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Magnetism in the magnetoelectric hexaferrite system $(\mathrm{Ba}_{1-x}\mathrm{Sr}_x)_2\mathrm{Zn}_2\mathrm{Fe}_{12}\mathrm{O}_{22}$

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The hexaferrite system $(\mathrm{Ba}_{1-x}\mathrm{Sr}_x)_2\mathrm{Zn}_2\mathrm{Fe}_{12}\mathrm{O}_{22}$ possesses a rich magnetic phase diagram and for strontium content $x=0.75$ exhibits a magnetoelectricity, the existence of which is intimately connected to the noncollinear arrangement of the iron spins. The system comprises seven cation sublattices, two of which have tetrahedral coordination. The tetrahedral sublattices are partly occupied by Fe and partly by Zn. Using *ab initio*–calculated exchange interactions we show that the magnetism in the $(\mathrm{Ba}_{1-x}\mathrm{Sr}_x)_2\mathrm{Zn}_2\mathrm{Fe}_{12}\mathrm{O}_{22}$ system is sensitive to the Fe and Zn distributions. The region of existence of the noncollinear spin structure and hence of ferroelectricity is determined and found to be rather narrow. The critical temperature of magnetic ordering is calculated using molecular field and random phase approximations. The results are in good agreement with the experiment.

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I. INTRODUCTION

The system $(\mathrm{Ba}_{1-x}\mathrm{Sr}_x)_2\mathrm{Zn}_2\mathrm{Fe}_{12}\mathrm{O}_{22}$ belongs to a large family of Y-type hexagonal ferrites. In the past its magnetism was studied frequently because of possible use in microwave applications[1] and because of the rich magnetic phase diagram.[2–4] Of special interest is the composition with $x=0.75$ as it was found recently that it exhibits a magnetoelectric effect with promising technical applications.[5] Similarly as in the manganites TbMnO_3 and DyMnO_3 the appearance of ferroelectricity in $\mathrm{Ba}_{0.5}\mathrm{Sr}_{1.5}\mathrm{Zn}_2\mathrm{Fe}_{12}\mathrm{O}_{22}$ is conditioned by a noncollinear spiral arrangement of the spins in this compound. In principle, ferroelectricity might exist above the room temperature, but electrical conductivity that increases with increasing temperature limits it to temperatures below ≈ 130 K. In a recent paper[6] we calculated the electronic structure of the $(\mathrm{Ba}_{1-x}\mathrm{Sr}_x)_2\mathrm{Zn}_2\mathrm{Fe}_{12}\mathrm{O}_{22}$ system using the GGA+U method as implemented in the WIEN2k package.[7] The results showed that the band gap and thus also the conductivity depend strongly on the distribution of Zn and Fe inside the two tetrahedral sublattices available for these cations. The goal of the present paper is the *ab initio* calculation of the magnetic interactions in the system with special attention paid to their dependence on the Zn and Fe distribution and on the concentration of Sr. In the following section we describe the crystal and magnetic structures of the $(\mathrm{Ba}_{1-x}\mathrm{Sr}_x)_2\mathrm{Zn}_2\mathrm{Fe}_{12}\mathrm{O}_{22}$ system and compile relevant experimental data. The method of calculating the Heisenberg exchange, the exchange energy between the block of spins, and magnetic transition temperatures is explained in Secs. III–V. The results are presented and discussed in Sec. VII. They clearly demonstrate the importance of Zn and Fe distributions for the magnetism of the system.

