Determination and structural application of anisotropic bond polarisabilities in complex crystals

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Abstract. It is shown that very small atomic displacements of about 10^{-9} Å can be detected by polarisation optical methods. The idea for such an optical determination of structural motions is based on an empirical model which considers the anisotropic polarisability and the orientation of the bonds as the origin of the optical anisotropy of a crystal. The polarisabilities and some other bond parameters are determined mainly from precise measurements of birefringence. The derivation of theoretical expressions and the selection of materials is done in such a way that the experimental data exceed the number of independent bond parameters even in complex compounds. As experimental examples the bonds S–O, M–O (M = K, Rb, Cs), and O–H–O are considered in several complex sulphates and in $KHCO_3$. Then the parameters of these bonds are used for the determination of atomic displacements induced by changes of temperature in K_2SO_4 and in $KHSO_4$. In both crystals there exist some structural displacements which show no direct relation to the macroscopic thermal expansion.

1. Introduction

In the past the microscopic model of bond polarisabilities, established by Phillips (1968) and Van Vechten (1969), has been used to characterise the ionicity of bonds (Phillips and Van Vechten 1969), to explain non-linear optical properties (Levine 1973a) and to calculate linear electro-optical coefficients (Shih and Yariv 1982). Whereas Phillips and Van Vechten considered mainly simple A–B compounds, Levine (1973b) extended their ideas to crystals with two different kinds of bonds. On the basis of the dielectric theory of Phillips and Van Vechten, we will work out the connection between the optical and structural anisotropy of complex crystals. In order to determine the parameters of the model precise optical and structural data are needed. Therefore we have performed exact measurements of the birefringence in a wide spectral range using crystals for which well refined structures are available. However, for Rb_2SO_4 and Cs_2SO_4 we were forced to perform new structure refinements.

In the early papers by Phillips, Van Vechten and Levine the main interest was to investigate the fundamental features of the physical model. Here the same model is applied to describe the optical anisotropy of a crystal as exactly as possible. For this purpose appropriate model parameters are the anisotropic bond polarisability $\Delta\beta$ and a quantity Δf which measures the dependence of $\Delta\beta$ on the bond length. The usefulness

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of this concept has already been demonstrated with earth alkaline carbonates and sulphates (Weber 1988). $\Delta\beta$ and Δf connect the birefringence of a crystal directly to its structure parameters. Therefore, if both parameters of all bonds of a crystal are known, it is possible to investigate structural properties by polarisation optical experiments, which can be performed with an extremely high sensitivity. In addition to $\Delta\beta$ and Δf, we determine also $\bar{\beta}$ and $\bar{f}$ which characterise the corresponding average optical properties of a bond.

The materials studied in the present paper are M_2SO_4 (M = K, Rb, Cs), $KHSO_4$, $CsHSO_4$, $K_2Ni(SO_4)\cdot 6H_2O$ and $KHCO_3$. They have been selected because their symmetry is low and because they show a wide variety of chemical, structural and optical properties. The availability of many experimental data, due to the low symmetry, is of special importance in complex compounds where the number of bond parameters exceeds the number of independent refractive indices. The wide variety of properties serves as a test of the universality of the bond parameters derived. In the above materials there are ionic M–O bonds, covalent S–O and C–O bonds and different kinds of hydrogen bonds, including chains, dimers and three-dimensional frames. The coordination number of the cation M^+ ranges from 8 to 11 and the birefringence ranges from $\Delta n = 0.002$ to the extremely large value $\Delta n = 0.18$.

In § 2 the basic formulae of the theory are derived and in § 3 we give a brief description of the experimental techniques applied in the present work. The experimental results and the relevant structural properties are presented in § 4. In § 5 we will show that a large number of bond parameters, as appear in complex compounds, can be determined by a comparative study of isomorphous crystals such as M_2SO_4. An application of the bond parameters is discussed in § 6. For K_2SO_4 and $KHSO_4$ the atomic displacements associated with the thermal expansion are determined. As we analyse very accurate optical data by a rather simple model it is not surprising that in some cases the limitations of the concept become evident. These are discussed in § 7.

2. Bond polarisabilities

The crystals studied in the present paper belong to the orthorhombic or to the monoclinic system. In orthorhombic crystals there exist the three susceptibilities χ_{11}, χ_{22} and χ_{33} which are referred to a cartesian coordinate system x_i parallel to the crystallographic axes. The treatment of monoclinic crystals is given further below. The connection between the susceptibilities and the bond polarisabilities and structural quantities is more conveniently worked out by the use of the tensor invariants

$$\bar{\chi} = \tfrac{1}{3}(\chi_1 + \chi_2 + \chi_3) \qquad \Delta\chi' = \chi_3 - \bar{\chi} \qquad \Delta\chi'' = \chi_2 - \bar{\chi} \qquad (1)$$

where we have used the abbreviation $\chi_{ii} = \chi_i$. Within the concept of bond polarisabilities the relations between the susceptibilities and microscopic quantities are given (Weber 1988) by

$$\bar{\chi} = \frac{1}{V}\sum_\mu (\bar{\beta}\bar{F})^\mu$$

$$\Delta\chi' = \frac{1}{V}\sum_\mu [\bar{\beta}\Delta F' + \tfrac{1}{2}\bar{F}\Delta\beta(3C_3^2 - 1)]^\mu \qquad (2)$$

$$\Delta\chi'' = \frac{1}{V}\sum_\mu [\bar{\beta}\Delta F'' + \tfrac{1}{2}\bar{F}\Delta\beta(3C_2^2 - 1]^\mu$$

where we have omitted some terms which are negligibly small for the materials under consideration. In (2) the index μ enumerates the bonds within one unit cell of the volume V. $\bar{\beta}$ is the average bond polarisability and $\Delta\beta$ its anisotropic part. $\bar{F}$, $\Delta F'$ and $\Delta F''$ are local field factors. The atomic positions are involved in $C_i = \cos \gamma_i$ where γ_i is the angle between the bond axis and the axis x_i of the reference system. For the sake of simplicity we have included the factor ε_0 in the definition of the polarisability by $\beta = \tilde{\beta}/\varepsilon_0$ where $\tilde{\beta}$ is the polarisability in SI units. The bond polarisabilities $\bar{\beta}$ and $\Delta\beta$ can be expressed in terms of a longitudinal (β^L) and a transverse (β^T) polarisability by

$$\bar{\beta} = \tfrac{1}{3}(\beta^L + 2\beta^T) \qquad \text{and} \qquad \Delta\beta = \tfrac{2}{3}(\beta^L - \beta^T).$$

