Origin of ferroelectricity in the multiferroic barium fluorides \( \text{BaMF}_4 \): A first principles study

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We present a first-principles study of the series of multiferroic barium fluorides with the composition \( \text{BaMF}_4 \), where \( M \) is Mn, Fe, Co, or Ni. We discuss trends in the structural, electronic, and magnetic properties, and we show that the ferroelectricity in these systems results from the freezing in of a single unstable polar phonon mode. In contrast to the case of the standard perovskite ferroelectrics, this structural distortion is not accompanied by charge transfer between cations and anions. Thus, the ferroelectric instability in the multiferroic barium fluorides arises solely due to size effects and the special geometrical constraints of the underlying crystal structure.

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I. INTRODUCTION

Magnetoelectric multiferroics are currently attracting much attention. These materials, which exhibit magnetic and dielectric order in the same phase, can give rise to interesting coupling effects between the two ferroic order parameters, with great potential for technological applications. Currently, the main research effort in multiferroics is directed toward Bi-containing perovskites such as \( \text{BiFeO}_3 \) or \( \text{BiMnO}_3 \) and toward both hexagonal and orthorhombic rare-earth manganites such as \( \text{HoMnO}_3 \) and \( \text{TbMnO}_3 \). In the present paper we reconsider another class of magnetic ferroelectrics: the barium fluorides \( \text{BaMF}_4 \), where \( M \) is Mn, Fe, Co, or Ni. This series of compounds attracted considerable interest from the late 1960s until the early 1980s (see Refs. 8 and references therein) but so far has not received much attention during the recent revival of multiferroic materials. We hope that our work will inspire further research in this interesting class of multiferroic materials, with the goal of exploring a broader range of non-oxide-based materials as candidates for magnetoelectric device applications.

The barium fluorides \( \text{BaMF}_4 \), \( M = \) Mn, Fe, Co, Ni, Zn, and Mg, form an isostuctural family of compounds with the polar space group \( \text{Cmc}_2_1 \) (Refs. 9 and 10). The corresponding crystal structure is shown in Fig. 1(a). In this base-centered orthorhombic structure the transition-metal cations are octahedrally surrounded by fluorine anions. Four of the six corners of the fluorine octahedra are shared with adjacent octahedra to form puckered sheets perpendicular to the orthorhombic \( b \) axis. These sheets of octahedra are separated by similar sheets of \( \text{Ba}^2+ \) cations. The structure is polar along the \( c \) direction, and ferroelectric switching has been demonstrated for \( M = \) Co, Ni, Zn, and Mg, but not for \( M = \) Mn and Fe. The dielectric constants \( \varepsilon_r \) show an increase with temperature that is characteristic for a ferroelectric phase transition, but all crystals melt before a transition into the paraelectric phase occurs. The melting temperatures range between 720 and 965 °C; the Curie-Weiss temperatures can be extrapolated from the temperature dependence of the dielectric constants and range between 810 and 1320 °C. In \( \text{BaMnF}_4 \) an additional structural phase transition occurs at \( \approx 255 \) K. The resulting low-temperature structure is incommensurate along the \( c \) axis. To facilitate a systematic comparison between the different \( \text{BaMF}_4 \) systems we do not consider this low-temperature structure of \( \text{BaMnF}_4 \) in the present study and instead use perfect \( \text{Cmc}_2_1 \) symmetry for all systems.

In addition to the polar distortion, the systems with \( M = \) Mn, Fe, Co, and Ni exhibit antiferromagnetic ordering below \( T_N = 20–80 \) K. These materials therefore exhibit multiferroic behavior, which is the motivation for the present investigation.

Here we present a comprehensive computational study of the structural, electronic, magnetic, and ferroelectric properties of \( \text{BaMF}_4 \), with \( M = \) Mn, Fe, Co, and Ni, using first-principles electronic structure calculations. The goal is to elucidate the origin of ferroelectricity in these materials, and to understand trends, such as why the systems with \( M = \) Mn and Fe do not exhibit ferroelectric switching. The origin of ferroelectricity is of fundamental interest, since \( \text{BaMF}_4 \) does not contain any ions that are usually considered to be “ferroelectrically active,” such as empty \( d \)-shell cations or lone-pair-active cations (e.g., \( \text{Bi}^{3+} \), \( \text{Pb}^{2+} \)). We show that the ferroelectricity in these systems is due to the softening of a single polar phonon mode, which involves both rotational motions of the fluorine octahedra and polar displacements of the \( \text{Ba}^2+ \) cations. The instability is caused solely by size effects and geometrical constraints; no charge transfer between anions and cations occurs as a result of the structural distortion. The \( \text{BaMF}_4 \) multiferroics therefore represent an example of proper “geometric ferroelectricity,” a mechanism that has
been proposed as a possible way to incorporate both magnetism and ferroelectricity in the same system.\footnote{16,17} Furthermore, our work represents an \textit{ab initio} study of a nonoxide multiferroic system, and we provide evidence that the local spin-density approximation (LSDA)\textit{+U} method results in a good description of the electronic structure of these materials.

