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Anisotropic Bond Polarizabilities in Birefringent Crystals

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Abstract

Based on the concept of bond polarizabilities the optical properties of a crystal are traced back to the orientation of its bonds and to the individual bond parameters $\bar{\beta}$ and $\Delta\beta$. A test with various sulfate compounds shows that the average bond parameters $\bar{\beta}$ describe the average refractive indices with a higher accuracy than the traditional model of ionic polarizabilities. The anisotropic part of a bond polarizability, $\Delta\beta$, is considered to be the origin of optical birefringence. Values for $\Delta\beta$ are evaluated in $M\text{CO}_3$ and $M\text{SO}_4$ (M = Mg, Ca, Sr, Ba). In different crystals the same values for $\Delta\beta$ have been discovered for the C–O and the S–O bonds. $\Delta\beta$ of the M–O bonds depends in a characteristic way on the bond length. A simple method is used to calculate local field effects in accordance with the model of bond

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polarizabilities. Possible applications of bond polarizabilities for the determination of structural quantities are discussed.

I. Introduction

In the present paper we develop an empirical model of optical birefringence. Microscopic parameters are defined in such a way that a direct and simple relation between birefringence and structural parameters is obtained even for complex crystals. From an analysis of the optical susceptibilities of different compounds, representative features and trends of the microscopic optical parameters have been observed.

The traditional approach for describing the relation between optical and structural properties is the 'point-dipole theory'. In this model the refractive index of a compound is calculated by adding together the ionic polarizabilities of its constituents. Especially successful examples of its application are the calculation of elastooptical coefficients in α-sulfur (Bounds & Munn, 1979) and the description of optical activity in various crystals (Devarajan & Glazer, 1986). However, the point-dipole approximation yields negative values for the polarizability of the Mg^{2+} ion (Pohl & Rath, 1979) and the polarizability of the same ion varies even in similar crystals (Lo, 1973).

An alternative dielectric theory is based on Penn's model of a semiconductor with an average band gap (Penn, 1962). With this model Phillips (1968) and Van Vechten (1969) have developed the concept of bond polarizabilities. This concept has been used in nonlinear optics (Levine, 1973*a*), for evaluating the ionicity of bonds (Phillips & Van Vechten, 1969), and for the calculation of linear electrooptical coefficients (Shih & Yariv, 1982). Pantelides (1975*a*) has pointed out that Phillips's and Van Vechten's theory is the extreme opposite of the point-dipole approximation. Whereas in the latter model only intra-ionic electronic transitions are considered, in the semiconductor model refractivity is exclusively based on interionic transitions.

The origin of optical anisotropy is different in each theory. The ionic polarizabilities are assumed to be isotropic and birefringence is a consequence of local field effects. In contrast to this picture bond polarizabilities are intrinsically anisotropic. In the present paper we assume that each bond has a rotational symmetry and is characterized by a longitudinal and a transverse polarizability, β^L and β^T respectively. Thus in a material with two different bonds at least four microscopic quantities have to be determined. Usually this is not possible because the number of experimentally available optical constants is too small. Therefore we start the evaluation of bond polarizabilities with simple *AB* compounds and extend the analysis step by step to more complex crystals.

In § II we summarize the formulae which are needed for the analysis of the optical susceptibilities and in § III some information about the materials under consideration is presented. The first class of compounds which are studied is the alkaline earth oxides (§ IV). In these crystals the influence of core excitations, which do not contribute to the bond polarizabilities (Weber 1986*a*), have to be taken into account. In § V the total polarizabilities of multibond compounds are divided into contributions from different bonds. In § VI the birefringence of alkaline earth carbonates and sulfates is considered. These two kinds of materials have been selected because their anisotropies may have different origins. Whereas the CO_3^{2-} ion is intrinsically anisotropic, birefringence in the sulfates must stem from interionic interactions.

II. Theoretical relationships

The macroscopic polarization

$$P_i = \varepsilon_0 \chi_{ij} E_j$$

is obtained by a summation of all microscopic dipoles which are given by

$$p_i^\mu = \tilde{\beta}_{ij}^\mu E_j^{\mu,\mathrm{loc}}.$$

$\tilde{\beta}_{ij}^\mu$ is the polarizability of a microscopic unit μ and $E_j^{\mu,\mathrm{loc}}$ is the corresponding component of the acting local field.