The correct treatment of local field effects is a delicate problem, and it is beyond the intention of the present paper. Here we use the standard treatment which is based on a spherical cavity dividing the dielectric material into a macroscopic phase with a homogeneous polarisation and a microscopic phase where the discrete nature of the lattice is taken into account (Aspnes 1982). The contribution from the polarisation of the uniform region outside the sphere is given (Weber 1988) by

$$\bar{F} = 1 + \tfrac{1}{3}\bar{\chi} \qquad \text{and} \qquad \Delta F = \tfrac{1}{3}\Delta\chi \tag{3}$$

where we have omitted the superscripts in the second expression. The contribution from the discrete phase to the local field factors is assumed to be included in the bond parameters.

In monoclinic crystals, in addition to the three quantities defined in (1), a further independent susceptibility, χ_{13}, exists. Its value depends on the orientation of the reference system. Using the axes of the optical indicatrix as reference system, χ_{13} is zero and in addition to equation (2) there exists the relation

$$\sum_{\mu} (C_1 C_3 \Delta\beta)^{\mu} = 0. \tag{4}$$

The dependence of the bond polarisabilities $\bar{\beta}$ and $\Delta\beta$ on the bond length is described by the two parameters $\bar{f}$ and Δf which are defined by the equations (Shih and Yariv 1982)

$$\partial\bar{\beta}/\bar{\beta} = \bar{f} \, \partial d/d \qquad \text{and} \qquad \partial\Delta\beta/\Delta\beta = \Delta f \, \partial d/d. \tag{5}$$

Furthermore the polarisabilities may depend on the coordination number N. Assuming that the effective electronic charge is the same in different coordinations, $\bar{\beta}$ of a bond A–B is given (Levine 1973b) by

$$\bar{\beta} \sim \frac{Z_A}{N_A} + \frac{Z_B}{B_B} \tag{6}$$

where Z_A and Z_B are the bond charge contributions of the cation A and the anion B, respectively. With the exception of M_2SO_4 we found that (6) works well also for $\Delta\beta$. M_2SO_4 is studied in detail in § 5.

With the theory outlined above the optical anisotropy is traced back to two kinds of structural anisotropies. The first one describes the orientational anisotropy and is measured by the geometrical factor G which is introduced as $G = \Sigma 3C^2 - 1$. The second one describes the anisotropy of the bond length and is measured by the geometrical factor $D = \Sigma(3C^2 - 1) \, \partial d/d$. The sum includes all bonds of one type. Inserting (3) and (5) in (2) we obtain a quantity $\Delta\chi^*$ which is directly related to D and G and to the bond parameters $\Delta\beta$ and Δf:

$$\Delta\chi^* = 2\Delta\chi V/(1 + \tfrac{1}{3}\bar{\chi})^2 = \sum_{\nu} (G \, \Delta\beta + D \, \Delta\beta \, \Delta f)^{\nu} \tag{7}$$

where the index ν denotes different types of bonds.

For the variation of the susceptibilities with temperature we obtain from (2), (3) and (7)

$$\frac{\partial \bar{\chi}}{\partial T} = -\bar{\chi}\bar{F}\frac{\partial \ln V}{\partial T} + \frac{\bar{F}^2}{V}\sum_{\mu} \bar{\beta}\bar{f}\frac{\partial \ln d}{\partial T} \tag{8}$$

$$\frac{\partial \Delta \chi}{\partial T} = -\Delta \chi \frac{\partial \ln V}{\partial T} + \frac{2\Delta \chi}{2\bar{F}}\frac{\partial \bar{\chi}}{\partial T} + \frac{\bar{F}^2}{2V}\frac{\partial \Delta \chi^*}{\partial T}. \tag{9}$$

The last term in (9) is the most interesting. It contains only contributions which are due to a change of atomic parameters. For a special bond A–B this term is given approximately by

$$\left.\frac{\partial \Delta \chi^*}{\partial T}\right|_{A-B} = G\Delta\beta\Delta f\frac{\partial \ln d}{\partial T} - 3\Delta\beta \sum \sin 2\gamma \frac{\partial \gamma}{\partial T}, \tag{10}$$

where the summation includes all bonds of this type. Notice that (9) represents two equations, one for $\Delta \chi'$ and one for $\Delta \chi''$. Furthermore in (10) $\gamma = \gamma_3$ in the case of $\Delta \chi = \Delta \chi'$ and $\gamma = \gamma_2$ if $\Delta \chi = \Delta \chi''$. In (8) and (9) $\partial \ln V/\partial T = \Sigma \alpha_i$ where α_i are the coefficients of thermal expansion. A similar simple relation does not necessarily hold for $\partial \ln d/\partial T$. If the fractional coordinates of both atoms of a bond do not change, $\partial \ln d/\partial T$ is given by

$$\partial \ln d/\partial T = \sum C_i^2 \alpha_i. \tag{11}$$

Of course, (11) is valid for the average behaviour of an assembly of many bonds, but a special bond such as O–H–O may behave in a completely different way. In K_2SO_4 and $KHSO_4$ the K–O bonds occupy about 90% to 95% of the volume. Therefore (11) must be true for these bonds, at least approximately.