This paper is organized as follows. We first describe the methods we use in our calculations, together with some technical details. We then present the results of our calculations for the structural, electronic, and magnetic properties of all systems. Finally, we focus on the ferroelectric properties and analyze the mechanism underlying the polar structural distortions in these systems. We end with a discussion and summary.

II. COMPUTATIONAL METHOD

All calculations in this work are performed using the projector augmented-wave method,\footnote{18} implemented in the Vienna \textit{ab initio} simulation package (VASP).\footnote{19,20} For the treatment of exchange and correlation we use both the local spin-density approximation\footnote{21} and the LSDA\textit{+U} method in the formulation of Dudarev et al.,\footnote{22} which is equivalent to the standard form of Anisimov et al.,\footnote{23} with the intra-atomic exchange parameter $J$ set to zero (see Ref. 24). For the Hubbard parameter $U_{\text{eff}}=U-J$ of the transition-metal $d$ states we use a typical value of 4 eV, and we test the sensitivity of our results with respect to the precise value of $U_{\text{eff}}$ where necessary (see also Sec. III B).

To obtain structural parameters we relax all ions until the Hellmann-Feynman forces are less than 0.01 eV/Å, and we adjust the lattice vectors such that all components of the stress tensor are smaller than 1 kbar. During the relaxations, except where otherwise noted, we impose the experimentally observed antiferromagnetic order (see Sec. III C), which doubles the size of the unit cell and reduces the space group symmetry to monoclinic. However, no monoclinic distortion has been found experimentally, and in our calculations the corresponding effect, if present, is too small to be resolved unambiguously. We therefore neglect a possible monoclinic distortion and restrict the lattice vectors to the orthorhombic symmetry. For test purposes, we also perform relaxations for different magnetic structures, e.g., ferromagnetic ordering.

To obtain local densities of states we define spheres around the ions with radius 1.0 Å for the $M$ cations and 0.9 Å for the fluorine anions. We use a $4 \times 4 \times 3$ Monkhorst-Pack $k$-point mesh (divisions with respect to the base-centered orthorhombic lattice vectors of the nonmagnetic unit cell) and a Gaussian smearing of 0.1 eV for Brillouin zone integrations. The plane-wave energy cutoff is set to 550 eV for relaxations and to 450 eV for all other calculations. To calculate the spontaneous polarization we use the Berry-phase approach\footnote{25,27} and integrate over eight homogeneously distributed $k$-point strings parallel to the reciprocal $c$ direction, each string containing eight $k$ points. For the calculation of the force-constant matrix we displace all the ions by 0.005 Å, corresponding to symmetry-adopted modes. To exclude eventual nonlinearities in the forces we repeat the calculation with displacements of 0.01 Å, which leads to identical values for the force-constant matrix.

III. RESULTS AND DISCUSSION

A. Structural properties

Table I shows the structural parameters for all systems obtained here by using both LSDA and LSDA\textit{+U} with $U_{\text{eff}}=4$ eV, together with experimental data. The overall agreement between calculated and experimental values is very good. The use of the LSDA leads to a typical underestimation of the lattice parameters between 1 and 4% whereas the internal structural parameters are consistent with the experimental values (especially if one considers that due to the large number of internal degrees of freedom the experimental data also contain a certain error). We point out that the corresponding uncertainties in the atomic positions are significantly smaller than the relevant displacements $d$ resulting from the structural distortion of the centrosymmetric reference structure (see below). The LSDA\textit{+U} method leads to a slightly larger distortion compared to the pure LSDA and therefore improves the agreement with experiment. This is very similar to what has been reported previously for several magnetic oxides.\footnote{4,32,33}

