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Molecular Distortion in Orthorhombic Sulphur; a Calculation

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A function for the intermolecular forces, based on atom–atom interactions, is used to calculate the distortion forces on the molecule of octasulphur in the orthorhombic structure. By making use of the internal force field resulting from spectroscopic studies the behaviour of the molecule under these forces is found. The calculated molecular distortion agrees very well with that found by performing constrained refinements, except that the distortions calculated are systematically too small. This calculation shows that measurable distortions are to be expected for molecules with fairly low internal-mode frequencies, and that simple models for intermolecular forces predict the observed effect. The energy involved in the molecular distortion is 0·0837 kcal/mole (5·81 × 10^{-22} joule/molecule).

Introduction

There are many examples in X-ray and neutron diffraction experiments indicating static distortions of molecules in the crystalline environment compared with their free-state shape. In some cases the shifts in the atomic positions are several times larger than the experimental errors.

The static distortions are due to the intermolecular forces in which the repulsive terms between nonbonded atoms must predominate. If we have a potential model for the interaction between these nonbonded atoms we are then able to calculate the force on every atom of each molecule. The response of the molecule depends on the force field between the atoms in the molecule itself. This force field can be found by spectroscopic methods, as described by Wilson, Decius & Cross (1955) or by Cyvin (1972).

We have made a calculation for the distortion of octasulphur molecules in the orthorhombic structure. The potential model from the lattice-statics calculations of Rinaldi & Pawley (1973) is used, along with the molecular force field of Cyvin (1970).

The calculation method

The potential between two non-bonded sulphur atoms located at positions $\mathbf{r}_i$ and $\mathbf{r}_j$ is assumed to be

$$V(r_{ij}) = -\frac{A}{r_{ij}^6} + B \exp(-\alpha r_{ij}) \qquad (1)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and A, B and α are constants determined from thermodynamic data and lattice statics calculations (Rinaldi & Pawley, 1973):

$$A = 2149 \text{ kcal Å}^6/\text{mole}$$
$$B = 199900 \text{ kcal/mole}$$
$$\alpha = 3·49 \text{ Å}^{-1}.$$

By summing over j we get the contribution to the crystal potential of atom i. Only interactions for interatomic distances smaller than 5 Å are taken into account, as the contribution to the potential from more distant contacts depends very little on the detailed atomic arrangement.

The static force on the atom i is the negative gradient of the atom potential, written

$$\mathbf{f}_i = -\text{grad}_i V_i = -\text{grad}_i \sum_j V(r_{ij}) \qquad (2)$$

where the gradient is taken with respect to the coordinates of atom i.

The total force on the eight-atom molecule can be represented by one 24-component vector

$$\mathbf{f} = \begin{pmatrix} \mathbf{f}_1 \\ \vdots \\ \mathbf{f}_i \\ \vdots \\ \mathbf{f}_8 \end{pmatrix}. \qquad (3)$$

This force must be balanced by the internal force field, which is considered to be harmonic. This leads to the equation

$$\mathbf{f} = \boldsymbol{\varphi}\mathbf{u} \qquad (4)$$

where φ is the harmonic force constant 24×24 tensor and $\mathbf{u}$ is the 24-component displacement vector, having three Cartesian components for every atom in the molecule. φ was obtained from Cyvin (1970) who fitted the symmetry force constants to the observed vibrational frequencies of the molecule. This resulted in an 18×18 tensor which we transform to the Cartesian system of the molecule, thereby enlarging it to 24×24. It is finally rotated to the orientation of the molecule in the crystal.

The transformation which enlarges this matrix introduces six zero roots, so that equation (4) cannot be solved for $\mathbf{u}$ simply by inversion. However the equation applies only when the molecule is in static equilibrium as it must be in a potential minimum in the crystal. This means that the net force and torque on it must be zero, or

$$\sum_{i=1}^{8} \mathbf{f}_i = 0 \tag{5}$$

and

$$\sum_{i=1}^{8} \mathbf{f}_i \times \mathbf{r}_i = 0 . \tag{6}$$

It is convenient but not necessary to have the coordinates of $\mathbf{r}$ with respect to the molecular centre of gravity. Under the above conditions equation (4) is soluble, except that an arbitrary rotational or translational displacement of the whole molecule can be added to the mathematical solution of $\mathbf{u}$. This is caused by the existence of the six zero roots of the enlarged matrix φ, whose eigenvectors are just the displacements mentioned. The conditions (5) and (6) mean that $\mathbf{f}$ is orthogonal to these six eigenvectors, which is a necessary and sufficient condition for the solubility of equation (4).

