Evaluation of photoelastic constants from first-order Raman intensities of MgF₂

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Abstract. A formalism to connect first-order Raman intensities of MgF₂ and its photoelastic constants is developed by developing a method of writing internal co-ordinates in terms of displacement gradients u_{ij} which are not symmetric. It is found that for crystals containing only one line in A_1 species, the ratios P_{13}/P_{33} and $(P_{11} + P_{12})/P_{31}$ can be directly evaluated from the intensities, without having to derive the intensity formulae; while $(P_{11} + P_{12})/P_{13}$ is independent of the intensities as well as the refractive index of the crystal. It is a function of only the dimensional parameters. In this crystal, since the species B_{1g} and B_{2g} also contain only one line each, the ratio $(P_{11} - P_{12})/P_{66}$ can also be directly obtained from the intensities.

Keywords. Photo-elastic constants; Raman intensities; displacement gradients

1. Introduction

When a crystal is stressed, the strains produced resolve themselves into phonons. Suitable groupings of Raman phonons manifest themselves as photoelastic constants according to their symmetry. This natural connection between Raman intensity and photoelasticity was recognised by Maradudin and Burstein (1967) who derived an expression for photo-elastic anisotropy $(P_{11} - P_{12} - P_{66})$ of diamond in terms of the intensity of its Raman line:

$$P = (a_0^2 \, \epsilon_0^2/8\pi) \, (P_{11} - P_{12} - P_{66})/[1 - 8 \, G/(a_0 \, M \, v_R^2)]. \tag{1}$$

P is the polarizability change with respect to the frequency v_R. ϵ_0 is equilibrium dielectric constant, a_0 radius of the carbon atom, M its mass and G an expression involving a product of force constant and length. P is the sign of the photoelastic anisotropy $(P_{11} - P_{12}) - P_{66}$. But this formalism does not seem to have been followed up later.

Nelson and his colleagues (Nelson and Lax 1970; Nelson and Lazay 1971) have connected intensities of Brillouin components of a crystal to its photoelastic constants. They have pointed out that, in place of strain tensor e_{ab}, we have to use u_{ab}, given by

$$2u_{ab} = u_{ab} + u_{ba} + u_{ab} - u_{ba} = e_{ab} + w_c \tag{2}$$

where a, b, c indicate the axes x, y, z; w_c is the rotation in the plane of ab. Thus, one has 9 components u_{ab} instead of 6 e_{ab} and the corresponding photoelastic constant

tensor is of order 9×9 instead of 6×6. It will be 9×9 if the polarizability tensor is taken to be unsymmetrical as in resonance or near resonance Raman spectra. For Raman spectra far from resonance the matrix is of the order 6×9. It is also pointed out that the photoelastic constant tensor does not follow the symmetry of the crystal for piezoelectric-type crystals, as the Raman phonons which are also infrared active create electric fields that produce additional polarizability changes.

Meera *et al* (1978) applied stress on a crystal of silicon and connected the changed intensities of Raman spectra to photoelastic constants. Briggs and Ramdas (1976) again studied the Raman spectra of CdS under properly stressed conditions and related the altered frequency changes to deformation potentials.

In this paper we try to relate the Raman intensities of a crystal (under unstrained conditions) and photoelastic constants. For this purpose, the bond polarizability theory of Raman intensities (Eliashevich and Wolkenstein 1945; Long 1953) has been applied to the crystals. A serious problem in this field is the sign ambiguity of the polarizability change $\partial \alpha_{ij}/\partial Q_k$. In papers published earlier (Kumar *et al* 1974; Buddha and Rajeswara Rao 1976, 1977; Pratibha *et al* 1979; Swarna Kumari and Rajeswara Rao 1981), it has been shown as to how this problem can be avoided. Maradudin and Burstein (1967) also pointed out the difficulty in obtaining photoelastic constants from Raman intensities.

A parallel theory of Raman intensities was earlier developed by Loudon (1963). But as pointed by Maradudin and Burstein (1967), 'the model of electric polarizability we choose, must contain as many parameters as there are pieces of experimental information, no more, no less'. Tubino and Piseri (1975) have justified this theory for crystals. Thus the bond polarizability theory has come to stay. It has also the advantage of understanding the properties of the crystal from molecules and may pave the way to relate photoelastic constants of different crystals having the same or similar molecules.