The calculated structural parameters shown in Table I are calculated for the experimentally observed antiferromagnetic order (see Sec. III C). If a different magnetic structure is imposed during the relaxation (results not shown here), we notice small, but distinct, structural changes. For example, LSDA relaxation of $\text{BaNiF}_4$ in a ferromagnetic configuration leads to a 0.8% increase in the lattice parameter $b$ and changes the Wyckoff parameters of those fluorine ions that mediate the magnetic superexchange interactions in the $M$-$F$-$M$ bonds from $(0, -0.483, -0.210)$ to $(0, -0.474, -0.187)$ for $F(1)$, and from $(0, -0.082, -0.002)$ to $(0, -0.075, 0.001)$ for $F(4)$. This indicates a certain degree of spin-lattice coupling in these systems, which can give rise to phenomena such as spin-phonon coupling\footnote{34} and magnetocapacitance.\footnote{35}

We also performed structural relaxations for all systems within the corresponding centrosymmetric prototype structure with space group symmetry $Cmcm$ [see Ref. 28 and Fig. 1(b)], which can be obtained from the ground-state structure by imposing an additional mirror symmetry perpendicular to the $c$ axis. It has been suggested that the $M$-$F(1)$-$M$ distance in this centrosymmetric $Cmcm$ structure is too small to accommodate two $M$-$F$ bonds, causing the structural instability in the $\text{BaMF}_4$ systems.\footnote{36} Here, $F(1)$ is the fluorine anion connecting neighboring octahedra along the $c$ direction. The $M$-$F(1)$-$M$ segment thus “bends” outward in order to increase the $M$-$F(1)$ bond length, leading to the observed collective distortion of the octahedral network. This distortion can be understood as collective alternate rotations of the fluorine octahedra around their respective centers with the rotation axis parallel to the $a$ direction, accompanied by displacements of the $M$ cations parallel to the polar $c$ axis. Table I shows the magnitude of the displacements $d$ of both the $M$-$F$-$M$ bond and the $F(1)$ ions leading from the centrosymmetric reference structure to the polar ground state structure. From

