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Dielectric Properties of Spinel, Garnet and Perovskite Oxides

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We suggest a definition of the effective ionic charges q_i^* of different pairs of ions connected in tetrahedral, octahedral and dodecahedral polyhedra in such oxide crystals as spinels, garnets and perovskites. The electronic polarizability α_i of cations and the O^{2-} atomic core polarizability are calculated by $\langle r_k^2 \rangle$ according to Kirkwood. The polarizability caused by O^{2-} valence electrons is determined from the empirical data relating $\alpha(O^{2-})$ to the amount of spin-uncompensated cation electrons. The static limits of electronic and ionic components of permittivity ε^* are calculated by using q_i^* and α_i according to Born-Szigeti and Lorentz-Lorenz relations, adapted to crystalline structures studied. The agreement of the calculated values with experimental data, obtained from the frequency dependences of ε_1 and ε_2 , is illustrated for a large number of ferrimagnetic and low magnetic mono- and polycrystals. The decrease of the electronic and ionic components of $\varepsilon_1(0)$ as a result of the substitution of magnetically active ions by diamagnetic ones is attributed to an increase of the degree of ionicity of the crystals. The optical spectra $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, calculated by the model of noninteracting quasiharmonic oscillators, which takes into account lattice and electronic resonances, allow to restore the spectra of the reflection coefficient $R(\omega)$, which are also in good agreement with the experiment.

1. Introduction

The present understanding of processes induced by electromagnetic field in oxide ionic crystals, including ferrimagnetic ones [1–14], allows us to proceed from the analysis of factors that influence their magnetic and dielectric properties, to the calculation of some properties for given compositions. Here we propose a definition of the effective ionic charges, and calculate (in the static limit) the components of complex permittivity $\varepsilon^* = \varepsilon_1 + i\varepsilon_2$, based on the crystal-chemical approach and oscillator simulation of frequency dependences of ε_1 and ε_2 , and of the reflection factor R .

In a number of our previous works [15–18] the experimental data on the main mechanisms of electrical polarizability, static components of permittivity ε_1 , frequency dependences $\varepsilon_1(\omega)$, and $\varepsilon_2(\omega)$ of both highly magnetic and diamagnetic-substituted crystals of spinels, garnets and perovskites are obtained. At low temperatures ($T \leq 100$ K) and high frequencies ($\omega \geq 10^8$ s⁻¹) the polarizability of the mentioned classes of crystals is caused mainly by the elastic displacement of ions and electrons, related to the ionic component of permittivity $\varepsilon_1^{\text{ion}}$ and electronic component of permittivity $\varepsilon_1^{\text{el}}$, respectively. The named mechanisms of polarization are of resonance origin. The possible relaxation mechanisms of polarization, related to the migration and exchange of valence (quasifree) electrons and the exchange of ions between equivalent crystallo-

graphic positions, at high frequencies and low temperatures neglect the participation in polarization.

The static value of ε_1 is the sum of $\varepsilon_1^{\text{ion}}$ and $\varepsilon_1^{\text{el}}$, which can be calculated from the Born-Szigeti [19] and Lorentz-Lorenz [20] relations,

$$\varepsilon_1 = 1 + \pi \sum_i (q_i^*)^2 \left(\frac{n^2 + 2}{3} \right)^2 \frac{N_A^2 d}{\omega_{0i}^2 M_{1i} M_2} + \frac{1 + (8\pi/3) \sum_k N_k \alpha_k}{1 - (4\pi/3) \sum_k N_k \alpha_k}. \quad (1)$$

Here q_i^* is the effective charge of a group of ions bound in different polyhedra of a crystalline lattice (for example, tetrahedra, octahedra or dodecahedra), ω_{0i} is the limiting frequency of transversal optical (TO) phonons, characteristic of a group of ions of the given coordination, n is the index of the refraction of a crystal, d is its density, M_{1i} is the mass of cations located in i -th polyhedrons, M_2 is the mass of anion $M_{O^{2-}}$, N_k , α_k are the concentration and electronic polarizability of ions, respectively.

The second and third terms in Eq. (1) correspond to static values of ionic and electronic polarizabilities, respectively. The frequencies of a noticeable ε^* dispersion lie above 10^{11} to 10^{14} s $^{-1}$. Therefore, it is possible to consider ε_1 determined in the MHz range as a static limit, assuming the condition of “freezing out” of relaxational mechanisms.

We have used Eq. (1) so far only for obtaining the effective charges of ions in oxide ferrosinels averaged over all value groups [15–17]. The dielectric properties of BiFeO $_3$ were studied in [18]. The values of q_i^* are calculated on the base of experimental data on the frequencies of lattice vibrations and components of permittivity. The results for Y $_3$ Fe $_5$ O $_{12}$ and Gd $_3$ Ga $_5$ O $_{12}$ garnets are obtained in this work. The plan of our work is the following:

1. semiempirical calculation of the values of partial effective ion charges bound in different (tetrahedral, octahedral or dodecahedral) coordinations not only of spinels but of garnets and perovskites as well;
2. evaluation of TO phonon frequencies for the named crystals and calculation of contributions of vibrations of different ion groups in the static limits of ionic components of permittivity;
3. estimations of the values of electronic components of permittivity;
4. simulation of dielectric spectra and the spectrum of reflection factor of the crystals by a set of quasiharmonic oscillators.