II. CRYSTAL AND MAGNETIC STRUCTURE

The crystal structure of the Y-type hexaferrite $(\mathrm{Ba}_{1-x}\mathrm{Sr}_x)_2\mathrm{Zn}_2\mathrm{Fe}_{12}\mathrm{O}_{22}$ (space group $R\bar{3}m$) consists of spinel ($\mathcal{S}$) and hexagonal $\mathcal{T}$ blocks alternating along the hexagonal axis (Fig. 1). Iron ions completely occupy four octahedral sublattices $6c$, $3b$, $18h$, and $3a$, while two tetrahedral sublattices $6c_{\mathcal{T}}$ and $6c_{\mathcal{S}}$ are filled partially by zinc and partially by iron. The fraction γ of Fe in the $6c_{\mathcal{T}}$ sublattice is equal to the fraction of Zn in the sublattice $6c_{\mathcal{S}}$. The experimental data on γ are rather controversial: Sizov *et al.*[8] found $\gamma=0.5$ for $x=0$ that increased to unity for $x=0.8$. On the other hand, the Mössbauer effect study[1] indicated that γ has a decreasing tendency with x: $\gamma=0.62(15)$ and 0.5(15) for $x=0$ and 0.8, respectively. X-ray single-crystal diffraction for $x=0$, 0.3, 0.5, and 0.7 (Ref. 9) yielded γ in the range 0.7–0.8 without any clear dependence on x. Finally Momozawa *et al.* reports $\gamma=0.661$ and 0.364 for two single crystals with close concentrations of Sr of $x=0.748$ and 0.807, respectively.[3] This indicates that γ may acquire various values, depending on

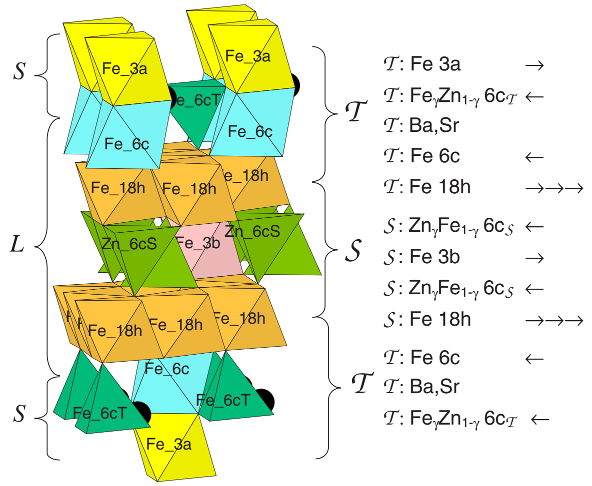

FIG. 1. (Color online) One formula unit of the $(\mathrm{Ba}_{1-x}\mathrm{Sr}_x)_2\mathrm{Zn}_2\mathrm{Fe}_{12}\mathrm{O}_{22}$ structure. Shown are Fe and Zn polyhedra and the sites of the large cations (solid circles). The arrows indicate the direction of spins corresponding to the $x=0$ collinear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

TABLE I. Fe and Zn sublattices in the $(Ba_{1-x}Sr_x)_2Zn_2Fe_{12}O_{22}$ system. n is number of sites per unit cell; spin direction refers to collinear ferrimagnet $Ba_2Zn_2Fe_{12}O_{22}$.

Subl.	Coordination	n	C block	M block	Spin	c_{Fe}
$6c_{\mathcal{T}}$	tetrahedral	6	$\mathcal{T}$	S	down	γ
$6c_{\mathcal{S}}$	tetrahedral	6	$\mathcal{S}$	L	down	$1-\gamma$
$6c$	octahedral	6	$\mathcal{T}$	L	down	1
$3b$	octahedral	3	$\mathcal{S}$	L	up	1
$18h$	octahedral	18	$\mathcal{T,S}$	L	up	1
$3a$	octahedral	3	$\mathcal{T}$	S	up	1

the growth and thermal history of the sample.

For a description of the magnetic structure, it is convenient to divide the unit cell into L (large) and S (small) blocks (Fig. 1). Within these blocks the Fe spins are collinear. The exchange interaction between the blocks is weak and, as a consequence, the relative directions of the total spins of the blocks change with the external magnetic field and with temperature, leading to a rich phase diagram. The spin structure also depends on the content x of Sr: in zero external field the $x=0$ compound is a collinear ferrimagnet with iron moments in tetrahedral $6c_{\mathcal{T}}$ and $6c_{\mathcal{S}}$ and, in the octahedral $6c$ sublattices, antiparallel to the magnetic moments of the remaining iron ions. As x increases, helical magnetism develops, which transforms to a commensurate antiferromagnetism as $x \to 1$.[3] As discussed in Refs. 4 and 10 the exchange between individual Fe(L)-Fe(S) pairs is expected to be relatively strong and it is the sum of the Fe(L)-Fe(S) exchange energies that is small. The weak Fe(L)-Fe(L) and Fe(S)-Fe(S) exchange interactions come then into play and the competition between the Fe(L)-Fe(L), Fe(S)-Fe(S), and Fe(L)-Fe(S) exchange interactions is the source of the spin noncollinearity.[4]

