

# Contribution to the microscopic theory of the quadratic susceptibility of crystals at optical frequencies

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A microscopic theory of nonlinear polarization of "ionic" crystals is developed. The nonlinearity at optical frequencies is due to the anharmonic motion of the outer electrons of an ion relative to their core. Only the Coulomb-induced anharmonicity is properly taken into account. In order to quantitatively verify the Coulomb-anharmonicity model, the components of the quadratic-susceptibility tensor of the non-cubic crystals  $AH_2XO_4$  ( $A = K, Rb, Cs; X = P, As$ ),  $BaTiO_3$ ,  $PbTiO_3$ ,  $LiIO_3$  and the cubic crystals  $CuCl$ ,  $CuBr$ ,  $ZnS$ ,  $ZnTe$ ,  $GaAs$  are computed. The results of the computation are compared with the experimental data. Qualitative and good quantitative agreement is found, in particular, for the ferroelectric substances KDP and  $BaTiO_3$  in a wide range of temperatures.

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## 1. INTRODUCTION

The source of the optical nonlinearity at frequencies much higher than the frequencies of infrared lattice vibrations is the distortion of the electron wave functions. There exists a relatively large number of papers devoted to the computation of this nonlinearity for specific compounds (see, for example, [1-10]). The greatest success in the computation of the spectral components  $d_{\alpha\beta\gamma}$  responsible for second-optical-harmonic generation has been achieved on the basis of Levine's macroscopic bond-charge model [9, 10].

However, the problem of the computation of the tensor components  $d_{\alpha\beta\gamma}$  is, generally speaking, a problem for a microscopic theory. The limited successes achieved in the computation of  $d_{\alpha\beta\gamma}$  on the basis of quantum-mechanical perturbation theory, which requires knowledge of the specific form of the electron dispersion law, the band structure, and the form of the wave functions, attest to the fact that more can be attained today on the basis of the classical crystal-polarization models. Therefore, in the present paper we develop a microscopic quantitative theory of nonlinear optical properties of crystals on the basis of the Born polarizable-ion model [11] and the ideas of the shell model [12].

The equation obtained in the paper for the spectral components  $d_{\alpha\beta\gamma}$  does not contain a single macroscopic parameter, and allows the computation of the  $d_{\alpha\beta\gamma}$  for crystals if the coordinates of the ions (atoms), the parameters of the unit cell, the electronic polarizabilities, and the charges of the shells of the ions are known. This equation is used to investigate the magnitude, sign, and temperature dependence of  $d_{\alpha\beta\gamma}$  of the noncubic crystals  $AH_2XO_4$  ( $A = K, Rb, Cs; X = P, As$ ),  $BaTiO_3$ ,  $PbTiO_3$ , and  $LiIO_3$  and the cubic crystals  $CuCl$ ,  $CuBr$ ,  $ZnS$ ,  $ZnTe$ , and  $GaAs$ . Owing to the allowance for the microstructure of crystals, the equation for  $d_{\alpha\beta\gamma}$  imparts all the characteristic features of the variation of the magnitude, sign, and temperature dependence of the  $d_{\alpha\beta\gamma}$  of the considered crystals, and also leads to important information about the individual characteristics of the ions, information which can subsequently be used in the investigation of other nonlinearities. In particular, in the present paper the information on the individual characteristics of the ions is used in the computation of the electro-optical constants  $r_{\alpha\beta\gamma}$  of the linear electro-

optical effect in the crystals  $KH_2PO_4$ ,  $RbH_2PO_4$  and their deuterated analogs, as well as in the crystals  $BaTiO_3$  and  $PbTiO_3$ .

The choice of the objects for investigation is not accidental. All the crystals under consideration have important practical meaning, and are interesting model crystals.

