Magnetic ferroelectrics that possess ferroelectricity together with some form of magnetic order like ferromagnetic, antiferromagnetic, or ferrimagnetic property in the same crystalline phase have attracted much interest due to their fundamental physics and a great promise for practical applications in future information technology. In particular, improper multiferroics in which a ferroelectric polarization is induced by electronic correlation effects such as non-centrosymmetric spin, charge, and orbital ordering, is currently under intensive study. This is related to the suggestion that a magneto-electric (ME) coupling in improper multiferroics is expected to be stronger than in proper case, because both dipolar and magnetic orderings share the same physical origin and occur at the same temperature.

In the early days of searching improper multiferroics, spin ordering was accepted to be a main driving force for the manifestation of ferroelectric polarization; examples include rare earth manganites RMnO$_3$ and R$_2$Mn$_2$O$_5$ ($R =$ Tb, Ho, Dy, Lu, ...) and Li-Cu-based oxides LiCu$_2$O$_2$ and LiCuVO$_4$. These compounds, however, have antiferromagnetic order, which makes their application strongly limited because of zero magnetization (and therefore uncontrollability), and what is worse, they have quite small electric polarization ($\leq 0.1 \mu C/cm^2$). On the other hand, it was found from first-principles and experiments that, in some ferrites including magnetite Fe$_3$O$_4$ and rare earth ferrites RF$_2$O$_4$ ($R =$ Y, Yb or Lu) and in some perovskites AA′BB′O$_6$, SrTiO$_3$/PbTiO$_3$ superlattice and LaMnWO$_6$ with a very large polarization of about $16 \mu C/cm^2$, and Ca$_3$Mn$_2$O$_7$ are typical compounds belonged to this materials class. These materials have weak ferromagnetism and thus a significant ME coupling is expected. Despite the great progress in the field of improper multiferroics, the effort to find new mechanism and design new materials is being continued.

In this letter, we present that spinel-type nickel ferrite NiFe$_2$O$_4$ (NFO) is a promising candidate for improper multiferroics with finite magnetization and considerably large polarization, based on the first-principles density functional theory (DFT) calculations. In fact, spinels exhibit several unusual features including magnetoelectricity and multiferroicity. From the experiment, it was established that the bulk NFO shows soft ferrimagnetic ordering below relatively high transition temperature of 850 K with a magnetization of 2 $\mu_B$ per formula unit (f.u.) in the recent experiment. Moreover, high dielectric permittivity was observed in NFO nanoparticles to be ranged from 60 to 600 at different frequencies and temperatures. This is comparable with the conventional ferroelectrics and therefore implies the presence of spontaneous polarization in the bulk NFO. However, the ferroelectricity of bulk NFO has neither been calculated nor measured yet, though the intensive studies of electronic, magnetic, and epitaxial strain and magnetoelastic properties have been conducted.

**Which is the most stable structure?** It is well accepted that NFO crystallizes in the completely inverse spinel structure with a face-centered cubic space group Fd$ar{3}$m (No. 227), half of the Fe$^{3+}$ cations occupy the tetrahedral A-sites (8a), the rest of Fe$^{3+}$ and Ni$^{2+}$ cations are equally distributed over the octahedral B-sites (16d), and the sites of oxygen anions are distinguished into O$_1$ and O$_2$. However, it was not clear how Fe$^{3+}$ and Ni$^{2+}$ cations are distributed over B-sites; when distributing factors (i.e., Jahn-Teller effects) were found to induce the breaking of inversion symmetry and produce a large ferroelectric polarization in the new class of double perovskites AA′BB′O$_6$. SrTiO$_3$/PbTiO$_3$ superlattice and LaMnWO$_6$ with a very large polarization of about $16 \mu C/cm^2$, and Ca$_3$Mn$_2$O$_7$ are typical compounds belonged to this materials class. These materials have weak ferromagnetism and thus a significant ME coupling is expected. Despite the great progress in the field of improper multiferroics, the effort to find new mechanism and design new materials is being continued.