Deriu *et al.*[1] found that the magnetic transition temperature decreases approximately linearly with the Sr content from 370 K for $x=0$ to ~300 K for $x=1$. There is, however, considerable dispersion in values of T_N: for the $Ba_2Zn_2Fe_{12}O_{22}$ different authors give T_N ranging from 367 K to 408 K.[11] As we will show below this may be caused by the variation of γ. We note, however, that the compounds in question are not precisely stoichiometric, containing a slight surplus of Fe at the expense of Zn. T_N of the magnetoelectric compound was found to be 326 K.[5]

In Table I the information on sublattices occupied by Fe and Zn is summarized.

III. *Ab initio* CALCULATION OF THE HEISENBERG EXCHANGE ENERGY

For the exchange interaction between two spins in the isotropic Heisenberg model we take the form

$$e_{12} = J(\vec{S}_1 \cdot \vec{S}_2). \tag{1}$$

The exchange energy per unit cell of the multisublattice magnetic system may be written as a sum of intersublattice exchange energies E_{ij},

$$E = \frac{1}{2}\sum_{i,j=1}^{N} E_{ij}, \tag{2}$$

where N is number of sublattices and

$$E_{ij} = n_i \mathcal{J}_{ij}(\vec{S}_i \cdot \vec{S}_j), \quad \mathcal{J}_{ij} = \sum_k z_{ij}^{(k)} J_{ij}^{(k)}. \tag{3}$$

n_i is number of sites of sublattice i in the unit cell, $z_{ij}^{(k)}$ is number of kth neighbors of spin from sublattice i that belong to sublattice j, and $J_{ij}^{(k)}$ are corresponding exchange integrals ($k=1$ corresponds to the nearest, $k=2$ to the second nearest neighbors, etc.). Note that $\mathcal{J}_{ij}$ is not symmetrical, but it holds that

$$n_i \mathcal{J}_{ij} = n_j \mathcal{J}_{ji}. \tag{4}$$

We now limit ourselves to the collinear spin configurations and assume that the *ab initio* calculations of the total energy of the ground state of the system as well as the excited states in which the spin of single sublattice or two sublattices is flipped with respect to the ground state may be converged. We denote $\mathcal{E}_0$ the total energy of the ground state, $\mathcal{E}_i$ ($\mathcal{E}_{ij}$) the total energy of excited states with the spins of the ith (ith and jth) sublattice flipped. Following the procedure for exchange between the nearest neighbors, as described in Ref. 17 we get

$$\mathcal{J}_{ij} = \frac{\Delta_{ij} - \Delta_i - \Delta_j}{4 S_i S_j n_i \sigma_i^{(0)} \sigma_j^{(0)}}, \tag{5}$$

where

$$\Delta_i = \mathcal{E}_i - \mathcal{E}_0, \quad \Delta_j = \mathcal{E}_j - \mathcal{E}_0, \quad \Delta_{ij} = \mathcal{E}_{ij} - \mathcal{E}_0 \tag{6}$$

and

$$\sigma_i^{(0)} = 1(-1) \tag{7}$$

if the ith spin in the ground state is up (down).

Note that if only the exchange between the nearest neighbors is considered, $\mathcal{J}_{ij}$ reduces to the Heisenberg exchange integral multiplied by the number of nearest neighbors:

$$J_{ij}^{(1)} = \mathcal{J}_{ij}/z_{ij}^{(1)}. \tag{8}$$

The molecular field approximation (MFA) may be formulated in terms of $\mathcal{J}_{ij}$ that are directly accessible by the *ab initio* calculation. This is not true, however, for the random phase approximation (RPA), where the exchange integrals

TABLE II. The nearest-neighbor Fe ions in $Ba_2Zn_2Fe_{12}O_{22}$. z_{ij} is the number of sites belonging to the sublattice j that are neighbors of the site from sublattice i, and r_{ij} is corresponding distance in Å. The data for the next nearest neighbors are also given if r_{ij} is smaller than 4 Å.

