First-principles study of the iron pnictide superconductor BaFe$_2$As$_2$

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This paper presents our study on the atomic, electronic, magnetic structures, and phonon modes of the low-temperature orthorhombic phase of undoped BaFe$_2$As$_2$ crystal. The electronic structure is characterized by a sharp Fe-$3d$ peak close to the Fermi level and is dominated by Fe-$3d$- and As-$4p$-hybridized states. Ba contribution occurs only at lower energies. The spin ordering of the magnetic ground state, which is determined by minimizing the total energy of different spin alignments on Fe atoms in the conventional cell, is in agreement with experimental findings but is different from the antiferromagnetic spin ordering obtained by assigning antiparallel spin directions on two Fe atoms in the primitive unit cell. Valuable information about the charge transfer and bonding is revealed through the analysis of the charge density. Electrons are transferred from Ba to Fe-As layers and also from Fe to As atoms. The magnetic phonon calculations of the ground state are carried out to predict Raman and infrared-active modes. Softening of some calculated spin-dependent phonon modes corroborates the contribution of spin-lattice coupling to the structural phase transition from $I4/mmm$ to $Fmmm$. DOI: 10.1103/PhysRevB.79.184523 PACS number(s): 74.25.Jb, 74.25.Kc, 74.25.Ha, 74.70.--b

I. INTRODUCTION

The superconductor phase occurring at the transition temperature $T_c$ as high as 55 K has initiated active research on iron-oxypnictide compounds.$^1$ BaFe$_2$As$_2$ has been found to be superconductor up to 38 K upon hole doping by the substitution of potassium for barium.$^2$ On the other hand, recent experiments predict that BaFe$_2$As$_2$ without doping has been made superconducting under high pressure by about 2–6 GPa.$^3$ In an effort to understand the mechanism of this superconducting state the atomic structure of parent (undoped) BaFe$_2$As$_2$ compound has been investigated experimentally by Rotter et al.$^4$ It has been found that undoped BaFe$_2$As$_2$ undergoes a structural phase transition at $-140$ K from tetragonal $I4/mmm$ symmetry to orthorhombic $Fmmm$ symmetry. The structural phase transition, which is confirmed also by a sharp peak observed in the variation in specific heat,$^5$ has been shown to strongly affect the electronic and magnetic properties of the crystal.$^6$ For example, the anomaly in resistivity is related to the structural phase transition.

The magnetic susceptibility of BaFe$_2$As$_2$ exhibits an antiferromagnetic (AFM) spin ordering at $\sim140$ K. The antiferromagnetic ordering has been investigated by neutron powder diffraction$^{4,7,8}$ and neutron-scattering$^9$ experiments on BaFe$_2$As$_2$. Huang et al.$^7$ have also observed a three-dimensional long-range AFM ordering occurring below $T \sim100$ K. It appears that the antiferromagnetism is destroyed upon doping and the metallic state changes into superconducting state. The metallic properties of undoped BaFe$_2$As$_2$ have been revealed at the high plasma frequencies, $\omega_p \geq 1.5$ eV.$^{10}$ Based on density-functional calculation, Yildirim$^{11}$ predicted that there is a strong interplay between structural and magnetic properties of Fe-pnictide system where the $c$ axis collapses with the loss of Fe magnetism. In contrast to cuprate superconductors (where localized electrons due to the large Coulomb repulsion give rise to the antiferromagnetic state) the metallicity of BaFe$_2$As$_2$ suggests relatively weaker $U$ and hence spin-density wave rather than localized AFM order.

In this paper we investigate atomic, electronic, magnetic structures, and phonon modes of the low-temperature $Fmmm$ phase of parent-undoped BaFe$_2$As$_2$. For the sake of comparison, we carried out calculations on the tetragonal high-temperature $I4/mmm$ phase. We presented an analysis of charge transfer and bonding between atoms. The ground-state spin ordering determined among six different spin configurations on Fe atoms is antiferromagnetic, but it is ferromagnetic (FM) only along Fe rows in the direction parallel to the shortest vector of orthorhombic lattice. We presented an extensive analysis of electronic structure and charge density. This AFM ground state is metallic with total and orbital projected density of states (DOS) is dominated by Fe-$3d$- and As-$4p$-hybridized states near but below the Fermi level. We found that phonon modes calculated for the AFM ground state at the center of the Brillouin zone (BZ) are compared with those observed experimentally. We believe that our findings are crucial for the understanding of this class of materials.