2. Effective Ionic Charges

To calculate the ionic components of permittivity in Eq. (1) it is necessary to know first the effective charges q_i^* of ions. Assuming a purely ionic character of interatomic binding, separate ions of a crystal can be assigned by the following charges implied from the valence of the elements that form a crystal and the conditions of its electroneutrality: 1. Me $^{2+}$ Fe $_2^{3+}$ O $_4^{2-}$ in ferrimagnetics such as spinel, 2. Me $_3^{3+}$ Fe $_5^{3+}$ O $_{12}^{2-}$ in ferrimagnetics with garnet structure, 3. Bi $^{3+}$ Fe $^{3+}$ O $_3^{2-}$ in bismuth ferrite having perovskite structure. These values of charges should be considered as ionic limit. It is known that even in ionic crystals chemical bonding is partly covalent, and oxygen ions could have the configurations $1s^2 2s^2 2p^5$ (O $^-$), and, probably, $1s^2 2s^2 2p^4$ (O). As a result, the charges of cations also diminish.

Disregarding the covalency effects so far we shall introduce the concept of an effective charge, outgoing from the consideration of the interaction of a couple of ions. Since the strength of the interaction of a couple of ions, as well as their Coulomb energy, and also the value of the electrical polarization related to the displacement of ions are directly proportional to the product of charges of ions q_1q_2 , then it is natural to define q_i^* of a separate ion as the average geometrical value q_1 and q_2 , i.e. to consider $q_i^* = \sqrt{q_1q_2}$.

Then we obtain the following limiting values of q_i^* , characterizing the averaged charge of each ion from a couple of a cation-anion types: $q_{\max}^* = \sqrt{2e2e} = 2e$ for couples of ions $\text{Me}^{2+}-\text{O}^{2-}$, bound in tetrahedral coordination of normal spinel (Me^{2+}) $[\text{Fe}_2^{3+}]\text{O}_4^{2-}$ and for couples $\text{Me}^{2+}-\text{O}^{2-}$ of the ions bound in octahedra of conversed spinel (Fe^{3+}) $[\text{Me}^{2+}\text{Fe}^{3+}]\text{O}_4^{2-}$. For couples of ions $\text{Fe}^{3+}-\text{O}^{2-}$ $q_{\max}^* = \sqrt{3e2e} \approx 2.45e$. We have the same value of q^* in all couples of ions such as $\text{Me}^{3+}-\text{O}^{2-}$ and in crystals such as garnet and in bismuth ferrite.

The effective charges q^* defined in this way are also to be understood as the greatest possible ones in the limit of purely ionic character of interatomic binding. The decrease

Table 1

The accepted distribution of ions and their effective charges q^*/e in some ferrimagnetic and low magnetic (\otimes) crystals