## 2. THE MICRO-OPTICAL EQUATION FOR THE SPECTRAL COMPONENTS $d_{\alpha\beta\gamma}$

Let us consider a crystal consisting of  $m$  ( $m \geq 2$ ) electrically different ions. The polarization of such a crystal can be interpreted in the following manner. When an ion is acted upon by an electric field, its electron cloud becomes deformed, and it acquires a dipole moment. If the field acting on an ion in the lattice is a high-intensity field, as in the case of the electric field of the light wave from a laser source, then the induced electronic dipole moment is not proportional to the field, i.e.,

$$\mu_{\alpha}^i = \mu_{\alpha}^i(\text{li}) + \mu_{\alpha}^i(\text{nl}) = \kappa_{\alpha}^i E_{\beta}(\omega) + \gamma_{\alpha\beta\gamma}^i E_{\beta}(\omega) E_{\gamma}(\omega), \quad (1)$$

where  $\mu^i(\text{li})$  and  $\mu^i(\text{nl})$  are the linear and nonlinear dipole moments of the  $i$ -th ion,  $\kappa^i$  is the linear susceptibility of the  $i$ -th ion,  $\mathbf{E}(\omega)$  is the electric field of the light wave, and  $\gamma_{\alpha\beta\gamma}^i$  is the lowest-order ionic nonlinearity. By definition, the  $\gamma_{\alpha\beta\gamma}^i$  are directly connected with the spectral components  $d_{\alpha\beta\gamma}$  [13].

From the point of view of the shell model [12], the dipole moment (1) of the ion can be represented as

$$\mu_{\alpha}^i = x_{\alpha}^i c^i = x_{\alpha}^i(\text{li}) a^i + x_{\alpha}^i(\text{nl}) a^i. \quad (2)$$

Here  $\mathbf{x}^i(\text{li})$  is the linear part of the displacement of the charge  $a^i$  of the shell of the  $i$ -th ion induced by the electric field, and  $\mathbf{x}^i(\text{nl})$  is the nonlinear part of the displacement.

It follows from (2) that the problem reduces to the problem of the determination of  $\mathbf{x}^i(\text{nl})$ , for which purpose it is necessary to solve a system of equations describing the motion of the charge of the ion shells in the anharmonic approximation. Let us write this system of equations for the case of the zero wave vector and in the absence of light absorption by the medium in the form

$$m^i \ddot{x}_{\alpha}^i + (R_{\alpha\beta}^{ik} - a^i g_{\alpha\beta}^{ik} a^k) x_{\beta}^k + (c_{\alpha\beta\gamma}^{ik} - 1/2 a^i f_{\alpha\beta\gamma}^{ik} a^k) x_{\beta}^k x_{\gamma}^k = a^i E_{\alpha}(\omega), \quad (3)$$

Here  $m^i$  is the mass of the  $i$ -th charge;  $R_{\alpha\beta}^{ik}$  and  $c_{\alpha\beta\gamma}^{ik}$  are constants of non-Coulomb origin<sup>[11]</sup>, while  $g_{\alpha\beta}^{ik} = \beta\alpha\beta\delta_{\alpha\beta} + f_{\alpha\beta}^{ik}$  and  $f_{\alpha\beta\gamma}^{ik}$  (where  $\beta\alpha\alpha$  is the Lorentz factor, which, according to its physical meaning, describes that part of the field acting on the lattice ions that is due to the medium outside the Lorentz cavity, and  $f_{\alpha\beta}^{ik}$  and  $f_{\alpha\beta\gamma}^{ik}$  describe the fields due to the medium inside the cavity) are constants of Coulomb origin;  $E(\omega)$  is the field from the external source; and  $\alpha$ ,  $\beta$ , and  $\gamma$ , which assume the values 1, 2, and 3, denote the axes of the Cartesian system of coordinates.

Let us find the solution to the system (3) under the assumption that the oscillations of the charge of the electron shells of the ions are normal-mode vibrations. Then we obtain for the displacement  $x^i$  at the frequency  $\omega$  the expression

$$x_{\alpha}^i(\omega) = a^i E_{\alpha}(\omega) \sum_j \frac{l_{\alpha}^i(j) l_{\alpha}^i(j)}{(\omega^2(j) - \omega^2) m(j)} = (a^i)^{-1} \alpha_{\alpha\beta}^i(\omega) A_{\alpha\beta}^i E_{\beta}(\omega). \quad (4)$$

Here  $\omega(j)$ ,  $l^i(j)$ , and  $m(j)$  are the eigenvalues, vectors, and mass of the  $j$ -th vibrational mode.

