

**Electronic structure and conductivity of ferroelectric hexaferrite: *Ab initio* calculations**

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$\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  is a promising multiferroic compound in which the electric polarization is intimately connected to the magnetic state. In principle, ferroelectricity might exist above the room temperature, but the electrical conductivity that increases with increasing temperature limits it to temperatures below  $\approx 130$  K. We present results of an *ab initio* electronic structure calculation of the  $(\text{BaSr})\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  system. To improve the description of strongly correlated  $3d$  electrons of iron, the GGA+ $U$  method is used. The results show that the electrical conductivity strongly depends on relative fractions of iron and zinc in the tetrahedral sublattice that belongs to the spinel block of the hexaferrite structure. If this sublattice is fully occupied by zinc, the system is an insulator with a gap of  $\approx 1.5$  eV. If it is occupied equally by Fe and Zn the gap decreases by a factor of 2, and the system is metallic when this sublattice is filled by iron only.

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In a recent paper<sup>1</sup> the discovery of ferroelectricity in a  $Y$ -type hexaferrite  $\text{Ba}_{2-x}\text{Sr}_x\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  ( $x=1.5$ ) was reported. In zero external magnetic field this compound is a nonferroelectric, helimagnetic insulator. When the field is applied it undergoes several magnetic transitions with some of the phases exhibiting ferroelectric order. The electric polarization is conditioned by a noncollinear arrangement of the electron spins, while with collinear spins the ferroelectricity is forbidden by symmetry. The magnetization lies in the plane perpendicular to the hexagonal axis and the in-plane magnetocrystalline anisotropy is very small. Electric polarization  $\vec{P}$  is also confined to the  $ab$  plane and it is perpendicular to the magnetization.  $\vec{P}$  can be thus easily rotated in the  $ab$  plane by an external magnetic field. The magnetic transition temperature is 326 K and the phase that exhibits the ferroelectricity persists up to room temperature. Thus, in principle, the system may possess both magnetism and ferroelectricity above the room temperature. These features promise important applications. The crucial problem is the electrical conductivity that increases with increasing temperature and prevents the ferroelectricity above  $\approx 130$  K.

In this paper we analyze the electronic structure of the system in question as obtained from the *ab initio* electron structure calculation, with special attention paid to electrical conductivity. In particular, we show that the value of the band gap is sensitive to the distribution of Zn atoms in the two tetrahedral sublattices of the hexaferrite. The distribution of atoms between different sublattices of the oxide ferrites may be influenced by a thermal treatment.<sup>2</sup> Our finding may thus open a way of raising the temperature up to which the ferroelectricity exists in  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ .

The crystal structure of the  $Y$ -type hexaferrite  $\text{Ba}_{2-x}\text{Sr}_x\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  (space group  $R\bar{3}m$ ) consists of the spinel ( $S$ ) and  $T$  blocks alternating along the hexagonal axis (Fig. 1). Iron ions completely occupy four octahedral sublattices,  $6c$ ,  $3b$ ,  $18h$ , and  $3a$ , while two tetrahedral sublattices  $6c_T$ ,  $6c_S$  are filled partially by zinc and partially by iron. The fraction  $\gamma$  of Fe in the  $6c_T$  sublattice is equal to the fraction of Zn in the sublattice  $6c_S$ . Experimentally  $\gamma$  was determined by the X-ray single-crystal diffraction to be around 0.7 for  $x$

ranging from 0 to 1.3.<sup>3</sup> On the other hand, from the neutron diffraction measurements on two single crystals with close concentration of Sr  $x=0.748$  and  $0.807$  different values of  $\gamma=0.661$  and  $0.364$  were found, respectively.<sup>4</sup> This indicates that  $\gamma$  may acquire various values, depending on the growth and thermal history of the sample.

For a description of the magnetic structure, it is convenient to divide the unit cell in the  $\mathcal{L}_m$  and  $\mathcal{S}_m$  blocks (Fig. 1). Within these blocks the Fe spins are collinear. The exchange interaction between the blocks is weak and depends on the composition. As a consequence the relative directions of the total spin of the blocks change with the content  $x$  of Sr and with the external magnetic field. For  $x=0$  the system is a collinear ferrimagnet with iron moments in tetrahedral  $6c_T$ ,  $6c_S$ , and in the octahedral  $6c$  sublattices antiparallel to the magnetic moments of the remaining iron. As  $x$  increases, helical magnetism develops which transforms to a commensurate antiferromagnetism as  $x \rightarrow 2$ .<sup>4-6</sup>