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
System & $a$ (Å) & $b$ (Å) \\
\hline
$\text{BaNiF}_4$ & 5.36 & 9.38 \\
$\text{BaFeF}_4$ & 5.38 & 9.40 \\
$\text{BaCoF}_4$ & 5.40 & 9.42 \\
$\text{BaNiF}_4$ & 5.37 & 9.39 \\
$\text{BaFeF}_4$ & 5.39 & 9.41 \\
$\text{BaCoF}_4$ & 5.41 & 9.43 \\
\hline
\end{tabular}
\caption{Lattice parameters for different systems.}
\end{table}
indeed the use of the LSDA+U method with \( U_{\text{eff}} = 4 \text{ eV} \) together with experimental data. \( a, b, \) and \( c \) are the usual orthorhomic lattice constants, \( V \) is the corresponding volume, and \( d \) represents the atomic displacements compared to the \( Cmcm \) centrosymmetric reference structure. All atomic positions correspond to Wyckoff positions 4\( a: (0, y, z) \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mn</th>
<th>( U_{\text{eff}} = 4 \text{ eV} )</th>
<th>Expt. (Ref. 28)</th>
<th>Fe</th>
<th>( U_{\text{eff}} = 4 \text{ eV} )</th>
<th>Expt. (Ref. 29)</th>
<th>Co</th>
<th>( U_{\text{eff}} = 4 \text{ eV} )</th>
<th>Expt. (Ref. 30)</th>
<th>Ni</th>
<th>( U_{\text{eff}} = 4 \text{ eV} )</th>
<th>Expt. (Ref. 31)</th>
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<td>( a (\text{Å}) )</td>
<td>4.18</td>
<td>4.18</td>
<td>4.22</td>
<td>4.20</td>
<td>4.21</td>
<td>4.24</td>
<td>4.15</td>
<td>4.10</td>
<td>4.21</td>
<td>4.08</td>
<td>4.08</td>
<td>4.14</td>
</tr>
<tr>
<td>( c (\text{Å}) )</td>
<td>5.81</td>
<td>5.85</td>
<td>5.98</td>
<td>5.63</td>
<td>5.59</td>
<td>5.83</td>
<td>5.65</td>
<td>5.78</td>
<td>5.85</td>
<td>5.65</td>
<td>5.67</td>
<td>5.78</td>
</tr>
<tr>
<td>( V (\text{Å}^3) )</td>
<td>354.4</td>
<td>359.5</td>
<td>381.4</td>
<td>338.0</td>
<td>341.4</td>
<td>367.2</td>
<td>328.9</td>
<td>333.4</td>
<td>360.3</td>
<td>319.4</td>
<td>323.0</td>
<td>345.1</td>
</tr>
<tr>
<td>Ba</td>
<td>( y )</td>
<td>0.152</td>
<td>0.154</td>
<td>0.156</td>
<td>0.145</td>
<td>0.148</td>
<td>0.151</td>
<td>0.142</td>
<td>0.143</td>
<td>0.148</td>
<td>0.139</td>
<td>0.141</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>-0.043</td>
<td>-0.047</td>
<td>-0.047</td>
<td>-0.035</td>
<td>-0.034</td>
<td>-0.041</td>
<td>-0.032</td>
<td>-0.040</td>
<td>-0.039</td>
<td>-0.026</td>
<td>-0.031</td>
</tr>
<tr>
<td>Ni</td>
<td>( y )</td>
<td>0.414</td>
<td>0.414</td>
<td>0.416</td>
<td>0.410</td>
<td>0.411</td>
<td>0.414</td>
<td>0.409</td>
<td>0.410</td>
<td>0.413</td>
<td>0.408</td>
<td>0.409</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
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<tr>
<td>F(1)</td>
<td>( y )</td>
<td>-0.464</td>
<td>-0.462</td>
<td>-0.465</td>
<td>-0.471</td>
<td>-0.468</td>
<td>-0.469</td>
<td>-0.477</td>
<td>-0.474</td>
<td>-0.472</td>
<td>-0.483</td>
<td>-0.479</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>-0.158</td>
<td>-0.157</td>
<td>-0.163</td>
<td>-0.171</td>
<td>-0.157</td>
<td>-0.166</td>
<td>-0.191</td>
<td>-0.191</td>
<td>-0.179</td>
<td>-0.210</td>
<td>-0.200</td>
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<tr>
<td>F(2)</td>
<td>( y )</td>
<td>0.298</td>
<td>0.298</td>
<td>0.298</td>
<td>0.299</td>
<td>0.300</td>
<td>0.301</td>
<td>0.300</td>
<td>0.299</td>
<td>0.302</td>
<td>0.302</td>
<td>0.301</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>0.205</td>
<td>0.202</td>
<td>0.196</td>
<td>0.212</td>
<td>0.208</td>
<td>0.198</td>
<td>0.213</td>
<td>0.204</td>
<td>0.198</td>
<td>0.217</td>
<td>0.211</td>
</tr>
<tr>
<td>F(3)</td>
<td>( y )</td>
<td>-0.327</td>
<td>-0.329</td>
<td>-0.336</td>
<td>-0.324</td>
<td>-0.323</td>
<td>-0.331</td>
<td>-0.325</td>
<td>-0.329</td>
<td>-0.334</td>
<td>-0.322</td>
<td>-0.325</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>0.224</td>
<td>0.225</td>
<td>0.225</td>
<td>0.229</td>
<td>0.230</td>
<td>0.223</td>
<td>0.221</td>
<td>0.227</td>
<td>0.227</td>
<td>0.236</td>
<td>0.234</td>
</tr>
<tr>
<td>F(4)</td>
<td>( y )</td>
<td>0.011</td>
<td>0.018</td>
<td>0.016</td>
<td>-0.001</td>
<td>-0.001</td>
<td>0.006</td>
<td>-0.001</td>
<td>0.007</td>
<td>0.011</td>
<td>-0.002</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>0.256</td>
<td>0.276</td>
<td>0.203</td>
<td>0.202</td>
<td>0.190</td>
<td>0.238</td>
<td>0.152</td>
<td>0.181</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>( d (\text{Å}) )</td>
<td>0.751</td>
<td>0.775</td>
<td>0.607</td>
<td>0.695</td>
<td>0.467</td>
<td>0.501</td>
<td>0.329</td>
<td>0.409</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

these displacements it can be seen that the structural distortion increases over the series from \( M = \text{Ni} \) to \( M = \text{Mn} \), which is also consistent with the experimental observations, and has been explained by a decrease in the ratio between the \( M-M \) distance and the minimum \( M-F \) bond length when \( M \) is changed from \( \text{Ni} \) to \( \text{Mn} \).28