structure type	distributions of ions and their limit charges	m	I	A couple of ions	q_{\max}^*	$q_{\max}^* \cdot I$
mixed spinel (monocryst.)	$(\text{Mn}_{0.8}^{2+} \text{Fe}_{0.2}^{3+})$ $[\text{Mn}_{0.2}^{2+} \text{Fe}_{1.8}^{3+}]$	5.00	0.71	$(\text{Me}^{2.2+}-\text{O}^{2-})$	2.10	1.49
				$[\text{Mn}^{2+}-\text{O}^{2-}]$	2.00	1.42
				$[\text{Fe}^{3+}-\text{O}^{2-}]$	2.45	1.74
conversed spinel (polycryst.)	$(\text{Fe}^{3+}) [\text{Fe}^{2+}\text{Fe}^{3+}]\text{O}_4^{2-}$	4.6(6)	0.73	$[\text{Fe}^{2+}-\text{O}^{2-}]$	2.00	1.46
				$(, [\text{Fe}^{3+}-\text{O}^{2-}])$	2.45	1.79
conversed spinel (polycryst.)	$(\text{Fe}^{3+}) [\text{Co}^{2+}\text{Fe}^{3+}]\text{O}_4^{2-}$	4.3(3)	0.75	$[\text{Co}^{2+}-\text{O}^{2-}]$	2.00	1.50
				$(, [\text{Fe}^{3+}-\text{O}^{2-}])$	2.45	1.84
conversed spinel (polycryst.)	$(\text{Fe}^{3+}) [\text{Ni}^{2+}\text{Fe}^{3+}]\text{O}_4^{2-}$	4.00	0.77	$[\text{Ni}^{2+}-\text{O}^{2-}]$	2.00	1.54
				$(, [\text{Fe}^{3+}-\text{O}^{2-}])$	2.45	1.87
conversed spinel (polycryst.)	$(\text{Fe}^{3+}) [\text{Li}_{0.5}^{+}\text{Fe}_{1.5}^{3+}]\text{O}_4^{2-}$	4.1(6)	0.79	$[\text{Li}^{+}-\text{O}^{2-}]$	1.41	1.41
				$(, [\text{Fe}^{3+}-\text{O}^{2-}])$	2.45	1.93
normal spinel	$(\text{Zn}^{2+}) [\text{Fe}_2^{3+}]\text{O}_4^{2-}$	3.3(3)	0.80	$[\text{Fe}^{3+}-\text{O}^{2-}]$	2.45	1.96
				$(\text{Zn}^{2+}-\text{O}^{2-})$	2.00	2.00
conversed spinel (polycryst.) (\otimes)	$(\text{Ga}^{3+}) [\text{Co}^{2+}\text{Ga}^{3+}]\text{O}_4^{2-}$	1.00	0.87	$[\text{Co}^{2+}-\text{O}^{2-}]$	2.00	1.74
				$(, [\text{Ga}^{3+}-\text{O}^{2-}])$	2.45	2.13
conversed spinel (polycryst.) (\otimes)	$(\text{Ga}^{3+}) \text{Li}_{0.5}^{+}\text{Ga}_{1.5}^{3+}]\text{O}_4^{2-}$	0.00	0.88	$[\text{Li}^{+}-\text{O}^{2-}]$	1.41	1.24
				$(, [\text{Ga}^{3+}-\text{O}^{2-}])$	2.45	2.15
garnet (monocryst.)	$\{\text{Y}^{3+}\} (\text{Fe}_3^{3+}) [\text{Fe}_2^{3+}]\text{O}_{12}^{2-}$	3.12	0.77	$\{\text{Y}^{3+}-\text{O}^{2-}\}$	2.45	1.88
				$(, [\text{Fe}^{3+}-\text{O}^{2-}])$	2.45	1.88
garnet (monocryst.) (\otimes)	$\{\text{Gd}^{3+}\} (\text{Ga}_3^{3+}) [\text{Gd}_2^{3+}]\text{O}_{12}^{2-}$	0.00	0.92	$\{[\text{Gd}^{3+}-\text{O}^{2-}]\}$	2.45	2.25
				$(\text{Ga}^{3+}-\text{O}^{2-})$	2.45	2.25
perovskite (polycryst.)	$\text{Bi}^{3+}\text{Fe}^{3+}\text{O}_3^{2-}$	2.50	0.79	$\text{Fe}^{3+}-\text{O}^{2-}$	2.45	1.93
				$\text{Bi}^{3+}-\text{O}^{2-}$	2.45	

of a charge compared with these maximum values occurs because cations exchange their valence electrons with the participation of oxygen ions. We shall try to take it into account on the base of interrelation between an effective charge after Szigeti averaged over all ions of the structural unit MeFe_2O_4 ,

$$\overline{q_s^*} = \frac{3\omega_0}{N_A(n^2 + 2)} \sqrt{\frac{(\varepsilon_1 - \varepsilon_\infty) \overline{M_1 M_2}}{\pi d}} \quad (2)$$

and an averaged (per one cation) number m of spin-uncompensated 3d electrons [17]

$$\overline{q_s^*} = (2 - 0.015m^2) e. \quad (3)$$

Here $2e$ is the value of the effective charge of ions in non-ferrimagnetic spinel ($m = 0$). We shall define the degree of ionicity I of a crystal as the ratio of the averaged charge (3) to the value q_{\max}^* in a structural chemical unit (MeFe_2O_4 , $\text{Me}_3\text{Fe}_5\text{O}_{12}$, or BiFeO_3) as

$$I = \overline{q_s^*} / q_{\max}^*. \quad (4)$$

For the spinel structure

$$q_{\max}^* = \frac{2e + 2(3e) + 4(2e)}{7} \approx 2.29e. \quad (5)$$

Multiplying $q_i^* = \sqrt{q_1 q_2}$ of different couples of ions by I we obtain their active effective charge. The obtained results are represented in Table 1. We observe an increase of the effective charge $q_{\max}^* I$ as a result of substitution of magnetically active Fe^{3+} , Co^{2+} , Ni^{2+} ions by diamagnetic Zn^{2+} , Ga^{3+} , Gd^{3+} ones.

3. Electronic Polarizability of Ions

We accept the square of refraction index n in (1) as equal to the established (not depending on frequency) limit of the electronic component of permittivity $n^2 = \varepsilon_\infty = \varepsilon_1^{\text{el}}$. As a matter of fact it is the third term in (1). It is possible to define the concentration of ions N_K , necessary for the calculation of $\varepsilon_1^{\text{el}}$ for each type of crystalline structure through the parameter a of its elementary unit cell: $N(\text{MeFe}_2\text{O}_4) = 8/a^3$, $N(\text{Me}_3\text{Fe}_5\text{O}_{12}) = 8/a^3$, $N(\text{BiFeO}_3) = 1/a^3$. The polarizability of cations which are included in the crystals being researched is evaluated after Kirkwood [21],

$$\alpha = \frac{4}{9Za_0} \left(\sum_k \langle r_k^2 \rangle \right)^2. \quad (6)$$

The average values of the squares "of orbit radii" $\langle r_k^2 \rangle$ are taken from the tables of Band and Trzhaskovskaya [22, 23]. The α values of Li^+ , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Ga^{3+} , Y^{3+} , Ba^{2+} , Bi^{3+} , Gd^{3+} cations obtained from (6) are equal to 0.016, 0.50, 1.09, 0.48, 0.62, 0.62, 0.47, 0.67, 0.75, 2.18, 1.38, 3.14 (in terms of 10^{-24} cm^3), respectively.

