2}{\pi} \mathbf{P} \int_0^\infty d\omega' \frac{\omega' \chi'^{(2)}(2\omega', \omega', \omega')}{\omega'^2 - \omega^2}. \quad (6)$$

In the present calculations, the δ functions are approximated by a Gaussian function with $\Gamma=0.1$ eV. The dense grid of k -points $16 \times 16 \times 16$ with total irreducible 417 k -points, 20 bands per atom, and the 50 eV of the maximum energy in the integrals of real part of ϵ and $\chi^{(2)}$ are used to guarantee the accuracy of the present optical calculations.

III. RESULTS AND DISCUSSION

A. Crystal structure and ferroelectric distortion

As shown in Fig. 1, BiFeO₃ has a $R3c$ symmetry. The unit cell contains two formula units with ten atoms therein. Such a polar structure arises from counter-rotation of neighboring O octahedra about the $[111]$ axis, and Bi, Fe, and O atoms are displaced relative to each other along this threefold axis, permitting the electric polarization developed along $[111]$ direction. The ferroelectric distortion in this Bi based multiferroic materials is related the $6s^2$ lone pair in Bi atom, which is evidenced by the ELF (Ref. 36) as shown in Fig. 2.

B. Electronic and magnetic properties

For the transition metal oxides, band gap predicted from density functional theory depends strongly on the choice of effective Hubbard U . With the increase in effective U , the band gap usually increases. Previous results are based on the effective U of up to 4 eV. It is noted that a small gap around 0.4 eV is found in LSDA, and the gap increases to 1.3 and

1.9 eV for $U_{\text{eff}}=2$ eV and $U_{\text{eff}}=4$ eV, respectively.¹⁴ The band gap is around 3.1 eV from hybrid functional.¹⁶ As shown in Fig. 3, band gap increases with the increase in U and reaches as high as 2.5 eV when U is larger than 7 eV. On the other hand, for the FM spin configuration (see Fig. 4), it is found that band gap increases a lot for the up spin channel and decreases a little in down spin channel. It is noted that G -type AFM configuration is the ground state, with 0.1569 eV/f.u. lower than FM one. In AFM state, the local magnetic moment of Fe in PAW sphere is around $4.31 \mu_B$, while for FM state, the local magnetic moment in of PAW sphere is around $4.41 \mu_B$.

The total and partial (Fe) densities of states are shown in Fig. 5. It is found that in both AFM and FM states, the lowest bands at -9 eV are mainly from Bi $6s$ states. Above these

FIG. 3. Band structure in BiFeO₃ with different Hubbard U .

FIG. 4. Band structure in BiFeO₃ ($U=7$ eV) with AFM ordering and FM (up spin and down spin) orderings, respectively.

bands are the bands of the Fe 3d states as well as the hybridized O 2p and Bi 6p. The CBs are from the unoccupied Fe 3d states and Bi 6p states. The hybridization between Bi and O is obvious, which is the driving force of ferroelectricity in such A-site driven ferroelectric materials. When the system transits from AFM spin configuration to FM case, the dispersion of Fe bands increases a little.

C. Linear optical response

For the $R3c$ symmetry, among the three components of linear dielectric function ϵ_{xx} , ϵ_{yy} , and ϵ_{zz} , $\epsilon_{xx}=\epsilon_{yy}$. As shown in Fig. 6, our GGA+ U ($U=7$ eV) calculations lead to a good agreement of $\epsilon=(2\epsilon_{xx}+\epsilon_{zz})/3$ with the recent experimental data.²⁰ Two absorption peaks located at 3.00 and 4.26 eV, respectively, are well reproduced via the imaginary part of linear dielectric function for the interband transition.

D. SHG

For the $R3c$ symmetry, among the SHG susceptibilities, there are eight nonvanishing components: $\chi_{xxx}^{(2)}$, $\chi_{xyy}^{(2)}$, $\chi_{yyz}^{(2)}$, $\chi_{xxz}^{(2)}$, $\chi_{yyz}^{(2)}$, $\chi_{zxx}^{(2)}$, $\chi_{zyy}^{(2)}$, and $\chi_{zzz}^{(2)}$, with $\chi_{xxx}^{(2)}=-\chi_{xyy}^{(2)}=-\chi_{yyz}^{(2)}$, $\chi_{xxz}^{(2)}=\chi_{yyz}^{(2)}$, and $\chi_{zxx}^{(2)}=\chi_{zyy}^{(2)}$.³⁷ The ME coupling of ionic origin is

FIG. 5. (Color online) Total and partial (Fe ion) DOS of BiFeO₃ ($U=7$ eV) with AFM ordering and FM ordering, respectively.