**B. Electronic structure**

The calculated total densities of states as well as the partial densities of the fluorine \( p \) and transition-metal \( d \) states for all systems are shown in Fig. 2. For \( M = \text{Mn} \) and \( \text{Ni} \), even the use of the LSDA leads to an insulating solution. In the case of the \( \text{Ni} \) system the gap is small and is due to the crystal field splitting of the localized \( d \) states, whereas in the \( \text{Mn} \) system the gap is larger and is produced mainly by the strong exchange splitting between the two spin channels. The Fe and Co systems are metallic in LSDA, as expected for the \( d^6 \) and \( d^7 \) electron configurations of the \( \text{Fe}^{2+} \) and \( \text{Co}^{2+} \) ions within the predominantly cubic crystal field. The very small band-width of the transition metal \( d \) states indicates an instability towards the formation of a Mott-Hubbard gap, and indeed the use of the LSDA+\( U \) method with \( U_{\text{eff}} = 4 \text{ eV} \) leads to the formation of a large gap of about 2–3 eV for \( M = \text{Fe} \) and \( \text{Co} \), and to a substantial increase in the width of the gap for the \( \text{Mn} \) and \( \text{Ni} \) systems. In all cases the gap is between occupied and unoccupied \( d \) states of the transition metal ion.

These results indicate that the use of the LSDA is inadequate for the \( \text{BaMF}_4 \) systems, whereas the LSDA+\( U \) method with an appropriate \( U \) value leads to a good description of the electronic structure. In this work, except where otherwise noted, we use \( U_{\text{eff}} = 4 \text{ eV} \), which is a typical value for transition-metal cations in oxide materials.36–38 Since the overall features of the transition-metal \( d \) states in the present fluorides are very similar to the oxide case, we expect that the same value of \( U \) is also appropriate for these systems. We point out that a variation of \( U \) within reasonable limits alters the electronic structure only qualitatively. Nevertheless, for quantities that are expected to depend critically on \( U \), we always consider the explicit \( U \) dependence.

It can be seen from Fig. 2 that all transition-metal cations are in a high-spin configuration, where the local majority spin states are fully occupied, and the minority spin states are filled with 0, 1, 2, 3 electrons for \( M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni} \), respectively. In the case of the LSDA, the transition-metal \( d \) states are energetically well separated from the fluorine \( p \) states, leading to only negligible hybridization between the two sets of states. The use of LSDA+\( U \) lowers the energy of the filled transition-metal \( d \) states, leading to energetic overlap of these states with the fluorine \( p \) levels and a certain degree of hybridization, which is most notable for \( M = \text{Ni} \). This increase in hybridization with increasing \( U \) could be an artifact of the LSDA+\( U \) method, which only corrects the transition-metal \( d \) states while leaving the fluorine \( p \) states unchanged.

The densities of states for the centrosymmetric \( Cmcm \) structures (not shown here) are indistinguishable from those...
etc., can lead to the preferred appearance of one or the other is generally assumed that extrinsic effects such as defects, energy difference between these two phases is very small, it

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level shown with negative sign. Zero energy corresponds to the Fermi

FIG. 2. Total densities of states (gray shaded), partial fluorine p (shaded with thin diagonal lines), and transition-metal d (black shaded) states (in states/eV), calculated within the LSDA (left panel) and by using $U_{\text{eff}}=4$ eV (right panel) for all BaMF$_4$ systems ($M=$Mn, Fe, Co, Ni from top to bottom). Minority spin states are shown with negative sign. Zero energy corresponds to the Fermi level (metallic systems) or the highest occupied state (insulating systems).

calculated for the ground-state structures (both in LSDA and LSDA+$U$). This indicates that the structural distortions in these systems do not lead to a significant change in covalent bonding, in contrast to the case of the ferroelectric perovskites, where the structural distortions lead to strong rehybridization between filled anion p and empty cation states.$^{39,40}$ We will further analyze the ferroelectric instability of the BaMF$_4$ systems in Sec. III D.

C. Magnetic properties

The experimentally observed magnetic structure is shown in Fig. 3.$^{31}$ The magnetic M cations form quasi-two-dimensional puckered rectangular grids “parallel” to the a-c planes. Within each rectangular grid the magnetic moments of nearest neighbors are aligned antiparallel to each other. The coupling between adjacent grids effectively cancels, so that the magnetic order along the b direction is determined by the weak coupling between the next-nearest-neighbor planes that are $\sim 14$ Å apart. This can lead to two different magnetic phases, in which the coupling along the b direction is either parallel (phase B) or antiparallel (phase A).