For the definition of polarizability of oxygen ions we used the empirical relationship obtained for crystals with the spinel structure [17],

$$\alpha(\text{O}^{2-}) = a_0 + am - bm^2. \quad (7)$$

Here $\alpha_0 = 1.45 \times 10^{-24} \text{ cm}^3$ is the polarizability of an oxygen ion in a low-magnetic spinel ($m = 0$); m is the number of spin-uncompensated 3d electrons of the cations; $a = 0.38 \times 10^{-24} \text{ cm}^3$ is the additional polarizability resulting from the establishing of two magnetic exchange bindings by a spin-uncompensated cation electron. This experimental value a is well correlated with quantum mechanical calculations [24] of the dipole moment and with the appropriate polarizability which depends on the overlap of atomic Fe^{3+} and O^{2-} orbitals. The constant $b = 0.042 \times 10^{-24} \text{ cm}^3$ takes into account the lowering of polarizability for large m as a result of simultaneous decrease of the participation of oxygen ions which have not been involved in magnetic exchange bindings.

4. Frequencies of Lattice Oscillations of Ions

The frequencies of optical phonons ω_{0i} for $\mathbf{k} = 0$ were defined through the effective ionic charges $q_i^* = q_{i\text{max}}^* I$, the interionic distances R_{0i} and the reduced masses \bar{M} of cations M_1 and anions M_2 from the relation

$$\omega_0 = q^* \sqrt{2/R_0^3 \bar{M}}. \quad (8)$$

It is obtained from the known equation connecting ω_0 of a crystal, that consists of two types of atoms, with a force constant C ($\omega_0 = \sqrt{2C/\bar{M}}$). The expression for $C = \left(\frac{d^2 U}{dR^2} \right)_{R=R_0}$ is obtained with by an interatomic interaction potential,

$$U(R) = A \exp(-R/\varrho) - (q^*)^2/R. \quad (9)$$

Here $\varrho = \frac{R_0}{n}$ and $\frac{1}{n}$ is the share of energy of repulsion from the total lattice energy. Excluding the constant A by minimization of expression (9) on R ,

$$C = \frac{(q^*)^2}{R_0^3} (n - 2) \quad (10)$$

is obtained. Assuming $n = 3$, which is close to the received value for oxide compounds [5], we obtain the Eq. (8). In spinels, $R_0^{\text{tetra}} = (\sqrt{3}/8) a$, $R_0^{\text{octa}} = a/4$.

The resonance frequencies of transverse optical phonons calculated from Eq. (8) are presented in the third column of Table 2.

Having defined the effective ionic charges, TO frequencies, electronic polarizabilities of ions and other parameters which are included in Eq. (1), it is possible to calculate now the static limits of the ionic and electronic components of permittivity of ferrimagnetic and low magnetic oxide crystals. However, difficulties arise while calculating the quantity of couples of ions in a structural unit and in a crystal as a whole: not each O^{2-} anion forms a pair with a cation. In an electric field, all ions of a negatively charged sublattice are displaced. This effect can be taken into account if we add two electrons from the not taken into account O^{2-} , by equal parts, to the ions O^{2-} , having already been taken into account in couples; and then calculate q_{max}^* and $q_{\text{max}}^* I$. Practically the same result occurs if we add shares from not taken into account ions of oxygen to components of ionic permittivity in (1): 1/4 in crystals with spinel structure, 1/3 in gar-

Table 2

The calculated frequencies of TO phonons ω_0 , oscillator strengths $\Delta\varepsilon'_i$, ionic $\varepsilon_1^{\text{ion}}$ and electronic $\varepsilon_1^{\text{el}}$ components of permittivity for crystals (the distribution of ions over sublattices in these crystals is presented in Table 1)