We investigate the ferrimagnetism and ferroelectricity of bulk NiFe$_2$O$_4$ with tetragonal $P4_2$2 symmetry by means of density functional calculations using generalized gradient approximation + Hubbard $U$ approach. Special attention is paid to finding the most energetically favorable configuration on magnetic ordering and further calculating the reliable spontaneous electric polarization. With the fully optimized crystalline structure of the most stable configuration, the spontaneous polarization is obtained to be $23 \mu C/cm^2$ along the z direction, which originates from the hybridization between the 3d states of the Fe$^{3+}$ cation and the 2p states of oxygen induced by Jahn-Teller effect. PACS numbers: 41.20.Gz, 77.80.-e, 75.85.+t, 31.15.E-
Fe	extsuperscript{3+} and Ni	extsuperscript{2+} over B-sites in the Fd	extit{3}m unit cell with the periodic boundary condition rather than in infinite bulk crystal, it might be possible to generate different space groups whose symmetries are lowered from Fd	extit{3}m. It is only recent year that, through the Raman spectra measurements, both NFO single crystals [39] and thin films [40] exhibit short range B-site ordering with tetragonal P4\textit{1}2\textit{1}2 (No. 91) (or equivalently P4\textit{1}22) symmetry, though the phase with orthorhombic Imma (No. 74) symmetry was not ruled out.

Such experimental finding that NFO has short range ordering was affirmed by the recent first-principles works [35–38]. Among possible space groups with symmetries lowering from Fd	extit{3}m created by distributing Fe	extsuperscript{3+} and Ni	extsuperscript{2+} cations on 8 B-sites, two relatively high-symmetry space groups P4\textit{1}2\textit{1}2 and Imma were found to be energetically the most favorable, and further P4\textit{1}22 slightly lower than Imma [35]. Therefore, it is only natural that we adopt the tetragonal P4\textit{1}22 and orthorhombic Imma structures as our starting phases of bulk NFO.

Next, we should consider the possible spin configurations of cations, which help to illustrate the nature of the magnetic property of bulk NFO. Denoting spin up and down as \( u \) and \( d \), there are eight spin configurations of cations, Fe\textsubscript{A}, Fe\textsubscript{B} and Ni\textsubscript{B} in due order: \( \text{ddd, ddu, dud, dww, udd, udv, uvd, and uvu} \). However, considering that spin inversion will give the same total energy to the origin with only opposite magnetization as confirmed by our calculation, the spin configurations to consider here reduce to four cases: \( \text{duu, dud, uud, and uuu} \). Fig. 1 shows the unit cells of two phases with the duu spin arrangement.

We carried out atomic relaxations for the four spin configurations with P4\textit{1}22 and Imma space groups respectively, using ultrasoft pseudopotential (USPP) plane wave method within spin-polarized DFT as implemented in Quantum ESPRESSO code (version 5.1) [41]. The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [42] was used for the exchange-correlation functional with on-site Coulomb interaction (i.e. GGA+\( U \)) to take into account the strong correlation effect of Fe and Ni 3d states [43]. As in the previous calculations [35, 43], the values of \( U \) and \( J \) for Fe are 4.5 eV and 0.89 eV, and for Ni, different \( U \) values ranged from 2 eV to 6 eV, all with \( J = 1 \) eV, were tested. The USPPs are provided in the code, where the valence electrons are taken as 10, 16, and 6 for Ni, Fe and O atoms [44]. The kinetic energy cutoff for plane-wave expansion was set to be 40 Ry and the \( k \)-points to be \( (5 \times 5 \times 3) \) for the Brillouin zone integration. Marzari-Vanderbilt cold smearing technique [45] with a gaussian spreading factor of 0.02 Ry was applied. We have used tetragonal unit cells containing 4 formula units (28 atoms) with fixed experimental lattice constants \( a = b = 5.89 \text{ Å} \) and \( c = 8.34 \text{ Å} \) [30]. The convergence threshold of forces on ions was set to be \( 1.0 \times 10^{-4} \text{ Ry/Bohr} \).