3. Experimental techniques

Large single crystals of K_2SO_4, Rb_2SO_4, Cs_2SO_4, $KHSO_4$, $CsHSO_4$, $K_2Ni(SO_4)_2 \cdot 6H_2O$ and $KHCO_3$ were grown by slow evaporation of aqueous solutions. Refractive indices of $KHSO_4$ and $CsHSO_4$ were measured with an optical goniometer between 400 and 700 nm. The values of n for all other crystals are taken from the literature (Landolt–Börnstein 1962). They are used only for calculating the average susceptibility $\bar{\chi}$.

For the measurement of birefringence 10 mm diameter plates with thicknesses between 0.1 and 4 mm were used. To achieve good results the surfaces of the samples must be exactly parallel and their thickness should be large when Δn is small. We measured Δn between $\lambda = 220$ nm and $\lambda = 2000$ nm with an optical spectrometer in which two polarisers had been mounted in the crossed position. The angle between the principal axes of the birefringent plate and the polarisation direction of the light was 45°. In this configuration the transmitted intensity I is given by

$$I \sim I_0 \sin^2(\pi/\lambda \, \Delta nL)$$

where L is the thickness of the sample. The intensity was recorded as a function of the wavelength λ. For the wavelengths at which $I = I_{min}$ we obtain

$$L \, \Delta n = k\lambda_k$$

and for $I = I_{max}$ the relation reads

$$L \, \Delta n = (k + 0.5) \, \lambda_{k+0.5}$$

where k denotes the order of the interference. k is determined by comparing the $I(\lambda)$ spectra of two samples with the same orientation but with different thickness.
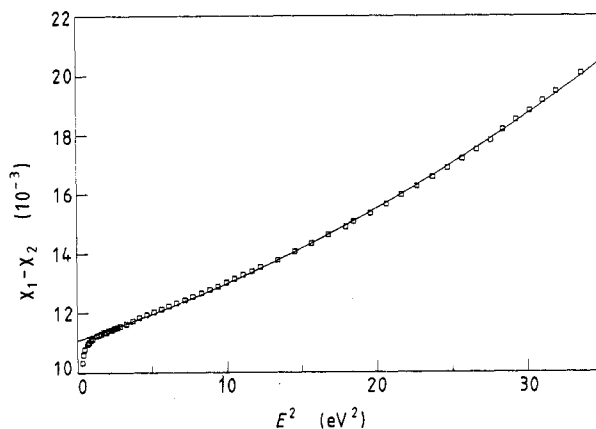
Figure 1. Dispersion of anisotropic optical susceptibilities in K_2SO_4. E is the photon energy. The curve is a fit with three terms of equation (12)

For a small birefringence Δn the susceptibility $\Delta \chi$ can be expressed as

$$\Delta \chi(E) = 2\bar{n}(E)\, \Delta n(E)$$

where $\bar{n}(E)$ is the average refractive index at the photon energy E. As $\bar{\beta}$ and $\Delta\beta$ in (2) are the electronic polarisabilities at $E = 0$ we need $\Delta \chi(0)$ which has been obtained from a least-squares fit of the coefficients in the power series

$$\Delta \chi(E) = \Delta \chi(0) + \Delta \chi^{(1)} E^2 + \Delta \chi^{(2)} E^4 + \ldots \tag{12}$$

to the experimental values of $\Delta \chi(E)$. In monoclinic crystals χ_{13} was obtained by determining the extinction position of a (010) cut in the spectrometer.

To refine the structure of Rb_2SO_4 and Cs_2SO_4 measurements were performed on an Enraf Nonius CAD-4 four-circle diffractometer with monochromated Ag Kα-radiation. For Rb_2SO_4 a total number of 3427 and for Cs_2SO_4 a total number of 2044 reflections were recorded by the $\omega/2\Theta$ scan technique. The data were reduced after applying Lorentz and polarisation factors and spherical absorption corrections (Dwiggins 1975) ($\mu(\text{Ag K}\alpha) = 108.1\ \text{cm}^{-1}$ for Rb_2SO_4 and $\mu = 68.97\ \text{cm}^{-1}$ for Cs_2SO_4). Finally 709 reflections for Rb_2SO_4 and 639 reflections for Cs_2SO_4 with intensities larger than $3\sigma(I)$ were considered. Both structures were refined by full matrix least-squares calculations using the ORXFLS 3 program system (Busing *et al* 1971). Atomic scattering factors and anomalous dispersion terms were taken from the *International Tables for X-ray Crystallography* (1974).

4. Optical and structural properties of crystals

4.1. M_2SO_4 (M = K, Rb, Cs)

In K_2SO_4 the differences $n_1 - n_2$ and $n_1 - n_3$ are both positive. In Cs_2SO_4 they are negative and Rb_2SO_4 shows an intermediate behaviour. Figure 1 shows the dependence of the difference $\chi_1 - \chi_2$ on E^2 in K_2SO_4. The appearance of the curve is typical for all M_2SO_4 compounds. Above 1.2 eV the power series (12) fits the experimental values with three coefficients. At smaller photon energies the dispersion changes drastically,

Table 1. Optical susceptibilities of M_2SO_4. The errors are always smaller than 1% for $\Delta\chi(0)$, 3% for $\Delta\chi^{(1)}$ and 5% for $\Delta\chi^{(2)}$.