II. METHOD

Our results are based on the first-principle plane-wave calculations within generalized gradient approximation using Perdew-Burke-Enzerhof. The band theory is applicable for iron pnictides, since the effective $U$ (which is estimated to be less than 0.5) is reduced by hybridization of localized Fe-$3d$ electrons with As-$4p$ electrons. We use ultrasoft pseudopotentials$^{12}$ and plane-wave basis set with kinetic-energy cutoff $\hbar^2|\mathbf{k}+\mathbf{G}|^2/2m=476$ eV. Numerical results have been obtained by using plane-wave self-consistent field (PWSCF) code.$^{13}$ In the self-consistent potential, total energy, and other calculations, the BZ is sampled in the $k$ space within Monkhorst-Pack scheme.$^{14}$ The numbers of these $k$ points...
The magnitude of magnetic moment on each Fe atom is less than \(10^{-3}\) eV/Fe. In addition to full structure optimization, calculations of phonon modes within linear-response theory have been performed with respect to the nonmagnetic state. The predicted AFM state and its spin order of BaFe$_2$As$_2$ in Fmmm are in agreement with the experimental observations. Another magnetic state specified as AFM2 has energy 92 meV/Fe higher than that of AFM3 and has perfect antiferromagnetic spin ordering not only inside the Fe planes but also between adjacent ones. As seen in Fig. 1, the magnetic moments of AFM2, AFM5, and AFM6 spin orderings are, respectively, 2.31, 2.61, and 2.26 \(\mu_B\), which are smaller than that of AFM3. It is important to note that earlier calculations have represented the antiferromagnetic state of the Fmmm phase in the primitive unit cell (see Fig. 1) by assigning opposite spins to two Fe atoms. However, this magnetic state, which is equivalent to AFM2 state is only an excited state and is 92 meV higher in energy relative to the true excited state AFM3 calculated in the conventional cell.

The total energies and optimized structural parameters of the undoped BaFe$_2$As$_2$ in Fmmm symmetry are presented in Table I for different magnetic states. For the sake of completeness, the calculated data of the nonmagnetic high-temperature phase having I4/mmm symmetry are also presented. These structure parameters are in agreement with neutron and x-ray data. The As-Fe-As tetrahedral angle and Fe-As distance are smallest for the NM but largest for the FM state, whereas the nearest As-As distance is largest in the AFM state. It is also seen that the calculated \(c\) of the nonmagnetic state is 0.54 Å smaller than \(c\) measured experimentally for I4/mmm.

### B. Electronic structure

Earlier the electronic band structure of the high-temperature I4/mmm phase of BaFe$_2$As$_2$ with experimental lattice constants has been thoroughly investigated. How-
one can trace the bands of individual Fe$_2$As$_2$ layer in the isolated configuration in BaFe$_2$As$_2$ crystal. The states due to the bands of the individual Ba layer despite their seemingly

we carried out band calculations on BaFe$_2$As$_2$ having $Fmmm$ symmetry. The energy bands corresponding to the NM and AFM2 states are calculated in the primitive cell of the optimized structure shown in Fig. 1. In order to reveal the effects of different atomic layers on the electronic structure, we also calculate the bands of individual Ba and Fe$_2$As$_2$ layers having the same atomic configuration in the optimized primitive cell. In addition to these the band structures of the AFM2 and AFM3 ground states calculated in the conventional cell are indicated in Fig. 1. The orbital-projected state densities and resulting total density of states (TDOS) of the AFM (AFM3) ground state is given to identify the character of bands. Energy bands together with the density of states in Fig. 2 provide a detailed information for the electronic structure of the $Fmmm$ phase.

The energy bands of BaFe$_2$As$_2$ crystal near the Fermi level ($E_F$=0) is dominated by the bands of Fe$_2$As$_2$ layers. In fact, one can trace the bands of individual Fe$_2$As$_2$ layer in the band structure of BaFe$_2$As$_2$. However, this is not the case for the bands of the individual Ba layer despite their seemingly isolated configuration in BaFe$_2$As$_2$ crystal. The states due to Ba atoms are shifted to lower energies due to significant charge transfer from Ba to As atoms as demonstrated by the charge distribution analysis later in this section. The contribution of Ba orbitals to the filled states between $E_F$ and $-5$ eV is rather small, but becomes significant between $-15$ and $-10$ eV. In fact, Ba-4$p$ orbitals give rise to a pronounced peak at approximately $-15$ eV in TDOS. Both structures, namely the NM and the AFM2 states of BaFe$_2$As$_2$ are metallic, but their energy bands are significantly different. Note that the crystal structure, magnetic order, and electronic structure of BaFe$_2$As$_2$ (Ref. 22) and SrFe$_2$As$_2$ (Ref. 23) are affected by pressure. For the NM state, the flat band between $\Gamma$-$Z$ direction of the BZ becomes above Fermi level, if the band structure were calculated using experimental lattice parameters. However, this band occurs below the Fermi level as in Fig. 2(c), since the optimized lattice parameters are used.