composition	A group of ions	ω_0 (10^{13} s^{-1})	$\Delta\varepsilon'_i$	$\varepsilon_1^{\text{ion}}$	$\varepsilon_1^{\text{el}}$	$\varepsilon_1^{\text{calc}} + 1$	$\varepsilon_1^{\text{exp}}$
MnFe ₂ O	[Mn ²⁺ -O ²⁻]	6.86	0.34	4.35	5.31	10.66	11.8
	[Fe ³⁺ -O ²⁻]	8.39	3.01				
	(Me ^{2,2+} -O ²⁻)	9.35	1.00				
Fe ₃ O ₄	[Fe ²⁺ -O ²⁻]	7.12	2.39	6.33	5.77	13.10	12.50
	[Fe ³⁺ -O ²⁻]	8.73	2.39				
	(Fe ³⁺ -O ²⁻)	10.8	1.55				
CoFe ₂ O ₄	[Co ²⁺ -O ²⁻]	7.31	1.85	5.20	5.77	12.00	12.00
	[Fe ³⁺ -O ²⁻]	9.02	1.92				
	(Fe ³⁺ -O ²⁻)	10.40	1.43				
NiFe ₂ O ₄	[Ni ²⁺ -O ²⁻]	7.59	1.97	5.40	5.99	12.40	12.00
	[Fe ³⁺ -O ²⁻]	9.26	2.08				
	(Fe ³⁺ -O ²⁻)	11.50	1.35				
Li _{0.5} Fe _{2.5} O ₄	[Li ⁺ -O ²⁻]	8.91	3.42	6.40	5.58	13.00	14.40
	[Fe ³⁺ -O ²⁻]	9.57	2.07				
	(Fe ³⁺ -O ²⁻)	11.90	0.90				
ZnFe ₂ O ₄	[Fe ³⁺ -O ²⁻]	9.54	3.38	4.36	5.18	10.54	9.52
	(Zn ²⁺ -O ²⁻)	11.90	0.98				
CoGa ₂ O ₄	[Co ²⁺ -O ²⁻]	8.54	1.38	3.33	4.31	8.64	7.30
	[Ga ³⁺ -O ²⁻]	10.30	1.20				
	(Ga ³⁺ -O ²⁻)	13.00	0.75				
Li _{0.5} Ga _{2.5} O ₄	[Li ⁺ -O ²⁻]	10.10	1.31	2.84	3.48	7.32	7.00
	[Ga ³⁺ -O ²⁻]	10.60	1.07				
	(Ga ³⁺ -O ²⁻)	13.10	0.46				
Y ₃ Fe ₅ O ₁₂	{Y ³⁺ -O ²⁻ }	7.58	2.07	5.34	5.74	12.10	12.50-
	[Fe ³⁺ -O ²⁻]	8.31	1.82				
	(Fe ³⁺ -O ²⁻)	11.40	1.45				
Gd ₃ Ga ₅ O ₁₂	{Gd ³⁺ -O ²⁻ }	7.94	0.85	3.10	5.06	9.16	10.00
	[Gd ³⁺ -O ²⁻]	9.99	0.90				
	(Ga ³⁺ -O ²⁻)	11.90	1.35				
BiFeO ₃	Fe ³⁺ -O ²⁻	10.10	2.54	3.31	5.12	9.43	25.00
	Bi ³⁺ -O ²⁻	12.00	0.77				

nets and 1/3 in perovskites. Then the resultant expression for the calculation of $\varepsilon_1^{\text{ion}}$ in conversed spinel takes the following form

$$\varepsilon_1^{\text{ion}} = \frac{5}{12} \pi \left(\frac{\varepsilon_1^{\text{el}} + 2}{3} \right)^2 N_A^2 d \times \left[\frac{(q_{1\text{octa}}^*)^2}{(\omega_{01}^{\text{octa}})^2 M_{1\text{octa}}^{2+} M_{\text{O}^{2-}}} + \frac{(q_{2\text{octa}}^*)^2}{(\omega_{02}^{\text{octa}})^2 M_{2\text{octa}}^{3+} M_{\text{O}^{2-}}} + \frac{(q_{\text{tetra}}^*)^2}{(\omega_0^{\text{tetra}})^2 M_{\text{tetra}}^{3+} M_{\text{O}^{2-}}} \right]. \quad (11)$$

5. Dependence of Permittivity on Chemical Composition

The results of the calculations of ionic and electronic components of permittivity with theoretical values of density d (calculated from the lattice parameter and chemical composition), as well as the corresponding experimental data are presented in Table 2. It is possible to speak about a satisfactory agreement of the calculated and experimental values of both electronic components of permittivity and the sum of electronic and ionic components of high-frequency ϵ_1 . The discrepancy between the calculated and experimental values of ϵ_1 can be related to the smaller density of real polycrystalline porous samples compared with the characteristics ϵ_1 of an ideally dense model crystal. The second reason for the discrepancy is that the relaxational components of polarization are not completely eliminated even at measuring at hundreds MHz and at 77 K. And finally, an obvious reason is the imperfection of the offered technique in calculating ϵ_1 , and also the experimental errors of its measurement. A significant (about 100%) exceeding of the experimental value ϵ_1 of bismuth ferrite compared with the calculated sum of electronic and ionic components is related to the existence of ferroelectric ordering [18, 29] in the given compound. On the basis of the calculation of the sum of electronic and ionic components of ϵ_1 and the optical limit of this sum, obtained from Kramers-Kronig analysis of the reflection spectrum of BiFeO₃, the value of the permittivity related to the reorientation of ferroelectric domains in the given compound is evaluated in the limits of 15 units.

It is seen from Table 2, that there is a reduction of both electronic and ionic components of ϵ_1 with the increase of the degree of ionicity of a crystal caused by substitution of magnetically active ions by diamagnetic ones. Such behaviour of permittivity and of the degree of ionicity is obviously related to the decrease of the degree of delocalization of valence electrons of ions as a result of the indicated replacement. The substitution of magnetically active ions by diamagnetic ones also reduces the indicated components of permittivity in the binary systems Ni_{1-c}Zn_cFe₂O₄, CoFe_{2(1-c)}Ga_{2c}O₄, Li_{0.5}Fe_{2.5(1-c)}Ga_{2.5c}O₄, (Li_{0.5}Fe_{0.5})_{1-c}Zn_cFe₂O₄.