In order to get rid of the unknown parameters  $l^i(j)$ ,  $\omega(j)$ , and  $m(j)$  in (4), we used the connection between the shell model and the polarizable-ion model<sup>[14]</sup> in solving the system (3), i.e.,

$$x_{\alpha}^i(1i) a^i = \alpha_{\alpha\beta}^i \mathcal{E}_{\beta}^i = \alpha_{\alpha\beta}^i A_{\alpha\beta}^i E_{\beta}(\omega). \quad (5)$$

In Eqs. (4) and (5),  $\alpha^i$  is the electronic polarizability of the  $i$ -th ion, while the tensor components  $A^k$  are found from the solution to the system of equations for the local fields:

$$\mathcal{E}_{\alpha}^i = E_{\alpha}(\omega) + g_{\alpha\beta}^{ik} \alpha_{\alpha\beta}^k \mathcal{E}_{\beta}^i.$$

In the lowest-order nonlinear approximation the displacements will be proportional to both  $f_{\alpha\beta\gamma}^{ik}$  and  $c_{\alpha\beta\gamma}^{ik}$ , i.e., to both the Coulomb and non-Coulomb parts of the anharmonic correction in (3).

Let us assume that the optical nonlinearity of ionic crystals can be described by taking only the Coulomb anharmonicity into account, i.e., let us assume that the overlap forces do not change during the generation of optical harmonics ( $c_{\alpha\beta\gamma}^{ik} = 0$ ). Then the displacement of the  $i$ -th charge at a harmonic frequency due to the anharmonic correction of Coulomb origin has the form

$$x_{\alpha}^i(2\omega) = x_{\alpha}^i(nl) = \sum_j \left[ \frac{l_{\alpha}^i(j) l_{\alpha}^i(j) a^i}{m(j) (4\omega^2(j) - 4\omega^2)} \right] \times \frac{1}{2} f_{\alpha\beta\gamma}^{ik} \alpha_{\alpha\beta}^k(\omega) A_{\alpha\beta}^k \alpha_{\alpha\gamma}^k(\omega) A_{\alpha\gamma}^k (a^k)^{-1} E_{\beta}(\omega) E_{\gamma}(\omega). \quad (6)$$

From the point of view of the polarizable-ion model, the term enclosed in the square brackets in (6) is equal to  $(a^1)^{-1} \alpha^1(2\omega) A^1$  (see (4) and (5)).

Thus, the polarization of the crystal at the frequency  $2\omega$  will contain only those terms that can be computed:

$$P_{\alpha}(2\omega) = d_{\alpha\beta\gamma} E_{\beta}(\omega) E_{\gamma}(\omega) = \sum_{i=1}^m N^i x_{\alpha}^i(2\omega) a^i = \frac{1}{2} \sum_{i=1}^m N^i \alpha_{\alpha\alpha}^i(2\omega) A_{\alpha\alpha}^i f_{\alpha\beta\gamma}^{ik} \alpha_{\alpha\beta}^k(\omega) A_{\alpha\beta}^k \alpha_{\alpha\gamma}^k(\omega) A_{\alpha\gamma}^k (a^k)^{-1} E_{\beta}(\omega) E_{\gamma}(\omega). \quad (7)$$

The investigation of (7) leads us to an equation for the computation of the spectral components  $d_{\alpha\beta\gamma}$ , an equation that does not include a single macroscopic parameter and that satisfies the symmetry requirements for

third-rank tensors, since  $f_{\alpha\beta\gamma}^{ik}$  is an odd function of the ion coordinates:

$$d_{\alpha\beta\gamma} = \frac{1}{2} \sum_{i=1}^m N^i \alpha_{\alpha\alpha}^i(2\omega) A_{\alpha\alpha}^i f_{\alpha\beta\gamma}^{ik} \alpha_{\alpha\beta}^k(\omega) A_{\alpha\beta}^k \alpha_{\alpha\gamma}^k(\omega) A_{\alpha\gamma}^k (a^k)^{-1} \quad (k=1, 2, 3, \dots, m). \quad (8)$$

Equation (8) can be derived in a different way, using the method considered in<sup>[14-17]</sup>, where the electro-optical properties of crystals are investigated. In these papers the nonlinear terms are introduced into the polarization by taking multipole corrections into account in the equation for the local field. It is, however, difficult to understand from such an approach the degree of approximation of the model; besides, an illusion is created that the nonlinear optical properties of crystals can be described under the assumption that the electric-field dependence of the displacements is linear in character.

