Cation-ordered $A'_{1/2}A''_{1/2}B_2X_4$ magnetic spinels as magnetoelectrics

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Abstract

We show that 1:1 ordering of $A'$ and $A''$ cations in $A'_{1/2}A''_{1/2}B_2X_4$ magnetic spinels results in appearance of magnetoelectric properties. Possible value of magnetically induced electric polarization is calculated using the recently proposed microscopic model, which takes into account spin-dependent electric dipole moments of magnetic ions located in noncentrosymmetric crystallographic positions. We build phenomenological models of magnetic phase transitions in cation-ordered spinels, which describe ferromagnetic and antiferromagnetic ordering patterns of B cation spins, and calculate the respective magnetoelectric responses. We find that magnetoelectric coefficients diverge at ferromagnetic or weak ferromagnetic phase transitions in ordered spinels.

Keywords: magnetoelectric, spinel, atomic ordering, multiferroic

1. Introduction

The search for new magnetoelectric materials has intensified in the last decade due to the discovery of whole new classes of magnetoelectrics and promising technological applications [1]. Multiferroic materials are sought among composite materials consisting of ferroelectric (piezoelectric) and magnetic (piezomagnetic) subsystems, as well as among single phase multiferroics. Single phase magnetoelectrics are usually divided into the so-called type-I and type-II multiferroics [2]. In the type-I magnetoelectrics, or ferroelectromagnets, ferrielectricity and magnetic order occur independently and have different sources. Ferroelectromagnets (the prominent example is BiFeO$_3$ [3]) usually possess high ferroelectric polarization, but the generally large difference between the ferroelectric and magnetic transition temperatures and the different causes of the two orders result in small coupling between them.

In contrast, the type-II magnetoelectrics, in which ferrielectricity occurs as a result of a magnetic phase transition, offer direct coupling between the magnetic and ferroelectric subsystems. Such magnetoelectrics, however, are characterized by much lower transition temperatures (10 – 40 K) and low electric polarization values (usually of the order of 10 – 100 $\mu C/m^2$). The prominent examples of such magnetoelectrics are rare-earth manganites RMnO$_3$ (R=Gd, Tb, and Dy) [4]. Cupric oxide CuO has the highest phase transition temperature (~230 K) among magnetoelectrics discovered to date [5], which is still very low for practical applications. Therefore, the search for new single phase magnetoelectrics with higher phase transition temperatures is of paramount importance.

The spinel class with the general chemical formula $AB_2X_4$, where $X$=O, S, Se, or Te, and A and B are metals, is one of the richest structural classes [6, 7]. Spinels offer very high temperatures of magnetic phase transitions of the order of 1000 K (e.g. 860 K in Fe$_3$O$_4$, 1020 K in $\gamma$-Fe$_2$O$_3$, and 790 K in CoFe$_2$O$_4$ [8]) and allow for great flexibility in both cation and anion substitution [6, 7, 8]. All this makes magnetoelectrics interesting from the point of view of searching for new materials and tailoring their properties.

The spinel compounds are widely used as constituents of multiferroic composites [9], whereas in single phase spinels the magnetoelectric effect (ME) has been found in a limited number of crystals. The ME effect was observed, for example, in CoCr$_2$O$_4$ [10] and ZnCr$_2$Se$_4$ [11]. However, these magnetoelectric spinels are characterized by low magnetic phase transition temperatures (of the order of 20 K) and incommensurately modulated magnetic order of the ferroelectric phase.

In this work we analyze magnetic spinels with the general chemical formula $A'_{1/2}A''_{1/2}B_2X_4$. We show that the chemical ordering of the $A'$ and $A''$ cations results in the appearance of magnetoelectricity in such spinels.

2. Atomic ordering in $A'_{1/2}A''_{1/2}B_2X_4$ spinels

The high symmetry AB$_2$X$_4$ cubic spinel structure is described by the space group Fd3m ($O_h^a$). If more than one sort of cations is present in one of the equivalent sublattices, a tendency generally exists to decrease the internal energy by ordering the cations. Such ordering may possess both short and long range characters, depending on the energy gain and thermodynamic history of the crystal. As a general rule one may state that the higher the difference in valences of inequivalent cations the stronger their tendency to order [6]. The examples of spinels exhibiting atomic ordering in the A sublattice are Li$_{1/2}$Ga$_{1/2}$Cr$_2$O$_4$, Li$_{1/2}$In$_{1/2}$Cr$_2$O$_4$ [12], Cu$_{1/2}$In$_{1/2}$Cr$_2$S$_4$ [13], and Fe$_{1/2}$Cu$_{1/2}$Cr$_2$S$_4$ [14, 15], whereas the atomic ordering in...
the B sublattice may be attained in Zn[LiNb]O₄, Zn[LiSb]O₄, and Fe[Li₁₋₁₂Fe₁₂]O₄ [6].

Various types of cation orderings in spinels (1:1 in the A sublattice, α and β 1:1 ordering in the B sublattice, and others) are considered in [16, 17] and possible orders of the order-disorder phase transitions are established. The atomic ordering results in loss of some symmetry elements, which reduces the cubic symmetry. In this work we focus on 1:1 cation ordering of A cations in A’/A”₁/₁₂B₂X₄ spinels, which results in every A’ cation surrounded by four A” cations and viceversa. Such ordering leads to reduction of the crystal symmetry to F43m (T₄ᵖ) [16] locally if only short range ordering is attained or globally if a long range order is established.

The distribution of atoms over the lattice sites measured by the degree of atomic ordering is an important property of multicomponent crystals. The atomic ordering degree depends on the thermodynamic history of the sample or synthesis conditions and frequently can be varied to a large extent. Among such crystals are ordering alloys and multiatomic compounds such as oxides and halogenides. If such crystals undergo structural transitions and the corresponding susceptibilities [23].

The 1:1 cation ordering in the A sublattice of A’/A”₁/₁₂B₂X₄ spinels is described by the order parameter s transforming according to the irreducible representation (IR) GM₃ which results in every A’ cation surrounded by four A” cations and viceversa. Such ordering leads to reduction of the crystal symmetry to F43m (T₄ᵖ) [16] locally if only short range ordering is attained or globally if a long range order is established.

When interpreting the influence of atomic ordering on properties of crystals one usually proceeds with the assumption that the degree of atomic ordering s makes quantitative contribution to the thermodynamic potential [21]. Within the framework of phenomenological theory this approach reduces to the introduction of the dependence on s of the coefficients in the thermodynamic potential expansion with respect to the relevant order parameters [22]. However, it was shown that the influence of atomic ordering can be much more substantial [23,24]. Namely, at s ≠ 0 additional contributions to the thermodynamical potential may arise, which are forbidden by symmetry in the disordered case s = 0. These contributions manifest themselves especially strong when they include degrees of freedom, which are described by macroscopic tensors. This results in formation of corresponding macroscopic fields during the phase transitions and divergencies in the corresponding susceptibilities [23].