2. Sign ambiguity in intensity analysis

The sign ambiguity problem connecting Raman intensities and electro-optical constants has earlier been solved for both molecules and crystals. The intensity formulae are of the type

$$I = L' A, \tag{3}$$

where $I = \partial P_i/\partial Q_k$ or $\partial \alpha_{ij}/\partial Q_k$ for IR or Raman intensities. I should not be confused with intensity which is proportional to I^2 and will be referred to later. L' is transpose of L matrix and A contains the electrooptical constants. I' can be plus or minus depending on the nature of the oscillation. It has been suggested that (3) may be written as

$$I' I = A' LL' A = A' GA. \tag{4}$$

We have one equation of this type for each species. If the parameters in A are larger in number than the equations, one may obtain the data from isotopic mole-

cules. *A* elements have thus been determined by us earlier in a number of molecules and crystals and these elements can be used to evaluate the photoelastic constants.

3. Internal co-ordinates and strains

For any crystal, polarizability change

$$\Delta a_{ij} = \frac{\partial a_{ij}}{\partial Q} \cdot \frac{\partial Q}{\partial S} \cdot \frac{\partial S}{\partial R} \cdot \Delta R, \tag{5}$$

S and R are symmetry and internal coordinates respectively. We seek to connect Δa_{ij} to photoelastic constants by deriving a relationship between ΔR and the strain parameters. For this purpose we start with

$$u_i^k = u_{ij} \, r_j^k \tag{6}$$

as explained by Born and Huang (1954). Repetition of the index j indicates summation. Here i and j stand for x, y, z, u_i^k is displacement of the kth atom in the ith direction. r^k is its position vector and $u_{ij} = \partial u_i / \partial r_j$ are related to strain parameters. In general $u_{ij} \neq u_{ji}$. However,

$$u_{ii} = e_{ii}, \tag{7a}$$

and $\qquad u_{ij} + u_{ji} = e_{ij}, \tag{7b}$

where e_{ij} are the strain parameters. The internal oscillations in a molecule (or crystal) are generated by displacements of atoms according to a system given by

$$\Delta R = \sum_k u^k \cdot s^k, \tag{8}$$

u^k is the displacement and s^k is the unit vector along the displacement. s^k are Wilson's (1955) s vectors and (8) is explained in detail in books on molecular physics. As an example, if ΔR is stretching between two atoms 1 and 2 of a bond, displacements u^1 and u^2 should be along the bond in opposite directions and s^1 and s^2 are unit vectors (figure 1). In this case, $s^1 = - s^2$.

Taking 0, midway between 1 and 2 as origin, the position vectors $r^1 = - r^2$, r_j^k in (6) is equal to $r^1 \, 1j$, $1j$ being the direction cosine of r^1. Since s^1 and r^1 are in the same direction, $1j$ are direction cosines of s^1 also. Similar direction cosines $2j$ apply to r^2 and s^2. Now, expanding (6) for atoms 1 and 2,

$$u_x^1 = (u_{xx} \, 1x + u_{xy} \, 1y + u_{xz} \, 1z) r^1, \tag{9a}$$

$$u_y^1 = (u_{yx} \, 1x + u_{yy} \, 1y + u_{yz} \, 1z) r^1, \tag{9b}$$

$$u_z^1 = (u_{zx} \, 1x + u_{zy} \, 1y + u_{zz} \, 1z) \, r^1. \tag{9c}$$

Writing similar equations for u_x^2, u_y^2 and u_z^2, we have

$$\Delta R = (u_x^1 \, 1x + u_y^1 \, 1y + u_z^1 \, 1z) + (u_x^2 \, 2x + u_y^2 \, 2y + u_z^2 \, 2z)$$

$$= R(e_{xx} \, 1x^2 + e_{yy} \, 1y^2 + e_{zz} \, 1z^2 + e_{xy} \, 1x \, 1y + e_{yz} \, 1y \, 1z + e_{zx} \, 1z \, 1x). \tag{10}$$

Here we have introduced a simplification $r^1 = r^2$ taking the origin at the centre of the bond. Also, since r^1 and r^2 are along the same line, but in opposite directions, $ij = -2j$. We have also put $R = 2r$.