	K_2SO_4	Rb_2SO_4	Cs_2SO_4
$\chi(0)$	1.206	1.257	1.404
$\chi^{(1)}$	6.58×10^{-3}	7.18×10^{-3}	9.21×10^{-3}
$\Delta\chi(0)'$	-1.46×10^{-3}	2.11×10^{-3}	8.50×10^{-3}
$\Delta\chi^{(1)'}$	-1.82×10^{-5}	2.40×10^{-5}	9.55×10^{-5}
$\Delta\chi^{(2)'}$	-6.83×10^{-7}	7.82×10^{-7}	24.7×10^{-7}
$\Delta\chi(0)''$	-4.83×10^{-3}	0.912×10^{-3}	2.88×10^{-3}
$\Delta\chi^{(1)''}$	-7.17×10^{-5}	-3.77×10^{-5}	1.95×10^{-5}
$\Delta\chi^{(2)''}$	-12.6×10^{-7}	-9.65×10^{-7}	10.5×10^{-7}

Table 2. Unit-cell dimensions of Rb_2SO_4 and Cs_2SO_4 in Å. Standard deviations are given in parentheses.

	Rb_2SO_4	Cs_2SO_4
a	7.820 (1)	8.239 (2)
b	10.441 (2)	10.937 (2)
c	5.979 (1)	6.256 (1)

indicating the influence of a near-lying IR resonance. This region of the spectrum is excluded from the least-squares fit. The numerical values for $\Delta\chi(0)$, $\Delta\chi^{(1)}$ and $\Delta\chi^{(2)}$ which are presented in table 1 show a nearly linear dependence on the radius r_M of the cation M^+ or on the bond length d_{M-O}.

The crystal structure of the isomorphous compounds M_2SO_4 (M = K, Rb, Cs) was determined for the first time by Ogg (1928). It is called the β-K_2SO_4 structure. The space group is P*nam* and the number of molecules in the unit cell is four. A structure refinement was carried out by McGinnety (1972) for K_2SO_4 and by Nord for Rb_2SO_4 (1974) and Cs_2SO_4 (1976). Calculating the geometrical factors G and D in equation (7) on the basis of the reported positional parameters, there is no monotonic trend of G_{S-O} and D_{S-O} with r_M or with d_{M-O} for the S–O bonds in spite of such a trend for $\Delta\chi$. Furthermore the errors in the values of G_{S-O} and D_{S-O} are extremely large (up to 100%), particularly in Rb_2SO_4 and Cs_2SO_4. Additionally the two densities, calculated from x-ray data and determined with large single crystals by Haussühl (1965), differ appreciably for Rb_2SO_4 and Cs_2SO_4. Both densities agree for K_2SO_4. Therefore we decided to redetermine the structure parameters of Rb_2SO_4 and Cs_2SO_4. For both compounds lattice constants have been determined from 25 independent reflections. The results are shown in table 2. As starting parameters for the initial cycle in the refinement process we used the values reported by Nord (1974, 1976). The final refinement included temperature factors and the isotropic secondary extinction parameter $g = 0.49$ for Rb_2SO_4 and $g = 0.58$ for Cs_2SO_4 (Zachariasen 1967). The final R value is 0.015 for both compounds. The positional parameters and the anisotropic temperature factors are listed in table 3.

There exist two kinds of M–O bonds. M(1) is surrounded by 11 and M(2) by 9 oxygens. The average bond length M(1)–O is larger than that of M(2)–O, but there is an overlap between the longest M(2)–O and the shortest M(1)–O contact of two compounds which are neighbours in the row K_2SO_4–Rb_2SO_4–Cs_2SO_4. These findings suggest that $\Delta\chi$ for all three crystals can be described by a common functional dependence on r_M or on d_{M-O}.

Table 3. Fractional atomic coordinates and anisotropic temperature factors B_{ij}. The form of the thermal ellipsoid is $\exp(-\sum_{ij} B_{ij}h_ih_j)$. The B_{ij} values are multiplied by 10^2.

| Rb$_2$SO$_4$	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rb(1)	0.67564 (4)	0.40923 (3)	0.25	0.665 (4)	0.369 (2)	1.006 (7)	−0.010 (2)	0	0
Rb(2)	−0.01208 (3)	0.70280 (3)	0.25	0.524 (4)	0.319 (2)	1.144 (7)	0.004 (2)	0	0
S	0.23734 (9)	0.41875 (6)	0.25	0.404 (9)	0.235 (5)	0.73 (2)	−0.001 (5)	0	0
O(1)	0.0500 (3)	0.4143 (3)	0.25	0.45 (3)	0.60 (2)	2.04 (8)	−0.07 (2)	0	0
O(2)	0.2974 (3)	0.5530 (2)	0.25	0.87 (4)	0.26 (2)	1.34 (6)	−0.11 (2)	0	0
O(3)	0.3037 (2)	0.3537 (2)	0.0483 (3)	0.95 (2)	0.44 (1)	0.98 (4)	0.09 (1)	0.16 (3)	−0.16 (2)
Cs$_2$SO$_4$									
Cs(1)	0.67704 (4)	0.40941 (3)	0.25	0.711 (5)	0.345 (3)	0.948 (8)	−0.007 (2)	0	0
Cs(2)	−0.01123 (4)	0.70145 (3)	0.25	0.543 (5)	0.329 (3)	1.111 (9)	0.002 (2)	0	0
S	0.2406 (1)	0.41726 (9)	0.25	0.44 (2)	0.257 (8)	0.74 (2)	0.010 (9)	0	0
O(1)	0.0626 (5)	0.4133 (4)	0.25	0.51 (5)	0.65 (4)	1.8 (1)	−0.03 (3)	0	0
O(2)	0.2977 (5)	0.5454 (3)	0.25	0.91 (6)	0.25 (3)	1.37 (9)	−0.08 (3)	0	0
O(3)	0.3039 (3)	0.3554 (4)	0.0576 (2)	0.98 (4)	0.46 (2)	1.05 (6)	0.07 (2)	0.21 (4)	−0.18 (3)
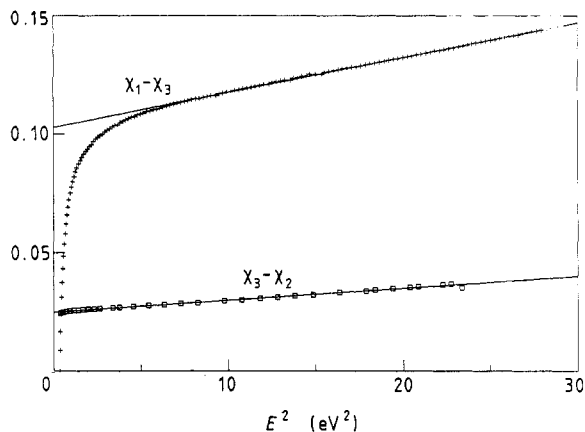
Figure 2. Dispersion of anisotropic optical susceptibilities in $KHSO_4$. Lines are fits with two terms of equation (12).