In the present paper, besides the  $d_{\alpha\beta\gamma}$ , we compute the electro-optical constants  $r_{\alpha\beta\gamma}$  from Eq. (1) of<sup>[17]</sup>, which equation was derived from the same position as the equation for  $d_{\alpha\beta\gamma}$ .

Let us write the equation for  $r_{\alpha\beta\gamma}$ , as well as the equation that describes the low-frequency permittivity  $\epsilon(0)$ <sup>[17]</sup>, and which will be required in connection with the computation of the  $r_{\alpha\beta\gamma}$ , in the implicit form<sup>[1]</sup>:

$$r_{\alpha\beta\gamma} = F(f_{\alpha\beta\gamma}^{ik}, g_{\alpha\beta}^{ik}, \alpha^k, \omega_c, a^k, (e^*)^k), \quad (9)$$

$$\epsilon_{\alpha\alpha}(0) = M(g_{\alpha\beta}^{ik}, \omega_c, (e^*)^k, \alpha^k). \quad (10)$$

For the computations carried out in the paper, we shall also need the generalized Lorenz-Lorentz equation, which is immediately obtained by taking (4) into account:

$$\epsilon_{\alpha\beta}(\omega) = \delta_{\alpha\beta} + 4\pi \sum_{i=1}^m N^i \alpha_{\alpha\beta}^i(\omega) A_{\alpha\beta}^i. \quad (11)$$

To compute the material constants from Eqs. (8)–(11), we must know the values of  $g_{\alpha\beta}^{ik}$ ,  $f_{\alpha\beta\gamma}^{ik}$ ,  $\alpha_{\alpha\beta}^i$ ,  $a^i$ ,  $(e^*)^i$ , and  $\omega_c$ . The local-field coefficients  $g_{\alpha\beta}^{ik}$  and  $f_{\alpha\beta\gamma}^{ik}$  for a perfect lattice are computed practically exactly<sup>[11]</sup>. Since, as a rule, the  $g_{\alpha\beta}^{ik}$  for  $\alpha \neq \beta$  make a negligibly small contribution to the linear dipole moment in comparison with the contribution of  $g_{\alpha\beta}^{ik}$  for  $\alpha = \beta$ , we took only the diagonal tensor components  $A^i$  and  $\alpha^i$  into account in the computations.

The electronic polarizabilities  $\alpha_{\beta\beta}^i$  were, if they were not known, estimated for the cations from refraction data and for the anions from Eq. (11), using experimental values for  $\epsilon_{\beta\beta}(\omega)$ .

The effective ion charge  $(e^*)^i = ez^i s^i$ , where  $e$  is the electron charge,  $z^i$  is the number of valence electrons, and  $s^i$  is the parameter of the theory (the degree of ionicity). If we replace  $s^i$  by some macroscopic quantity that is the same for all the ions of the lattice (phenomenologically, nothing prevents this), then in determining  $(e^*)^i$  we can use the data available in the literature on the degree of ionicity of the compounds (see, for example, <sup>[11, 18]</sup>). In the opposite case, it is possible to choose the quantity  $s^i$  on the basis of an analysis of the structure in question and the data on the electro-negativity of the atoms<sup>[19, 20]</sup>. There are other approaches to the estimation of  $s^i$  for the individual bonds in a lattice<sup>[10]</sup>.

The ion-shell charge  $a^i$  was assumed in our computations to be equal to

$$a^i = e[z_{at}^i + s^i z_{val}^i] / \sigma^i, \quad (12)$$

where  $z_{at}^i$  is the number of electrons in the outermost shell of the neutral atom and  $\sigma^i$  is the screening constant. The second term in (12) takes account of the charge that an atom receives (gives away) as a result of a redistribution of the electronic charges in the crystal, i.e., it is the effective ion charge. The quantity  $\sigma^i$  depends on the specific form of the electron-density distribution, and is different for the different types of ions entering into the crystal. Nevertheless, as a first approximation, we can assume  $\sigma^i$  to be the same for all the ions and approximate it by the quantity  $\sigma^i = \epsilon(\omega)^{[10]}$ .