Equation (10) is derived in standard books on elasticity (for example by Love 1952) though in a different manner. We may point out at this stage that this formula is derived for two points in a continuous medium but is applied for a bond between two atoms. We follow this approximation in all these calculations (as Dayal 1950, Saxena 1944 and others have done). We have considered this format as it can be adopted to any internal coordinate, bending, out-of-plane oscillation, rotation, etc. We shall demonstrate this for rotation.

Taking a simple linear molecule MgF_2 (figure 2) with Mg at the centre, we shall derive an expression for rotation about y-axis which takes place by F_1 and F_2 moving along z in the opposite directions. According to (8),

$$R_y = u^1 \cdot s^1 + u^2 \cdot s^2 = u_z^1 \, (- e_z/R) + u_z^2 \, (e_z/R). \tag{11}$$
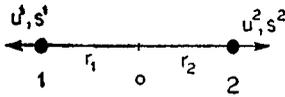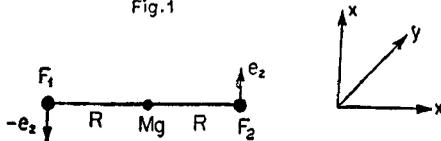

Figure 1. Symmetric stretching of atoms 1 and 2. u^1 and u^2 are displacements, s^1 and s^2 are unit vectors in those directions.
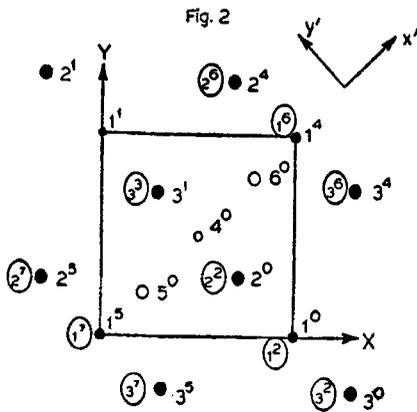

Figure 2. Rotation about Y-axis

Figure 3. Unit cell of MgF_2. The light shaded atoms are in the plane of the paper. The dark ones are above or below the plane of the paper at a distance $c/2$. Those in circles are above the plane of paper. The superscripts represent the cell numbers.

Here, we have used $s^1 = -e_z/R$ (e_z is the unit vector along z direction) as it indicates bending of the bond MF_1. Since $u_x = u_y = 0$

$$-\frac{1}{R} u_z^1 = u_{zx} \, 1x \, R \times \frac{1}{R},$$ (12a)

and, $$\frac{1}{R} u_z^2 = u_{zx} \, 2x R \times \frac{1}{R}.$$ (12b)

Therefore $R_y = 2u_{zx} = u_{zx} + u_{xz} + u_{zx} - u_{xz} = e_{zx} + w_y,$ (13)

in the notation used by Love (1952). Thus ΔR in (5) can be replaced by the appropriate expressions involving strains. Equation (10) can be written in the form Rle. R is a diagonal matrix of bonds, l row matrix of products of direction cosines taken two at a time (writing l, m, n for $1x$, $1y$, $1z$) and e column matrix of strains. Substituting in (5)

$$\Delta a_{ij} = I' \, L^{-1} \, URle,$$ (14)

I' is row matrix of $\partial a_{ij}/\partial Q$. We have put $S = LQ$ and $S = UR$. Now, photoelastic constants are defined by (Born and Huang 1954)

$$\Delta \, (\epsilon^{-1})_{ij} = P_{ijkl} \, e_{kl}$$ (15)

From, $$\epsilon \, \epsilon^{-1} = 1, \Delta \, \epsilon = - \epsilon_0 \, \Delta \, \epsilon^{-1} \, \epsilon_0$$ (16)

Here we have written ϵ_0 for ϵ as an approximation. ϵ_0 is the dielectric constant of the unstrained crystal and ϵ is that of the strained crystal. Substituting in (16)

$$\Delta \epsilon_{ab} = (\epsilon_0)_{ai} \, P_{ijkl} \, (\epsilon_0)_{bj} \, e_{kl} = P'_{ijkl} \, e_{kl}.$$ (17)