4.2. $KHSO_4$ and $CsHSO_4$

The striking difference between M_2SO_4 and the corresponding compounds containing hydrogen bonds, $KHSO_4$ and $CsHSO_4$, is the significant larger optical anisotropy of the latter compounds. In $KHSO_4$ the direction of all O–H–O bonds is nearly parallel to [100]. As a consequence $\chi_3 - \chi_2$, which contains diminishingly small contributions from O–H–O-bonds, is significantly smaller than the electronic part of $\chi_1 - \chi_3$ as shown in figure 2. In addition, at small photon energies we observe a strong decrease of $\chi_1 - \chi_3$ which is due to the infrared resonance of the O–H–O bonds. The decrease of $\Delta\chi$ at small photon energies was observed in all compounds containing hydrogen bonds. The influence of this decrease on $\Delta\chi$ in the visible part of the spectrum makes a careful measurement of the dispersion of Δn necessary. Otherwise a reliable decomposition of $\Delta\chi$ into an electronic and an ionic part and an extrapolation of the electronic part to $E = 0$ is not possible. Whereas the dispersion of $\Delta\chi$ contains a quadratic term in K_2SO_4 (figure 1), figure 2 shows a pure linear dependence on E^2. We have observed this linearity in all compounds with hydrogen bonds.

   $KHSO_4$ is orthorhombic with 16 molecules in the unit cell. The potassium ion is surrounded by 9 oxygen ions. There are two kinds of O–H–O bonds. The first one forms a dimer with two sulphate groups of the S(1) atom and the second one connects the sulphate group of the S(2) atom to a continuous chain (Loopstra and MacGillavry 1958). The direction of both kinds of O–H–O bonds is approximately that of [100]. Two refinements of the structure have been reported at nearly the same time (Cotton *et al* 1975, Payan and Haser 1976). We used average values of both sets of data for the calculation of the geometrical factors G and D.

   $CsHSO_4$ is monoclinic (Itoh *et al* 1981). The coordination number of Cs is 10. Hydrogen-bonded zigzag chains of SO_4 groups run along the b axis; however, the direction of each O–H–O bond is nearly parallel to the x_3 axis which belongs to the largest index of refraction and forms an angle of 39.5° with the crystallographic c axis. The optical data for $KHSO_4$ and $CsHSO_4$ as well as those for the other compounds containing hydrogen bonds are given in table 4.

4.3. $K_2Ni(SO_4)_2 \cdot 6H_2O$

This compound, abbreviated in the following as KNiS, belongs to the large family of Tutton's salts which are all of monoclinic symmetry. For our calculations we have

Table 4. Optical susceptibilities of compounds containing hydrogen bonds. $\Delta\chi(0)$ and $\Delta\chi^{(1)}$ are multiplied by 10^3.

	KHSO$_4$	CsHSO$_4$	KNiS	KHCO$_3$
$\bar{\chi}(0)$	1.100	1.285	1.195	1.154
$\bar{\chi}^{(1)}$	0.00665	0.00858	0.00802	0.0084
$\Delta\chi(0)'$	-25.98	58.1	-26.83	-267
$\Delta\chi^{(1)'}$	0.32	0.90	-0.26	4.49
$\Delta\chi(0)''$	-50.74	-26.4	-4.88	3
$\Delta\chi^{(1)''}$	-1.83	-0.37	-0.06	0
$\sphericalangle a^*, x_1$		39.5°	$-8.7°$	27.2°

used the structure data reported by Hodgeson *et al* (1975). KNiS is the most complex compound studied in the present paper. Its structure may be considered as an assembly of potassium ions and the two units SO$_4$ and Ni(H$_2$O)$_6$ which are connected by hydrogen bonds. There is no outstanding direction for the O–H–O bonds as in KHSO$_4$ and CsHSO$_4$. The coordination number is well defined only for the cations: $N = 4$ for S, $N = 6$ for Ni and $N = 10$ for K. The Ni(H$_2$O)$_6$ complex possesses a nearly tetragonal symmetry with a compressed tetragonal axis. The optical properties of most Tutton's salts were determined by Tutton himself (Winchell and Winchell 1964). We have measured the birefringence with higher accuracy. To determine the orientation of the indicatrix a careful consideration of the dichroism near the absorption bands was necessary. We observed no influence of these bands on the birefringence Δn.

4.4. KHCO$_3$

The structure of KHCO$_3$ shows $(HCO_3)_2^{2-}$ dimers with some disorder of the H atoms as revealed by a neutron diffraction study (Thomas *et al* 1974b). Order–disorder processes of protons are assumed to be the origin of a ferroelastic phase transition at 318 K (Haussühl 1986). In our calculations we neglect this disorder and use the structure data obtained from x-ray diffraction (Thomas *et al* 1974a).

The birefringence in KHCO$_3$ is extremely large, and this can easily be explained by the fact that the O–H–O bonds and the CO$_3$ planes are nearly parallel and that the optical anisotropy of both structural units is large.