This approximation is applied in our paper to all the crystals, with the exception of the KDP group of crystals. In computing the electro-optical constants of the ferroelectric crystals KDP, RDP, DKDP, DRDP, BaTiO<sub>3</sub>, and PbTiO<sub>3</sub> the frequency  $\omega_c$  of the soft lattice vibration mode was eliminated from (9) with the aid of (10). The quantity  $\Delta\epsilon = \epsilon(0) - \epsilon(\omega)$  was assumed to be equal to the experimental value.

### 3. THE KDP GROUP OF CRYSTALS

A good verification of the theory is its applicability to the ferroelectric crystals AH<sub>2</sub>XO<sub>4</sub> (A = K, Rb, Cs; X = P, As). Let us restrict ourselves to the consideration of the nonlinear properties in the paraelectric phase. In this phase there are two nonvanishing components:  $d_{312}$  and  $d_{231} = d_{123} \approx d_{312}$  and two electro-optical coefficients:  $r_{123}$  and  $r_{232}$ . We shall compute only the constants  $d_{312}$  and  $r_{123}$ .

The theory should give the correct sign and order of magnitude of the quantities  $d_{\alpha\beta\gamma}$  and  $r_{\alpha\beta\gamma}$ , reflect the nature of their variation within the isomorphous series of crystals, and, as applied to the crystals of the KDP group, also impart the variation of  $r_{\alpha\beta\gamma}$  with temperature and the dependence of  $r_{\alpha\beta\gamma}$  on the degree of deuteration of the crystals of this group.

The results of the calculations with Eqs. (8) and (9) are presented in Figs. 1–3. Also shown in the figures are experimental data. It can be seen that the theoretical results are in qualitative and excellent quantitative agreement with the experimental data. The magnitude and sign of  $d_{312}$  are predicted for a new crystal, CDP, of the KDP group.

The theory leads to  $d_{312}(\text{KDP}) = d_{312}(\text{DKDP})$ , but to different  $r_{123}$  values for KDP type of crystals and their deuterated analogs (see Fig. 2 and the Table), which is in agreement with experiment. The differences in the  $r_{123}$  values for the crystals KDP and DKDP, RDP and DRDP arise from the differences in the soft-mode frequencies of the deuterated and undeuterated lattices, i.e., from the inequality of the values of  $\Delta\epsilon$  for these lattices. Figure 3 shows the theoretical and experimental temperature dependences of  $r_{123}$  for the crystal KDP. The only—to all intents and purposes—parameter determining the temperature dependence of  $r_{123}$  is the variation with temperature of the soft-mode frequency  $\omega_c$ . This dependence of  $\omega_c$  ( $\nu_c = \omega_c / 2\pi c$ ) is shown in Fig. 3.

Thus, Eqs. (8) and (9) gave all the principal distinctive features of the nonlinear optical characteristics of the ferroelectric members of the KDP group. In calculating these characteristics, the local-field coefficients were computed on a computer for the actual positions of

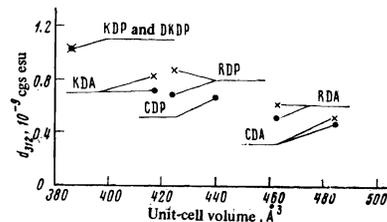


FIG. 1. Dependence of  $d_{312}$  on the unit-cell volume for crystals of the KDP group: ● calculated from (8), X mean experimental values [23,24].

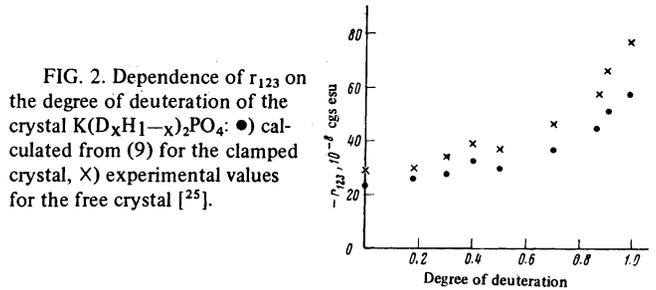


FIG. 2. Dependence of  $r_{123}$  on the degree of deuteration of the crystal  $\text{K}(\text{D}_x\text{H}_{1-x})_2\text{PO}_4$ : ● calculated from (9) for the clamped crystal, X experimental values for the free crystal [25].