For all the tested \( U_{\text{Ni}} \) values of 2, 4 and 6 eV, the order of four spin configurations in total energy was always like \( \text{duu} < \text{udu} < \text{udd} < \text{uuu} \) with the almost equal energy difference of 0.2 eV/f.u. between two spin configurations in turn, and this is the same in both P4\textit{1}22 and Imma space groups. Eventually the lowest energy structure was turned out to be duu (or udd) configuration for both P4\textit{1}22 and Imma. It was also found that P4\textit{1}22 phase is \( \sim 0.02 \text{ eV/f.u. lower in energy than Imma phase in each spin configuration and this does not change with the } U_{\text{Ni}} \text{ value.} \)

Our calculations show that the total magnetization varies with change of \( U_{\text{Ni}} \) value; in the case of duu spin configuration, the \( U_{\text{Ni}} \) value that gives the total magnetization of 2 \( \mu_{\text{B}}/\text{f.u.} \) consistent with the experimental value for the bulk NFO [30], was 3.24 eV. Therefore, we will use the \( U_{\text{Ni}} \) value of 3.24 eV for the following calculations and analysis.

In Table I, we show the obtained coordinates of atoms and geometries of oxygen octahedra around B-sites cations for the lowest spin configuration duu phases with both P4\textit{1}22 and Imma space groups. While both distortions and tiltings of octahedra due to Jahn-Teller effect are observed in P4\textit{1}22 phase, only slight tiltings are observed in Imma phase.

**Multiferroicity of bulk NFO**—Here we focus our major interest on the ferroelectricity of NFO because its magnetic property with ferrimagnetic order is well accepted at present [33] as also confirmed in this study. Let us consider the aforementioned crystalline symmetries of two phases of bulk NFO. As shown clearly in Fig. 1, the P4\textit{1}22 phase does not have inversion symmetry but the Imma phase has a space inversion center. Therefore, the P4\textit{1}22 phase is allowed to have a spontaneous polarization, while for the Imma phase the spontaneous polarization could not be expected. In addition, the Imma phase can be a centrosymmetric reference phase for the calculation of spontaneous polarization of the P4\textit{1}22 phase.

What leads to whether or not the presence of inversion symmetry is just B-sites ordering of cations; in the former...
TABLE I: Relaxed atomic coordinates and geometries of oxygen octahedra around B-sites cations for spin configuration duu phases with $P4_122$ and Imma space groups.

|       | $P4_122$                          | Imma                          |
|-------|----------------------------------|-------------------------------|
| FeA   | $4c$ (x,x,3/8) x 0.2480           | $4e$ (0,1/4,z) z 0.1282       |
| FeB   | $4a$ (0,y,0) y 0.7412             | $4b$ (0,0.1/2)                |
| NiB   | $4b$ (1/2,y,0) y 0.7435           | $4c$ (1/4,1/4,1/4)            |
| O1    | $8d$ (x,y,z) x 0.0144             | $8h$ (0,y,z) y 0.0125         |
|       | $y$ 0.7535                        | z 0.7416                      |
|       | $z$ 0.2423                        |                               |
| O2    | $8d$ (x,y,z) x 0.4904             | $8i$ (x,1/4,z) x 0.7640       |
|       | $y$ 0.7526                        | z 0.5028                      |
|       | $z$ 0.2432                        |                               |
| ∠ $O_1$-FeB-O$_2$ (')             | 94.32, 92.05                   | 92.20, 92.17                 |
|       |                                  | 88.50, 85.04                  | 87.80, 87.83                 |
| ∠ $O_1$-NiB-O$_2$                 | 93.33, 91.89                   | 93.64, 93.61                 |
|       |                                  | 88.72, 86.02                  | 86.36, 86.39                 |
| O$_1$-FeB, O$_1$-NiB (Å)          | 2.024, 2.047                   | 2.017, 2.064                 |
| O$_2$-FeB                           | 2.046, 1.997                   | 2.026                        |
| O$_2$-NiB                           | 2.067, 2.029                   | 2.033                        |