The 1:1 cation ordering in the A sublattice of A’/A”₁/₁₂B₂X₄ spinels is described by the order parameter s transforming according to the irreducible representation (IR) GM₃ of the space group Fd3m. Denoting by Nᵥ and Nᵥ’ the number of atoms A’ and A”, respectively, in one of the sublattices appearing upon atomic ordering, we can define the atomic ordering degree as

\[ s = \frac{Nᵥ - Nᵥ’}{Nᵥ + Nᵥ’}. \]

Thus, s varies from zero for completely disordered crystal to ±1 for completely ordered one. Nonzero s results in disappearance of center of inversion and lowering of the crystal symmetry to F43m. The emergence of noncentrosymmetric structure upon 1:1 cation ordering in A’₁/₁₂A”₁/₁₂B₂X₄ spinels is to be contrasted with 1:1 cation ordering in A’₁/₁₂A”₁/₁₂BO₃ or A’B”₁/₁₂O₂ perovskites, where such ordering results in centrosymmetric crystal lattice.

3. Magnetic phase transitions in spinels and atomic ordering

Spinels exhibit a variety of magnetic structures including ferromagnetic (e.g. CuCrZnS₄ [25]), ferrimagnetic (e.g. FeCr₂S₄ [26]), antiferromagnetic (e.g. MgV₂O₄ [27]) and incommensurate (e.g. CoCr₂O₄ [10]), which is explained by the fact that both the A and B sublattices can incorporate magnetic ions. The B ions also form the so-called pyrochlore lattice, which is known to give rise to very strong geometrical frustration effects [28].

Detailed representation analysis of possible magnetic structures in spinels is given in [29]. Most of the magnetic structures observed in spinels, especially those appearing at high temperatures, are described by the wave vector k = 0, i.e. the magnetic unit cell coincides with the crystal cell [30]. Incommensurate magnetic structures are found in some spinels at temperatures below 20 – 50 K and some of them are also shown to be ferroelectric (e.g. CoCr₂O₄ [10] and ZnCr₂S₄ [11]). Therefore, despite the fact that spinels exhibit high temperature magnetic properties, ME effect in spinels is observed only at rather low temperatures. Here we show that chemical substitution in the A sublattice of spinels with sufficient degree of cationic ordering results in high temperature magnetically ordered phases becoming magnetoelectric.

The magnetic representation for the A and B positions in ABₓX₄ for k = 0 is given by [29]

\[ d_M = GM^{+} \otimes GM^{-}, \]
\[ d_M' = GM^{+} \otimes GM^{+} \otimes GM^{+} \otimes GM^{+}, \]
respectively. The basis functions for IRs entering into the magnetic representations dₘ and dₘ’ are given in [29]. It has to be noted, that since the spinel structure possesses spatial inversion I a magnetic structure described by a single IR with \( \vec{k} = 0 \) cannot induce electric polarization [31]. This is explained by the following. The symmetry of the paramagnetic phase is G ⊗ R, where G is the space group and R is time inversion. When \( \vec{k} = 0 \), for any of the IR’s of G ⊗ R a unit matrix corresponds to either I or IR. Therefore, upon a phase transition according to this IR one of these symmetry elements preserves in the ordered phase, but non of them allows non-zero electric polarization.

However, a magnetic phase transition with respect to IR GM⁻¹, which corresponds to appearance of a simple collinear antiferromagnetic ordering of spins of A cations, results in appearance of a linear ME effect. Denoting the antiferromagnetic ordering of A cation spins by (Lₓ, Lᵧ, Lẑ) the magnetoelectric interaction can be written in the form

\[ Lₓ(MₓPₓ + MᵧPᵧ) + Lᵧ(MₓPₓ + MᵧPᵧ) + Lẑ(MₓPₓ + MᵧPᵧ), \]
where $\vec{M}$ and $\vec{P}$ are magnetic moment and electric polarization, respectively. (Here and in the following we define the orthogonal $x$, $y$, and $z$ axes along the cubic edges.) Therefore, the magnetic structures with antiferromagnetically ordered spins of A cations possess linear ME effect. Such magnetic structures appear, for example, in MnAl$_2$O$_4$ below $T_N = 42$ K [32], Co$_3$O$_4$ below $T_N = 40$ K [33], and CoRh$_2$O$_4$ below $T_N = 25$ K [34]. The linear ME effect in A-site antiferromagnetic spinels has to be demonstrated experimentally yet.

The A-site antiferromagnetic structures in spinels, however, are rarely observed and occur at rather low temperatures. The magnetic phase transitions in spinels, and especially those taking place at high temperatures, more often occur with respect to IRs even under space inversion and entering into $d_M^b$. The resulting magnetic structures neither induce electric polarization nor allow ME effect, since they do not break inversion symmetry. However, cation substitution spinels $A'_1/2 A''_{1/2} B_2 X_4$ with partial or full ordering of $A'$ and $A''$ cations will possess magneto-electric properties.

The $\vec{k} = 0$ magnetic structures in spinels are most often described by IRs GM$^{4+}$ or GM$^{5+}$. The latter describes antiferromagnetic ordering of B cations. IR GM$^{4+}$ enters into both $d_M^a$ and $d_M^b$ and can induce ferromagnetic, ferrimagnetic or weak ferromagnetic structures, which, besides other causes, depends on whether both the A and B ions are magnetic or not. We denote by $(f_x, f_y, f_z)$ and $(g_x, g_y, g_z)$ the magnetic order parameters transforming according to GM$^{4+}$ and describing ferromagnetic and antiferromagnetic ordering of B cations, respectively, whereas by $(a_1, a_2, a_3)$ the antiferromagnetic order parameter that transforms according to GM$^{5+}$. The following ME interactions in spinels can be obtained

\[
s(P_x f_x + P_y f_x + P_z f_x), \tag{2}
\]
\[
s(P_y f_y + P_y f_y + P_z f_y), \tag{3}
\]
\[
s(P_y f_y + P_z f_y + P_z f_y) + P_z (g_x f_y + g_y f_y) + P_z (g_x f_y + g_y f_y), \tag{4}
\]
\[
s(P_x a_1 a_1 + P_y a_1 a_2 + P_y a_1 a_3), \tag{5}
\]
\[
s(P_x a_2 a_2 + a_3 a_3) + P_x (a_1 a_2 - a_1 a_2) + P_x (a_1 a_3 - a_2 a_3), \tag{6}
\]
\[
s(P_x a_1 f_y + a_3 f_y) + P_y (a_2 f_y - a_1 f_y) + P_z (a_3 f_y - a_2 f_y). \tag{7}
\]

It follows from (2) - (7) that nonzero A cation ordering ($s \neq 0$) in $A'_1/2 A''_{1/2} B_2 X_4$ spinels results in the fact that the in the thermodynamic potential. The ME coefficients are, thus, directly proportional to the degree of A ordering $s$.

4. Magneto-electric coupling

A microscopic model of ME interactions based on local noncentrosymmetric surroundings of magnetic ions was recently suggested [35]. In current work we use this model to estimate the ME coefficients in cation-ordered spinels. In cation-disordered spinels with the cubic Fd$\bar{3}$m structure the A cations are located in noncentrosymmetric tetragonal positions (8a) with local symmetry $T_d$, whereas the B cations are in positions (16d) with centrosymmetric rhombohedral symmetry $D_{3d}$. Therefore, according to the microscopic model [35] the A cations and the oxygen ions, whose surrounding is polar with symmetry $C_{3v}$, can contribute to the ME effect in spinels with the symmetry Fd$3m$.