The correlated character of the behaviour of ϵ_1^{ion} and ϵ_1^{el} at the change of the composition is not casual. In Eqs. (1) and (11) for the ionic component of ϵ_1 , it is possible to exclude $(q^*)^2$, since ω_0^2 is proportional to $(q^*)^2$. Then

$$\epsilon_1^{\text{ion}} = \frac{\pi}{2} \left(\frac{\epsilon_1^{\text{el}} + 2}{3} \right)^2 \frac{N_A^2 d R_0^3 \bar{M}}{M_1 M_2} \quad (12)$$

depends mainly on the electronic component of permittivity ϵ_1^{el} and on the sizes of ions which are included in (12) through the interion distances R_0 . Since ϵ_1^{el} is proportional to the sizes of the ions (see (6)), then expression (12) includes the radii of ions practically in the ninth degree. It predetermines that the radii of electronic shells of ions, especially outer ones, check the behaviour of both electronic and ionic components of permittivity if the composition changes.

6. Simulation of Spectra of Permittivity by a Sum of Quasiharmonic Oscillators and the Calculation of Optical Reflection Spectra

The application of classical-oscillator theory to the analysis of lattice-vibrational and electronic spectra of solids has been extensively reviewed and discussed [11–13]. The

relevant equations for the real and imaginary parts of the complex dielectric constants according to the classical oscillator analysis are

$$\varepsilon_1(\omega) - 1 = n^2 - k^2 = \sum_i \frac{\Delta\varepsilon_i^{\text{ion}} \omega_{0i}^2 (\omega_{0i}^2 - \omega^2)}{(\omega_{0i}^2 - \omega^2)^2 + (\Gamma_i \omega)^2} + \sum_j \frac{\Delta\varepsilon_j^{\text{el}} (\omega_{0j}^2 - \omega^2)}{(\omega_{0j}^2 - \omega^2)^2 + (\Gamma_j \omega)^2}, \quad (13)$$

and

$$\varepsilon_2(\omega) = 2nk = \sum_i \frac{\Delta\varepsilon_i^{\text{ion}} \omega_{0i}^2 \Gamma_i \omega}{(\omega_{0i}^2 - \omega^2)^2 + (\Gamma_i \omega)^2} + \sum_j \frac{\Delta\varepsilon_j^{\text{el}} \Gamma_j \omega}{(\omega_{0j}^2 - \omega^2)^2 + (\Gamma_j \omega)^2}, \quad (14)$$

where $\Delta\varepsilon_i^{\text{ion}}$, $\Delta\varepsilon_j^{\text{el}}$ are the strengths, Γ_i , Γ_j are the damping constants and ω_{0i} , ω_{0j} are the frequencies of the i -th lattice and the j -th electronic resonances. The reflectivity R

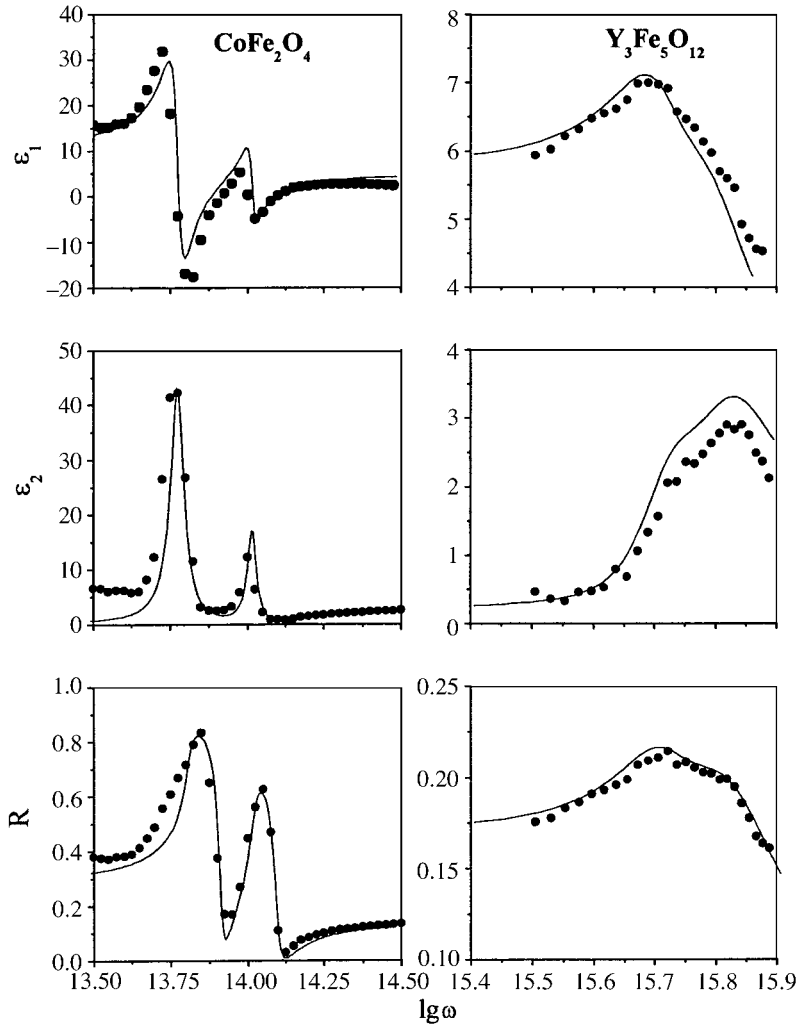


Fig. 1. Calculated (solid line) and experimental (solid circles) spectra of high-frequency permittivity components $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$ and of the reflection coefficient $R(\omega)$ for CoFe_2O_4 [17] and $\text{Y}_3\text{Fe}_5\text{O}_{12}$