Since $\epsilon = 1 + 4\pi abN$, where a is the polarizability tensor and N, the number of molecules per unit volume; b is related to crystal structure

$$\Delta \epsilon = 4\pi bN \Delta a,$$ (18)

and Δa_{ij} in (14) can be replaced by $\Delta \epsilon_{ij}$. As we propose to derive expressions for photoelastic constants in units of polarizability derivatives, $4\pi bN$ cancels off. In order to compare with experimental photoelastic constants, we have to multiply them with ϵ_0 elements according to the scheme given by (16). To make such multiplication simple, we take the coordinates along the symmetry axes of the crystal and make ϵ_0 a diagonal tensor having only the principal elements. For a crystal like MgF₂ for which we shall derive the photoelastic constants, P' and P are related as follows. Here $(\epsilon_0)_{xx} = n_x^2$ and $(\epsilon_0)_{zz} = n_z^2$, are refractive indices along a and c axes of the crystal:

$$P'_{11} = n_x^4 \, P_{11}, \qquad\qquad P'_{22} = n_x^4 \, P_{22},$$

$$P'_{33} = n_z^4 \, P_{33}, \qquad\qquad P'_{44} = n_x^2 \, n_z^2 \, P_{44}.$$ (19)

P_{11}, P_{22} etc have the usual meaning (Born and Huang 1954) with respect to the co-ordinate axes x, y, z.   Then, we have from (14)

$$P' = I'L^{-1} URle.$$

(20)

4. Raman intensity analysis of MgF_2

As we propose to get $\partial \alpha_{ij}/\partial Q$ from Raman intensities, we shall first derive formulae connecting intensities and bond polarizabilities of this crystal as was done earlier for other cyrstals (Kumar *et al* 1974).

MgF_2 is a rutile-type crystal of symmetry D_{4h}^{17}, with two molecules in the unit cell. The molecules are oriented perpendicular to each other and their levels separated by $c/2$.   But the a_1 and a_2 axes of the cell are oriented at 45° to the orientations of the molecules (figure 3).   We shall refer to molecule 213 as 1 and 546 as 2.   As it becomes necessary to take into account distances of the atoms in the neighbouring unit cells also, to construct symmetry coordinates, the central cell is marked 0, and the other cells with different numbers.   The bonds like 12, 13, 45 and 46 are mostly of covalent nature while bonds like 42 or 51 are ionic but have also some covalent nature and oscillations are possible between them.

The dimensions of the crystal and of the bonds (Wyckoff 1962) are calculated to be $a_1 = a_2 = 4\cdot623\text{Å}$, $c = 3\cdot052\text{Å}$, $r_{12} = r_{13} = r_{45} = r_{46} = 2\cdot026\text{Å}$, $r_{42} = 1\cdot967\text{Å}$. The angle 42 makes with XY plane is θ which is equal to 50°51′.

Since there are 6 atoms in the unit cell, there are 15 optical modes and they are distributed among the species as $1A_{1g}$, $1B_{1g}$, $1B_{2g}$, $1E_g$, $1A_{2g}$, $2A_{2u}$, $2B_{1u}$, $4E_u$. Among them, $1A_{2u}$, and $1E_u$ are translations.   In addition to the ungerade modes, A_{2g} is inactive.   Raman modes are of frequencies 410, 515, 92 and 295 cm^{-1} 410 being observed in α_{xx}, α_{yy} and α_{zz} spectra, 92 in α_{xx} and α_{yy}, 515 in α_{xy} and 295 in α_{zx} and α_{yz}.   These spectra are taken by Porto (1967).

5. Intensity formulae

To derive intensity formulae, it is necessary to determine the symmetry coordinates in the way explained in our earlier papers.   They are

$$S_1^{A_{1g}} = \frac{1}{\sqrt{2}}\Big[(1/2)\{(1^020 + 1^131) + (4^050 + 4^060)\}$$

$$- \frac{1}{2\sqrt{2}} \{(4^020 + 4^022) + (4^031 + 4^033) + (5^015 + 5^017)$$

$$+ (6^014 + 6^016)\} \Big],$$

(21a)

$$S_2^{B_{1g}} = \frac{1}{\sqrt{2}} \left[(1/2)\{(4^05^0 + 4^06^0) - (1^02^0 + 1^13^1)\} \right.$$

$$+ \frac{1}{2\sqrt{2}} \{(4^02^0 + 4^02^2) + (4^03^1 + 4^03^3) - (5^01^5 + 5^01^7)$$

$$\left. - (6^01^4 + 6^01^6)\} \right], \tag{21b}$$

$$S_3^{B_{2g}} = -\frac{1}{\sqrt{2}} [R_{z1} + R_{z2}] = R_z, \tag{21c}$$

$$S_{4a}^{E_g} = \frac{1}{\sqrt{2}} [R_{y'} + R_{x'}] = R_x, \tag{21d}$$

$$S_{4b}^{E_g} = \frac{1}{\sqrt{2}} [R_{y'} - R_{x'}] = R_y, \tag{21e}$$

x' and y' are directions along molecules 2 and 1. The first coordinate shows that both the molecules stretch in and out while in the second, one stretches, and the other contracts. The other coordinates describe R_z, R_x and R_y rotations of these coordinates about the axes.