The ordering of A cations in $A'_1/2 A''_{1/2} B_2 X_4$ spinels results in disappearance of the inversion symmetry operation and lowering of the crystal lattice symmetry to F43m. In the tetrahedral structure the atoms $A'$, $A''$, B, and X are located in positions (4a), (4d), (16e), and (16e), respectively, as shown in Fig. 1(b). Therefore, local symmetry around the B cations becomes polar $C_3$, and the local electric dipole moments of these ions can contribute to the ME effect.

The primitive unit cell of the tetrahedral structure F43m contains four B cations $B_i$ ($i = 1, 2, 3, 4$) located in positions $(x, x, x), (1 - x, 1 - x), (1 - x, 1 - x)$, and $(1 - x, 1 - x)$, respectively. Their respective electric dipole moments $\vec{d}_{0i}$ induced by local polar surroundings are equal in size and directed parallel to [111], [111], [111], and [111], respectively, as shown in Fig. 1(a). This ensures absence of macroscopic electric polarization ($\sum_i \vec{d}_{0i} = 0$).

According to the microscopic model of ME interactions suggested earlier [35], the spins $\vec{S}_i$ of the cations $B_i$ modify the electric dipole moments $\vec{d}_{0i}$ due to spin-orbit interaction as schematically shown in Fig. 1(b). This results in spin-dependent electric dipole moments $\vec{d}_i$ of the cations $B_i$, which may lead to nonzero macroscopic electric polarization $\vec{P}$ for certain spin configurations if $\sum_i \vec{d}_i \neq 0$.

In order to build the microscopic model we closely follow the scheme developed in [35]. In the cubic Fd$3m$ structure the B cations are located in trigonally distorted oxygen octahedra. The local $D_{3d}$ symmetry splits the triply degenerate low lying $\delta_2$ electron states into one $a_{1g}$ orbital and two degenerate $e'_{g}$ states. Therefore, for simplicity, as a zeroth order perturbation...
where \( |0\rangle = |a_{1g}\rangle \), \( H_0 \) is the Hamiltonian including the crystal field of \( D_{3h} \) symmetry and \( E_d \) is the \( a_{1g} \) energy level. In order to obtain spin-dependent electric dipole moments, we consider a single cation \( B_1 \), whereas the dipole moments of the remaining \( B \) cations can be obtained from \( B_1 \) by crystal symmetry operations. The \( A \)-site cation ordering reduces the crystal field symmetry around the \( B \) cations to \( C_{3v} \), which is treated perturbatively. Compared to the \( D_{3h} \) symmetry the \( C_{3v} \) polar distortion gives additional contribution to the crystal field

\[
V_{CF} = s c Z, \tag{8}
\]

where \( c \) is coefficient and \( s \) is included in order to reflect the fact that only \( s \neq 0 \) results \( V_{CF} \neq 0 \). In (8), we consider only the lowest powers in crystal field coordinate expansion around the \( B \) cation. Here and in the following we define the orthogonal axes

\[
X = \frac{1}{\sqrt{2}} (x - y),
\]

\[
Y = \frac{1}{\sqrt{6}} (x + y - 2z),
\]

\[
Z = \frac{1}{\sqrt{3}} (x + y + z).
\]

The spin-orbit coupling is given by

\[
V_{SO} = -\lambda (\vec{L} \cdot \vec{S}),
\]

where \( \vec{L} \) is the angular momentum operator, \( \vec{S} \) is the spin, and \( \lambda \) is the spin-orbit coupling constant. Thus, the perturbed Hamiltonian has the form \( H = H_0 + V \), with \( V = V_{CF} + V_{SO} \).

The perturbation \( V \) mixes the unperturbed \( a_{1g} \) state with other states and for simplicity it is sufficient to consider only the \( 4p \) states \( H_0 |p_\alpha\rangle = E_p |p_\alpha\rangle \) with the energy \( E_p \), \( \alpha = x, y, z \). One can write the perturbed eigenvector in the form

\[
|\psi\rangle = |0\rangle + \sum_\alpha A_\alpha |p_\alpha\rangle,
\]

where \( A_\alpha \) are coefficients. The electric dipole moment is given then by

\[
\vec{d} = \langle \psi | \vec{r} | \psi \rangle = \sum_\alpha A_\alpha \langle 0 | \vec{r} | p_\alpha \rangle + c.c.,
\]

where \( e \) is the electron charge. Performing the perturbations up to the third order we obtain the electric dipole moment of the \( B_1 \) cation as

\[
d_x = \frac{d_0}{\Delta} \frac{\Delta^2}{2} x S_x S_z,
\]

\[
d_y = \frac{d_0}{\Delta} \frac{\Delta^2}{2} y S_y S_z,
\]

\[
d_z = \frac{d_0}{\Delta} \frac{\Delta^2}{2} (S_x^2 + S_y^2),
\]

with

\[
\bar{d}_0 = 2e \sum_\alpha V_{a\alpha}(0|\alpha|p_\alpha)/\Delta,
\]

where \( \Delta = E_{d} - E_F \) and \( V_{a\alpha} = \langle \alpha \mid p_\alpha \rangle |0\rangle \). Thus, in addition to \( \bar{d}_0 \), which is the electric dipole moment induced by the local polar crystal field, the spin-orbit coupling gives rise to spin-dependent contribution to the electric dipole moment \( \bar{d} \).

Obtaining similarly the remaining electric dipole moments of the cations \( B_2, B_3 \), and \( B_4 \), we find the macroscopic electric polarization \( \bar{P} = \sum_i \bar{d}_i / v \) (i = 1, 2, 3, 4) as

\[
P_x = q(3(a_1 g_z - a_2 g_x) + g_1 f_y + g_3 f_z - 2a_1 a_3 + 3(a_3 f_z - a_1 f_x) - 4 f_y f_z),
\]

\[
P_y = q(3(a_2 g_z - a_1 g_x) + g_2 f_y + g_3 f_x - 2a_2 a_2 + 3(a_1 f_x - a_2 f_z) - 4 f_x f_z),
\]

\[
P_z = q(3(a_3 g_z - a_3 g_x) + g_3 f_y + g_3 f_x - 2a_2 a_2 + 3(a_2 f_y - a_3 f_x) - 4 f_y f_x),
\]

where \( v \) is the volume of the primitive cell, \( q = d_{00}^F / (16 \sqrt{3} v \Delta^2) \), and where we used the basis functions given in [29] to rewrite the spins \( \vec{S} \) of the cations \( B_i \) in terms of the magnetic order parameters. The electric polarization \( \bar{P} \), obtained from microscopic considerations, reflects the ME invariants \( (2), (4), (5), (6), \) and \( (7) \) and can be used to estimate the respective coefficients in the thermodynamic potential expansion. Performing the quantum perturbations to higher orders one can obtain additional contributions to polarization \( \bar{P} \), which reflect in particular the existence of invariant \( (3) \).