According to the modern theory of polarization [46, 47], the spontaneous polarization of $P4_122$ NFO is obtained by calculating the polarization difference between ferroelectric $P4_122$ phase and centrosymmetric Imma reference phase, $\Delta P = P_{FE} - P_{Ref} = \Delta P_{ion} + \Delta P_{el}$. The ionic contribution $P_{ion}$ is calculated by the simple “point charge model”, while the electronic contribution $P_{el}$ by the Berry phase method as already applied to perovskite ferroelectrics by one of the authors [43]. The calculations were carried out on the most stable duu spin configurations. The polarization of $P4_122$ NFO for all kinds of spin configurations were calculated to be zero, i.e., both ionic and electronic contributions to be zero. In $P4_122$ NFO, the ionic contributions to the polarization were also zero, but the electronic contributions were calculated to be $-23.0 \, \mu C/cm^2$ along the $c$ direction with the polarization quantum $\alpha |c|/\Omega = 46.0 \, \mu C/cm^2$ ($|c| = 8.34 \AA$, and $\Omega = 289.33 \AA^3$). This indicates the $P4_122$ NFO to be improper multiferroics (with the ferromagnetic order as discussed below). When comparing with the conventional improper multiferroics, the calculated polarization is remarkably large, but not very surprising as compared to other recently found spin ferroelectrics like Fe$_3$O$_4$, LuFe$_2$O$_4$ and NaLaMnWO$_6$ [20, 22, 26, 28]. We note that the polarization comes from spin down electrons for the case of duu spin configuration, while for the case of uudd spin configuration (another lowest-energy spin configuration with the opposite magnetic moment to the duu configuration) it is from spin up electrons. This feature is very precious for spintronic applications because it gives the way to control the only electrons with a certain spin direction by applying external electric field.

To see an electronic essence behind having large polarization, we resort to the electronic properties of bulk NFO. The plots of density of states (DOS) (Fig. 2) calculated for $P4_122$ NFO with duu spin configuration show the band gaps of 1.88 eV for spin up electrons and 2.30 eV for spin down ones, which are in good agreement with the recent theoretical and experimental values [32]. The atom-projected partial DOS indicates that the 3d states of cations hybridize strongly with the $O 2p$ states for both spin up and down electrons. Moreover, we can see that below Fermi level the NiB 3d electrons play the major role for both spin up and down, while above Fermi level the FeA 3d electrons for spin up and the FeB 3d electrons for spin down play the dominant role.

To illustrate how $P4_122$ NFO has large polarization, we calculated maximally localized Wannier functions (MLWF) of valence bands for spin up and down states in the duu spin configuration, and recalculated the polarization by summing up the displacements of MLWF centers $\Delta \mathbf{r}$ using the following equation,

$$P_{el} = -\frac{e}{\Omega} \sum_m (\Delta r_{m,\uparrow} + \Delta r_{m,\downarrow}),$$

where $m$ runs over MLWF centers (with a charge $-e$ located at $r_m$) in the unit cell with the volume $\Omega$ and arrows denote the spin states. In accordance with the Berry phase calculation, the sum of the displacements of MLWF centers for spin up state was calculated to be zero in all Cartesian directions (i.e., $\sum_m \Delta \alpha_{m,\uparrow} = 0; \alpha = x, y, z$),

![FIG. 2: (color online) Density of states of NiFe$_2$O$_4$ with $P4_122$ space group and duu spin configuration. $E_F$ is set to be zero.](image-url)
The calculated MLWFs pointed towards the importance of the lowest empty $d_{z^2}$ state of spin down channel in conduction bands of Fe$^{3+}$ cation, introducing the hybridization with the $p_z$ state of oxygen. This p-d hybridization leads to breaking of the inversion symmetry driven by the electronic degree of freedom. In order to illustrate how the p-d hybridization breaks the inversion symmetry, we display the MLWFs associated with the 3d states of Fe$^{3+}$ cations in the relaxed $P4_122$ phase and centrosymmetric $Imma$ phase. We note that such properties give rise to the valuable applications for magnetoelectric actuators, spintronics and so on, since they are originated from the same electronic degree of freedom.