The intensities are functions of the bond polarizabilities and their derivatives. The derivation is described in our papers. The intensities are

$$I_{xx}^{A_{1g}} = I_{yy}^{A_{1g}} = (14 \cdot 19) \, K = \left[\sqrt{2} \, a_{12}^{\prime T} + \frac{1}{\sqrt{2}} \gamma_{12}^{\prime} - a \, \gamma_{42} \right] L_{11} = A_1 L_{11}, \tag{22a}$$

$$I_{zz}^{A_{1g}} = (?) = [\sqrt{2} \, a_{12}^{\prime T} + 2a \, \gamma_{42}] L_{11} = A_1^{\prime} L_{11}, \tag{22b}$$

$$I_{xy}^{B_{1g}} = (3 \cdot 527) \, K = \left(\frac{1}{\sqrt{2}} \gamma_{12}^{\prime} - a \, \gamma_{42} \right) L_{22} = A_2 L_{22}, \tag{22c}$$

$$I_{xx}^{B_{2g}} = I_{yy}^{B_{2g}} = (1 \cdot 017) \, K = [\sqrt{2} \, \gamma_{12} - b \, \gamma_{42}] L_{33} = A_3 L_{33}, \tag{22d}$$

$$I_{yz}^{E_g} = I_{zx}^{E_g} = (?) = [\gamma_{12} - c \, \gamma_{42}] L_{44} = A_4 L_{44}. \tag{22e}$$

These equations are expanded forms of (3). These A elements are transferred to table 1.

where $$a_{12}^{\prime T} = \frac{\partial}{\partial r_{12}} (a_{12}^T + a_{13}^T),$$

$$\gamma_{12}^{\prime} = \frac{\partial}{\partial r_{12}} (\gamma_{12} + \gamma_{13}),$$

$$a = \frac{4 \cos \theta \cdot \sin^2 \theta}{r_{42} \left[(1/\sqrt{2}) + \cos \theta \right]} = 0.5667,$$

$$b = (2 \sqrt{2} \, r_{12} \cos \theta)/r_{42} = 1.8386,$$

$$c = (2 \, r_{12} \cos \theta \cdot \cos 2 \, \theta)/r_{42} = -0.2640.$$

L elements are the square roots of the G elements which are calculated in the usual way and are given below:

$$G_{11} = G_{22} = \left[(1/\sqrt{2}) + \cos \theta \right]^2 \mu_F = (0.0568) \times 10^{24},$$

$$G_{33} = G_{44} = (2/r_{12}^2) \mu_F = (0.0154) \times 10^{24}$$

γ_{12} is the difference between the polarizability along the bond 12 and perpendicular to it. γ_{12}' is its derivative. $\alpha_{12}'^T$ is polarizability derivative perpendicular to the bond. γ_{42}' is taken to be negligible as it is mostly electrovalent.

The areas A under the lines 515, 410 and 92 cm^{-1} are taken and I^2, the intensity, is defined by the formula

$$I^2 = \frac{K^2 \, A \, \nu_i \left[1 - \exp \left(- hc \, \nu_i/kT \right) \right] n^2}{(\nu_0 - \nu_i)^4} . \tag{23}$$

K is a constant of proportionality, ν_i the frequency of the line, ν_0 the frequency of the exciting line. Exp $(hc\nu_i/kT)$ is the usual Boltzmann factor. These values are also shown in the intensity formulae (22).

K, which is a function of the experimental conditions, has the same value for these three lines, as they are recorded in the same spectrum. It is not possible to say if the experimental conditions for zz and xz spectra are the same as for those lines. Hence, we cannot use these intensities and are shown as (?) in (22). Equations (22) contain five parameters to be determined, γ_{12}, γ_{42}, γ'_{12}, $\alpha_{12}'^T$ and K while we have only three equations (22a, c and d).