FIG. 6. (Color online) Real and imaginary parts of the averaged dielectric function ϵ . *Ab initio* results with $U=7$ eV (red solid line) in good agreement with experimental data (Ref. 20) (blue round dot).

usually extremely small in these conventional multiferroic materials, and optical response revealed in our paper, which arises mainly from the electrons, does not depend on the small change in crystal structure between different magnetic orderings. Based on the same crystal structure, we calculate and compare the SHG between AFM and FM spin configurations. As shown in Fig. 7, there is little difference in ϵ between AFM and FM states. However, SHG coefficients display great contrast between each other. In particular, the relative changes in the low frequency SHG susceptibilities reach as high as 97.83% (Table II). While the low frequency (electronic part) ϵ_{xx} and ϵ_{zz} hardly changes (within 1%). Such a large change in SHG will provide a novel functionality of BiFeO₃ since the linear electro-optical effect, which describes the change in refraction under an external electric field, will also be magnetic ordering dependent.

In order to clarify the microscopic origin of NOME effects, we plot the absolute value of imaginary part of $\chi^{(2)}$ in

FIG. 7. (Color online) Real part of $\epsilon(\omega)$ and $\chi^{(2)}$ (10^{-6} esu) of the AFM (blue solid line) and FM (red dashed line) BiFeO₃.

TABLE II. Low frequency dielectric constant (ϵ), SHG susceptibilities ($\chi^{(2)}$) (10^{-8} esu), and corresponding OME effects in BiFeO₃.

	AFM	FM	OME (%)
ϵ_{xx}	7.030	7.025	0.07
ϵ_{zz}	6.507	6.462	0.69
$\chi_{xxx}^{(2)}$	3.10	6.14	49.51
$\chi_{xxz}^{(2)}$	-0.015	0.69	97.83
$\chi_{xzz}^{(2)}$	-1.69	-0.75	55.62
$\chi_{zzz}^{(2)}$	-1.88	-2.95	36.27

contrast with $\epsilon'(\omega)$ and $\epsilon''(\omega/2)$ (Fig. 8). First, we can find that the SHG spectrum can be divided into three regions: The regime with $\hbar\omega \leq 2.7$ eV, corresponding to double-photon resonance; the regime with $2.7 \text{ eV} \leq \hbar\omega \leq 3.7$ eV, corresponding to joint double-photon and single-photon resonances; and the regime beyond, related to single-photon resonance. Second, between AFM and FM states, little difference, except the peak around 2.1 eV in $\epsilon''(\omega/2)$ (as well as 4.2 eV in $\epsilon''(\omega)$), is observed. However, $\chi^{(2)}$ differs significantly in the height of the peaks. In particular, great contrast in the magnitude of first several peaks ($\hbar\omega \leq 2.7$ eV, i.e., linear absorption edge) is observed. This also agrees with the variation in low frequency $\chi^{(2)}$ as listed in Table II, showing the enhanced contrast in double-photon resonance between the AFM and FM configurations.

E. Spin-pair correlation function and ME effect

In multiferroic materials, the finite-temperature properties of ME effects are determined by the spin fluctuation and its coupling with electric order. For BiFeO₃, in addition to ferroelectric and antiferrodistortive (AFD) motions, the ef-

fective Hamiltonian should include magnetic degree of freedom, which is composed of the exchange interaction associated with local magnetic moments ($\mathbf{S}_i$), as well as its modification due to local soft-mode, strain, and AFD degrees of freedoms (Eq. (1) in Ref. 18). For the static dielectric function, the evolution of spin-spin correlation function ($\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$) as a function of external magnetic field gives rise to the MD effect.¹⁸ For the higher order susceptibility $\chi^{(2)}$, the evolution of the coupling between $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ and the higher order term in electric order (e.g., P^4) leads to NOME effects.

Therefore, to investigate the intrinsic NOME effects in BiFeO₃ from room temperature to Néel transition temperature, we apply a magnetic field and compute the change in SHG. Since the magnetic moments are localized at the Fe two sublattices, the effective model for the spin degrees of freedom of BiFeO₃ is a Heisenberg model. In the meantime, as described above, in these conventional multiferroic systems, the ferroelectric transition temperature is much higher than the magnetic Néel transition temperature, so the electric order is invariant around the Néel temperature. For the spin fluctuation dependence of SHG, the evolution of spin-pair correlation function between two sublattices ($\langle S_i S_j \rangle$) plays the key role. Therefore, we can have a further knowledge of the temperature dependence of SHG by mapping the exchange interaction in a Heisenberg model,