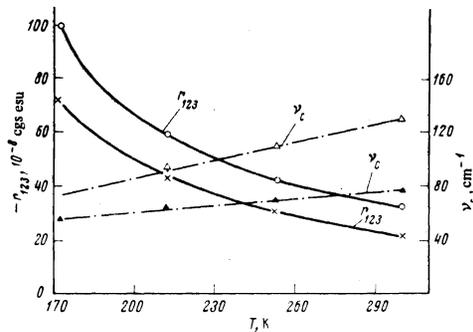


FIG. 3. Temperature dependence of the constants  $r_{123}$  and  $\nu_c$  of the crystal KDP. X, Δ) calculated from (9) and (10); ○) experimental values of  $r_{123}$  for the free crystal [26]; ▲) experimental values of  $\nu_c$  [27].

the ions of the KDP lattice<sup>[21]</sup>. In going over to the other crystals of this group we took into account, using the data given in<sup>[22]</sup>, only the variation of the parameters of the unit cell. As the electronic polarizabilities, the degrees of ionicity of the ions, and the screening constants, we used the following values<sup>2)</sup>:  $\alpha^X = 0.5 \text{ \AA}^3$ ,  $\alpha^A = 1.3 \text{ \AA}^3$ ,  $\alpha^O = 0.9 \text{ \AA}^3$ ,  $s^A = 1$ ,  $s^H = 1$ ,  $s^X = 0.3$ ,  $s^O = 0.55$ ;  $\sigma^A = 2.25$ ,  $\sigma^X = 1.3$ ,  $\sigma^O = 4.4$ .

### 4. TETRAGONAL BARIUM AND LEAD TITANATES

The crystals BaTiO<sub>3</sub> and PbTiO<sub>3</sub> are isomorphous crystals, which belong at room temperature to the crystal class 4mm. From the theoretical point of view the nonlinear optical properties of these crystals are of interest in connection with the change in sign of the components  $d_{333}$  and  $r_{333}$  when we go over from BaTiO<sub>3</sub> to PbTiO<sub>3</sub><sup>[30,32]</sup>.

Our calculations showed that the primary source of such an unusual behavior of the sign of the nonlinear coefficients is connected with the fact that the static displacements undergone by the oxygen ions in BaTiO<sub>3</sub> and PbTiO<sub>3</sub> crystals during the phase transitions are oppositely directed<sup>[33]</sup>. This leads to different signs for the coefficients  $r_{333}^k$ , with which  $d_{333}$  and  $r_{333}$  are connected by a linear relation.

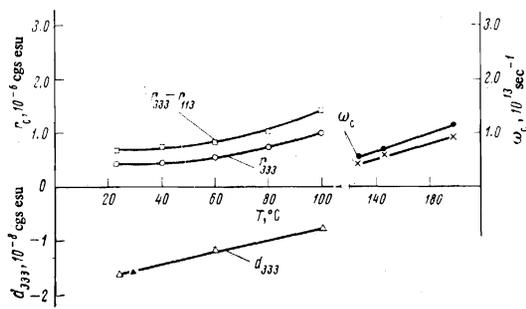


FIG. 4. Temperature dependence of  $d_{333}$ ,  $r_{333}$ , and  $\omega_c$  for tetragonal barium titanate.  $\Delta$ ,  $\circ$ ,  $\bullet$ ) calculated respectively from (8), (9), and (10);  $\square$ ) experimental values of  $r_{333} - r_{113}$  [28];  $\times$ ) experimental values of  $\omega_c$  [29];  $\blacktriangle$ ) measured [35].