In order to estimate the electric polarization \( \bar{P} \) we use the hydrogen-like orbitals and obtain \( \langle 0|\vec{r} |p_\alpha\rangle \approx 0.37a_0/Z (a, b, c = x, y, z) \), where \( a_0 \) is the Bohr radius and \( Z \) is the charge of the nucleus and core electrons in units of e. Taking \( Li_{1/2}Ga_{1/2}Cr_2O_4 \) as example [12] we obtain \( c \approx 1.9 \cdot 10^{-5} \) N and \( \nu \approx 140 \) Å. Using \( Z \approx 5, \lambda \approx 0.05 \) eV, \( \Delta \approx 1 \) eV, \( \beta = 1 \), and \( \lambda a_0 \approx a_0 - a_0 \approx 1 \) we find \( d_0 \approx 2 \cdot 10^{-31} \) C m and \( q \approx 0.13 \) µC/m². The electric polarization \( \bar{P} \) can, therefore, take values of the order of 0.1 – 0.5 µC/m².

5. Phenomenological models

5.1. Ferromagnetic ordering

In this section we study ferromagnetic ordering in cation-ordered spinels, which is described by IR GM⁺. The thermodynamic potential expansion can be written in the form

\[
\Phi = \frac{A_f}{2} I_1 + \frac{b_1}{4} I_2 + \frac{b_2}{4} I_3 + \kappa I_{ME} + \frac{A_p}{2} I_p - (f_x H_x + f_y H_y + f_z H_z), \tag{10}
\]

where \( A_f, b_1, b_2, A_p, \kappa \) and \( \alpha \) are coefficients, \( \vec{H} \) is magnetic field, \( I_1 = f_x^2 + f_y^2 + f_z^2, I_2 = f_x^4 + f_y^4 + f_z^4, I_{ME} = s(P_x f_x f_z + P_y f_y f_z + P_z f_z f_x + P_x f_x f_y), \) and \( I_p = P_x^2 + P_y^2 + P_z^2. \) Following the usual premise of the phenomenological theory we assume \( A_f = a_f (T - T_c) \), where \( T \) is temperature, \( T_c \) the Curie temperature, and \( a_f \) is
a coefficient independent of $T$. Since the system is far from a proper ferroelectric phase transition we take $A_f \gg 0$.

In the paramagnetic and paraelectric phase $A_f = 0$, $f_x = f_y = f_z = 0$, $P_x = P_y = P_z = 0$, and the magnetic susceptibility

$$\chi_{\alpha\beta} = \frac{\partial f_{\alpha}}{\partial H_\beta},$$

where $\alpha, \beta = x, y, z$, has the form $\chi_{\alpha\beta} = 1/A_f$ with other components equal to zero. The linear magnetoelectric coefficient

$$\Lambda_{\alpha\beta} = \frac{\partial P_{\alpha}}{\partial H_\beta},$$

is also zero. The potential (10) allows two ferromagnetic phases, either of which may occur at $T = T_c$: an improper ferroelectric phase with $f_x = f_y = f_z = 0$ and a paraelectric phase with $f_x = f_y = 0$ and $f_z = 0$.

5.1.1. The phase $f_x = f_y = f_z = 0$.

In this phase (phase I), which is stable for $b_1 > 0$, the order parameters are given by $f_x = f_y = f_z = f$ and

$$P_x = P_y = P_z = \frac{-s_k}{A_p} f^2$$

with

$$f^2 = \frac{A_p A_p}{A_p (b_1 + 3b_3) - 2s_k^2}.$$

The magnetic susceptibility and magnetoelectric tensors represented in the $(X, Y, Z)$ coordinates are given by

$$\chi_{XX} = \chi_{YY} = -\frac{A_p (b_1 + 3b_3) - 2s_k^2}{2A_p (b_1 + s_k^2)}, \quad \chi_{ZZ} = -\frac{1}{2A_f},$$

$$\Lambda = \begin{pmatrix}
\frac{s_k}{2A_p} & 0 & 0 \\
0 & \frac{s_k}{2A_p} & 0 \\
0 & 0 & \frac{s_k}{A_p s_k}
\end{pmatrix},$$

respectively. Nondiagonal components of $\chi$ equal zero. Therefore, the ME tensor components are proportional to the degree of atomic ordering $s$ and diverge as $s/\sqrt{T_c - T}$ at $T < T_c$. As shown in Fig. 2a, since $f^2 \sim (T_c - T)$.

5.1.2. The phase $f_x = f_y = f_z = 0$.

In this phase (phase II), which is stable for $b_1 < 0$, the order parameters are given by $f_x = f_y = f_z = f$ and $P_x = P_y = P_z = 0$ with

$$f^2 = -\frac{A_f}{b_1 + b_2}$$

(12)

The magnetic susceptibility and magnetoelectric tensors represented in the $(x, y, z)$ coordinates are given by

$$\chi_{xx} = \chi_{yy} = -\frac{A_p (b_1 + b_2)}{A_p (A_p + s_k^2)}, \quad \chi_{zz} = -\frac{1}{2A_f},$$

and

$$\Lambda = \begin{pmatrix}
0 & \frac{s_k}{2A_p (b_1 + b_2 + s_k^2)} & 0 \\
\frac{s_k}{2A_p (b_1 + b_2 + s_k^2)} & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}.$$  

Figure 2: (a) Schematic temperature dependence of nonzero ME coefficients $\Lambda_{\alpha\beta}$ close to $T' (T' = T_c$ or $T_N)$ for the magnetic phase transitions described by IR GM$^+$. (b) The same as (a) but for IR GM$^{-}$. respectively. Nondiagonal components of $\chi$ equal zero. Similar to the previous case the ME tensor components are proportional to the degree of atomic ordering $s$ and diverge as $1/\sqrt{T_c - T}$ at $T < T_c$. As shown in Fig. 2a).

5.1.3. Estimation of ME effect.

To make an order of magnitude estimation of the ME coefficient in the paraelectric phase II we proceed in the following way. We assume that the order parameter $f_x$ in (10) represents the magnetic moment of the B cation measured in Bohr magnetons $\mu_B$. It is convenient to introduce three constants

$$c_1 = \frac{a_f}{b_1 + b_2}, \quad c_2 = \frac{2A_p (b_1 + b_2)}{b_1 A_p + k^2}, \quad c_3 = \frac{\kappa}{A_p},$$

and

$$c_1 = \frac{a_f}{b_1 + b_2}, \quad c_2 = \frac{2A_p (b_1 + b_2)}{b_1 A_p + k^2},$$

and

$$c_3 = \frac{\kappa}{A_p},$$

respectively. Nondiagonal components of $\chi$ equal zero. Therefore, the ME tensor components are proportional to the degree of atomic ordering $s$ and diverge as $s/\sqrt{T_c - T}$ at $T < T_c$.