$$H = -J \sum_{\text{NN}} S_i S_j - h \sum_{\text{all}} S_i, \quad (7)$$

where J (−4.18 meV) is the nearest neighboring (NN) exchange coupling constant obtained from the above GGA + U total energy results, h is the external magnetic field, and S_i (5 μ_B) is the magnetic moment of the Fe³⁺ ions. Monte Carlo Metropolis simulation is performed on a 20^3 grid to obtain the temperature dependence of $\langle S_i S_j \rangle$. As shown in Fig. 9(a), $\langle S_i S_j \rangle$ transits from the perfect AFM spin configuration at a low temperature to the random spin configuration when crossing magnetic transition temperature T_N . T_N , which is obtained from finite size scaling of specific heat C_V over several N^3 ($N=10-20$) grids, is about 330 K. According to Anderson's theory, the superexchange interaction between Fe³⁺ ions originates from two parts: kinetic exchange (due to the mixing of the ligand-field orbitals) and potential exchange (direct exchange interaction between these ligand-field orbitals). The former is AFM and is proportional to b^2/U , while the latter is FM. Since the strong $dp\sigma$ bonding between the Fe e_g electrons in BiFeO₃, AFM coupling dominates. Compared with the smaller U (3.8 eV) used by Kornev *et al.*,¹⁸ the AFM coupling in the present study is slightly reduced but still leads to a reasonable T_N with experimental data (625–643 K). On the other hand, when an external magnetic field is applied, $\langle S_i S_j \rangle$ gets a little increased. Figure 9(b) shows the field dependence of $\Delta \langle S_i S_j \rangle$ around T_N . A large change in spin-pair correlation function is found. Although the magnetic field applied here is still very large, compared with the linear MD effect as shown by Kornev *et al.*,¹⁸ NOME revealed here is much larger than linear MD effect ($2.4 \times 10^{-5} \text{ T}^{-1}$).¹⁸

FIG. 8. (Color online) Absolute value of the imaginary part of $\chi^{(2)}$ as well as $\epsilon''(\omega)$ (black solid line) and $\epsilon''(\omega/2)$ (red dotted line) in BiFeO₃.

FIG. 9. (Color online) (a) Temperature dependence of spin-pair correlation function ($\langle S_i S_j \rangle$) under different magnetic fields. Inset shows specific heat ($C_V = \langle E^2 \rangle - \langle E \rangle^2 / T^2$) peaked at T_N . (b) Magnetic field dependence of spin-pair correlation function ($\Delta \langle S_i S_j \rangle = \langle S_i S_j \rangle_h - \langle S_i S_j \rangle_{h=0}$). Here we use the normalized magnetic field $h = \mu_B H / (k_B T_N)$.

F. Discussion of ME coupling in other conventional ferroelectric magnets and improper ferroelectric materials

From the above calculations, strong magnetic ordering dependence of SHG is well established in BiFeO₃. NOME effects similar to those described above are also expected in the AFM BiCoO₃ and PbVO₃ as well as FM BiMnO₃. In fact, consistent with the suggestion by Tokura,⁷ these conventional polar magnets can show very interesting linear and nonlinear optical properties arising from the ME response in the optical frequency region, yet the coupling between electric polarization P and magnetization M at their electronic ground state appears to remain very small. On the other hand, it is also expected that colossal NOME effects exist in the improper ferroelectrics, where the spontaneous electric polarization is induced by particular spin, charge, or orbital ordering. In the improper ferroelectrics, the spontaneous electric polarization P itself is M dependent, so $\chi^{(2)}$ should change strongly between different magnetic configurations.

IV. CONCLUSION

In conclusion, a combined density functional theory and Monte Carlo simulation have been performed to explore the nonlinear optical response in BiFeO₃. GGA+ U calculations reproduce very well the experimental optical band gap and linear dielectric function. For SHG, colossal NOME effects are revealed. Such NOME effects are much larger than linear MD effects and can be induced by either the change in the magnetic ordering with external magnetic field or the presence of spin fluctuations near magnetic phase transition. We hope this study will stimulate further experiments on the NOME effects in various kinds of multiferroic systems.