Both phases have been observed for BaCoF$_4$, and since the energy difference between these two phases is very small, it is generally assumed that extrinsic effects such as defects, etc., can lead to the preferred appearance of one or the other phase. In our calculations we consider only phase A where the coupling between second-nearest-neighbor planes along the b direction is antiparallel. In all systems except BaCoF$_4$ the magnetic moments are oriented parallel to the b axis, whereas in BaCoF$_4$ the magnetic moments are oriented parallel to the c axis (in both phases A and B).$^{42}$

The magnetic structure of BaMnF$_4$ exhibits two distinct variations of the structure described in the previous paragraph and shown in Fig. 3: first, the antiferromagnetic axis is rotated by 9° from the b toward the a direction,$^{43}$ and in addition all magnetic moments are slightly canted towards the c direction by about 0.1°, resulting in a very small magnetization.$^{44}$

We do not attempt to reconstruct the full magnetic structure of all BaMF$_4$ systems from first principles, but to check if the LSDA+$U$ treatment of the electron-electron interaction leads to a correct description of the magnetic properties of the multiferroic barium fluorides, we determine the nearest-neighbor magnetic coupling constants for all systems. To do this, we first calculate the energy differences corresponding to different magnetic configurations of the four spins in the unit cell. We then map the calculated energies on a simple Heisenberg model, where we write the magnetic interaction as $E_{ij}=-2J_{ij}s_i\cdot s_j$ ($s_i$ is the spin of cation $i$; $J_{ij}$ is the coupling constant between ions $i$ and $j$) and consider only nearest-neighbor interactions. Within our sign convention a negative $J_{ij}$ corresponds to antiferromagnetic coupling.

Figure 4 shows the calculated Heisenberg coupling constants $J_a$ and $J_c$ corresponding to pairs of nearest-neighbor spins along the a and c directions, respectively, for $M=$Mn, Fe, Co, and Ni. All nearest-neighbor couplings are antiferromagnetic, in agreement with the experimentally observed magnetic structure. The coupling becomes stronger from $M=$Mn–Ni, which is a consequence of the successive filling of the $t_{2g}$ states (see Ref. 45). In addition, the stronger hybrid-
ization between the transition metal $d$ and fluorine $p$ states in the case of the Ni system further increases the strength of the superexchange interaction, leading to particularly strong antiferromagnetic nearest-neighbor coupling in BaNiF$_4$.

For BaMnF$_4$ we obtain the exchange coupling constants $J_a = -0.270$ meV and $J_c = -0.173$ meV (using $U_{\text{eff}}=4$ eV). This compares extremely well with experimental values that have been extracted from the measured spin-wave dispersion: $J_a = -0.282$ meV and $J_c = -0.197$ meV. This very good agreement might be to some extent fortuitous, but can also be regarded as strong indication that the value of $U_{\text{eff}}$ indeed provides a good description of the electronic structure, since the magnetic superexchange coupling depends very strongly on $U$ (see Fig. 5 and the following paragraph).

From the theory of superexchange it follows that the corresponding coupling constant is proportional to $1/U$. One therefore expects a rather strong influence of the Hubbard parameter on the strength of the magnetic coupling, if this coupling is mediated mainly by the superexchange interaction. Indeed, strong $U$ dependence of the magnetic coupling constants has been found for various oxides. Figure 5 shows the variation of $J_a$ and $J_c$ in BaNiF$_4$ with the Hubbard parameter $U_{\text{eff}}$ used in the LSDA+$U$ treatment of the electron-electron interaction. To see the pure electronic effect on the coupling constant, the structural parameters are kept fixed to their values obtained by the LSDA relaxation. It is apparent that the coupling strength significantly decreases with increasing $U_{\text{eff}}$, although the variation does not show an exact $1/U$ dependence. This is due to the fact that a variation of $U$ in the band structure calculation also changes the overlap of the wave functions and therefore the transfer integrals, which are considered as constant in the theory of superexchange.

The values corresponding to the relaxed structural parameters for $U_{\text{eff}}=4$ eV are also shown in Fig. 5. It can be seen that there is only a negligible change of $J_a$, whereas $J_c$ is reduced by 20% due to the slightly different structure. This is due to the fact that the bond lengths and angles for the Ni-F(4)-Ni bond, which determines $J_a$, are nearly identical in LSDA and LSDA+$U$, whereas the Ni-F(1)-Ni bond angle, which determines $J_c$, is reduced from 160.5° (LSDA) to 155.8° ($U_{\text{eff}}=4$ eV). The Ni-F(1) distance increases slightly from 1.94 Å (LSDA) to 1.96 Å ($U_{\text{eff}}=4$ eV).

In addition, if spin-orbit coupling is taken into account, there are small deviations from the collinear antiferromagnetic structure, which are due to the antisymmetric exchange or Dzyaloshinskii-Moriya interaction. This small canting does not influence the structural and ferroelectric properties studied in the present paper, and we therefore neglect all effects due to spin-orbit coupling here.