The first of them determines the magnetic moment $f^2 = -c_1 (T - T_c)$ in (12) and can be estimated as $c_1 = 0.25 \mu_B^2/K$. The second constant represents the ratio of susceptibilities $c_2 = \chi_{xx}/\chi_{zz}$, which we estimate as $c_2 = 1/2$. The third constant $c_3$ can be estimated from (11) using the results of section 3. Assuming that $f \approx 5 \mu_B$ induces improper polarization of 0.5 $\mu C/m^2$ we obtain $c_3 = -0.02 \mu C/(\mu_B m)^2$ (here and in the following we assume $s = 1$). The phenomenological constant $a_f$, which is related to the paramagnetic susceptibility as $\chi^{-1} = a_f (T - T_c)$ can be estimated as $a_f = 9.9 \cdot 10^{-7} m^3 K^{-1}$, where we used the molar susceptibility $\chi_{mol} = C/(T - \Theta)$ of ferromagnetic spinel CuCr$_2$Te$_4$ with $C = 4.28$ K-emu/mol-f.u. [36]. The components of the ME tensor (13) can then be expressed in the form

$$\Lambda_{xx} = \Lambda_{yy} = \frac{c_2 c_1 \sqrt{c_1}}{2a_f \sqrt{T_c - T}} = -\gamma \sqrt{\frac{K}{T_c - T}},$$

where $\gamma = 2.17 \cdot 10^{-6} \mu C/(m^2-Oe) = 0.027$ ps/m, which is about two orders of magnitude smaller than the maximum ME coefficient observed in Cr$_2$O$_3$ [37]. Assuming a dielectric constant of $\varepsilon = 5.5$ observed in CoCr$_2$O$_4$ [38] we obtain
\[ \gamma = 0.45 \text{ mV/(cm-Oe)}, \] which is comparable to that of some BaTiO\(_3\)-based bulk particulate magnetoelastic composites [9].

5.2. Antiferromagnetic ordering described by GM\(^{4+}\)

In this section we study antiferromagnetic ordering of B cations described by IR GM\(^{4+}\). The thermodynamic potential expansion can be written in the form

\[ \Phi = \frac{A_f}{2} I_1 + \frac{A_g}{2} I_g + \frac{b_{g1}}{4} I_{g1}^2 + \frac{b_{g2}}{4} I_{g2}^2 + wJ + \kappa_1 \chi_{ME1} + \frac{A_p}{2} Ip - (f_x H_x + f_y H_y + f_z H_z), \] (14)

where \( A_f, b_{g1}, b_{g2}, \) and \( \kappa_1 \) are coefficients, \( I_{g1} = g_x^2 + g_y^2 + g_z^2, \) \( I_{g2} = g_x^4 + g_y^4 + g_z^4, \) \( I_{ME1} = s(P_x (g_x f_x + g_y f_y) + P_y (g_x f_x + g_y f_y) + \) \( P_z (g_y f_y + g_z f_z)), \) and \( J = g_x f_x + g_y f_y + g_z f_z. \) As discussed in section 4, the ME interaction appears only upon perturbations to higher orders and can be considered smaller than the other ME interactions. Therefore, we do not include this term in the expansion [14]. Since the system is far from both the pure ferromagnetic and ferroelectric phase transitions we assume \( A_f > 0 \) and \( A_g > 0. \) Minimization of potential [14] shows that the paramagnetic phase is unstable at \( A_g = A_g^0 = w^2/A_f \) and experiences a phase transition either to the ferromagnetic phase (phase I) with \( g_x = g_y = g_z \neq 0, f_x = f_y = f_z \neq 0, \) and \( P_x = P_y = P_z \neq 0 \) or a paraelectric phase (phase II) with \( g_x = g_y = 0, g_z \neq 0, f_x = f_y = 0, f_z \neq 0, \) and \( P_x = P_y = P_z = 0. \) Here we consider only the latter phase for simplicity. Minimization of potential [14] yields the order parameters

\[ f_x = -\frac{w}{A_f} g_x, \] \[ f_y = -\frac{w}{A_f} g_y, \] \[ f_z = -\frac{w}{A_f} g_z. \] (15)

The antiferromagnetic phase transition according to IR GM\(^{4+}\) is a quasiproper ferromagnetic transition since the ferromagnetic moment transforms according to the same IR. The weak ferromagnetic moment arising due to (15) is usually about two orders of magnitudes smaller than the antiferromagnetic one. Therefore, the ratio \( w/A_f \) can be estimated as 0.01 – 0.05 and will be used as a small parameter in expansions.

Similar to the above case of a ferromagnetic phase transition, we assume \( A_g = A_g^0 (T - T^*) \) with \( T^* = T_N - w^2/(A_f A_g) \), where \( T_N \) is the Néel temperature of the magnetic susceptibility tensor. The paramagnetic susceptibility tensor is given by

\[ \chi_{aa} = \frac{A_g}{A_f A_g^0 - w^2} = \frac{1}{A_f} + \frac{w^2}{A_f^2 A_g^0 (T - T_N)}, \]

whereas the magnetoelectric tensor \( \Lambda \) is equal to zero. Therefore, \( \chi_{aa} \) diverges at \( T = T_N \). However, due to the smallness of \( w/A_f \), the temperature region of high \( \chi_{aa} \) is very narrow.

In the phase II at temperatures below \( T_N \) the nonzero components of magnetic susceptibility tensor are given by

\[ \chi_{xx} = \chi_{yy} = -\frac{w^2 (b_{g1} + b_{g2})}{A_f^2 A_g b_{g1}(T_N - T)}, \] \[ \chi_{zz} = \frac{1}{A_f} + \frac{w^2}{2A_f^2 A_g (T_N - T)} \]

where for \( \chi_{xx} \) and \( \chi_{yy} \) we consider only the first term in their expansions with respect to \( w/A_f \).

At temperatures close to \( T_N \) the magnetoelectric tensor is given by

\[ \Lambda = \begin{pmatrix} 0 & \frac{2w x^2}{A_f A_g b_{g1}} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \] (16)

i.e., diverges at \( T_N \) as \( 1/\sqrt{T_N - T} \) as shown in Fig. (2a), since

\[ g_z^2 = \frac{a_g (T_N - T)}{b_{g1} + b_{g2}}. \]

At temperatures significantly lower than \( T_N \) we obtain

\[ \Lambda = \begin{pmatrix} 0 & \frac{-2w x^2}{A_f A_g b_{g1}^0 z^1} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \] (17)

Here we again considered only the leading term in expansion of \( \Lambda \) with respect to \( w/A_f \).

To estimate the ME effect we introduce two constants

\[ c_1 = \frac{a_g}{b_{g1} + b_{g2}}, \] \[ c_2 = -\frac{a_g b_{g2}}{b_{g1} + b_{g2}}. \]

The first of them determines the temperature dependence of the order parameter as \( g_z^2 = c_1 (T_N - T) \), whereas \( c_2 \) reflects the temperature dependence of magnetic susceptibility as \( \chi_{xy} = \chi_{yz} = w^2/A_f (c_2 (T_N - T)). \) The ME coefficients in (16) take then the form

\[ \Lambda_{xy} = \Lambda_{yz} = \frac{2\sqrt{c_1 w^2} x^1}{c_2 A_f^2 A_g^0 \sqrt{T_N - T}}. \]

Similarly to the case of section 5.1.3, we can use the estimates \( c_1 = 0.25 \mu_B^2/K \) and \( k_1/A_g = 0.02 \mu_C/(\mu_B) \), whereas \( c_2 \) can be tentatively taken equal to \( a_f = 9.9 \cdot 10^{-27} \text{ m}^3 \cdot \text{K}^{-1} \) from section 5.1.3 both \( c_1 \) in the current case and \( a_f \) in section 5.1.3 determine the temperature dependence of magnetic susceptibility, whereas in the current case the fact that the weak ferromagnetism is considered for by the factor \( (w/A_f)^2 \) in the expression for \( \chi_{xx} \) and \( \chi_{yy} \). Assuming \( w/A_f = 0.05 \) we obtain

\[ \Lambda_{xy} = \Lambda_{yz} = \gamma \sqrt{K/T_N - T}. \]

where \( \gamma = 5.4 \cdot 10^{-4} \text{ ps/m}, \) which is about two orders of magnitude smaller than that in section 5.1.