of unpolarized radiation at normal angle of incidence is related to the refractive index n and extinction coefficient k

$$R = ((n - 1)^2 + k^2) / ((n + 1)^2 + k^2). \quad (15)$$

In Eqs. (13) and (14) the first sum is related to ionic polarization whereas the second sum describes the permittivity of bound electrons. Static limits of the ionic components of permittivity $\Delta\epsilon_i^{\text{ion}}$ have been found by the division of ϵ_1^{ion} into portions that refer to ionic oscillations of different coordinations: tetrahedral, octahedral, dodecahedral. The frequencies of transverse optical phonons ω_{0i} have been calculated in terms of the effective ionic charges and interion distances (8). Depending on composition and structure of the crystals the permittivity of core electrons is represented by a sum of 101–328 Lorentz oscillators per formula unit of MeFe_2O_4 , $\text{Me}_3\text{Fe}_5\text{O}_{12}$, BiFeO_3 . The frequencies ω_{0j} of the oscillators have been determined from the eigenvalues of energies for the pertinent electronic states $\omega_{0k} = E_{0k}/\hbar$ [22, 23]. While calculating permittivity, related to the transition of valence electrons, their indirect exchange was taken into account. On the base of the used values of effective charge probability the valence electron localization on oxygen anions was evaluated. Frequencies, corresponding to transitions of electrons of O^{2-} on Fe^{3+} were taken for the resonance frequencies of six external O^{2-} electrons situated on $2p^{1/2}$ and $2p^{3/2}$ subshells. Their values were taken from the experimental data on the reflexion of light in the range of electronic resonances received in this work, as well as from literature sources. In particular, we used the values of transition energy carrying a charge in FeO_4 and FeO_6 complexes, calculated in [30, 31]. The calculated and experimental spectra of the permittivity components $\epsilon_1(\omega)$, $\epsilon_2(\omega)$ and of the reflection coefficient $R(\omega)$ in the range of lattice (CoFe_2O_4) and electronic ($\text{Y}_3\text{Fe}_5\text{O}_{12}$) resonances are presented in Fig. 1. The parameters of oscillators describing the lattice spectra are presented in Table 3.

Table 3

Parameters of oscillators, simulating dielectric spectra of crystals in the range of lattice resonances

composition	ω_{0i} (10^{13} s^{-1})	$\Delta\epsilon_i^{\text{ion}}$	Γ_i (10^{12} s^{-1})
MnFe_2O_4	6.90	1.80	1.37
	8.35	2.60	6.71
	9.42	0.65	1.87
CoFe_2O_4	6.50	5.20	3.90
	10.40	1.35	8.32
NiFe_2O_4	7.59	3.05	1.52
	11.5	1.35	5.75
$\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$	7.76	5.28	7.76
	10.90	2.72	10.90
$\text{Y}_3\text{Fe}_5\text{O}_{12}$	7.19	2.65	3.61
	9.71	5.08	9.70
	10.89	3.17	10.09
BiFeO_3	3.59	5.00	2.87
	7.80	2.56	6.24
	10.00	0.60	2.53

The real spectra of the dielectric functions of crystals have a more complex structure, which is related to the distortions of the crystalline lattices, and also to the presence of interion interactions not taken into account within the limits of the suggested model. However, in the considered types of crystals there are always oscillation modes depending on the displacement of ions situated in tetrahedral and octahedral (in spinel), in tetrahedral, octahedral and dodecahedral (in garnets), and in octahedral (in perovskites) crystallographic positions. This gives the possibility to simulate dielectric functions of the indicated types of crystals by the sum of non-interactive quasiharmonic oscillators. The obtained results are in good agreement with $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$ and $R(\omega)$ both on parts independent of frequency, and in the range of resonance absorption of electromagnetic radiation by the crystals.

7. Conclusions

With the use of empirical data within the crystal-chemical approach we have defined effective ionic charges (q_i^*) for ion groups connected in tetrahedral, octahedral and dodecahedral polyhedra in such oxide crystals as spinels, garnets and perovskites. On the base of the obtained q_i^* values and the values of interionic distances, we have calculated the frequencies of TO phonons and the values of contributions of lattice vibrations of different types of ions in the static limits of ionic components of permittivity. Electronic polarizabilities of ions and values of electronic components of permittivity have been calculated. The obtained sums of electronic and ionic contributions are in good agreement with the experimental high-frequency ($\omega = 10^8 \text{ s}^{-1}$) values of $\varepsilon_1(\omega)$, measured at 77 K. Dielectric spectra and reflection coefficient spectra of the crystals are simulated by a set of quasiharmonic oscillators.