Defining a local field tensor F_{ij} by

$$E_i^{\mu,\mathrm{loc}} = F_{ij}^\mu E_j$$

and including ε_0 in the definition of the polarizability by $\beta = \tilde{\beta}/\varepsilon_0$ we obtain

$$\chi_{ij} = (1/V)\sum_\mu \beta_{ik}^\mu F_{kj}^\mu, \tag{1}$$

where V is the volume of the unit cell. Here we assume that there are only longitudinal and transverse bond polarizabilities β^L and β^T. The relation of β^L and β^T to the β_{ij}, which are related to a crystal-physical reference system, is given by (Weber, 1986*a*)

$$\beta_{ij} = (\alpha_{i1}\alpha_{j1} + \alpha_{i2}\alpha_{j2})\beta^T + \alpha_{i3}\alpha_{j3}\beta^L. \tag{2}$$

α_{ij} are elements of the transformation matrix

$$\alpha_{ij} = \begin{pmatrix} C_2/S_3 & C_1C_3/S_3 & C_1 \\ -C_1/S_3 & C_2C_3/S_3 & C_2 \\ 0 & -S_3 & C_3 \end{pmatrix},$$

where $C_i = \cos\gamma_i$ and $S_i = \sin\gamma_i$. γ_i denotes the angle between the bond axis and the x_i direction of the reference system. Equation (2) describes the influence of structural parameters on optical properties.

It is possible to choose the reference system in such a way that all χ_{ij} which have $i \neq j$ vanish. Then a maximum of three independent components of χ_{ij} and β_{ij} exists, *i.e.* $\chi_{11}, \chi_{22}, \chi_{33}$. In addition we assume that the local field tensor possesses the same kind of coefficients. This assumption means that the local field is parallel to the macroscopic field. Instead of $\chi_{11}, \chi_{22}, \chi_{33}$ we use throughout this paper the tensor invariants (Jerphagnon, Chemla & Bonneville, 1978)

$$\bar{\chi} = \tfrac{1}{3}(\chi_{11} + \chi_{22} + \chi_{33})$$

$$\Delta\chi' = \chi_{33} - \bar{\chi}$$

$$\Delta\chi'' = \chi_{11} - \bar{\chi}.$$

In a similar way we define the local field components F, $\Delta F'$, $\Delta F''$ and the bond polarizabilities

$$\bar{\beta} = \tfrac{1}{3}(\beta^{L} + 2\beta^{T})$$

$$\Delta\beta = \tfrac{2}{3}(\beta^{L} - \beta^{T}).$$

With these definitions the susceptibilities are given by

$$\bar{\chi} = (1/V)\sum_{\mu}\{\bar{\beta}\bar{F} + \tfrac{1}{2}\Delta\beta[\Delta F'(C_3^2 - C_2^2) + \Delta F''(C_1^2 - C_2^2)]\}^{\mu} \tag{3a}$$

$$\begin{aligned}\Delta\chi' = (1/V)\sum_{\mu}\{&\bar{\beta}\Delta F' + \tfrac{1}{2}\Delta\beta\bar{F}(3C_3^2 - 1)\\ &+ \tfrac{1}{2}\Delta\beta[\Delta F'(C_3^2 - C_1^2) - \Delta F''(C_1^2 - C_2^2)]\}^{\mu}\\ \Delta\chi'' = (1/V)\sum_{\mu}\{&\bar{\beta}\Delta F'' + \tfrac{1}{2}\Delta\beta\bar{F}(3C_1^2 - 1)\\ &+ \tfrac{1}{2}\Delta\beta[\Delta F''(C_1^2 - C_3^2) - \Delta F'(C_3^2 - C_2^2)]\}^{\mu}.\end{aligned} \tag{3b}$$

For optically uniaxial crystals the above equations reduce to those reported by Chemla (1975).