6. Photoelastic constants

As explained earlier, formulae (22) are like $I = L'A$, where I is a column vector. Transposing and substituting in (20)

$$P' = A'URle. \tag{24}$$

We thus get rid of a very inconvenient factor L^{-1}. Though, in the case of MgF$_2$, the species contain only one line each and calculation of L^{-1} elements is not difficult, in other crystals each species may contain more than one line and calculation of L elements requires correct evaluation of force constants which is generally not possible, particularly for crystals. In simple molecules, the secular determinant is supple-

mented by data on Coriolis interaction constants and the force constants can be evaluated to some degree of reliability. For crystals, this facility is not always available.

Formulation of (24) avoids another important hurdle, that is, the sign ambiguity of *I*. The sign ambiguity arises because, the polarizability can increase or decrease during an oscillation, depending on the *A* elements and their interaction with *L* elements. But, we have the same set of *A* elements for all the lines of a species. Hence, this ambiguity is avoided. Elements of *A* can be determined in the manner explained in our previous papers.

7. Determination of URle

There are only two types of coordinates, ΔR and rotation which are connected to strains by (10) and (13). While (10) is a general equation suitable for any coordinate system, (13) is derived for X axis along molecule 2, (figure 3). As the axes of the crystal are inclined to it by 45°, the equation can be modified as

$$R_{x'} = - \sqrt{2} \ (u_{zx} - u_{zy}), \qquad \text{for molecule 1,}$$

$$R_{y'} = \sqrt{2} \ (u_{zx} + u_{zy}), \qquad \text{for molecule 2,}$$

$$R_x = R_{x'} + R_{y'} = 2\sqrt{2} \ u_{zy} = \sqrt{2} \ (e_{yz} + w_x). \tag{25a}$$

Similarly,

$$R_y = \sqrt{2} \ (e_{zx} + w_z), \tag{25b}$$

and $\qquad R_x = - 2 \ (e_{xx} - e_{yy}). \tag{25c}$

It is seen that w_x and w_y occur in these equations but not w_z. This is due to the crystal having symmetry about z axis.

URle can be computed and writing *A* and this matrix separately, we have in table 1

Table 1. A' and *URle* matrices.

A	$S_1^{A_{1g}}$	$S_2^{B_{1g}}$	$S_3^{B_{2g}}$	$S_{4a}^{E_g}$	$S_{4b}^{E_g}$	URle
a_{xx}	A_1	—	A_3	—	—	$S_1^{A_{1g}} (e_{xx} + e_{yy})(P) - e_{zz}(Q)$
a_{yy}	A_1	—	$-A_3$	—	—	$S_2^{B_{1g}} e_{xy} (P)$
a_{zz}	A_1'	—	—	—	—	$S_3^{B_{2g}} 2 (e_{xx} - e_{yy})$
a_{yz}	—	—	—	A_4	—	$S_{4a}^{E_g} e_{yz} + w_x = 2u_{zy}$
a_{zx}	—	—	—	—	A_4	$S_{4b}^{E_g} e_{zx} + w_y = 2 u_{zx}$
a_{xy}	—	A_2	—	—	—	

P' is obtained by multiplying these two matrices as in eq. (24).

Here

$$P = \left(\frac{\gamma_{12}}{\sqrt{2}} - r_{42} \cos^2 \theta \right) = (0.6491),$$

$$Q = 2 \sin^2 \theta \cdot r_{42} = (2.367).$$

In the 9×9 photoelastic constant matrix, in place of P_{44}, P_{55} and P_{66}, Grimsditch and Ramdas (1980) have given

$$\begin{vmatrix} P_{yz\ yz} & P_{yz\ zy} \\ P_{zy\ yz} & P_{zy\ zy} \end{vmatrix} \quad \text{etc.}$$

Since the Raman spectra used here are of non-resonance type, we have $a_{yz} = a_{zy}$. Also, in our formalism, R_x is a function of only u_{zy}. Therefore, there is only one term $P_{yz\ zy}$ or $P_{zy\ zy}$. Therefore, one should write $P_{44} = 2A_4\,u_{zy}$ or $A_4\,e_{yz}$ assuming $w_x = 0$. Since the experimental value available is for P_{44} we have put $w_x = 0$ and used the equation $P_{44} = A_4\,e_{yz}$.

8. Calculation of photoelastic constants

Expressions for A elements are taken from (22) and we obtain the equations for the photoelastic constants in terms of the electro-optical constants and strains.