The coefficients  $f_{333}^{ik}$  were computed for the actual positions of the ions of the  $BaTiO_3$  and  $PbTiO_3$  lattices<sup>[33]</sup> and the  $g_{33}^{ik}$  were assumed to be equal to their values in the cubic phase<sup>[34]</sup>. According to refraction data<sup>[19,20]</sup>,  $\alpha^{Ba} \approx 1.7 \text{ \AA}^3$  and  $\alpha^{Ti} \approx 0.6 \text{ \AA}^3$ ;  $\alpha^0$  was computed from (11) for  $BaTiO_3$ , and is equal to  $2.5 \text{ \AA}^3$ . These same values were assumed for the ions of the  $PbTiO_3$  lattice. According to the numerous data available in the literature, the degree of ionicity of the crystals in question is equal to  $\sim 0.5$ . The values obtained in the calculation for  $d_{333}$  and  $r_{333}$  are presented in the Table and shown in Fig. 4. As can be seen, there is qualitative and quantitative agreement between the theory and experiment.

## 5. LITHIUM IODATE

For the hexagonal crystal  $LiIO_3$ , let us restrict ourselves to the computation of the spectral components  $d_{322}$  and  $d_{333}$ . The electronic polarizabilities of the extraordinary and ordinary rays are equal to:  $\alpha_{33}^0 = 2.4 \text{ \AA}^3$ ,  $\alpha_{33}^I = 1.0 \text{ \AA}^3$ , and  $\alpha_{33}^{Li} = 0.03 \text{ \AA}^3$ <sup>[36]</sup>;  $\alpha_{22}^0 = 1.6 \text{ \AA}^3$ ;  $\alpha_{22}^I = 1.25 \text{ \AA}^3$ , and  $\alpha_{22}^{Li} = 0.03 \text{ \AA}^3$ . According to the data of the same paper, the degree of ionicity of the compound  $LiIO_3$  is roughly equal to 0.3. Let us attribute this value to the I-O bond (which then makes the dominant contribution to  $d_{\alpha\beta\gamma}$ ) and assume the Li-O bond to be purely ionic. Then the charges of the shells of the ions in  $LiIO_3$  will be equal to:  $a^0 = 6.8 e/\sigma^0$ ,  $a^I = 3.5 e/\sigma^I$ ,  $a^{Li} = 2e/\sigma^{Li}$  (in the case of lithium the next electron sheath was taken into account). Let us assume the screening constant to be the same for all the ions and approximate it by the quantity  $(n_e^2 + n_o^2)/2 = 3.3$ <sup>[30]</sup>. The local-field coefficients were computed for the actual positions of the atoms of the  $LiIO_3$  lattice. The results of the computation are presented in the Table.

## 6. CUBIC CRYSTALS OF THE TYPE AB

From the point of view of the theory the crystals AB are of interest in connection with the different signs of the values of the only nonvanishing component  $d_{312}$  for different members of the group; for example,  $d_{312}(CuCl) < 0$ , while  $d_{321}(ZnS) > 0$ <sup>[30]</sup>. In contrast to the crystals  $BaTiO_3$  and  $PbTiO_3$ , for the crystals  $CuCl$  and  $ZnS$  the local-field coefficients  $f_{\alpha\beta\gamma}^{ik}$  are not only of the same sign, they are of the same magnitude as well<sup>[14]</sup>:

$$f_{312}^{AA} = f_{312}^{BB} = 0, \quad f_{312}^{BA} = -f_{312}^{AB} = 306 v^{-1/2}.$$

Therefore, it is clear that the cause of the sign difference between the  $d_{312}$  values for the crystals in ques-

Comparison of the theoretical and experimental values of  $d_{\alpha\beta\gamma}$  and  $r_{\alpha\beta\gamma}$  for a number of crystals.

