

SHORT COMMUNICATIONS

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Point-dipole theory and optical birefringence of calcite-type carbonates. By D. POHL & R. RATH, *Mineralogisch–Petrographisches Institut der Universität Hamburg, Grindelallee 48, D2000 Hamburg 13, Federal Republic of Germany*

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Abstract

A critical survey of the literature has revealed that recent structure determinations and optical data are available for only three calcite-type carbonates: calcite, rhodochrosite and magnesite. For these structures, the limitations of the point-dipole approximation are discussed.

The point-dipole model was introduced by Bragg (1924) to explain quantitatively the birefringence of calcite and aragonite with respect to the crystal structures. In this approach optical anisotropy arises from differences in dipole–dipole coupling along different crystallographic directions. This source of anisotropy is connected with the Lorentz-factor tensor. In addition, however, optical anisotropy may arise from an intrinsic anisotropy in the constituent ions. In this case electronic polarizability tensors should be considered.

In order to investigate the relation between atomic arrangement and double refraction, the crystals of carbonates have been used repeatedly. The latest studies are those given by Isherwood & James (1976) and Pohl (1978). In his paper Pohl (1978) has developed a method to determine the electronic polarizabilities of ions from structural and optical data by a least-squares fit. The method is based on Bragg's (1924) model of point dipoles and on an exact calculation of Lorentz-factor tensors. This model satisfactorily accounts for the double refraction of aragonite-type carbonates. In the present paper we discuss the application of the method to calcite-type carbonates.

Structural parameters of only three calcite-type carbonates have been determined: calcite (Chessin, Hamilton & Post, 1965), rhodochrosite (Brown & Forsyth, 1967) and magnesite (Oh, Morikawa, Iwai & Aoki, 1973). Optical constants are given by Winchell & Winchell (1964). Application of Pohl's (1978) method yields the electronic polariz-

abilities listed in Table 1. Indications of deficiencies in the method are the negative value of the polarizability of Mg^{2+} and the low values obtained for the Mn^{2+} and Ca^{2+} ions.

The strong double refraction displayed by calcite-type carbonates cannot be explained by isotropic polarizabilities. Based on Bragg's (1924) ideas, the birefringence arises from the oxygens within the isolated CO_3^{2-} groups: the stronger the birefringence the stronger the influence of the O^{2-} ions on each other. Strengthening of the oxygen interaction can take place in two ways. Firstly, the distance between the carbon and oxygen can be diminished. Secondly, the polarizability of the oxygen ion can be increased. Since the C–O distance is fixed according to the structure determination, only an increased polarizability of the O^{2-} ion remains. However, this results in an increased mean refractivity which in return is compensated by a smaller polarizability of the cation, thus explaining the above results.

To overcome the shortcomings encountered with the Bragg model of point dipoles, two improvements may be considered. Firstly, the point dipoles can be positioned outside the atomic centers, because the outer electrons responsible for the optical effects may have a center of gravity distinct from that determined by X-rays. Secondly, an intrinsic anisotropy can be allocated to the polarizability of the ions. Both of these improvements involve the introduction of at least one extra parameter. Thus the number of adjustable parameters will exceed the number of experimentally known refractive indices. This difficulty may be handled by adopting polarizability data for the cation from other investigations. There are however additional difficulties with every improved model, leading to the conclusion that the problem of too many coefficients and not enough data cannot be easily removed. As pointed out by a number of authors (Spangenberg, 1923; Fajans & Joos, 1924; Born & Heisenberg, 1924; Bragg, 1925; Batsanov, 1966; Pohl, 1978; Pohl, Eck & Klaska, 1978) the polarizability of the anions varies with the size of the cation. Specifically, small cations tend to reduce the polarizability of the anions. This is the reason why Lawless & Devries (1964) had to exclude $MgCO_3$ when they determined the least-squares oxygen polarizability ellipsoid in fitting the refractive indices of carbonate minerals. In his study, Lo (1973) computed the polarizabilities of the planar nitrate, carbonate and borate anions in crystals and concluded that the deduced polarizability values are strongly dependent on the crystalline environment.

Table 1. *Calcite-type carbonates: electronic polarizabilities of ions (in \AA^3)*

Compound	α_{cation}	$\alpha_{\text{O}^{2-}}$
$CaCO_3$	2.0	19.5
$MnCO_3$	0.2	20.1
$MgCO_3$	-1.9	17.1

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A matrix formulation for choosing starting sets in direct methods. By LAWRENCE C. ANDREWS, *Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, USA*

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Abstract

A method for finding the strongest starting set of reflections for multiresolution direct methods is proposed and compared with the Convergence Method of Germain, Main & Woolfson [*Acta Cryst.* (1970), **B26**, 274–285].

The program *MULTAN* uses a powerful procedure called the 'Convergence Method' (Germain, Main & Woolfson, 1970) to determine starting sets of reflections for multiresolution direct methods and to determine the path of phase determination. While the Convergence Method (CM) has been described as a method for finding the strongest set of starting reflections, in fact it finds the least weak by eliminating the weakest reflection at each step of the iterative procedure. The formulation presented here directly seeks the strongest starting set of reflections. An additional advantage of this formulation is that at each stage the information required to build trees for phasing is entirely available after the starting set has been chosen. In the CM, trees must be constructed separately for each starting set.

Form the matrix

$$\sum_i \begin{pmatrix} W_i \left(\frac{\partial \varphi_1}{\partial \varphi_1} \right)_i & W_i \left(\frac{\partial \varphi_2}{\partial \varphi_1} \right)_i & \dots \\ W_i \left(\frac{\partial \varphi_1}{\partial \varphi_2} \right)_i & W_i \left(\frac{\partial \varphi_2}{\partial \varphi_2} \right)_i & \dots \\ \vdots & & \end{pmatrix},$$

where the φ_j are the phase angles for the reflections, j , that participate in phase relationship i , where the matrix is summed over all the relationships, and where W_i is the weight associated with relationship i . The weights may be calculated by any appropriate method for evaluating the

relative importance of the relationship; for phase triplets a possible choice of weights is the κ of Germain, Main & Woolfson (1970). Some thought should be given to the method of combining the weights as they are summed into the matrix. In the examples below, the κ 's were summed, but some other weighting scheme (for example, like the computation of α 's in Germain, Main & Woolfson, 1970) might be more effective. A contribution from a quartet relationship with phase sum Φ_i to the matrix sum is computed as follows:

$$\varphi_1 + \varphi_6 - \varphi_2 + \varphi_4 = \Phi_i \text{ with weight} = g_i;$$

where Φ_i is the phase sum (if this is the i th phase relationship). From the equation, compute

$$\frac{\partial \varphi_1}{\partial \varphi_1} = 1, \quad \frac{\partial \varphi_1}{\partial \varphi_6} = -1, \quad \frac{\partial \varphi_1}{\partial \varphi_2} = 1, \quad \frac{\partial \varphi_1}{\partial \varphi_4} = -1,$$

$$\frac{\partial \varphi_6}{\partial \varphi_1} = -1, \quad \frac{\partial \varphi_6}{\partial \varphi_6} = 1, \quad \dots$$

⋮

$$\frac{\partial \Phi_i}{\partial \varphi_j} = 0.$$

Thus the matrix contribution to the sum is

$$\begin{pmatrix} g & g & 0 & -g & 0 & -g \\ g & g & 0 & g & 0 & g \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -g & g & 0 & g & 0 & -g \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -g & g & 0 & -g & 0 & g \end{pmatrix}.$$