	$6c_{\mathcal{T}}$		$6c_{\mathcal{S}}$		$6c$		$3b$		$18h$		$3a$	
	z_{ij}	r_{ij}	z_{ij}	r_{ij}	z_{ij}	r_{ij}	z_{ij}	r_{ij}	z_{ij}	r_{ij}	z_{ij}	r_{ij}
$6c_{\mathcal{T}}$	3	5.03	3	5.86	3	3.35	1	5.41	3	3.40	3	3.87
$6c_{\mathcal{S}}$	3	5.86	3	3.62	1	3.79	3	3.45	6	3.47	1	6.63
									3	3.53		
$6c$	3	3.53	1	3.79	1	5.69	3	5.57	6	3.52	1	2.84
$3b$	2	5.41	6	3.45	6	5.57	6	5.88	6	3.02	6	8.01
$18h$	1	3.40	2	3.47	2	3.52	1	3.022	2	2.88	2	5.61
			4	3.53					2	2.99		
$3a$	6	3.87	2	6.63	2	2.85	6	8.01	12	5.61	6	5.88

must be inserted. When using the RPA we have therefore to make an additional assumption concerning the range of the exchange interaction. Particularly, we assumed that the exchange interactions are of short range. Therefore the exchange energies were ascribed to the nearest-neighbor exchange integrals, though there are a few exceptions. These exceptions are shown in Table II, where the second nearest-neighbor distance is below 4 Å. In these cases the exchange energy was evenly split between all the first and second nearest neighbors.

The procedure described above can be applied to insulators, as the total spin of the system is integer and it does not change during the iteration procedure. For metallic systems the situation is more complex. It often happens that the calculation started from the configuration with the flipped spin converges to a different spin configuration. Even if this is not the case, the change of the electron structure caused by flipping the spin may be so large that the differences of total energy cannot be mapped onto the Heisenberg model.

IV. INTERACTION BETWEEN BLOCKS OF SPINS

To calculate completely the magnetic phase diagram of the $(Ba_{1-x}Sr_x)_2Zn_2Fe_{12}O_{22}$ system would require knowledge of the exchange interaction of the Fe spins that are far apart. To this end a very large supercell would be needed and corresponding calculations are beyond our present computer capabilities. However, the existence of the noncollinear spin structure and thus also the ferroelectricity is conditioned by the weak exchange interaction between the magnetic L and S blocks. In what follows we calculate the energy $E(S,L)$ of flipping the total spin of block S. The reorientation of the total spins of the S and L blocks may only occur if $E(S,L)$ is comparable to the energy of these blocks in a relatively weak external magnetic field where the phase transitions take place ($B_{ext} \leqslant 2$ T).

Summing over the interactions gives for the energy in the ground (nonflipped) state (the quantities $\sigma_i^{(0)}$, and $\sigma_j^{(0)}$ refer to the ground state)

$$E_0(S,L) = \sum_{i \in S} \sum_{j \in L} n_i S_i S_j \sigma_i^{(0)} \sigma_j^{(0)} E_{ij}, \tag{9}$$

while for S spin flipped, the minus sign is obtained. $E(S,L)$ is thus

$$E(S,L) = 2 \sum_{i \in S} \sum_{j \in L} n_i S_i S_j \sigma_i^{(0)} \sigma_j^{(0)} E_{ij}. \tag{10}$$

If the sublattice i is partly occupied by the magnetic atoms and partly by nonmagnetic ones we can, in the spirit of the molecular field approximation, substitute

$$J_{ij} \to c_i J_{ij}, \tag{11}$$

where c_i is the concentration of magnetic atoms in sublattice i. Equation (10) then reads

$$E(S,L) = 2 \sum_{i \in S} \sum_{j \in L} n_i c_i c_j S_i S_j \sigma_i^{(0)} \sigma_j^{(0)} E_{ij}. \tag{12}$$

V. TRANSITION TEMPERATURE

When deriving the transition temperature within the MFA we follow the procedure of Smart,[12] but with $\mathcal{J}_{ij}$ replacing the exchange integrals. The single-spin Hamiltonianan is

$$\hat{h}_i = -\vec{\mu}_i \cdot \vec{H}_i = -g\mu_B \vec{S}_i \cdot \vec{H}_i, \tag{13}$$

where $g = 2.0023$, μ_B the Bohr magneton, and the molecular field $\vec{H}_i$ is given by

$$\vec{H}_i = -\frac{1}{g\mu_B} \sum_j \mathcal{J}_{ij} \langle \vec{S}_j \rangle. \tag{14}$$