When a special bond A–B appears in different crystals, the coordination number N may differ and, as a consequence, its polarizabilities may change. If the total number of bond charges is independent of the coordination, the proportionality

$$\beta \sim Z_A/N_A + Z_B/N_B \tag{4}$$

is valid (Levine, 1973*b*). Z_A and Z_B enumerate the valence electrons of the cation A and of the anion B, respectively.

A crucial problem in the application of (3) is the determination of the local field factors. Usually local field effects are assumed to be automatically included in the definition of bond polarizabilities (Chemla, 1971). This approximation may not be valid in birefringent crystals (Chemla, 1975). In the present study we apply the Lorentz factor $\bar{F} = 1 + \bar{\chi}/3$. This factor was derived from the idea that the bond under consideration is placed at the centre of a spherical cavity within a homogeneously polarized medium and the local field is created by the charges on the surface of this sphere. The contribution of these charges to ΔF is $\Delta\chi/3$. The dipoles within the spherical cavity do not contribute to $\bar{F}$ but they affect ΔF as shown below.

III. Characterization of materials

For the present study we have selected those crystals whose structural and optical data are known with a high degree of accuracy. These materials include different structural types: NaCl structure (alkaline earth oxides), calcite structure ($MgCO_3$, $CaCO_3$, $NaNO_3$), CaF_2 structure [$Sr(NO_3)_2$, $Ba(NO_3)_2$] and various kinds of complex sulfate structures. Cell volumes and bond lengths have been calculated using average lattice constants tabulated in Landolt-Börnstein (1979*a*, 1982). When the atomic parameters reported by different authors vary we have calculated average values by giving recent data more importance than earlier data. For the analysis of birefringence exact structural data are especially important because in the sum $\sum(3C_i^2 - 1)$ in (3) negative and positive contributions cancel each other out.

Values of refractive indices have been taken from Landolt-Börnstein (1962) and from the *Handbook of Optics* (1978). For orthorhombic and monoclinic crystals the relations between optical data and crystallographic axes have been obtained from standard mineralogical text books (Winchell & Winchell, 1964).

The power series

$$\chi = \chi^{0} + \chi^{(1)}E^{2} + \ldots$$

has been fitted to the values of the susceptibility $\chi = n^2 - 1$ at different photon energies E. Only the coefficients χ^0 have been used for the determination of bond polarizabilities.

IV. Alkaline earth oxides

Most of the birefringent crystals considered here contain M–O bonds, where M designates an alkaline earth metal. The parameters of these bonds have been determined from the corresponding oxides.

From the $\varepsilon^{(2)}$ spectra of alkali halides ($\varepsilon^{(2)}$ is the imaginary part of the complex dielectric constant) it is well known that two kinds of electronic transitions can be distinguished (Pantelides, 1975*b*). The first corresponds to the excitation of valence electrons and the second to the transition between cation states. As only the excitation of valence electrons represents an interionic transition the second mechanism does not contribute to the bond polarizabilities. Therefore it is necessary to divide the total susceptibility χ^0 into two parts,

$$\chi^{0} = \chi^{0\prime} + \chi^{0\prime\prime}.$$

Only $\chi^{0\prime}$ is assumed to represent the bond polarizability. Both kinds of mechanisms have also been observed in the $\varepsilon^{(2)}$ spectra of alkaline earth oxides (Whited & Walker, 1969; Hanson, Arakawa & Williams, 1972).

$\chi^{0\prime}$ and $\chi^{0\prime\prime}$ for these compounds have been determined with the same technique we have recently applied with alkali halides (Weber, 1986*a*). This technique is based on a Kramers-Kronig transformation of the $\varepsilon^{(2)}$ spectrum and an analysis of the dispersion

Table 1. *Optical susceptibility χ, bond length d, and average bond polarizabilities $\bar{\beta}$ in alkaline earth oxides*

	MgO	CaO	SrO	BaO
d (Å)	2·1059	2·4048	2·5800	2·7696
χ^{0} *	1·941	2·271	2·261	2·540
$\chi^{0\prime}$ †	1·895	2·056	1·975	2·140
$\chi^{0\prime\prime}$ ‡	0·046	0·215	0·286	0·400
$\bar{\beta}$ (Å^3) §	3·582	5·425	6·447	8·207

* Total susceptibility $\chi^{0}=\chi^{0\prime}+\chi^{0\prime\prime}$ for the photon energy $E=0$.