To estimate the ME coefficients in (17) we assume \( A_f A_g \gg g_z^2 s^2 z^1 \) since the system is far from ferroelectric and ferromagnetic phase transitions. Therefore, nonzero coefficients in (17) can be written as \( \Lambda_{xy} = \Lambda_{yz} = -g_z s^2 k_1/A_f A_g. \) From the paramagnetic susceptibility \( \chi = 5 \cdot 10^{-3} \mu_B/\text{T of Cr spins in LiGaCrO}_8 \) we can estimate \( A_f \) as \( A_f = \chi^{-1}. \) Taking \( g_z = 1 \mu_B \) we obtain the components of ME tensor (17) of the order of \( 1.3 \cdot 10^{-4} \text{ ps/m}. \)
5.3. Antiferromagnetic ordering described by GM$^{3+}$

In this section we study antiferromagnetic ordering of B cations described by IR GM$^{3+}$. The thermodynamic potential expansion can be written in the form

\[ \Phi = \frac{A_1}{2} I_1 + \frac{A_2}{2} I_2 + \frac{b_{\text{b}}}{4} I_{\text{b}} + \frac{b_{\text{a}}}{4} I_{\text{a}} + \kappa_2 I_{\text{ME2}} + k_3 I_{\text{ME3}} + \frac{A_0}{2} \text{Tr} - (f_x H_x + f_y H_y + f_z H_z), \]  

(18)

where \( A_a, b_{\text{b}}, b_{\text{a}}, \) and \( \kappa_2 \) are coefficients, \( I_1, I_2, I_{\text{b}}, I_{\text{a}}, I_{\text{ME2}}, \) and \( I_{\text{ME3}} \) are given in section 5. The three suggested models describe (phase II). In the paramagnetic phase at \( T > 0 \), the non-zero magnetic susceptibility tensor components are given by \( \chi_{xx} = 1/\alpha_f \), whereas the ME tensor \( \alpha \) is zero.

The thermodynamic potential (18) allows two antiferromagnetic phases, either of which becomes stable for \( A_a > 0 \): a ferroelectric phase with \( f_x = f_y = f_z = 0, P_x = P_y = P_z = P \), and \( A_1 = A_2 = a = \alpha (\text{phase I}) \) and a paraelectric phase with \( f_x = f_y = f_z = 0, P_x = P_y = P_z = 0, A_1 = a, \) and \( A_2 = A_3 = 0 \) (phase II). Phase I is stable for \( A_{>0} \geq -2\kappa f^2/\alpha_f \), whereas phase II for \( b_{>0} \leq -2\kappa f^2/\alpha_f \).

In the phase I the order parameters are given by

\[ P = -\frac{a f}{a^2} \]

and

\[ a^2 = \frac{A_a}{b_{\text{b}} + b_{\text{a}}} \]

The magnetic susceptibility and ME tensors represented in the \((X, Y, Z)\) coordinates take the forms (here and in the following we do not consider the term in (18) proportional to \( \kappa_3 \), since it gives minor contribution compared to the other terms)

\[ \chi_{XX} = \chi_{YY} = \frac{A_p}{A_f A_p - 3a^2 s^2 f_2}, \quad \chi_{ZZ} = \frac{1}{A_f} \]

and

\[ \Lambda = \begin{pmatrix} 0 & -\frac{a f}{a^2} & 0 \\ -\frac{a f}{a^2} & \frac{A_p}{A_f A_p - 3a^2 s^2 f_2} & 0 \\ 0 & 0 & 0 \end{pmatrix} \]

(19)

respectively. Nondiagonal components of \( \chi \) equal zero.

In the phase II the order parameter is given by

\[ a^2 = -\frac{A_a}{b_{\text{b}} + b_{\text{a}}} \]

whereas \( \chi \) and \( \Lambda \) take the forms

\[ \chi_{xx} = \chi_{yy} = \frac{A_p}{A_f A_p - a^2 s^2 f_2}, \quad \chi_{zz} = \frac{1}{A_f} \]

and

\[ \Lambda = \begin{pmatrix} 0 & -\frac{a f}{a^2} & 0 \\ -\frac{a f}{a^2} & \frac{A_p}{A_f A_p - a^2 s^2 f_2} & 0 \\ 0 & 0 & 0 \end{pmatrix} \]

(20)

respectively. Nondiagonal components of \( \chi \) equal zero.

At temperatures \( T \lesssim T_N \) below the antiferromagnetic transition temperature \( T_N \), the ME coefficients (19) and (20) grow as \( \sqrt{T_N - T} \) with decreasing temperature as shown in Fig. (2) (b) since \( a^2 \sim A_a \sim (T - T_N) \). Similarly to the estimation of ME coefficients (14) performed in section 5.2 we can estimate the ME tensor components \( \chi_{xx} = -\chi_{yy} \) in (19) and (20) to be of the order of \( 10^{-4} \) ps/nm.

6. Discussion

In this work we have studied the magnetoelectric properties of \( \alpha_1^{s}, \alpha_2^{s}, \alpha_3^{s}, B_2X_4 \) spinels with nonzero degree \( s \) of \( A' \) and \( A'' \) cation order. Disordered \( \alpha_1^{s}, \alpha_2^{s}, \alpha_3^{s}, B_2X_4 \) spinels possess cubic \( Fd\bar{3}m \) structure at high temperatures, whereas nonzero \( s \) results in lowering of crystal symmetry to \( F43m \) and disappearance of inversion symmetry operation. Spinels often exhibit high temperature magnetic phase transitions, which are usually governed by magnetic B cations and result in magnetic structures with unit cells coinciding with the crystallographic ones, i.e. with \( k = 0 \). The \( k = 0 \) magnetic representation of B cations (11) consists of IRs even under space inversion, which do not allow ME effect as shown in section [3]. However, cation ordering results in disappearance of inversion operation and emergence of ME effect due to interactions (2) – (7).

The microscopic model of magnetoically induced electric polarization is suggested in section [4]. The model is based on the recently proposed mechanism of ME effect (35) and directly takes into account the disappearance of inversion symmetry at the B cation sites upon atomic ordering in spinels. It is shown that in cation-ordered spinels local electric dipole moments at B positions are spin-dependent and result in macroscopic electric polarization for a spin configuration. The electric polarization obtained from microscopic theory is in accordance with macroscopic interactions (36) – (7). The obtained value of magnetically induced polarization of the order of \( 0.5 \mu C/m^2 \) is comparable to that of magnetoelectric CoCr$_2$O$_4$ with incommensurate magnetic ordering (10). The maximum possible electric polarization value depends on the cation ordering degree \( s \) as well as on the degree of polar distortion reflected by the coefficient \( c \) in (8). Therefore, in order to obtain higher polarization one has to increase \( c \), which strongly depends on the difference of ionic radii of the ordering \( A' \) and \( A'' \) cations. The spinels with substantially different ionic radii of \( A' \) and \( A'' \) cations should generally possess stronger tendency to atomic ordering as well as larger \( c \).