The energy spectrum of the spin i is then

$$\varepsilon_{im} = -g\mu_B m H_i, \quad m = -S_i, \ldots, S_i. \tag{15}$$

Let $z \| \vec{H}_i$. The mean value $\langle S_{iz} \rangle$ is

$$\langle S_{iz} \rangle = \frac{\sum_{m=-S_i}^{S_i} m e^{-\varepsilon_{im}/kT}}{\sum_{m=-S_i}^{S_i} e^{-\varepsilon_{im}/kT}}, \tag{16}$$

which can be written using the Brillouin function B_S:

$$\langle S_{iz} \rangle = S_i B_{S_i}(x_i), \quad x_i = g\mu_B H_i / kT. \tag{17}$$

At high temperatures $x_i \ll 1$ and

$$B_S(x) = \frac{1}{3}(S+1)x, \tag{18}$$

i.e.,

$$\langle S_{iz}\rangle = \frac{1}{3kT} S_i(S_i+1) g\mu_B H_i. \tag{19}$$

Inserting there the expression (5) for H_i we get

$$\langle S_{iz}\rangle = -\frac{1}{3kT} S_i(S_i+1)\sum_j \mathcal{J}_{ij}\langle S_{jz}\rangle. \tag{20}$$

Denoting

$$y_i = \langle S_{iz}\rangle, \tag{21}$$

we obtain a system of linear homogeneous equations for y_i:

$$Ty_i + \frac{1}{3kT} S_i(S_i+1)\sum_j \mathcal{J}_{ij} y_j = 0, \tag{22}$$

which has nonzero solution only if the determinant

$$\begin{vmatrix} a_{11}-T & a_{12} & \cdots & a_{1n} \\ \cdots & \cdots & \cdots & \cdots \\ a_{n1} & a_{n2} & \cdots & a_{nn}-T \end{vmatrix} = 0, \tag{23}$$

where (expressing now the exchange integrals in K)

$$a_{ij} = -\frac{1}{3} S_i(S_i+1)\mathcal{J}_{ij}. \tag{24}$$

In many sublattices system (23) has n solutions. The highest positive T_α is the critical temperature. The eigenvector y_α gives a corresponding spin mode which becomes soft at T_α. Calculation of the transition temperatures of many sublattice systems within the RPA is based on the crystal structure and exchange integrals. It was described in detail in Ref. 13.

VI. CALCULATION OF ELECTRON STRUCTURE

The random distribution of Zn and Fe in $6c_T$ and $6c_S$ sublattices, as well as the one of Ba and Sr in the sublattice of large cations, brings a lot of disorder to the $(Ba_{1-x}Sr_x)_2Zn_2Fe_{12}O_{22}$ system. This conflicts with the band structure calculation, which requires translational symmetry. To overcome this problem the disorder is often simulated by distributing the atoms in question over a large supercell. The rhombohedral unit cell of $Ba_2Zn_2Fe_{12}O_{22}$ contains 38 lattice sites, which already makes the calculation demanding, however. For this reason we neglect the disorder and limit our calculations to three Sr concentrations $(x=0,0.5,1)$ and two values of $\gamma=0.5,1$ as the translational symmetry is then maintained with the original unit cell. The same is true for $\gamma=0$; however, in this case the GGA+U calculation results in a metallic state[6] and our way of calculating the exchange cannot be applied.

To calculate the electron structure we have employed the WIEN2k program,[7] which is based on the density functional theory (DFT) and uses the full-potential linearized augmented plane-wave method with the dual-basis set. The number of $\vec{k}$ points in the irreducible part of the Brillouin zone was 10—a typical number of basis functions was 2700. For the exchange correlation potential we adopted the generalized gradient approximation (GGA) form.[15] 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.

To improve the description of Fe $3d$ states we used the rotationally invariant version of the GGA+U method as described by Liechtenstein *et al.*[16] 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[17] the effective U parameter for iron in barium hexaferrite is most likely to be slightly larger than 6 eV so that the present calculations were performed with $U=6.1$ eV.