† Partial susceptibility due to excitation of valence electrons.

‡ Partial susceptibility due to excitation of core electrons.

§ All $\bar{\beta}$ are related to the coordination number $N_M=6$ of the cation in MO.

of refractive indices. The results are presented in Table 1. Table 1 also shows the average bond polarizabilities $\bar{\beta}$ which have been derived from $\chi^{0\prime}$.

In cubic crystals the anisotropic part of β can be determined by the elastooptical effect (Weber, 1986*b*). The birefringence which is induced by the shear strain ε_6 is described by

$$\chi_{12}=\chi_6=-n^4 p_{66}\varepsilon_6.$$

χ_{12}, in turn, is given by (Weber 1986*b*)

$$\chi_{12}=(3\bar{F}/4V)\sum_{\mu}[(C_1^2+C_2^2)\Delta\beta]^{\mu}.$$

From the value $p_{66}=-0{\cdot}096$ for MgO (Landolt-Börnstein, 1979*b*) we obtain $\Delta\beta_{\text{Mg–O}}=3{\cdot}14$ Å^3. Unfortunately no elastooptical coefficients are available for the other alkaline earth oxides.

V. Average bond polarizabilities of multibond compounds

For complex materials little information is available about their $\varepsilon^{(2)}$ spectra and about their electronic band structure. Therefore the contribution of intra-ionic transitions to the optical susceptibility cannot be clarified beyond doubt. The analysis of the $\varepsilon^{(2)}$ spectra of some ferroelectric oxides suggests that excitations of core electrons are of less importance than in simple *AB* crystals (Mamedov, Shilnikov, Mehdiev & Ibragimova, 1984). Furthermore, in our analysis of carbonates and sulfates we did not find it necessary to consider intra-ionic transitions. Therefore with these materials we neglect them completely. As a further approximation we neglect the influence of the slightly varying bond lengths on the bond polarizability.

In Fig. 1 the average polarizabilities $\bar{\beta}_c$ and $\bar{\beta}_s$ of MCO$_3$ and MSO$_4$ compounds are plotted against the values of $\bar{\beta}_{ox}$ obtained from the alkaline earth oxides MO. The two values for CaCO$_3$ represent calcite and aragonite, respectively. $\bar{\beta}$ of MgSO$_4$ has been derived from MgSO$_4$.7H$_2$O and the second value for CaSO$_4$ from CaSO$_4$.2H$_2$O. In both cases $\bar{\beta}_{\text{H}_2\text{O}}=18{\cdot}3$ Å^3, as determined from ice, has been used for an H$_2$O molecule. With the help of (4) all $\bar{\beta}_c$ and $\bar{\beta}_s$ values have been related to the coordination number $N_M=6$ for the alkaline earth ion. Terms containing the quantity $\Delta\beta\Delta F$ in (3*a*) have been neglected.

Table 2. *Average bond polarizabilities $\bar{\beta}$ (Å^3) (N_{cat} = coordination number of the cation)*

Bond	N_{cat}	$\bar{\beta}$
C–O	3	9·25
S–O	4	10·60
N–O	3	12·80
Na–O	6	2·54
K–O	6	4·24
Rb–O	6	5·54
Cs–O	6	7·70

As shown in Fig. 1 the relationship for both kinds of materials is linear with a slope of 1. This fact proves the universality of $\bar{\beta}_{M\text{–O}}$ in all materials under investigation. By extrapolating both curves in Fig. 1 $\bar{\beta}_{\text{C–O}}$ and $\bar{\beta}_{\text{S–O}}$ have been obtained. In the same way we determined $\bar{\beta}_{\text{N–O}}$ from Sr(NO$_3$)$_2$ and Ba(NO$_3$)$_2$. Then it was possible to evaluate $\bar{\beta}_{\text{Na–O}}$ and $\bar{\beta}_{\text{K–O}}$ from NaNO$_3$ and KNO$_3$ and from Na$_2$SO$_4$ and K$_2$SO$_4$, respectively. The final results, which include $\bar{\beta}_{\text{Rb–O}}$ and $\bar{\beta}_{\text{Cs–O}}$ as determined from Rb$_2$SO$_4$ and CsSO$_4$, are shown in Table 2.