The bands of AFM2 presented in the conventional cell as presented in Fig. 2(e) are different from those of the AFM ground state (namely, AFM3) presented in Fig. 2(f). The flat band just below the Fermi level of the AFM3 state in Fig. 2(f) gives rise to a sharp peak in the total density of states close to the Fermi level. However, this peak is sharper in the AFM2 state. The states of this band originate from the strongly localized Fe-3$d_{xz}$ orbitals. Hybridization of Fe-3$d$ orbitals with As-4$p$ orbitals is minute in the states of this particular flat band, but becomes crucial for the states between $-4$ and $-1$ eV. While the contribution of Fe-3$d$ orbitals in the states between $-6$ and $-4$ eV recedes, the contribution of As-4$p$ orbitals increases.

The Fermi surface of BaFe$_2$As$_2$ in the nonmagnetic $I4/mmm$ symmetry consists of two holelike orbitals near the zone center and two electronlike orbitals near X point. This is in agreement with the results of angle-resolved photoemission spectroscopy (ARPES). The Fermi surface of the AFM ground state constructed from the calculated electronic structure consists of four separated sheets at the four edges of the Brillouin zone, which are combined to nonuniform tubes leading to holelike orbitals and a single circular tube along $Z$-$\Gamma$-$Z$ direction leading to electronlike orbitals.

### C. Phonons

The magnetic properties and superconductivity of Fe-pnictide compounds exhibit strong sensitivity to the lattice and hence to the corresponding phonon spectrum. Here we carried out magnetic phonon calculations of BaFe$_2$As$_2$ crystal for the AFM (AFM3) ground state at the $\Gamma$ point of the conventional cell. In these calculations we used the optimized lattice parameters and determined the infrared (IR)

### Table I. Optimized structure parameters of the undoped BaFe$_2$As$_2$ crystal and their total energies calculated for different phases and different magnetic states. The total energies $E_d$ are given relative to the total energy of the NM state calculated for optimized crystal structure. Calculated results for the high-temperature $I4/mmm$ phase in NM state are also given.

<table>
<thead>
<tr>
<th>State</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>Fe-Fe (Å)</th>
<th>Fe-As (Å)</th>
<th>As-As (Å)</th>
<th>Ba-As (Å)</th>
<th>$E_d$ (meV/Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NM</td>
<td>5.696</td>
<td>5.586</td>
<td>12.856</td>
<td>2.84;2.79</td>
<td>2.41;</td>
<td>3.92;</td>
<td>3.74;</td>
<td>3.39;3.403;</td>
</tr>
<tr>
<td>Expt.</td>
<td>5.614</td>
<td>5.574</td>
<td>12.950</td>
<td>2.81;2.79</td>
<td>2.39;</td>
<td>3.91;</td>
<td>3.75;</td>
<td>3.36;3.38;</td>
</tr>
</tbody>
</table>

For the NM state, the flat band occurring below the Fermi level is a holelike orbital. The other bands just above the Fermi level are electronlike orbitals. The band just below the Fermi level is a combination of holelike and electronlike orbitals. The band just above the Fermi level is a single circular tube along $Z$-$\Gamma$-$Z$ direction leading to electronlike orbitals.
and Raman-active (R) modes. Calculations are performed using the density-functional perturbation theory with plane-wave methods as implemented in PWSCF package. Our results are presented in Table II. While Ba atoms contribute to the low-energy part of the calculated spectrum at Γ point, Fe and As atoms contribute to the frequency range 10–37 meV of the spectrum. The Fmmm phase has six Raman-active modes. In this respect, the IR data are crucial, since they can provide reliable information about the atomic structure. The analysis of symmetry and frequency shows that $E_u$ and $E_g$ modes of $I4/mmm$ phase are doubly degenerate for normal phase, but are split under the applied pressure or collapse of $c$ axis. These modes are also nondegenerate in the Fmmm phase.