As already stated, there are 5 parameters while only 3 intensity equations are available. We are, therefore, adding to them equations for P_{44} and P_{66}. Afanas' ev *et al* (1975) published the photoelastic data for this crystal (tables 2 and 3). Values of the 5 parameters are obtained by solving the following equations:

$$K = 0.0174 \times 10^{12}; \qquad \gamma_{12} = 0.2536$$

$$\gamma_{42} = 0.1175; \qquad a'^{T}_{12} = 0.5516 \text{ and}$$

$$\gamma'_{12} = 0.4605.$$

Table 2. Photoelastic constants.

	P'	P	MgF$_2$ (Afanas' ev *et al* 1975)	P for rutile (Grims-ditch and Ramdas 1980)
$P_{11} = P_{22}$	0.8754	0.2345		0.017
$P_{12} = P_{21}$	0.4720	0.1264		0.143
$P_{13} = P_{23}$	−2.456	−0.6581		−0.139
$P_{31} = P_{32}$	0.5942	0.1648		−0.080
P_{33}	−2.167	−0.6010		−0.057
$P_{44} = P_{55}$	0.2847	0.0776	0.0776	−0.009
P_{66}	0.1674	0.0448	0.04485	−0.060

Table 3. Combinations of photoelastic constants.

	Calculated values MgF₂	Experimental values	
		Afanas'ev *et al* (1975) MgF₂	Rutile
$P_{11} - P_{12}$	0·1080	0·0892	− 0·126
$P_{11} - P_{31}$	0·0696	0·0695	0·097
$P_{33} - P_{13}$	0·0571	0·1128	0·082

For this purpose, we assume that all the I values are positive. Since there is only one line in each species, it is not necessary to use (4) to avoid the sign of I. Using these parameters, the other P' values are calculated and given in table 2. Afanas'ev *et al* (1975), however, have given only the combinations $P_{11} - P_{12}$, $P_{11} - P_{31}$ and $P_{33} - P_{13}$. To compare with these values we have prepared similar combinations and given in table 3. The agreement seems to be satisfactory.

There are some interesting relations among these photoelastic constants.

$$\frac{P_{11} - P_{12}}{P_{66}} = \frac{2A_3(1·414)}{A_2(0·6491)} = \frac{2(1·414)}{(0·6491)} \times \frac{I_{xx}^{B_{2g}}}{I_{xy}^{B_{1g}}} \times \frac{L_{22}}{L_{33}} = 2·409 \qquad (26a)$$

$$\frac{P'_{13}}{P'_{33}} = \frac{A_1}{A'_1} = \frac{I_{xx}^{A_{1g}} \cdot n_x}{I_{zz}^{A_{1g}} \cdot n_z} \qquad (26b)$$

$$\frac{P'_{11} + P'_{12}}{P'_{31}} = \frac{2A_1}{A'_1} = \frac{2I_{xx}^{A_{1g}} \cdot n_x}{I_{zz}^{A_{1g}} \cdot n_z} \qquad (26c)$$

$$(P_{11} + P_{12})/P_{13} = 2A_1(0·6491)/A_1(- 2·36) = - 0·55 \qquad (26d)$$

Equations (26a, b, c) show that the photoelastic constant ratios can be determined using the intensities directly and without having to derive the intensity formulae (22). For (26a) the experimental value 1·99 is very near the ratio calculated by the above method 2·41. Unfortunately, the intensities $I_{xy}^{B_{1g}}$ and $I_{xx}^{B_{2g}}$ are very low and their experimental determination is uncertain. Hence, the nearness of these values can be taken to be satisfactory. The ratio of the ratios given by (26a) and (26b) is really equal to 2. Equation (26d) indicates that this ratio is independent of even intensities or refractive index of the crystal. It is a function only of the dimensional parameters.

Equations (22) show that the photoelastic constants can be obtained from only 4 electro-optical constants. This does not violate the group theoretical result that there are 7 independent constants. Group theory simply says that any one of them cannot be transformed into the other or a combination of them by symmetry operation. It does not preclude a relation among them through some independent parameters smaller or larger in number. As an example, for calcite, n_x and n_y are two independent quantities in the second-order tensor. But they are calculated in terms of a single parameter (Bhagavantam 1940) polarizability of the oxygen atom.