D. Ferroelectric properties

Figure 6 shows the energy differences per formula unit between the ferroelectric and the centrosymmetric prototype structures, calculated within the LSDA (circles) and by using $U_{\text{eff}}=4$ eV (triangles).

This energy barrier is exactly the energy difference shown in Fig. 6. The values for $M=\text{Ni}$ and $M=\text{Mn}$ are comparable with the corresponding energy differences between ferroelectric and centrosymmetric prototype structures in the perovskite ferroelectrics BaTiO$_3$ ($\approx$18 meV/f.u.) and PbTiO$_3$. 

FIG. 4. (Color online) Heisenberg nearest-neighbor exchange coupling constants $J_a$ (circles) and $J_c$ (triangles).

FIG. 5. (Color online) Heisenberg coupling constants for BaNiF$_4$ as a function of $U_{\text{eff}}$ ($J_a$, circles; $J_c$, triangles). Open symbols correspond to calculations done with structural parameters obtained within the LSDA. Filled symbols correspond to fully relaxed calculations.

FIG. 6. (Color online) Energy differences $\Delta E$ per formula unit between the ferroelectric and the centrosymmetric prototype structures, calculated within the LSDA (circles) and by using $U_{\text{eff}}=4$ eV (triangles).
TABLE II. Spontaneous polarizations (in $\mu$C/cm$^2$) calculated with an ionic model using formal charges and by using the Berry-phase approach ($U_{\text{eff}}=4$ eV), together with available experimental data.

<table>
<thead>
<tr>
<th>$M$</th>
<th>Ionic model</th>
<th>Berry phase</th>
<th>Expt. (Ref. 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>13.68</td>
<td>13.60</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>10.34</td>
<td>10.88</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>8.57</td>
<td>9.02</td>
<td>8.0</td>
</tr>
<tr>
<td>Ni</td>
<td>6.34</td>
<td>6.79</td>
<td>6.7</td>
</tr>
</tbody>
</table>

(=200 meV/f. u.), respectively.\textsuperscript{39} Although it is not likely that ferroelectric switching actually takes place through the centrosymmetric reference structure, this energy difference can be viewed as an upper limit for the switching barrier. It is apparent that a classification of the Co and Ni systems as ferroelectric and the Mn and Fe systems as merely pyroelectric is probably not very instructive, since there is only a gradual quantitative difference between these systems. It seems feasible that ferroelectric switching could be achieved at least for the Fe system if highly resistive samples were available that could sustain higher electric fields.

From the displacements of the ions between the centrosymmetric prototype and the polar ground state structure it is possible to calculate an estimate of the spontaneous polarization using the formal charges of the ions (+2 for the cations and −1 for the fluoride anions). Table II lists the polarization values calculated from such an ionic model together with the corresponding values obtained by \textit{ab initio} calculation using the Berry-phase theory of electric polarization.\textsuperscript{25–27} The good agreement between the Berry-phase result and the ionic model indicates that the Born effective charges\textsuperscript{51} are very close to their formal values for all systems. This is consistent with the lack of significant changes in the electronic densities of states between the centrosymmetric and distorted structures as described in Sec. III B. Thus, no significant charge transfer occurs as a result of the polar distortion. This again indicates that the ferroelectricity in these systems is of different origin than in the prototypical perovskite ferroelectrics where charge transfer between the transition-metal $d$ and the anion $p$ states is crucial for stabilizing the ferroelectric state.\textsuperscript{39}

To obtain further insight into the ferroelectric instability of these systems, we calculate the TO phonon frequencies of the centrosymmetric structure for BaNiF$_4$. Since we are interested only in the phonon modes that are compatible with the observed ground-state symmetry (only these modes can give rise to the corresponding structural distortions), we transform the dynamical matrix to block-diagonal form using symmetry-adapted modes, and diagonalize only the blocks corresponding to the irreducible representations $A_g$ and $B_{1u}$ of space group $Cmcm$. The nonpolar $A_g$ phonons do not change the symmetry of the system, whereas the infrared-active $B_{1u}$ modes reduce the symmetry to the ground-state $Cmc2_1$ space group. There are five $A_g$ and seven $B_{1u}$ modes. The calculated phonon frequencies are listed in Table III. One of the seven $B_{1u}$ modes corresponds to an acoustic mode with zero frequency at the $\Gamma$ point and is not included in Table III.