References

- [1] A. FAIRWEATHER and E. J. FROST, *Proc. IEEE A* **100**, 15 (1953).
- [2] R. D. WALDRON, *Phys. Rev.* **99**, 1727 (1955).
- [3] P. A. MILS, W. B. WESTPHALEN, and A. A. HIPPEL, *Rev. Mod. Phys.* **29**, 279 (1957).
- [4] W. B. WHITE and B. A. DE'ANGELIS, *Spectrochim. Acta A* **23**, 985 (1967).
- [5] S. KRUPÍČKA, *Fyzika feritů a příbuzných magnetykých kysličníků*, NCAV, Praha 1969 (p. 594).
- [6] M. I. KLINGER and A. A. SAMOKHVALOV, *phys. stat. sol. (b)* **79**, 9 (1977).
- [7] V. P. MIROSHKIN, YA. I. PANOVA, and V. V. PASSYNKOV, *phys. stat. sol. (a)* **66**, 779 (1981).
- [8] H. SHIRAI, Y. MORIOKA, and J. NAKAGAWA, *J. Phys. Soc. Jpn.* **51**, 592 (1982).
- [9] H. D. LUTZ, J. HIMMIRICH, and H. HAEUSELER, *Z. Naturf.* **45a**, 893 (1990).
- [10] M. KUČERA, V. N. KOLOBANOV, V. V. MIKHAILIN, P. A. OREKHANOV, and V. N. MAKHOV, *phys. stat. sol. (b)* **157**, 745 (1990).
- [11] S. TAJIMA, A. MASAKI, S. UCHIDA, T. MATSUURA, K. FUEKI, and S. SUGAI, *J. Phys. C* **20**, 3469 (1987).
- [12] A. M. HOFMEISTER and K. R. CAMPBELL, *J. Appl. Phys.* **72**, 638 (1992).
- [13] D. A. CRANDLES, T. TIMUSK, J. D. GARRET, and J. E. GREEDAN, *Phys. Rev. B* **48**, 4299 (1994).
- [14] C. N. W. DARLINGTON, *phys. stat. sol. (a)* **155**, 31 (1996).
- [15] M. I. DANILKEVITCH, *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.* **17**, 860 (1981).
- [16] M. I. DANILKEVITCH and A. V. LEONTEV, *Zh. Prikl. Spektrosk.* **45**, 639 (1986).
- [17] M. I. DANILKEVITCH, *Inorg. Mater.* **33**, 313 (1997).
- [18] I. I. MAKOED and M. I. DANILKEVICH, *Inorg. Mater.* **34**, 737 (1998).
- [19] B. SZIGETI, *Proc. Roy. Soc. A* **204**, 51 (1950).
- [20] A. R. V. HIPPEL, *Dielectrics and Waves*, Wiley, New York 1954.
- [21] J. G. KIRKWOOD, *Phys. Z.* **33**, 57 (1931).

- [22] I. M. BAND and M. B. TRZHASKOVSKAYA, Tables of Eigenvalues for Electrons, Densities near Zero Temperature, and Mean Values in Self-Consistent Fields of Atoms and Ions with $2 \leq Z \leq 52$, Leningradsk. Inst. Yadernoi Fiziki, 1974 (in Russian).
- [23] I. M. BAND and M. B. TRZHASKOVSKAYA, Tables of Eigenvalues for Electrons, Densities near Zero Temperature, and Mean Values in Self-Consistent Fields of Atoms and Ions with $64 \leq Z \leq 94$, Leningradsk. Inst. Yadernoi Fiziki, 1974 (in Russian).
- [24] M. I. DANILKEVITCH and A. V. LEONTEV, Proc. Natl. Acad. Sci. BSSR, Physico-Mathematical Ser. **6**, 78 (1988) (in Russian).
- [25] A. J. M. KUIPERS and V. A. M. BRABERS, Phys. Rev. Lett. **39**, 488 (1977).
- [26] M. I. DANILKEVITCH, Vestnik Belorussk. Universiteta, Ser. 1., Fiz. Mat. and Mech. **3**, 21 (1993).
- [27] M. I. DANILKEVITCH and A. V. LEONTEV, Vestnik Belorussk. Universiteta, Ser. 1., Fiz. Mat. and Mech. **3**, 17 (1984).
- [28] M. I. DANILKEVITCH and A. V. LEONTEV, Vestnik Belorussk. Universiteta, Ser. 1., Fiz. Mat. and Mech. **2**, 29 (1986).
- [29] A. STEINER, O. TABARES-MUNOZ, and H. SCHMID, Helv. Phys. Acta **60**, 294 (1987).
- [30] A. V. ZENKOV and A. S. MOSKVIN, Fiz. Tverd. Tela **32**, 3674 (1990).
- [31] E. A. GANSHINA, A. V. ZENKOV, G. S. KRINCHIK, A. S. MOSKVIN, and A. YU. TRIFONOV, Fiz. Tverd. Tela **33**, 1122 (1991).