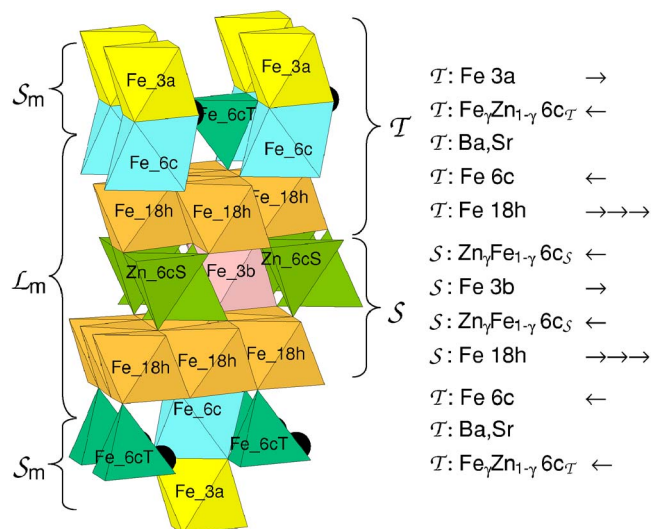


FIG. 1. (Color online) One formula unit of  $\text{Ba}_{2-x}\text{Sr}_x\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  structure. Shown are Fe and Zn polyhedra and the sites of the large cations (black bullets). The arrows indicate direction of spins corresponding to the  $x=0$  collinear ferrimagnetic structure.

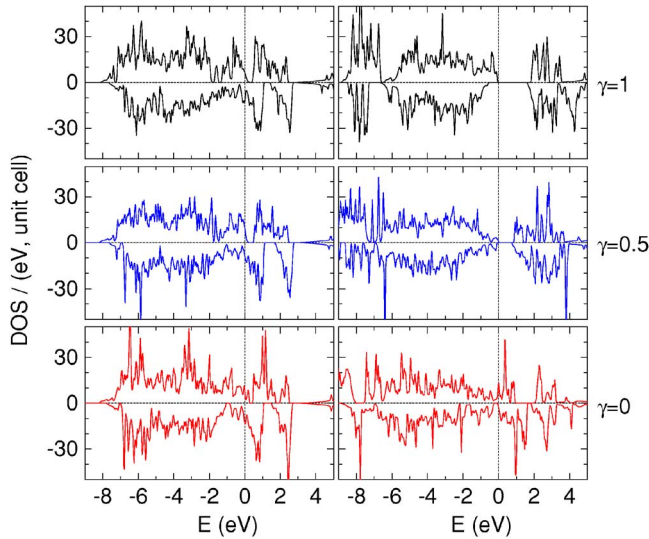


FIG. 2. (Color online) Evolution of the total density for  $\text{Sr}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  of majority spin states (positive) and minority spin states (negative) with  $\gamma$ , for  $U=0$  (left panels) and  $U=6.1$  eV (right panels).

Barium and strontium have a stable valency 2+, their energy levels are far from the Fermi energy  $E_F$  and, as a consequence, these atoms influence the geometry of the crystal lattice, but have little direct effect on magnetic and transport properties. If the disorder in the sublattice of large cations is neglected, the band structure in the vicinity of  $E_F$  should be insensitive to  $x$ . Note, however, that the indirect effect of  $x$  on magnetism is large as it qualitatively modifies the magnetic structure as described above. The calculations of the electronic structure were done for  $x=0, 1$ , and  $2$ , for which values the system retains the periodicity with an unchanged number of atoms in the unit cell.

The electronic structure is more seriously affected by the distribution of Fe and Zn in sublattices  $6c_T, 6c_S$ . All iron ions in the system in question are nominally trivalent, while zinc is divalent. Interchanging  $\text{Fe}^{3+}$  for  $\text{Zn}^{2+}$  changes the Coulomb potential which has direct consequences for the properties of the system. To get qualitative information on how the electronic structure depends on the Zn preference for the  $6c_S$  sublattice, calculations that correspond to limiting cases of the full occupation of  $6c_S$  by zinc ( $\gamma=1$ ), by iron ( $\gamma=0$ ), as well as to the equal zinc and iron concentration ( $\gamma=0.5$ ), were performed. In the last case we assumed that Fe occupies one of the two sites belonging to each of the two tetrahedral sublattices, and Zn occupies the remaining one. The translational symmetry is thus preserved and any effect of the disorder is disregarded.

The calculations for  $x=0$  were performed with the experimental crystal structure parameters,<sup>7</sup> while for  $x=1$  and  $x=2$  the parameters were extrapolated using the data from Ref. 3, since no experimental data were available for these compositions. We have employed the WIEN2k program<sup>8</sup> that is based on the density functional theory (DFT) and uses the full-potential linearized augmented plane wave method with the dual basis set.