Using inelastic neutron scattering, Mittal et al. measured the temperature dependence of the phonon density of states of BaFe$_2$As$_2$ and determined the Raman-active modes. They also performed calculations of phonon spectrum for the nonmagnetic state. Our results are in fair agreement with the experimental data on Raman-active modes. We are predicting a phonon peak at 20 meV using spin-polarized calculation, which originates from vibrations of As atoms in Fmmm phase. This mode is observed experimentally at 21.5 meV, but is not predicted by direct method with nonmagnetic calculations. Earlier, phonon-dispersion curves of LaOFeAs have been obtained by Boeri et al. and Singh et al. In addition, Zbiri et al. have obtained Raman-active modes for $Fmmm$ and $I4/mmm$ phases of BaFe$_2$As$_2$ by nonmagnetic calculations using experimental lattice parameters. Present results indicate however that the phonon spectrum of BaFe$_2$As$_2$ cannot properly be described by nonmagnetic phonon calculations which are performed using experimental lattice parameters.

As for IR-active modes, until now there is no theoretical treatment for the antiferromagnetic spin configuration of BaFe$_2$As$_2$ crystal. Experimentally, at the zone center, an IR-active Fe-As out-of-plane vibration mode is observed at $\sim$35 meV. We are predicting this mode at 33.28 meV. Note that our results indicate softening and shift of some modes. As seen in Table II, almost all of Raman and IR frequencies are softened to smaller values when the effect of magnetic order is taken into account in phonon calculations. For example, IR-active $E_g$ modes of Fe in $I4/mmm$ are lowered from 36.45 and 36.79 meV to 34.82 and 32.71 meV in Fmmm. The Fe and As $B_2g$ Raman modes show a giant phonon softening: Raman-active $E_g$ modes of As in $I4/mmm$ are lowered from 18.31 and 19.20 meV to 13.93 and 18.52 meV, respectively. Similarly, Raman-active $E_g$ modes of Fe in $I4/mmm$ are lowered from 32.624 and 37.64 meV to 31.43 and 32.55 meV in Fmmm, respectively. All these results show spin-lattice interaction in the structural phase transition from the high temperature to the low-temperature phase as found earlier by Yildirim for LaOFeAs and by Hou et al. for BaFe$_2$As$_2$.

D. Analysis of charge distribution

The analysis of charge distribution is carried out to reveal valuable information about the character of the bonding and basic features of the structures. In spite of ambiguities in determining the rigorous values, the calculation of charge transfer between atoms or atomic layers may be useful in understanding the system under consideration. Here we present the isosurfaces of total charge density of the AFM ground state in the conventional cell in Fig. 3. In the same figure the counterplots of the total charge are also shown on...
TABLE II. Calculated frequencies of Raman-active (R) and IR-active modes (in meV) of Fmmm and I4/mmm phases at the Γ point and their symmetry analysis. The subscripts u and g represent antisymmetric and symmetric vibrations, respectively. The other subscript i (i = 1, 2, 3) indicates the stretching modes. Modes of the AFM ground state corresponding to AFM3 spin configuration are calculated in the conventional cell with optimized lattice parameters. As for the phonon modes, specified as AFM3 (expt.) and NM (expt.), are calculated by using experimental lattice constant with experimental As coordinate, \( z_{\text{As}} \).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>Fmmm</th>
<th>Phonon modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>4a</td>
<td></td>
<td>( B_{1u} + B_{2u} + B_{3u} )</td>
</tr>
<tr>
<td>Fe</td>
<td>8f</td>
<td></td>
<td>( B_{1g} + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u} )</td>
</tr>
<tr>
<td>As</td>
<td>8i</td>
<td></td>
<td>( A_{i} + B_{1u} + B_{2u} + B_{3u} + B_{2g} + B_{3g} )</td>
</tr>
</tbody>
</table>

\[ \text{Raman} = A_{i} + B_{1g} + 2B_{2g} + 2B_{3g} \]

\[ \text{IR} = 3B_{1u} + 3B_{2u} + 3B_{3u} \]

<table>
<thead>
<tr>
<th>State</th>
<th>IR (meV)</th>
<th>R (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM3 (Expt.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AFM3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>I4/mmm</th>
<th>Phonon modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>2a</td>
<td></td>
<td>( A_{2u} + E_{u} )</td>
</tr>
<tr>
<td>Fe</td>
<td>4d</td>
<td></td>
<td>( B_{1g} + E_{g} + A_{2u} + E_{u} )</td>
</tr>
<tr>
<td>As</td>
<td>4e</td>
<td></td>
<td>( A_{1g} + A_{2u} + E_{g} + E_{u} )</td>
</tr>
</tbody>
</table>

\[ \text{Raman} = 2E_{g} + A_{1g} + B_{1g} \]

\[ \text{IR} = 3A_{2u} + 3E_{u} \]