As a test of the accuracy of the $\bar{\beta}$ values in Tables 1 and 2 we have calculated the average refractive indices in 15 different sulfates. In Table 3 the results are compared with the experimental values. The average deviation is less than 0·2%. In comparison we notice that in the point-dipole approximation the corresponding value is 1% (Cowley, 1970).

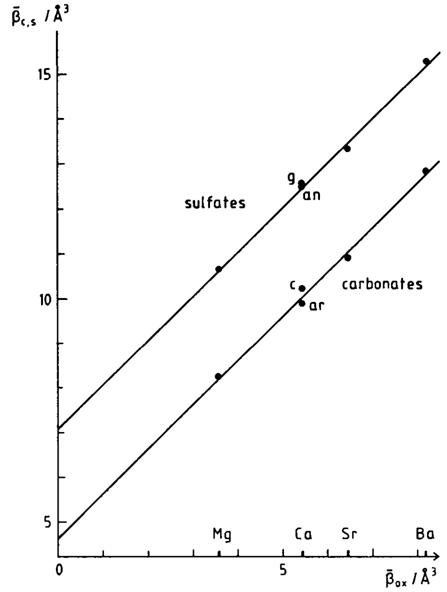

Fig. 1. Average polarizabilities $\bar{\beta}_c$ of MCO$_3$ and $\bar{\beta}_s$ of MSO$_4$ *versus* $\bar{\beta}_{ox}$ of MO (M = Mg, Ca, Sr, Ba). Values are related to one M–O bond. The modifications of Ca compounds are: *g* gypsum, *an* anhydrite, *c* calcite, *ar* aragonite.

Table 3. *Experimental and calculated average refractive indices of sulfates for photon energy $E = 0$ (Δ is the difference in percent)*

	n_{exp}	n_{calc}	Δ
$MgSO_4.7H_2O$	1·4379	1·4376	−0·02
$CaSO_4$	1·5735	1·5689	−0·29
$CaSO_4.2H_2O$	1·5134	1·5137	0·02
$SrSO_4$	1·6163	1·6215	0·32
$BaSO_4$	1·6227	1·6221	−0·04
Na_2SO_4	1·4636	1·4613	−0·15
K_2SO_4	1·4852	1·4851	−0·01
Rb_2SO_4	1·5029	1·5090	0·40
Cs_2SO_4	1·5508	1·5499	−0·06
$K_2Mg_2(SO_4)_3$	1·5199	1·5156	−0·29
$K_2Mg(SO_4)_2.6H_2O$	1·4521	1·4516	0·04
$Rb_2Mg(SO_4)_2.6H_2O$	1·4602	1·4585	−0·12
$Cs_2Mg(SO_4)_2.6H_2O$	1·4757	1·4763	0·04
$K_2Ca(SO_4)_2.H_2O$	1·5060	1·5062	0·02
$Na_2Mg(SO_4)_2.4H_2O$	1·4870	1·4898	0·19

VI. Anisotropy in carbonates and sulfates

In the past carbonate minerals repeatedly served as model compounds for investigating structural sources of optical anisotropy (Lawless & Devries, 1964; Lo, 1973; Pohl & Rath, 1979). Most authors considered ionic polarizabilities and used the Lorentz local field method in the point-dipole approximation. Kinase, Tanaka & Nomura (1979) attributed a part of the birefringence in calcite to the anisotropy of the C–O bond and determined $\beta^L/\beta^T = 1{\cdot}64$. On the basis of birefringence data Pohl (1978) determined cation and O_2 polarizabilities in carbonates and sulfates. He observed an unsystematical variation of O_2 polarizabilities by more than 10% in aragonite-type carbonates and by more than 20% in sulfates.