Crystal	$d_{\alpha\beta\gamma}, 10^{-7}$ cgs esu		$r_{\alpha\beta\gamma}, 10^{-7}$ cgs esu	
	Calculated from (8)	Experiment [24,30,31]	Calculated from (9)	Experiment [24,31]
RDP	$d_{312} = +0.68$	$d_{312} =  0.72 $	$r_{123} = -2.5$	$r_{123} =  2.3 $
DRDP	$d_{312} = +0.68$	$d_{312} =  0.72 $	$r_{123} = -6.5$	$r_{123} =  6.8 $
$BaTiO_3$	$d_{333} = -16.3$	$d_{333} = -16; -19$	$r_{333} = +4.0$	$r_{333} = +8.4$
$PbTiO_3$	$d_{333} = +20.7$	$d_{333} = +20.0$	$r_{333} = -2.3$	$r_{333} = -1.8^*$
$LiIO_3$	$d_{333} = -0.3$	$d_{333} = -0.9$	—	—
	$d_{322} = -0.71$	$d_{322} = -1.1$	—	—
$CuCl$	$d_{312} = -0.21$	$d_{312} = -0.23$	—	—
$CuBr$	$d_{312} = -0.20$	$d_{312} = -0.23$	—	—
$ZnS$	$d_{312} = +0.36$	$d_{312} = +0.58$	—	—
$ZnTe$	$d_{312} = +1.8$	$d_{312} = +2.2$	—	—
$GaAs$	$d_{312} = +11.8$	$d_{312} = +6.5$	—	—

\*The sign of the coefficient  $r_{333}$  ( $PbTiO_3$ ) was measured by Yu. V. Shaldin.

tion does not lie in a change in sign of the coefficients  $d_{312}$ .

The contributions of the ions A and B to the  $d_{312}$  of the crystal  $CuCl$  or  $ZnS$  have opposite signs. Which of the terms will predominate in the case of  $CuCl$  or  $ZnS$  depends on the values of  $\alpha^I$  and  $a^I$ .

The electronic polarizability of the A ions was calculated from refraction data for these ions (see Table 29 in<sup>[20]</sup>), and the polarizability of the B-type ions was calculated from (11). The degree of ionicity of the A-B bonds was chosen in accordance with the data on the electronegativity of these bonds in the lattice (see Batsanov's book<sup>[19]</sup>) and Szigetti's data, which are also given in<sup>[19]</sup>. On the basis of these data the degree of ionicity of the Cu-Cl and Cu-Br bonds is roughly equal to 0.7, while for the other AB-type crystals considered in our paper it is equal to 0.5.

The  $d_{312}$  values computed from (8) and the experimental values are presented in the Table above.

The method developed for the computation of the  $d_{\alpha\beta\gamma}$  gives also in the case of crystals of the AB type results that are in qualitative and quantitative agreement with the experimental results (see the Table), the sign difference between the  $d_{\alpha\beta\gamma}$  values for  $CuCl$ - and  $ZnS$ -type crystals being due primarily to the charge difference between the shells of the Cu and Zn ions.

## 7. CONCLUSION

The above-described method of computing the spectral components  $d_{\alpha\beta\gamma}$  and the electro-optical constants  $r_{\alpha\beta\gamma}$ , which takes into account the nonlinear polarization due only to the anharmonic terms of Coulomb origin, gave results that are in qualitative and reasonably good quantitative agreement with the experimental data for simple, as well as complex, compounds. This apparently means that the Coulomb anharmonicity in ionic crystals makes the dominant contribution to the nonlinear polarization, i.e., that the approximation considered in the present paper is entirely admissible. For a more detailed investigation of this problem, it is advisable to compute the contribution from  $c_{\alpha\beta\gamma}^{ik}$  to  $d_{\alpha\beta\gamma}$ , even if for simple compounds of the type AB. This should, however, be done together with the refinement of the scheme for the determination of the free parameters  $\alpha^I$  and  $a^I$  in Eqs. (8) and (9).

A further quantitative verification of the theory would be the computation of the third-order susceptibilities. The point is that for these susceptibilities experiment

gives the absolute sign, while theoretically the sign of the third-order susceptibilities is determined only by the sign of the local-field coefficients  $f_{\alpha\beta\gamma\theta}^{ik}$ , since the ion-shell charge and the effective charge enter into equations of the type (8) and (9) in the quadratic form. The first estimates for the third- and higher-order nonlinearities for the crystals KDP and  $\text{CaCO}_3$  were in agreement with the experimental results<sup>[37]</sup>.

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<sup>1)</sup>The factor  $a^\alpha$  in the basic equation (1) in [17] should be replaced by the tensor  $A^i$ . In the limiting case of cubic diatomic crystals  $a^\alpha = A^i$ .

<sup>2)</sup>The anisotropy of the electronic polarizability was neglected.

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