5. Determination of bond parameters

In a complex crystal several kinds of bonds exist and usually the length d of each bond type varies. In addition each type of bond is characterised by four quantities which are $\Delta\beta, \Delta f, \bar{\beta}$ and $\bar{f}$. As a consequence, for one crystal the number of independent parameters is *always* larger than the number of available experimental data. Therefore we study different materials containing similar bonds and we introduce assumptions in such a way that the final number of bond parameters is essentially smaller than the experimental data used.

Let us start with the characterisation of SO$_4$ groups. They form nearly ideal tetrahedra in M$_2$SO$_4$. Thus $\Delta\beta_{S-O}$ and Δf_{S-O} cannot be determined from the birefringence of M$_2$SO$_4$ with a sufficient degree of reliability. Therefore we consider suitable materials

Table 5. Bond parameters $\bar{\beta}$, $\Delta\beta$, $\bar{f}$ and Δf. Values are referred to the bond length d_R and to the coordination number N.

Bond	N	d_R (Å)	$\bar{\beta}$ (Å^3)	$\Delta\beta$ (Å^3)	$\bar{f}$	Δf
S–O	4	1.47	—	11.7 (2)	—	−1.0 (2)
K–O	10	2.944	2.83 (2)	0.063 (8)	6.2 (6)	3.1 (3)
Rb–O	10	3.078	3.65 (3)	0.30 (1)	5.4 (6)	2.3 (3)
Cs–O	10	3.248	4.81 (4)	0.75 (2)	4.5 (6) .	1.5 (2)
O–H–O	(chain)	2.6	9.0 (3)	5.12 (6)	1.1 (5)	−2.0 (2)
O–H–O	(dimer)	2.6	18 (1)	5.12 (6)	1.1 (5)	−2.0 (2)

which show a larger birefringence than M_2SO_4. These are the orthorhombic compounds Na_2SO_4 and $KHSO_4$. In Na_2SO_4 all S–O bonds possess the same length (Nord 1973); thus the geometrical factor D_{S-O} vanishes. Within the accuracy of structural and optical data the two values for $\Delta\chi$ are described by the bond parameter $\Delta\beta_{S-O}$. In $KHSO_4$ d_{S-O} varies strongly, leading to a large value for D_{S-O}. Therefore a reliable value for Δf_{S-O} can be determined from its birefringence. The values for $\Delta\beta_{S-O}$ and Δf_{S-O} obtained from Na_2SO_4 and $KHSO_4$ are shown in table 5. They were used as input data in the calculations for all compounds containing the sulphate group.

In the next step we analyse the susceptibilities of M_2SO_4 to determine the parameters of the ionic M–O bonds. They are similar to the bonds in alkali halides and may be treated in the same way. In alkali halides we found that the longitudinal and transverse bond polarisabilities can be described (Weber 1986) by

$$\beta = \beta_0 \exp(-f_0/d^s) \tag{13}$$

with the value $s = 3$ for the exponent of the bond length d and with two different values f_0^L and f_0^T for f_0. Quantities with the superscripts L and T are referred to the longitudinal and transverse polarisability, respectively. From (13) it follows that

$$f = \frac{\partial\beta}{\partial d}\frac{d}{\beta} = sf_0/d^s. \tag{14}$$

In alkali halides β_0 is a characteristic quantity of the anion and f_0 depends on the kind of cation. Based on these results we assume that in all three M–O bonds β_0 has the same value, that f_0 depends linearly on the cation radius r_M and that $\beta_0^L = \beta_0^T$. With these assumptions we are left with five independent bond parameters for the three M–O bonds. These are β_0, f_0^L, f_0^T, $\partial f_0^L/\partial r_M$ and $\partial f_0^T/\partial r_M$. The equality $\beta_0^L = \beta_0^T$ ensures that the anisotropic bond polarisability vanishes for $d \to \infty$. There still remains the problem that two different coordinations exist. Even a rough inspection of $\Delta\chi$ and of the geometrical factors for both coordinations shows that M(2)–O bonds are optically more important than M(1)–O bonds. Therefore we introduce another factor δ which increases the contribution of $\Delta\beta_{M(2)-O}$ and decreases that of $\Delta\beta_{M(1)-O}$ accordingly to

$$\Delta\beta^{[11]} = \tfrac{10}{11}(1 - \delta)\Delta\beta^{[10]} \qquad \text{and} \qquad \Delta\beta_{M-O}^{[9]} = \tfrac{10}{9}(1 + \delta)\Delta\beta_{M-O}^{[10]}. \tag{15}$$

The five bond parameters noted above and δ have been fitted to the nine experimental data for $\bar{\chi}(0)$ and $\Delta\chi(0)$ given in table 1. In table 5 the result is presented in a way which allows a direct comparison of the bond parameters of the different M–O bonds. By (15) all parameters have been referred to the coordination number $N = 10$. The value for δ in (15) is $\delta = 0.45$. A calculation with the parameters of table 5, for the birefringence in M_2SO_4 the average error in Δn is 8×10^{-5} or 6%.

Table 6. Temperature dependence of optical susceptibilities in K_2SO_4 and $KHSO_4$ (units: 10^{-5} K^{-1}). Different contributions according to equations (8) and (9) are given in brackets: $(-\bar{\chi}\bar{F} \, \partial \ln V/\partial T)$, $[-\Delta\chi \, \partial \ln V/\partial T]$, $\{\frac{2}{3}(\Delta\chi/\bar{F})(\partial\bar{\chi}/\partial T)\}$.