For an analysis of the optical anisotropy we used the materials listed in Tables 4 and 5. As a first step we attempted to describe $\Delta\chi$ of different compounds with as few parameters as possible. For MCO_3 only one quantity was needed: $\Delta\beta_{\text{C–O}} = 5{\cdot}3$ Å^3. In MSO_4 birefringence can be described using the two quantities $\Delta\beta_{\text{S–O}} = 15{\cdot}0$ Å^3 and $\Delta\beta_{M\text{–O}} = 1{\cdot}17$ Å^3. In this fit we have assumed that ΔF equals the Lorentz factor $\Delta\chi/3$. When we calculated the $\Delta\chi$'s using the above values for $\Delta\beta$, they disagreed with experimental $\Delta\chi$ values by about 10% in the carbonates and by about 20% in the sulfates. This result shows that in both kinds of materials the anisotropy of the anion group is the main source of birefringence. However, the above fit is not good enough and the result $\Delta\beta_{M\text{–O}} = 0$ in carbonates and $\Delta\beta_{M\text{–O}} \neq 0$ in sulfates is not satisfactory.

Inspecting the discrepancies obtained with the above values in detail we noticed that $\Delta F = \Delta\chi/3$ is an oversimplified local field factor. Usually ΔF is determined by considering the mutual interactions of point dipoles situated at lattice points. This treatment of local field effects does not agree with the concept of bond polarizabilities. Therefore we need an alternative approach. Let us consider each MO_N complex as a unit with a total polarizability $N\beta$, where N is the coordination number. With the exception of the highly anisotropic CO_3 group we used the values of $\bar{\beta}$ for β. The total polarizability is assumed to be concentrated at the centre of the complex which coincides with the cation M. The dipole field of the polarized complexes is calculated at the centre of a sphere and the magnitude of these contributions to ΔF is determined by an adjustable factor q which turned out to be the same in all crystals with the same anion group. Thus the local field factor ΔF^μ for a special bond μ reads

$$\Delta F^\mu = \Delta\chi/3 + qE^\mu_D/E. \qquad (5)$$

Table 4. *Structural and optical data for MCO_3*

The values $3C_i^2 - 1$ and E_D/E are valid for one molecular unit. Z is the number of molecules in the unit cell, N_M the coordination number of the cation M, and $d_{M\text{–O}}$ is the bond length of the M–O bond. All other symbols are defined in equations (3) and (5).

M	Mg*	Ca*	Ca†‡	Sr†
Structure	Calcite	Calcite	Aragonite	Aragonite
V (Å^3)	279·1	367·2	226·6	259·1
Z	6	6	4	4
N_M	6	6	9	9
$d_{M\text{–O}}$ (Å)	2·104	2·358	2·527	2·636
$\Delta\chi'$	−0·3745	−0·3335	−0·3048	−0·2671
$\Delta\chi''$			0·1459	0·1252
$\bar{F}$	1·5478	1·5050	1·5384	1·5107
M–O bonds				
$3C_3^2-1$	0·3698	0·5209	−0·9207	−0·9686
$3C_1^2-1$			1·0464	0·9171
$(E_D/E)'$	−0·1928	−0·1338	0·0352	0·0064
$(E_D/E)''$			−0·1229	−0·0999
C–O bonds				
$3C_3^2-1$	−3	−3	−2·9938	−2·9948
$3C_1^2-1$			1·4566	1·4744
$(E_D/E)'$	−0·2023	−0·2023	−0·0395	−0·0208
$(E_D/E)''$			0·1226	0·0763

References for structural data:
* Landolt-Börnstein (1979*a*);
† De Villiers (1971);
‡ Dal Negro & Ungaretti (1971).