Basic phenomenological models of magnetic phase transitions according to the main ordering patterns of B cation spins are given in section [5]. The three suggested models describe the magnetic ordering according to the three-dimensional representations entering into the magnetic representation (1) and representing: (i) ferromagnetic (IR GM$^{3+}$), (ii) antiferromagnetic with weak ferromagnetism (IR GM$^{3+}$), and (iii) purely antiferromagnetic (IR GM$^{3+}$) ordering patterns of B cation spins. The temperature dependencies of the magnetic susceptibility and magnetoelectric tensors are determined. It is found that in
the first two cases described by IR GM\textsuperscript{45} the ME tensor components diverge as \(\sqrt{T - T_c}\) below the phase transitions temperatures \(T'\) (\(T' < T_c\) or \(T' > T_c\)) as shown in Fig. [2](a). The coefficient \(\gamma\) is about two orders of magnitude larger in the purely ferromagnetic case (i), than in the case of a weak ferromagnetic phase transition (ii). In case (iii) the ME tensor components grow below \(T_N\) as \(\sqrt{T_N - T}\) with decreasing temperature as shown in Fig. [2](b).

In the upper limit for the magnetic susceptibility, which is given by \((g_A)_{\text{eff}}\) \(\chi_0\), we find that to the fact that \(\gamma\) diverges at \(T_c\), the ME susceptibility is largest in the case of a ferromagnetic phase transition (i), for which we obtain the ME coefficient of the order of 0.01 ps/m. In case (ii) the ME constants also diverge at \(T_N\) since \(\chi\) diverges, but possess additional factor \((w/A)^2 \sim 2.5 \times 10^{-3}\) due to the fact that in this case the crystal is weakly ferromagnetic. In case (iii) the obtained values of ME coefficients are rather low (of the order of \(10^{-4}\) ps/m), because \(\chi\) remains low at antiferromagnetic phase transitions. Therefore, from the point of view of practical applications ordered spinels with purely ferromagnetic (or ferrimagnetic) phase transition are of primary interest. To this class belong, for example, ferrimagnetic \(\text{Fe}_{0.5}\text{Cu}_{0.5}\text{Cr}_{2}\text{S}_4\) \([40]\) and ferromagnetic \(\text{Cu}_{0.5}\text{In}_{0.5}\text{Cr}_{2}\text{Se}_4\) \([41]\). The former spinnel, however, is semiconducting and displays colossal magnetoresistance \([42]\).

The ME properties of \(\text{A}'_{1/2}\text{A}''_{1/2}\text{B}_2\text{X}_4\) spinels claimed in this work are due to the presence of 1:1 cation order at the A site. Therefore, as a result the ME coefficients become proportional to the degree of atomic ordering \(s\). Complete order of \(A'\) and \(A''\) cations, which we assumed in current work, corresponds to \(s = 1\) and results in maximal ME properties. However, different crystal preparation conditions or thermodynamic history of the sample may result in only partial atomic ordering, which will reduce the ME response, or even in inhomogenous cation ordering when the order parameter \(s\) becomes spatially dependent. For the description of the latter case one will have to employ averaging techniques, such as the one performed in \([24]\).

Because ME response the appearance of ME properties in cation-ordered magnetic spinels \(\text{A}'_{1/2}\text{A}''_{1/2}\text{B}_2\text{X}_4\) should be also observed, for example, in infrared studies. Compared to non-substituted spinels \(\text{AB}_2\text{X}_4\), which possess four active infrared modes \([43]\), cation-ordered spinels \(\text{A}'_{1/2}\text{A}''_{1/2}\text{B}_2\text{X}_4\) have seven active modes \([44]\), which belong to the same IR T\text{2} of the F\text{4}3m space group. It has to be noted, that the infrared spectra of ordered and disordered \(\text{Li}_{0.5}\text{Ga}_{0.5}\text{Cr}_2\text{O}_4\) possess no drastic differences, which may be due to the difficulty of completely disordering the sample and the presence of locally ordered regions \([45]\).

The magnetic phase transitions in ordered spinels to the phase states (\(f, f, f\), (\(g, g, g\)), and (\(a, a, a\)) of the cases (i), (ii), and (iii), respectively, are improper ferroelectric. Therefore, the temperature dependencies of the frequencies of infrared active modes should experience a kink at the phase transition. In contrast, under applied magnetic field the magnetic phase transitions with respect to both \(\text{GM}^{+4}\) and \(\text{GM}^{-8}\) become proper ferroelectric as seen from ME interactions \([3\), (4), and (7)]. Therefore, the frequencies of infrared active modes should experience strong temperature and magnetic field dependence close to these magnetic phase transitions.

The suggested model can be used to estimate the magnetoelectric response in all cation-ordered \(\text{A}'_{1/2}\text{A}''_{1/2}\text{B}_2\text{X}_4\) magnetic spinels. The prominent examples of such spinels are \(\text{Li}_{1/2}\text{Ga}_{1/2}\text{Cr}_2\text{O}_4\) and \(\text{Li}_{1/2}\text{In}_{1/2}\text{Cr}_2\text{O}_4\) \([12]\), \(\text{Cu}_{1/2}\text{Mn}_{1/2}\text{Cr}_2\text{S}_4\) \([13]\), \(\text{Fe}_{1/2}\text{Cu}_{1/2}\text{Cr}_2\text{S}_4\) \([14\), (15]\), \(\text{Li}_{1/2}\text{FeRh}_3\text{O}_4\) \([45]\), and \(\text{ALi}_{0.5}\text{Mn}_{1.5}\text{O}_4\) \([46]\). The model can be also applied to \(\text{AB}_2\text{X}_4\) spinels with sufficient degree of inversion and 1:1 cation ordering at the tetrahedral site, such as, for example, in \(\text{FeIn}_2\text{S}_4\) \([47]\). In section 5 macroscopic magnetoelectric response calculation for such spinels experiencing magnetic ordering with \(\vec{k} = 0\) is presented, which is based on the microscopic model given in section 4. For spinels with complex magnetic ordering, such as when, for example, the magnetic unit cell is a multiple of the crystallographic one or when an incommensurate magnetic structure appears (i.e., when \(\vec{k} \neq 0\)), the phenomenological description should be rewritten accordingly, whereas the results of the macroscopic approach can still be used \([35]\).

7. Conclusions

In summary, we theoretically show that cation-ordered \(\text{A}'_{1/2}\text{A}''_{1/2}\text{B}_2\text{X}_4\) magnetic spinels should display magnetoelectric properties. The value of ME effect is estimated using recently proposed microscopic model based on spin-dependent electric dipole moments of ions located in noncentrosymmetric positions. Three phenomenological models describing various ferromagnetic and antiferromagnetic ordering patterns of B cation spins are build and the corresponding ME responses are calculated.