	K_2SO_4	$KHSO_4$
$\partial\bar{\chi}(0)/\partial T$	$-13.5\,(9)$	$-16\,(1)$
	$(-18.4$	$-18)$
$\partial\Delta\chi(0)'/\partial T$	$0.59\,(3)$	$7.5\,(3)$
	$[0.02$	$0.3]$
	$\{0.01$	$0.2\}$
$\partial\Delta\chi(0)''/\partial T$	$0.85\,(5)$	$6.6\,(3)$
	$[0.05$	$0.6]$
	$\{0.03$	$0.4\}$

In $KHSO_4$, $CsHSO_4$, $KHCO_3$ and KNiS the hydrogen bonds appear in different forms. Usually both O–H contacts of one bond are different in length and the angle O–H–O differs from $180°$. The bonds appear as chains, dimers and three-dimensional frames. Furthermore the coordination of the oxygen atoms is different in different compounds. In spite of these structural variations the birefringence in all materials examined by us depends in a similar way on the orientation of the hydrogen bonds. Therefore we neglect the differences and regard the positions of the two oxygen atoms of an O–H–O bond as the characteristic structural entities. There are slight but significant variations in the bond length. The shortest bond is observed in $CsHSO_4$ ($d_{O-H-O} = 2.58$ Å), the longest one in KNiS ($d_{O-H-O} = 2.72$ Å). These variations allow a determination of Δf_{O-H-O} and $\bar{f}_{O-H-O}$.

To describe the contribution of the hydrogen bonds to the birefringence of $CsHSO_4$, $KHCO_3$, $KHSO_4$ and KNiS only two bond parameters are needed. Their values are presented in table 5. In addition we have checked that these two values also agree with the birefringence in ice.

The decomposition of the average susceptibilities does not yield such a simple result. $\bar{\beta}_{O-H-O}$ is significantly larger in $KHCO_3$ and $KHSO_4$ than in $CsHSO_4$ and KNiS. Therefore we consider $\bar{\chi}$ of some further compounds to comparing $\bar{\beta}_{O-H-O}$ in a wider range of the bond length. These additional substances are $M_2Cu(SO_4)_2 \cdot 6H_2O$ (M = K, Rb, Cs), ice, $CaSO_4 \cdot 2H_2O$ and $MgSO_4 \cdot 7H_2O$. We find that $\bar{\beta}_{O-H-O}$ is different for hydrogen bonds occurring in a chain and in a dimer. The final results are shown in table 5.

6. Structural applications

After determining the individual bond parameters, by relating the optical anisotropy of a crystal to its structural anisotropy, we are now in the position to analyse structural properties by measurement of the birefringence. The method is demonstrated by investigating the temperature dependence of the optical susceptibilities in K_2SO_4 and in $KHSO_4$. In both crystals $\bar{\chi}$ and $\Delta\chi$ depend linearly on T between 160 K and 300 K. The experimental results are shown in table 6.

6.1. General features of the experimental results

As shown in equations (8) and (9), $\partial\bar{\chi}/\partial T$ and $\partial\Delta\chi/\partial T$ depend on different contributions. The change of the optical density, which is described by the first term in both equations,

can be computed with the coefficients of thermal expansion (Haussühl 1965, Gerlich and Siegert 1975). Furthermore the second term in equation (9) is obtained from the results of $\partial \bar{\chi}/\partial T$ measurements. In table 6 the magnitude of the different contributions to $\partial \bar{\chi}/\partial T$ and $\partial \Delta \chi/\partial T$ are compared. Obviously in both crystals $\partial \bar{\chi}/\partial T$ is produced mainly by the change in the optical density and to a small degree by the changes in the bond lengths, but the mechanism which governs the temperature dependence of $\Delta \chi$ is different. Practically the whole value for $\partial \Delta \chi/\partial T$ is produced by $\partial \Delta \chi^{*}/\partial T$ which contains the structural motions.

To obtain a survey of possible structural displacements we consulted some results from the literature. Hathaway and Hewat (1984) have determined the structure of the deuterated Tutton's salt $(ND_4)_2Cu(SO_4)_2 \cdot 6D_2O$ at different temperatures by neutron powder diffraction. There is some indication that the bond lengths d_{S-O} and d_{O-H-O} decrease with increasing temperature: $(\partial \ln d/\partial T)|_{S-O} = -0.6 \times 10^{-4} \text{ K}^{-1}$ and $(\partial \ln d/\partial T)|_{O-H-O} = -2 \times 10^{-4} \text{ K}^{-1}$. Unfortunately the experimental error is much larger than these values. However, Thomas *et al* (1974a) have investigated $KHCO_3$ by single-crystal x-ray experiments and also observed a negative value $(\partial \ln d/\partial T)|_{O-H-O} = (-3.4 \pm 1.4) \times 10^{-4} \text{ K}^{-1}$ for the hydrogen bond. The increase of d_{K-O} with T is the same as the average coefficient of thermal expansion $\bar{\alpha}$: $(\partial \ln d/\partial T)|_{K-O} = (4 \pm 1) \times 10^{-5} \text{ K}^{-1}$, $\bar{\alpha} = 3.5 \times 10^{-5} \text{ K}^{-1}$. The thermal expansion of the C–O bonds is negative: $(\partial \ln d/\partial T)|_{C-O} = (-2 \pm 2) \times 10^{-5} \text{ K}^{-1}$. The examples show that the response of some bonds, investigated in the present work, to the temperature changes may be opposite to that of the macroscopic dimensions of the relevant crystals. The examples also show that the accuracy of diffraction experiments is usually too small to derive reliable conclusions. In contrast to the results in $(ND_4)_2Cu(SO_4)_2 \cdot 6D_2O$ and $KHCO_3$ the thermal expansion of the hydrogen bond in KH_2PO_4 (KDP) is positive: $(\partial \ln d/\partial T)|_{O-H-O} = (2.7 \pm 0.2) \times 10^{-5} \text{ K}^{-1}$ (Nelmes *et al* 1982). The small error shows that the hydrogen bond in KDP has been investigated with a high accuracy. It should be noted that for KDP we have used structural data which have been obtained in the vicinity of its ferroelectric phase transition.