Table 5. *Structural and optical data for MSO_4 (for explanations see Table 4)*

M	Ca*	Sr*	Ba*	Na_2†
V (Å^3)	305·1	307·2	346·9	707·8
Z	4	4	4	8
N_M	8	12	12	6
$d_{M\text{–O}}$ (Å)	2·468	2·831	2·952	2·431
$\Delta\chi'$	0·0840	−0·0051	−0·0102	0·0203
$\Delta\chi''$	−0·0502	−0·0110	−0·0134	−0·0011
$\bar{F}$	1·4923	1·5328	1·5484	1·3807
M–O bonds				
$3C_3^2-1$	2·2099	1·6354	1·3388	−0·3906
$3C_1^2-1$	−1·4269	−0·2730	−0·3532	−0·5028
$(E_D/E)'$	0·1638	0·0135	−0·0188	0·1255
$(E_D/E)''$	−0·2250	−0·0004	0·0216	0·0254
S–O bonds				
$3C_3^2-1$	0·2578	−0·0694	−0·0792	0·1754
$3C_1^2-1$	−0·1025	−0·0642	−0·0856	−0·0083
$(E_D/E)'$	0·0943	0·0410	0·0173	0·0778
$(E_D/E)''$	−0·2247	−0·0259	−0·0039	−0·0931

References for structural data:
* Miyake *et al.* (1978);
† Nord (1973).

The ratio E''_D/E contains the contribution of all induced dipoles in the neighbourhood of this bond which is in the centre of a sphere.

All structural and optical data which are needed for a determination of $\Delta\beta$ and q are gathered in Tables 4 and 5. In calculating E_D/E the radius of each sphere was smaller than 7 Å. The values for the bond length in both tables represent average values. Thus the influence of slightly varying bond lengths within the same complex or in different crystals has been neglected. Furthermore, we have assumed that (4) describes the behaviour of $\Delta\beta$ correctly for different coordination numbers. The compound $BaCO_3$ has been excluded because the available data do not allow an accurate extrapolation of $\Delta\chi$ to long wavelengths. Hydrated sulfates have been excluded to avoid any problem with hydrogen bonds. The optical properties of these bonds will be discussed elsewhere.

In the course of our calculations we noticed that the birefringence of calcite-type $CaCO_3$ is unreasonably large. A possible reason for this is the existence of highly anisotropic absorption bands in the near infrared region (Kashintseva, Kolyadin & Shustov, 1983). Therefore the average $\Delta\beta_{C\text{-}O}$ value has been determined without the value of calcite. The quantity $3C_1^2-1=-0{\cdot}0856$ of $BaSO_4$ in Table 5 is about 1·5 times larger than the value one extracts from the original structural data. The value for $3C_1^2-1$ has been changed within the limit of the experimental error reported by Miyake, Minato, Morikawa & Iwai (1978). The change was necessary because otherwise the optical and structural data of the two isotypic crystals, $BaSO_4$ and $SrSO_4$, contradict each other.

For reducing the number of free parameters we used for the Mg–O bond the $\Delta\beta$ value which is obtained from the elastooptical effect as described in § IV ($\Delta\beta_{Mg\text{-}O}=3{\cdot}14$ Å^3). In a similar way we obtained from the elastooptic coefficient p_{44} of calcite-type $CaCO_3$ $\Delta\beta_{Ca\text{-}O}=2{\cdot}97$ Å^3. Finally we are left with 13 experimental values and nine bond parameters.

The result of a least-squares fit is $\Delta\beta_{C\text{-}O}=4{\cdot}86(9)$ Å^3 and $q_{carb}=0{\cdot}22(4)$ for the carbonates and $\Delta\beta_{S\text{-}O}=10{\cdot}13(11)$ Å^3 and $q_{sul}=0{\cdot}024(4)$ for the sulfates. The standard deviations are given in parentheses. In addition we have determined $\Delta\beta$ of the bonds Ca–O, Sr–O, and Ba–O in aragonite-type and sulfate crystals. The result is shown in Fig. 2 together with the values obtained from the elastooptical effect in MgO and calcite as described above. As demonstrated in Fig. 2, the $\Delta\beta$'s of the M–O bonds follow approximately the relation

$$\Delta\beta/\bar{\beta}=\alpha(d-d_0)^2 \qquad (6)$$

with $\alpha=0{\cdot}92(10)$ Å^{-2} and $d_0=3{\cdot}06(36)$ Å.