All calculations were spin-polarized with the spin direc-

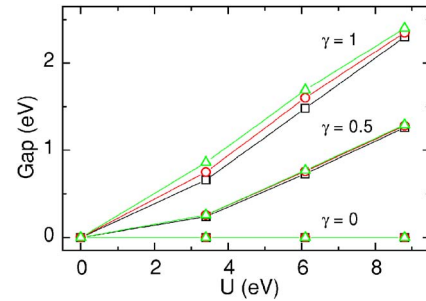


FIG. 3. (Color online) Dependence of the gap on  $U$  for three values of  $\gamma$  and for  $x=0$  ( $\square$ ),  $x=1$  ( $\circ$ ), and  $x=2$  ( $\triangle$ ). For  $\gamma=0$  the gap is zero irrespective of the  $x$  and  $U$  values.

tions corresponding to the  $x=0$  collinear ferrimagnetic structure. The modification of this structure that occurs, when Sr is substituted for Ba, is connected with a change of the weak exchange interaction between iron ions in octahedral  $6c$  and tetrahedral  $6c_T$  sublattices. The gap in the band structure is essentially determined by a strong on-site Coulomb interaction and it should be practically independent of the assumed directions of the  $\mathcal{L}_m$  and  $\mathcal{S}_m$  block's spins.

The number of  $\vec{k}$  points in the irreducible part of the Brillouin zone was 10, the typical number of the basis functions was 2700. For the exchange correlation potential we adopted the GGA form.<sup>9</sup> The radii of the atomic spheres were taken to be 2.4 a.u. for Ba and Sr, 1.86 a.u. for Fe and Zn, and 1.65 a.u. for oxygen.

The electronic structure methods based on local and semilocal approximations to the DFT have problems in describing strongly correlated states. In particular, the splitting in Hubbard subbands is too small or even missing, which often results in an incorrect metallicity of the system. To improve the description of Fe  $3d$  states we thus used the rotationally invariant version of the local density approximation LDA+ $U$  method as described by Liechtenstein *et al.*<sup>10</sup> To simplify the situation in the present calculation we used an effective value of  $U=U(\text{Hubbard})-J$ , where  $J$  is the exchange parameter. As discussed in detail in a recent paper<sup>11</sup> the effective  $U$  parameter for iron in barium hexaferrite is most likely to be slightly larger than 6 eV. The present calculations were performed for  $U=3.4, 6.1$ , and  $8.8$  eV in addition to the GGA ( $U=0$ ) to see how the results evolve when the value of  $U$  is changed. We prefer to use GGA+ $U$ , instead of the more common LDA+ $U$  method because, comparing to LSDA, the GGA yields better equilibrium geometry in the  $3d$  metal oxides. The value of the gap is larger, reflecting the fact that GGA describes the correlation better than LSDA (for comparison of LDA+ $U$  and GGA+ $U$  in the copper oxides see Ref. 12).

We discuss first the results for  $\gamma=1$ , when all tetrahedral sites in the spinel block are filled by Zn. As pointed out above, it is not surprising that the electronic structure calculated with GGA ( $U=0$ ) corresponds to a metal, irrespective of the Sr content  $x$ . The bands intersecting the Fermi energy  $E_F$  have Fe  $3d$  character hybridized with the oxygen  $2p$  states. The total magnetic moment is smaller than its nominal value  $20\mu_B$ , reflecting the metallic character of the system. The orbital potential, introduced by GGA+ $U$  and applied to

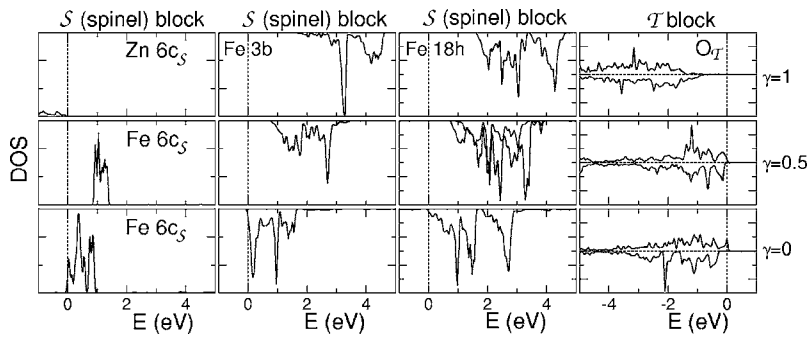


FIG. 4. Density of states projected on the minority spin states of iron ions in the spinel block and on the majority (positive) and minority (negative) spin states of oxygen ions in the  $T$  block for three values of  $\gamma$ .

the  $3d$  states of iron, lowers the energy of the occupied states having the Fe  $3d$  character and increases the energy of the unoccupied ones. As a result, for nonzero  $U$  a gap opens, which depends approximately linearly on the value of  $U$ . The magnetic moment attains its nominal value  $20\mu_B$ , independently of  $U$ . As the energy of the occupied Fe  $3d$  states decreases, the character of the highest occupied states changes from Fe  $3d$  to oxygen  $2p$ .