<table>
<thead>
<tr>
<th>State</th>
<th>IR (meV)</th>
<th>R (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NM (expt.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NM expt.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The specific planes. Isosurfaces of the total charge clearly show the bonds between As atoms in the (100) plane. The counterplots of charge density on the (100) plane quantify these isosurface plots on the faces of orthorhombic cell. However, neither isosurface, nor contour plots calculated on the (100) plane present any evidence for directional (covalent) bonding between Ba and As atoms. Such a bond is also absent between two As atoms below and above the Ba atomic layer. The low value of charge density (0.005 unit) between As atoms above and below Ba atom is actually due to the metallic charge in the Ba layer. In the case of collapse (nonmagnetic) phase of BaFe\(_2\)As\(_2\) crystal the bond between these As ions do not occur due to the interaction between Ba ions and As ions.

The metallic bond between Ba atoms within the Ba layers is revealed only if the isosurface values were lowered. It is, however, clearly seen in the charge density counterplots on the (110) plane. High charge density around Fe ions is due to Fe-3d orbitals. Each Fe atom forms four Fe-As bonds in tetrahedral directions, which are achieved through the hybridization of Fe-3d and As-4p orbitals. Even if one cannot calculate rigorously, the charge transfer from Fe to As atoms (which is estimated to be 0.16 electrons using Bader scheme)\(^{32}\) attributes a minute ionic character to the four Fe-As bonds. Our charge density analysis based on Bader scheme also estimates that 1.24 electrons are transferred from Ba atoms. Considering the charge transferred from Fe and Ba atoms, the excess charge on the As atoms amounts to 0.78 electrons. Moreover, Mulliken\(^{33}\) population analysis indicates that the Mulliken charge of Ba, Fe, and As in BaFe\(_2\)As\(_2\) crystal in the AFM ground state were approximately, +1.20, +0.26, and −0.86, respectively. These values corroborate the charge-transfer values revealed by Bader analysis and both Bader and Mulliken charge analyses demonstrate that electrons are transferred from Ba layer to FeAs layer.

Despite the ambiguities in quantitative determination of the charge transfer between constituent atoms, critical information can be revealed from the calculation of the difference charge density. We first plot the difference charge density obtained by subtracting the charges of Fe-As and Ba layers from the total charge density of the AFM ground state,
phase for the sake of completeness. Among different spin Brillouin zone. While our study is focused on the orthorhombic structures, as well as phonon modes at the center of the theory. Our analysis comprises atomic, electronic, and magnetic structures, as well as phonon modes at the center of the Brillouin zone. Our calculations are essential to distinguish the correct spin configurations we determined the magnetic ground state of the Fmmm phase. The complex spin configuration of this ground state agrees with the experimental results, but differs from that of the antiferromagnetic state achieved by the antiparallel spin alignment on two Fe atoms in the primitive unit cell. We found that the electronic state density of the antiferromagnetic ground state close to the Fermi level is characterized by a sharp peak, which is derived mainly from Fe-3d_{xy} orbitals with a small contribution from the As-4p orbitals. Whereas states originating from Ba orbitals become pronounced at the lower part of the spectrum. The analysis of charge transfer reveals valuable information about charge states and bonding between atoms. The magnetic phonon calculations are essential to distinguish the correct spin configuration. Our analysis of the phonon modes of the AFM ground state at the $\Gamma$ point predicts Raman- and IR-active modes, some of which were softened.

IV. CONCLUSIONS

In conclusion, we presented a theoretical study of the undoped iron-pnictide $\text{BaFe}_2\text{As}_2$ crystal based on first-principles plane-wave calculations within density-functional theory. Our analysis comprises atomic, electronic, and magnetic structures, as well as phonon modes at the center of the Brillouin zone. While our study is focused on the orthorhombic Fmmm phase, we also considered the tetragonal I4/mmm phase for the sake of completeness. Among different spin configurations we determined the magnetic ground state of the Fmmm phase. The complex spin configuration of this ground state agrees with the experimental results, but differs from that of the antiferromagnetic state achieved by the antiparallel spin alignment on two Fe atoms in the primitive unit cell. We found that the electronic state density of the antiferromagnetic ground state close to the Fermi level is characterized by a sharp peak, which is derived mainly from Fe-3d_{xy} orbitals with a small contribution from the As-4p orbitals. Whereas states originating from Ba orbitals become pronounced at the lower part of the spectrum. The analysis of charge transfer reveals valuable information about charge states and bonding between atoms. The magnetic phonon calculations are essential to distinguish the correct spin configuration. Our analysis of the phonon modes of the AFM ground state at the $\Gamma$ point predicts Raman- and IR-active modes, some of which were softened.

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