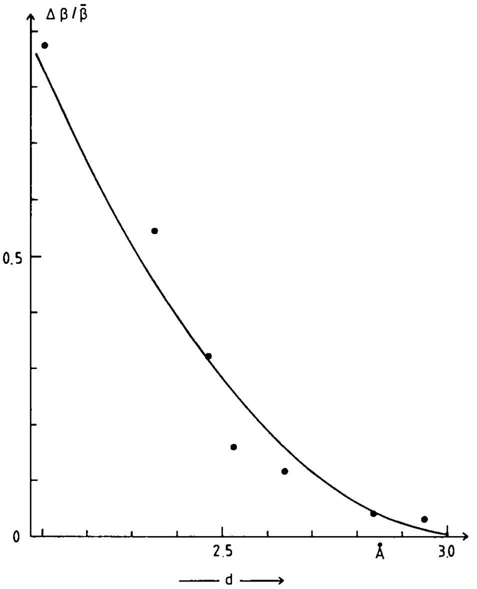

Fig. 2. Relative anisotropic bond polarizabilities $\Delta\beta/\bar{\beta}$ of M–O bonds as a function of the bond length d (M = Mg, Ca, Sr, Ba). The results presented can be identified with the help of Tables 4 and 5. The full line represents a fit according to equation (6).

VII. Discussion

It is highly surprising that the anisotropic part of the polarizabilities of the ionic M–O bonds obeys the simple relation (6), although the values have been gained from different materials and effects. This result suggests a universal meaning of (6). The universality of $\Delta\beta_{S\text{-}O}$ is stressed by the fact that the same value is observed in the alkaline earth sulfates and in Na_2SO_4.

Let us assume that (6) is exactly valid. Then we need the six quantities $\Delta\beta_{C\text{-}O}$, q_{carb}, $\Delta\beta_{S\text{-}O}$, q_{sul}, α and d_0 for a description of birefringence in all alkaline earth carbonates and sulfates. The average deviation between experimental and fitted $\Delta\chi$ values is 0·015 or about 5% in the carbonates and 0·001 or 2% in the sulfates. An error of 0·001 for $\Delta\chi$ corresponds to an error of about 0·0005 of the birefringence Δn. This is near to the experimental limit of refractive index data. Another source of discrepancies is the errors in structural data, as already discussed for $BaSO_4$. In principle the birefringence Δn itself can be measured with a sensitivity of 10^{-6}. Thus it should be possible to improve structural parameters by a measurement of birefringence if the individual bond parameters are known.

Another attractive application of bond polarizabilities is the determination of atomic displacements which are induced by an external field. Without difficulty it is possible to measure as a function of a uniaxial stress or an electrical field changes of Δn which are as small as 10^{-11}. The corresponding atomic displacements are estimated to be 10^{-8} to 10^{-9} Å. This seems to be a new class of sensitivity for studying structural properties.

It should be mentioned that a modification of the local field factor by the term qE_D/E in (5) is not the only way to improve the description of $\Delta\chi$ in the crystals considered, but it is the most effective one. In a systematic way we have tested different possible influences on $\Delta\chi$. With the use of a modified local field factor we obtained the highest accuracy with the smallest number of fit parameters.

The present results demonstrate that the anisotropic polarizability of the bonds is the origin of optical birefringence Δn. In the crystals studied here the main contribution to Δn stems from the covalent bonds C–O and S–O. We observed in a preliminary study a different behaviour of crystals with the β-K_2SO_4 structure. In those crystals the birefringence is even smaller than in the alkaline earth sulfates. As a consequence the interpretation of $\Delta\chi$ in terms of bond polarizabilities requires simultaneously a critical consideration of structural data. Therefore, with the exception of Na_2SO_4, we excluded alkali sulfates from the present work.

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Definition of an Asymmetric Domain for Intercrystalline Misorientation in Cubic Materials in the Space of Euler Angles

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Abstract

A new asymmetric domain for intercrystalline misorientation is defined in the space of Euler angles for materials exhibiting cubic (O_h point-group) lattice symmetry. The invariant measure for this new domain is nearly constant; this is in significant contrast to the previous domain defined by MacKenzie [*Biometrika* (1958), **45**, 229-240]. Distribution functions in the misorientation can now be represented with greater clarity and convenience in the new domain. A detailed theoretical analysis of special misorientations exhibiting multiplicities $m > 1$ is described. It is demonstrated that all such special misorientations fall upon the surfaces separating distinct asymmetric domains. This result convincingly proves that the derived asym-

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