The calculations for $x=0$ were performed with the experimental crystal structure parameters,[14] while for $x=1/2$ and $x=1$ the parameters were extrapolated using the Ref. 9, since no experimental data were available for these compositions.

VII. RESULTS AND DISCUSSION

In all cases the band structure has a gap and the total magnetic spin moment M (per formula unit) has its nominal value

$$M = 5\mu_B[2\gamma\sigma_{6c_T} + 2(1-\gamma)\sigma_{6c_S} + 2\sigma_{6c} + 6\sigma_{18h} + \sigma_{3a} + \sigma_{3b}], \tag{25}$$

where $\sigma=1$ (-1) if the spin of sublattice in question is up (down).

From Eq. (5) follows that in order to determine any of the exchange energies $\mathcal{J}_{ij}$ the selfconsitent procedure must be converged for three different spin configurations. $\mathcal{J}_{ij}$ calculated from the converged E_{tot} of these configurations are summarized in Table III. As seen from this table, the dependence of $\mathcal{J}_{ij}$ on the strontium content is relatively weak and smooth. The change with γ is more pronounced, but also not dramatic which allows us to expand $\mathcal{J}_{ij}$ in the Taylor series

$$\mathcal{J}_{ij} = \sum_{l=0}^{2}\sum_{m=0}^{1} j_{ij}^{(lm)} x^l \gamma^m, \tag{26}$$

where the coefficients $j_{ij}^{(lm)}$ are determined using Table III. The exchange energy $E(S,L)$ can now be calculated using Eq. (10) for the whole range of x and γ. In Fig. 2 the $E(S,L)$ as a function of x is displayed for several values of γ and compared with the energy of the magnetic L block in an external magnetic field. It can be seen from this figure how fragile the existence of the ferroelectricity in $(Ba_{1-x}Sr_x)_2Zn_2Fe_{12}O_{22}$ system is: to keep the $E(S,L)$ energy comparable to energy of flipping the spin of the block in an external magnetic field, γ is limited to a narrow interval around $\gamma=0.5$ (equal number of Zn and Fe in both tetrahedral sublattices). Moreover, this interval depends on the strontium content.

The critical temperatures may be also calculated using $\mathcal{J}_{ij}(x,\gamma)$ as obtained from Eq. (26). The corresponding de-

TABLE III. Exchange energies $\mathcal{J}_{ij}$ in meV. The energies $\mathcal{J}_{ji}=(n_j/n_i)\mathcal{J}_{ij}$. The only intrasublattice interaction was calculated for Fe(5), as in this case the Fe(5)-Fe(5) distance is short. x is the concentration of Sr, γ is the fraction of Fe in the $6c_T$ sublattice.

	$\gamma=1/2$			$\gamma=1$		
	$x=0$	$x=0.5$	$x=1$	$x=0$	$x=0.5$	$x=1$
$\mathcal{J}_{21}$	0.238	0.227	0.224	-	-	-
$\mathcal{J}_{31}$	10.514	10.914	12.021	8.462	9.372	10.182
$\mathcal{J}_{32}$	1.059	1.245	1.154	-	-	-
$\mathcal{J}_{41}$	0.208	0.308	0.412	0.384	0.416	0.390
$\mathcal{J}_{42}$	31.370	28.478	27.338	-	-	-
$\mathcal{J}_{43}$	−0.140	−0.134	−0.132	0.100	0.016	-0.018
$\mathcal{J}_{51}$	4.364	4.334	4.377	4.222	4.412	4.541
$\mathcal{J}_{52}$	11.752	11.866	12.287	-	-	-
$\mathcal{J}_{53}$	11.650	11.644	11.050	11.829	11.590	11.392
$\mathcal{J}_{54}$	0.499	0.434	0.663	0.701	0.697	0.734
$\mathcal{J}_{55}$	1.154	1.397	1.154	1.154	1.397	1.566
$\mathcal{J}_{61}$	36.984	37.312	37.038	41.620	40.724	40.412
$\mathcal{J}_{62}$	0.352	0.496	0.528	-	-	-
$\mathcal{J}_{63}$	0.376	−0.162	1.044	−0.108	0.026	0.480
$\mathcal{J}_{64}$	−0.095	0.035	0.030	0.041	0.074	0.028
$\mathcal{J}_{65}$	2.610	3.012	3.270	2.100	2.376	2.580