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References

[1] A. P. Pyatakov, A. K. Zvezdin, Usp. Phys. Nauk [Sov. Phys.-Usp.] 55 (2012) 557.
[2] D. Khomskii, Physics 2 (2009) 20.
[3] G. Catalan, J. F. Scott, Adv. Mater. 21 (2009) 1.
[4] T. Kimura, G. Lawes, T. Goto, Y. Tokura, A. P. Ramirez, Phys. Rev. B 71 (2005) 224425.
[5] T. Kimura, Y. Sekio, H. Nakamura, T. Siegrist, A. P. Ramirez, Nat. Mater. 7 (2008) 291.
[6] S. Krupička, P. Novák. Oxide spinels, in: E. P. Wohlfarth (Ed.), Handbook of magnetic materials, volume 3, North-Holland Publishing Company, 1982.
[7] R. P. van Stapele, Sulphospinels, in: E. P. Wohlfarth (Ed.), Handbook of magnetic materials, volume 3, North-Holland Publishing Company, 1982.
[8] V. A. M. Brabers, Progress in spinel ferrite research, in: K. H. J. Buschow (Ed.), Handbook of magnetic materials, volume 8, Elsevier, 1995.
[9] C. A. Vaz, J. Hoffman, C. H. Ahn, R. Ramesh, Adv. Mater. 22 (2010) 2900.
[10] Y. Yamashita, S. Miyasaka, Y. Kaneko, J.-P. He, T. Arima, Y. Tokura, Phys. Rev. Lett. 96 (2006) 207204.
[11] H. Murakawa, Y. Onose, K. Ohgushi, S. Ishiwata, Y. Tokura, J. Phys. Soc. Jap. 77 (2008) 043709.
[12] Y. Okamoto, G. J. Nilsen, J. P. Attfield, Z. Hiroi, Phys. Rev. Lett. 110 (2013) 097203.
[13] Y. A. Kesler, E. G. Zhukov, D. S. Filimonov, E. S. Polulyak, T. K. Menchikova, V. A. Fedorov, Inorg. Mater. 41 (2005) 914.
[14] H. M. Palmer, C. Greaves, J. Mater. Chem. 9 (1999) 637.
[15] T. G. Aminov, D. I. Kirdyankin, G. G. Shabunina, V. M. Novotortsev, Russ. J. Inorg. Chem. 57 (2012) 991.
[16] C. Haas, J. Phys. Chem. Sol. 26 (1965) 1225.
[17] V. M. Talanov, V. B. Shirokov, Acta Cryst. A70 (2014) 49.
[18] F. Chu, N. Setter, A. K. Tagantsev, J. Appl. Phys. 74 (1993) 5129.
[19] D. S. Sarma, E. V. Sampathkumaran, S. Ray, R. Nagarajan, S. Majumdar, A. Kumar, G. Nalini, T. N. G. Row, Solid State Commun. 114 (2000) 465.
[20] D. Sánchez-Soria, J. A. Alonso, M. García-Hernández, M. J. Martínez-Lope, J. L. Martínez, A. Mellergård, Appl. Phys. A 74 (2002) s1752.
[21] D. Wagner, A. Y. Romanov, V. P. Silin, JETP 82 (1996) 945.
[22] A. A. Bokov, Ferroelectrics 90 (1989) 155.
[23] V. P. Sakhnenko, N. V. Ter-Oganessian, Crystallogr. Rep. 48 (2003) 443.
[24] V. P. Sakhnenko, N. V. Ter-Oganessian, Ferroelectrics 314 (2005) 1.
[25] Y. Iijima, Y. Kamei, N. Kobayashi, J. Awaka, T. Iwasa, S. Ebisu, S. Chukazawa, S. Nagata, Philos. Mag. 83 (2003) 2521.
[26] G. M. Kalvius, A. Krimmel, O. Hartmann, R. Wäppling, F. E. Wagner, F. J. Litterst, V. Tsurkan, A. Loidl, J. Phys.: Condens. Matter 22 (2010) 052205.
[27] E. M. Wheeler, B. Lake, A. T. M. N. Islam, M. Reehuis, P. S. T. Guidi, A. H. Hill, Phys. Rev. B 82 (2010) 140406(R).
[28] H. Takagi, S. Nishida, Highly frustrated magnetism in spinels, in: C. Lacroix, P. Mendels, F. Mila (Eds.), Introduction to frustrated magnetism, Springer, 2011.
[29] Y. A. Izyumov, V. E. Naish, S. B. Petrov, J. Magn. Magn. Mater. 13 (1979) 267.
[30] A. Oles, F. Kajzar, M. Kucab, W. Sikora, Magnetic structures determined by neutron diffraction, Warszawa, Krakow, 1976.
[31] O. V. Kovalev, Kristallografiya 18 (1973) 221.
[32] A. Krimmel, V. Tsurkan, D. Sheptyakov, A. Loidl, Physica B 378-380 (2006) 583.
[33] W. L. Roth, J. Phys. Chem. Solids 25 (1964) 1.
[34] T. Suzuki, H. Nagai, M. Nohara, H. Takagi, J. Phys.: Condens. Matter 19 (2007) 145265.
[35] V. P. Sakhnenko, N. V. Ter-Oganessian, J. Phys.: Condens. Matter 24 (2012) 266002.
[36] T. Suzuki, T. Awaka, H. Yamamoto, S. Ebisu, M. Ito, T. Suzuki, T. Nakama, K. Yagasaki, S. Nagata, J. Solid State Chem. 179 (2006) 140.
[37] H. Wiegelmann, A. G. M. Jansen, P. Wyder, J.-P. Rivera, H. Schmid, Ferroelectrics 162 (1994) 141.
[38] G. Lawes, B. Melot, K. Page, C. Ederer, M. A. Hayward, T. Proffen, R. Seshadri, Phys. Rev. B 74 (2006) 024413.
[39] W. F. Brown, R. M. Hornreich, S. Shtrikman, Phys. Rev. 168 (1968) 574.
[40] E. Z. Kurmaev, A. V. Postnikov, H. M. Palmer, C. Greaves, S. Bartkowski, V. Tsurkan, M. Demeter, D. Hartmann, M. Neumann, D. A. Zatsepin, V. R. Galakhov, S. N. Shamin, V. Trofimova, J. Phys.: Condens. Matter 12 (2000) 5411.
[41] H. Yokoyama, S. Chiba, J. Phys. Soc. Jap. 27 (1969) 505.
[42] A. P. Ramirez, R. J. Cava, J. Krajewski, Nature 386 (1997) 156.
[43] J. Preudhomme, P. Tart, Spectrochimica Acta 27A (1971) 1817.
[44] P. Tart, J. Preudhomme, Spectrochimica Acta 29A (1973) 1301.
[45] K. U. Kang, C. S. Kim, Hyperfine Interact. 168 (2006) 1181.
[46] C. M. Julien, F. Gendron, A. Amouni, M. Massot, Mater. Sci. Eng. B 130 (2006) 41.
[47] R. J. Hill, J. A. Craig, G. V. Gibbs, J. Phys. Chem. Solids 39 (1978) 1105.