TABLE III. TO phonon frequencies $\omega$ of $A_g$ and $B_{1u}$ symmetry for BaNiF$_4$. $x$ gives the contribution of the corresponding mode to the ground state distortion.

<table>
<thead>
<tr>
<th>$\omega$ (cm$^{-1}$)</th>
<th>96</th>
<th>168</th>
<th>256</th>
<th>300</th>
<th>502</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$ (%)</td>
<td>7</td>
<td>3</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\omega$ (cm$^{-1}$)</td>
<td>i58</td>
<td>151</td>
<td>212</td>
<td>256</td>
<td>397</td>
</tr>
<tr>
<td>$x$ (%)</td>
<td>87</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

We find that there is one unstable $B_{1u}$ mode with $\omega = i58$ cm$^{-1}$. If we decompose the structural distortion leading from the centrosymmetric reference structure to the relaxed ground-state structure into contributions from the different phonon modes, we see that the unstable $B_{1u}$ mode is responsible for about 87% of the final distortion. This indicates that the ferroelectricity in the barium fluorides originates from the softening of a single polar phonon mode which freezes in to form the ferroelectric ground state of the system. In contrast to the well-known case of perovskite ferroelectrics such as BaTiO$_3$ or PbTiO$_3$ no charge transfer between anions and cations occurs as a result of the displacements, which would lead to anomalous values of the Born effective charges, but instead the structural distortion in the BaMF$_4$ systems is driven purely by size effects, which, together with the special geometric connectivity realized in these compounds, leads to an inversion symmetry breaking and the appearance of a spontaneous electric polarization.

IV. DISCUSSION AND SUMMARY

It is well known that size effects can drive structural distortions. For example, in the perovskite system the relative ionic radii of the $A$ and $B$ cations determine the stability towards tilts of the anion octahedra.\textsuperscript{52}

The idea that ionic polarizability is, in general, not necessary for achieving ferroelectricity was already formulated in Ref. 53, when a ferroelectric ground state was predicted for perovskite-like NaCaF$_3$ on the basis of atomistic simulations using Gordon-Kim pair potentials.\textsuperscript{54} Since the possibility of covalent bond formation is excluded within this method, it became clear that a different mechanism is driving the ferroelectric distortion in NaCaF$_3$. Although the underlying mechanism was not investigated any further, it was assumed that ionic polarizability would significantly enhance the ferroelectricity in NaCaF$_3$. The present study shows that this does not necessarily have to be the case. Ferroelectricity was also predicted recently for a variety of perovskitelike fluorides, such as LiMgF$_3$, LiNiF$_3$, and NaCdF$_3$.\textsuperscript{55,56} It is reasonable to assume that the ferroelectricity in all these fluoride systems is driven purely by size effects and that no charge transfer between anions and cations occurs.

It was pointed out recently that such a mechanism for ferroelectricity is compatible with the simultaneous occurrence of magnetic ordering.\textsuperscript{15} Using first-principles electronic structure calculations, the hexagonal multiferroic YMnO$_3$ was identified as an example for such a scenario. In
this material no charge transfer occurs as a result of the structural distortion, and the dynamical charges are very close to their formal values. This suggests that in YMnO$_3$, similar to the BaMF$_4$ systems discussed in the present paper, ionic polarizability does not have any effect on the ferroelectric properties. A subsequent analysis of the phonon modes of the corresponding centrosymmetric reference structure suggested that YMnO$_3$ is in fact an \textit{improper ferroelectric}, where the ferroelectricity is due to the symmetry-allowed unstable zone-boundary mode.

The present study shows that such geometric ferroelectricity is not restricted to improper ferroelectrics, but that size effects can also directly lead to unstable polar zone-center phonon modes. Thus, BaNiF$_4$, and with it the whole class of BaMF$_4$ multiferroics, represents a confirmed example of a proper geometric ferroelectric.

In summary, we have presented an \textit{ab initio} study of the structural, electronic, and magnetic properties of the multiferroic barium fluorides BaMF$_3$ with $M$=Mn, Fe, Co, and Ni. The ferroelectricity in these systems is due to a single unstable polar zone-center phonon. The instability is triggered solely by size effects, and no charge transfer occurs as a result of the structural distortion. In addition, we have shown that the LSDA+U method results in a good description of the electronic structure of these systems. Thus, our work represents an \textit{ab initio} demonstration of a proper geometric ferroelectric. In addition, we have shown that the LSDA+U method results in a good description of the electronic structure of these nonoxide multiferroics.

**ACKNOWLEDGMENTS**

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