9. Comparison with rutile

The photoelastic constants of rutile taken from the data given by Grimsditch and Ramdas (1980) are also given in table 2, for comparison, as this is of the same structure. It is interesting to note that:

(a) P_{11} and P_{12} are so different for MgF_2 and TiO_2. But $P_{11} + P_{12}$, which is a function of the intensity of A_{1g} line, is comparable and assumes similar importance in the two cases.

(b) Equation (26b) shows, that P_{13} being proportional to A_1 is larger than P_{33}. A_1 and A'_1 are proportional to the intensities of 410 in xx and zz spectra. Generally, the intensity in zz, being proportional to the polarizability of the bond perpendicular to it, is smaller. Therefore, P_{13} is generally larger than P_{33}. But experiment shows that $P_{33} - P_{13}$ is positive and small. This is possible only if both P_{33} and P_{13} are negative. This shows that the negative value of P_{33} is correct.

10. Discussion

This crystal is particularly suitable to determine photoelastic constants from Raman intensities as each species consists of only one line. Equations (26a, b, c, d) are possible only if the A_1 type oscillation consists of one line, for example, for calcite-like crystals also.

Table 2 shows that the photoelastic constants of rutile are much smaller than that of MgF_2. Partly it may be due to its large refractive index ($n=2.584$) compared to 1.39 of MgF_2. The P' values are divided by n^4, to get P. $n^4=44.58$ for rutile and 3.73 for MgF_2. Hence, smaller values for rutile are understandable. P' will be comparable and hence they stand a better chance to be called the photoelastic constants, similar to q's defined by Gavini and Cardona (1969) by

$$\Delta \epsilon_{ij} = q_{ijkl} \, \sigma_{kl}$$

It is obvious that with a similar procedure one can evaluate piezo-electric constants from infrared intensities.

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References

Afanas'ev I I, Andrianova L K, Mamontov I Ya and Reiterov V M 1975 *Sov. Phys. Solid State* **17** 2006
Bhagavantam, S 1940 *Light scattering and Raman effect* (Andhra University Press), p. 111
Born M and Huang K 1954 *Dynamical theory of crystal lattices* (Oxford University press)
Briggs R J and Ramdas A K 1976 *Phys. Rev.* **B13** 5518

Buddha Addepalli V and Rajeswara Rao N 1976 *Indian J. Pure Appl. Phys.* **14** 117
Buddha Addepalli V and Rajeswara Rao N 1977 *Indian J. Pure Appl. Phys.* **15** 157
Dayal B 1950 Proc. Indian *Acad. Sci.* **A32** 304
Eliashevich M and Wolkenstein M W 1945 *J. Chem. Phys.* **9** 101 326
Gavini A and Cardona M 1969 *Phys. Rev.* **177** 1351
Grimsditch M H and Ramdas A K 1980 *Phys. Rev.* **B22** 4094
Kumar S P, Padma V A and Rajeswara Rao N 1974 *J. Chem. Phys.* **60** 4156
Long D A 1953 *Proc. R. Soc. London* **217** 203
Loudon R 1963 *Proc. R. Soc. London* **A275** 218
Love A E H 1952 *Treatiseon the mathematical theory of elasticity*   4th Edn
Maradudin A A and Burstein E 1967 *Phys. Rev.* **164** 1081
Meera Chandrasekhar, Grimsditch M H and Gardona M 1978 *J. Opt. Soc. Am.* **68** 523
Nelson D F and Lax M 1970 *Phys. Rev. Lett.* **24** 379
Nelson D F and Lazay P D 1971 *Phys. Rev. Lett.* **25** 1187
Nelson D F and Lax M 1971 *Phys. Rev.* **B3** 2778
Porto S P S 1967 *Phys. Rev.* **154** 522
Pratibha Naik, Padma V A and Rajeswara Rao N 1979 *Pramana* **13** 111
Saxena B D 1944 *Proc. Indian Acad. Sci.* **A19** 357
Swarna Kumari G and Rajeswara Rao N 1981 *Indian J. Pure Appl. Phys.* **19** 326
Tubino R and Piseri L 1975 *Phys. Rev.* **B11** 5145
Wilson Jr. E S, Decius J C and Cross P C 1955 *Molecular vibrations* (New York: McGraw Hill)
Wyckoff R W G 1962 *Crystal srructures* (New York: Interscience), Vol. 1, p. 15