pendence on γ for several values of x is displayed in Fig. 3. In the same figure the experimentally determined critical temperatures are also shown. It is seen that the dependence on the Sr content is weak. As a function of γ the critical temperature exhibits a minimum in both molecular field and random phase approximations. It is known that MFA overestimates and the RPA underestimates the actual critical temperature, and this fact is corroborated by our results. We note that the results obtained for $\gamma \rightarrow 0$ must not be taken too seriously: the Taylor series is linear in γ, the coefficients were obtained using the values of $\mathcal{J}_{ij}$ for $\gamma=1/2$, 1, and we know that for $\gamma \rightarrow 0$ the calculation corresponds to a metallic state.

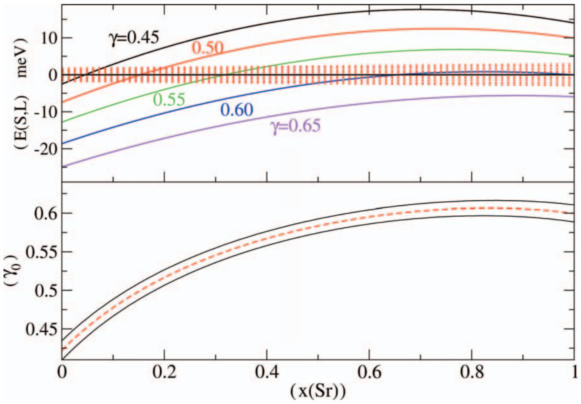

FIG. 2. (Color online) Upper panel: exchange energy $E(S,L)$ between the magnetic S and L blocks as a function of Sr concentration for several values of γ. The hatched area corresponds to the region of L-block energies in an external magnetic field $B_{ext} \leqslant 1$ T and it approximately set bounds for existence of the noncollinear spin structure. Lower panel: dependence of parameter γ_0 on x (dashed curve). γ_0 is the value of γ for which the exchange energy E_{LS} is zero. The solid curves correspond to those γ for which $E_{S,L}$ is equal to the energy of the L block in the field 1 T.

VIII. CONCLUSIONS

There are two important conclusions that follow from our theoretical results.

(i) The ferroelectricity in the hexaferrite in question is a fragile phenomenon as its existence depends on whether or

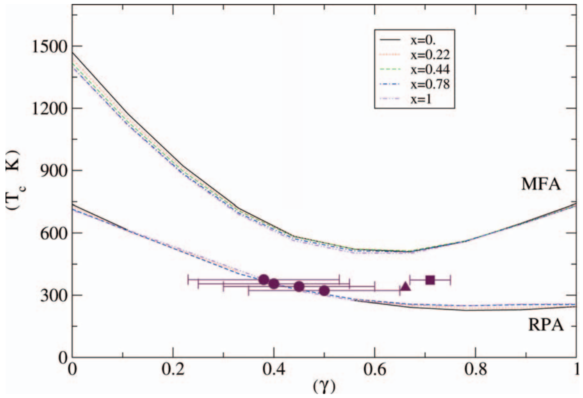

FIG. 3. (Color online) Critical magnetic temperature as a function of γ for several Sr concentrations x calculated using the molecular field approximation (MFA) and random phase approximation (RPA). The experimental data are those of (Ref. 1) (solid circles, $x=0$, 0.25, 0.5, and 0.8), Momozawa and Yamaguchi (Ref. 4) ($x=0.748$, triangle), and Collomb (Ref. 11) (square, $x=0$).

not the parameter γ falls in a narrow interval. Knowledge of γ is rather poor; its control would not be easy and to our knowledge it was never attempted.

(ii) Once control of γ is achieved, the ferroelectricity may be found not only for a single concentration of strontium, but in a much broader class of compounds. Moreover, the desired values of γ lie in the interval $0.44 \lesssim \gamma \lesssim 0.62$ (Fig. 2)—i.e., not far from $\gamma=0.5$, which that corresponds to a random distribution of Fe and Zn. Such a random distribution may be presumably accessed by rapidly quenching the samples from high temperatures.

At present these conclusions are hypotheses only, being based on calculations that are burdened by approximations. Nevertheless, in view of the potential important applications of the compounds in question, we believe that it is worth testing them experimentally.[18]

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