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- ¹N. A. Hill, *J. Phys. Chem. B* **104**, 6694 (2000).
- ²M. Fiebig, *J. Phys. D* **38**, R123 (2005).
- ³W. Eerenstein, N. D. Mathur, and J. F. Scott, *Nature (London)* **442**, 759 (2006).
- ⁴C. Ederer and N. A. Spaldin, *Curr. Opin. Solid State Mater. Sci.* **9**, 128 (2005).
- ⁵S.-W. Cheong and M. Mostovoy, *Nature Mater.* **6**, 13 (2007).
- ⁶R. Ramesh and N. A. Spaldin, *Nature Mater.* **6**, 21 (2007).
- ⁷Y. Tokura, *J. Magn. Magn. Mater.* **310**, 1145 (2007).
- ⁸S. Ju, T.-Y. Cai, G.-Y. Guo, and Z.-Y. Li, *Phys. Rev. B* **75**, 064419 (2007).
- ⁹F. Kubel and H. Schmid, *Acta Crystallogr., Sect. B: Struct. Sci.* **46**, 698 (1990).
- ¹⁰J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, *Science* **299**, 1719 (2003).
- ¹¹H. Bea, M. Bibes, A. Barthelemy, K. Bouzehouane, E. Jacquet, A. Khodan, J. P. Contour, S. Fusil, F. Wyczisk, A. Forget, D. Lebeugle, D. Colson, and M. Viret, *Appl. Phys. Lett.* **87**, 072508 (2005).
- ¹²H. Bea, M. Bibes, S. Fusil, K. Bouzehouane, E. Jacquet, K. Rode, P. Bencok, and A. Barthelemy, *Phys. Rev. B* **74**, 020101(R) (2006).
- ¹³H. Bea, M. Bibes, M. Sirena, G. Herranz, K. Bouzehouane, E. Jacquet, S. Fusil, P. Paruch, M. Dawber, J. P. Contour, and A. Barthelemy, *Appl. Phys. Lett.* **88**, 062502 (2006).
- ¹⁴J. B. Neaton, C. Ederer, U. V. Waghmare, N. A. Spaldin, and K. M. Rabe, *Phys. Rev. B* **71**, 014113 (2005).
- ¹⁵P. Ravindran, R. Vidya, A. Kjekshus, H. Fjellvag, and O. Eriksson, *Phys. Rev. B* **74**, 224412 (2006).
- ¹⁶M. Goffinet, P. Hermet, D. I. Bilec, and Ph. Ghosez, *Phys. Rev. B* **79**, 014403 (2009).
- ¹⁷C. Ederer and N. A. Spaldin, *Phys. Rev. B* **71**, 060401(R) (2005).
- ¹⁸I. A. Kornev, S. Lisenkov, R. Haumont, B. Dkhil, and L. Bellaiche, *Phys. Rev. Lett.* **99**, 227602 (2007).
- ¹⁹T. Kimura, S. Kawamoto, I. Yamada, M. Azuma, M. Takano, and Y. Tokura, *Phys. Rev. B* **67**, 180401(R) (2003).
- ²⁰J. F. Ihlefeld, N. J. Podraza, Z. K. Liu, R. C. Rai, X. Xu, T. Heeg, Y. B. Chen, J. Li, R. W. Collins, J. L. Musfeldt, X. Q. Pan, J. Schubert, R. Ramesh, and D. G. Schlom, *Appl. Phys. Lett.* **92**, 142908 (2008).
- ²¹S. R. Basu, L. W. Martin, Y. H. Chu, M. Gajek, R. Ramesh, R. C. Rai, X. Xu, and J. L. Musfeldt, *Appl. Phys. Lett.* **92**, 091905 (2008).
- ²²A. J. Hauser, J. Zhang, L. Mier, R. A. Ricciardo, P. M. Woodward, T. L. Gustafson, L. J. Brillson, and F. Y. Zhang, *Appl. Phys. Lett.* **92**, 222901 (2008).
- ²³A. Kumar, R. C. Rai, N. J. Podraza, S. Denev, M. Ramirez, Y. H. Chu, L. W. Martin, J. Ihlefeld, T. Heeg, J. Schubert, D. G. Schlom, J. Orenstein, R. Ramesh, R. W. Collins, J. L. Musfeldt, and V. Gopalan, *Appl. Phys. Lett.* **92**, 121915 (2008).
- ²⁴Y. Xu and M. R. Shen, *Mater. Lett.* **62**, 3600 (2008).
- ²⁵R. C. Rai, J. Cao, J. L. Musfeldt, D. J. Singh, X. Wei, R. Jin, Z. X. Zhou, B. C. Sales, and D. Mandrus, *Phys. Rev. B* **76**, 174414 (2007).
- ²⁶S. Ju and G. Y. Guo, *Appl. Phys. Lett.* **92**, 202504 (2008).
- ²⁷P. E. Blochl, *Phys. Rev. B* **50**, 17953 (1994).
- ²⁸G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).
- ²⁹G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (1994).
- ³⁰G. Kresse and J. Furthmuller, *Comput. Mater. Sci.* **6**, 15 (1996).
- ³¹G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ³²A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, *Phys. Rev. B* **52**, R5467 (1995).
- ³³P. E. Blochl, O. Jepsen, and O. K. Andersen, *Phys. Rev. B* **49**, 16223 (1994).
- ³⁴G. Y. Guo, K. C. Chu, D. S. Wang, and C. G. Duan, *Phys. Rev. B* **69**, 205416 (2004); G. Y. Guo and J. C. Lin, *ibid.* **72**, 075416 (2005); **77**, 049901(E) (2008).
- ³⁵S. Ju and G. Y. Guo, *J. Chem. Phys.* **129**, 194704 (2008).
- ³⁶B. Silvi and A. Savin, *Nature (London)* **371**, 683 (1994).
- ³⁷R. W. Boyd, *Nonlinear Optics* (Elsevier, Amsterdam, 2003).