The change of the electronic structure of the  $\gamma=0.5$  system with  $U$  is similar to that of  $\gamma=1$ , albeit the gap is approximately halved. The situation for the system with all tetrahedral sites in the  $S$  block filled by Fe ( $\gamma=0$ ) is different, however, as in this case the system remains metallic even for the highest value  $U=8.8$  eV used in the present calculation. The evolution of the density of states with  $\gamma$  for  $U=0$  and 6.1 eV is shown in Fig. 2. The dependence of the gap on  $U$  for all cases considered is displayed in Fig. 3.

The dependence of the gap on  $\gamma$  has a simple interpretation. First we note that all iron atoms are nominally trivalent with the half-filled  $3d$  shell (electron configuration  $d^5$ ). The majority spin states of individual ferric atoms correspond to spin parallel to the total magnetization  $\vec{M}$  for Fe in  $18h$ ,  $3b$ , and  $3a$  sublattices and to spins antiparallel to  $\vec{M}$  for Fe on the  $6c$ ,  $6c_T$ , and  $6c_S$  sites. For nonzero  $U$  the majority spin states of Fe are fully occupied and they are situated deep below the Fermi energy. If  $6c_T$  sites are occupied by the iron only ( $\gamma=1$ ) the composition of the spinel block corresponds to the zinc ferrite  $\text{ZnFe}_2\text{O}_4$ , while the  $T$  block is  $\text{Ba}_{1-x}\text{Sr}_x\text{Fe}_4\text{O}_7$ . Neither the  $S$  nor the  $T$  block is electrically charged. As  $\gamma$  decreases, divalent  $\text{Zn}^{2+}$  ions in the spinel block are replaced by  $\text{Fe}^{3+}$  and the spinel block acquires a positive charge. As a consequence the energy of the electron states in the  $S$  block decreases, for the critical value  $\gamma_{crit}$  the energy of the minority spin states of  $\text{Fe}^{3+}$  intersects the Fermi energy and the system becomes metallic. The  $T$  block acquires a negative charge as  $\gamma$  decreases and the energy levels of ions in this block increase. While the levels of Fe from  $T$  block still remain deep below  $E_F$ , the  $2p$  levels of oxygen are pinned to  $E_F$ , for  $\gamma > \gamma_{crit}$  they become partially occupied, and holes appear in the corresponding electron band. The situation is illustrated in Fig. 4, where the density of states projected on the spinel block Fe  $3d$  and  $T$  block oxygen  $2p$  states are displayed for  $U=6.1$  eV and for  $\gamma=0, 0.5$ , and 1.

The value of  $\gamma_{crit}$  deduced from our calculations is  $\approx 0.1$  and, to some extent, it depends on the parameter  $U$ . This

value is thus smaller than  $\gamma$  determined experimentally<sup>4</sup> and the stoichiometric compound is likely to be an insulator. The conductivity observed at elevated temperatures is probably connected with the small amount of ferrous ions<sup>4</sup> induced by nonstoichiometry and defects. To show that even in this situation the gap is important, we note that for  $U=6.1$  eV and  $\gamma=0.5$  (values that are likely to be close to the actual ones) the gap is  $\approx 0.75$  eV. The energy needed to create a charge carrier (either an extra electron represented by an  $\text{Fe}^{2+}$  ion excited to the conduction band or the electron from the valence band excited to unoccupied state of the ferrous ion) will be smaller than  $\approx 0.4$  eV. Moreover, due to the disorder in the (ZnFe) and (BaSr) sublattices, there will be a spread of the defect energy levels that could achieve several tenths of eV. It is then conceivable that some of the defects will yield the charge carriers at temperatures as low as 130 K. Increasing the gap will increase the average energy difference between the defect levels and the band edges and thus it will probably lead to a decrease of the conductivity in the system in question.

We only considered an idealized model in which any disorder connected with the random distribution of Zn and Fe (and also Ba and Sr) was neglected. We believe, however, that the qualitative features of the results will still hold even if the disorder is taken into account. Our prediction is important for the ferroelectricity and it may be tested experimentally by comparing the conductivity of the system with the same Sr content, but subjected to different thermal treatments (quenching the system from different temperatures).

In conclusion the calculation of the electronic structure of the  $\text{Ba}_{2-x}\text{Sr}_x\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  showed that the compound is metallic if the tetrahedral sublattice in the spinel block is fully occupied by iron, while it is insulating if it is occupied by zinc or if the fraction of iron equals the fraction of zinc atoms. As the occupation may be changed by suitable thermal treatment, this represents an experimental challenge and it could lead to an increase of the temperature range in which the ferroelectricity and magnetic state coexist.

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