6.2. Determination of structural motions

As already discussed, the temperature dependence of birefringence in K_2SO_4 and $KHSO_4$ reflects mainly the changes of structural parameters. Although there are usually more free parameters than available experimental data, we will demonstrate that an idea of the dominant structural displacements can be obtained.

By determining, from the results of $\partial \bar{\chi}/\partial T$ measurements, upper limits for the values of $\partial \ln d/\partial T$ the magnitude of the first term in equation (10), $G\Delta\beta\Delta f\partial \ln d/\partial T$, can be estimated. In K_2SO_4 this term turns out to be very small and is neglected in the following analysis. Only one free structural parameter is involved in $\partial \Delta \chi'/\partial T$. This is the z component of $O(3)$. Its variation with temperature is definitely determined by the optical experiment. The result is $\partial z_{O(3)}/\partial T = (-1.32 \pm 0.08) \times 10^{-6} \text{ K}^{-1}$. This value should be compared with the standard errors for the oxygen parameters in table 3. Although the R value of 0.015 which has been achieved in the refinement of Rb_2SO_4 and Cs_2SO_4 is very small, the smallest error is as large as 2×10^{-4}. Thus it is not possible to detect the thermal shift of the $O(3)$ atom by such diffraction experiments. The displacement of $O(3)$ can be elucidated as an increase of the angle $O(3)–S–O(3)'$ by $1.03 \times 10^{-3} \text{ deg K}^{-1}$ with increasing temperature.

Six free structural parameters are involved in $\partial \Delta \chi''/\partial T$. However, as the contributions which are produced by the change of bond lengths can be neglected, the only

possible movement of the oxygen atoms is a rotation of the $S-O_4$ group around the z axis by 1.8×10^{-3} deg K^{-1}. This is an average rotation. We are not able to decide whether the rotations of the three different S–O bonds are the same or not.

The structure of $KHSO_4$ is much more complex than that of K_2SO_4. There is a total of 36 free parameters. On the other side, only three optical data are available. Therefore it is necessary to introduce some assumptions. Even then it is only possible to derive average features of the thermal shifts of atoms. First of all we assume that equation (11) is valid for the K–O bonds as discussed in § 2. Secondly, we do not distinguish between both kinds of hydrogen bonds and between S–O bonds which are in contact with hydrogen bonds or not. Thirdly, the movements of those S–O and O–H–O bonds which form a continuous chain along [100] are connected to the coefficient of thermal expansion α_1 by

$$\alpha_1 = \sum x \frac{\partial \ln d}{\partial T} - \frac{d}{a} \sin \gamma_1 \frac{\partial \gamma_1}{\partial T} \tag{16}$$

where the summation has to be executed over all S–O and O–H–O bonds. In (16) x represents the differences of fractional coordinates $x_O - x_S$, etc, and a is the lattice constant. Some combinations of the sign of different terms in (16) result in improbably large displacements and can be excluded. With these restrictions we identify from our results a contraction of the hydrogen bonds with increasing temperature by

$$\left. \frac{\ln d}{\partial T} \right|_{O-H-O} = -1.3 \times 10^{-4} \ K^{-1}.$$

This contraction is compensated by an increase of the angle O–S–O' for those S–O bonds which form the chain O–S–O'–H–O–S–O' by about 0.01 deg K^{-1}.

The negative thermal expansion of the hydrogen bonds supports the results of diffraction experiments in $(ND_4)_2Cu(SO_4)_2 \cdot 6D_2O$ and in $KHCO_3$ and suggests that the positive value in KDP is caused by mechanisms which are related to the ferroelectric phase transition in KDP.

7. Final remarks

Based on the concept of bond polarisabilities, we have demonstrated that the optical susceptibilities of a complex crystal can be decomposed into additive contributions of single bonds. This was possible by precise measurements of optical birefringence in a wide spectral range and by a comparative study of various compounds. The parameters which we have used for a characterisation of the bonds are empirical quantities. Of course, it is possible to derive from our results more fundamental quantities of a physical model. However, the loss of accuracy involved impairs the achievement of the second goal of the present paper, the determination of induced structural displacements. Such a determination has been demonstrated using the thermal expansion of K_2SO_4 and $KHSO_4$. In a similar way the structural origin of electro-optical and elasto-optical effects can be investigated which may lead to a new understanding of elastic and dielectric properties of crystals. In this context it is interesting to estimate the sensitivity of such an optical determination of structural displacements. As an example we assume that in $CsHSO_4$ the length of the hydrogen bonds change. A change of the birefringence Δn by

10^{-12}, which is a value that can be detected using modern polarisation optical methods, corresponds to a relative displacement of the two oxygen atoms in the hydrogen bond of $CsHSO_4$ which is as small as 10^{-9} Å.

The number of experimental data which have been used for the determination of the bond parameters exceeds the number of fitting parameters by a factor of two. Furthermore the materials represent a wide spectrum of structural and optical anisotropy. Therefore the results reflect a considerable amount of reliability and universality. However, in deriving the bond parameters we have observed two kinds of limitations of the model applied. The first one is related to the occurrence of different coordination numbers in complex crystals. As an example, in M_2SO_4 the birefringence measurements show very clearly that both M–O coordinations are not equivalent, which can be explained by an exchange of effective charges between both kinds of bonds. A similar reason may be responsible for the errors in the parameters of hydrogen bonds which are larger than the errors for M–O and S–O bonds. The second limitation concerns the discrepancy in the sensitivity of optical and diffraction experiments. The limited accuracy of structural data becomes important in the analysis of crystals with a small anisotropy, such as M_2SO_4, and in the determination of f^L and f^T, which requires very precise bond lengths.

As shown in the last section for the example of $KHSO_4$, the problem in the optical determination of structural properties is the limited number of experimental data. However, an essential step forward in the investigation of small structural displacements can be achieved by combining the high sensitivity of optical experiments with the large amount of information obtained from x-ray diffraction experiments.

Acknowledgments

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