In conclusion, we have investigated the ferroelectricity induced by p-d hybridization in ferrimagnetic NiFe$_2$O$_4$ with $P4_122$ space group symmetry by means of GGA+U method. The polarization of 23 $\mu$C/cm$^2$ is considerably large, compared to other improper multiferroics, and the net magnetic moment of 2 $\mu_B$/f.u. is also large. This work sheds light on that the driving force of the large ferroelectric polarization is just the hybridization between the empty 3$d$-states of Fe$^{3+}$ cations on B-sites and the 2$p$-states of the oxygen anions, induced by Jahn-Teller effect, and the magnetic property also comes from the 3$d$ states of cations. We note that such properties give rise to the valuable applications for magnetoelectric actuators, spintronics and so on, since they are originated from the same electronic degree of freedom.

We thank Stefaan Cottenier at the Center for Molecular Modeling (CMM) & Department of Materials Science and Engineering (DMSE), Ghent University, for his careful reading of the manuscript and invaluable comments. This work was supported partially by the Committee of Education, DPR Korea under the project en-
titled “Strong correlation phenomena at superhard, superconducting and nano materials”.

[1] H. Schmidt, J. Phys.:Condens. Matter 20, 434201 (2008).
[2] N. A. Spaldin and M. Fiebig, Science 309, 391 (2005).
[3] S.-W. Cheong and M. Mostvoy, Nature Materials 6, 13 (2007).
[4] R. Ramesh and N. A. Spaldin, Nature Materials 6, 21 (2007).
[5] J. F. Scott, Science 315, 954 (2007).
[6] W. Eerenstein, N. D. Mathur, and J. F. Scott, Nature 442, 759 (2006).
[7] C.-W. Nan, M. I. Bichurin, S. Dong, D. Viehland, and G. Srinivasan, J. Appl. Phys. 103, 031101 (2008).
[8] S. Picozzi and A. Stroppa, Eur. Phys. J. B 85, 240 (2012).
[9] N. A. Benedek and C. J. Fennie, Phys. Rev. Lett. 106, 107204 (2011).
[10] T. Fukushima, S. Picozzi, and U. Gösele, Adv. Mater. 21, 177202 (2009).
[11] B. S. Holinsworth, D. Mazumdar, H. Sims, Q.-C. Sun, M. K. Yurtisig, S. K. Sarker, A. Gupta, W. H. Butler, and J. L. Musfeldt, Appl. Phys. Lett. 103, 082406 (2013).
[12] C. Cheng, J. Magn. Magn. Mater. 34, 144 (2013).
[13] D. Fritsch and C. Ederer, Phys. Rev. B 82, 104117 (2010).
[14] D. Fritsch and C. Ederer, Appl. Phys. Lett. 99, 081916 (2011).
[15] D. Fritsch and C. Ederer, Phys. Rev. B 86, 014406 (2012).
[16] V. G. Ivanov, M. V. Abrashev, M. M. Gospodinov, J. Meen, and M. I. Aroyo, Phys. Rev. B 82, 024104 (2010).
[17] M. N. Iliev, D. Mazumdar, J. X. Ma, A. Gupta, F. Rigato, and J. Fontcuberta, Phys. Rev. B 83, 014108 (2011).
[18] P. Giannozzi et al., J. Phys.:Condens. Matter 21, 395502 (2009).
[19] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[20] A. I. Liechtenstein, V. Anisimov, and J. Zaanen, Phys. Rev. B 52, R5467 (1995).
[21] We used the pseudopotentials Ni.pbe-nd-rrkjus.upf, Fe.pbe-sp-van.upf, and O.pbe-van_\krkjkp.upf from http://www.quantum-espresso.org.
[22] N. Marzari, D. Vanderbilt, A. D. Vita, and M. C. Payne, Phys. Rev. Lett. 82, 3296 (1999).
[23] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B 47, 1651 (1993).
[24] D. Vanderbilt, J. Phys. Chem. Solids 61, 147 (2000).