The problem is most easily solved by changing basis to the normal coordinates of the vibrations of the molecule. These are defined as the column vectors of the orthogonal transformation $\mathbf{U}$ which diagonalizes φ, while φ transforms to

$$\mathbf{U}\varphi\mathbf{U}^T = \text{diag} (\lambda_1, \lambda_2, \ldots \lambda_{24}) . \tag{7}$$

The elements λ_i are the 24 squares of the angular frequencies of the fundamental vibrations of the molecule, multiplied by the mass of the sulphur atom. The displacement vector $\mathbf{u}$ has an expansion in the new basis given by

$$\mathbf{u} = \sum_{i=1}^{24} \alpha_i \mathbf{e}_i \tag{8}$$

where α_i and $\mathbf{e}_i$ are the expansion coefficients and the unit normal displacements respectively. Equation (4) can now be written, using (8)

$$\mathbf{f} = \varphi \sum_i \alpha_i \mathbf{e}_i = \sum_i \alpha_i \lambda_i \mathbf{e}_i \tag{9}$$

because $\mathbf{e}_i$ are the eigenvectors of φ. Finally by taking the scalar product of $\mathbf{e}_i^T$ and $\mathbf{f}$ of equation (9), we get

$$\mathbf{e}_i^T . \mathbf{f} = \alpha_i \lambda_i \tag{10}$$

where the orthonormality of the $\mathbf{e}_i$ vectors has been used.

Equation (10) can be used for determining the α_i values, but λ_i are only the non-zero eigenvalues. The forces in this equation are at first those calculated when the molecule is undistorted, but as the force must correspond to the final positions of the atoms an iterative procedure is necessary. The final distortion is

$$\mathbf{u} = \sum_{i=1}^{18} \left\{ \frac{\mathbf{e}_i^T . \mathbf{f}}{\lambda_i} \right\} \mathbf{e}_i . \tag{11}$$

Calculation for sulphur

(i) Crystal and molecular structure

The space group of orthorhombic sulphur (α-sulphur) is *Fddd* and there are four molecules in the primitive unit cell, as shown by Abrahams (1955). Taking the unit-cell origin at a centre of symmetry, the centre of one molecule is placed at $(\frac{7}{8}a, \frac{7}{8}b, z)$, and the others are related by symmetry. The molecular site symmetry is 2_z, denoting a twofold axis parallel to the crystal z axis. The experimental cell parameters from Caron & Donohue (1961) are

$$a = 10\cdot467, \ b = 12\cdot870, \ c = 24\cdot473 \text{ Å} .$$

The angle between the xz plane and the mean plane of the molecule taken from Pawley & Rinaldi (1972) is $\theta = 141\cdot3°$, and $z = 4\cdot0295$ Å. The free-state symmetry of the molecule is assumed to be $\bar{8}m$. Projection of the molecular structure in the plane perpendicular to the $\bar{8}$ axis is presented in Fig. 1.
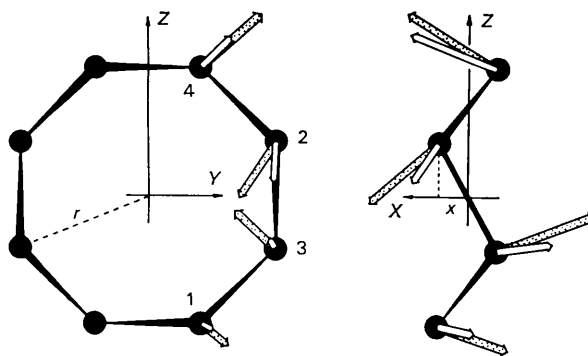

Fig. 1. Two views of the octasulphur molecule. The first is projected perpendicular to the plane of the molecule, and r is the radial distance of all atoms projected in the YZ plane. The other view is down the Y axis, showing the definition of x. Two sets of displacement vectors are shown; the stippled vectors are from the constrained refinement and the unstippled are from the present calculation. The vectors are enlarged by a factor of 50. Because the Z axis coincides with the crystal z axis, the vectors for the atoms in one half of the molecule have been omitted.

The structure of the symmetric molecule can be described by two parameters r and x. In Fig. 1 r is the projected distance of the atoms from the centre of the molecule. The atoms which have numbers 1 and 2 are at a distance x above the projection plane while those numbered 3 and 4 are at $-x$. The remaining atoms are related to these by the diad axis, 2_z, which is common to the molecule and the crystal. The values for r and x are $r = 2\cdot3441$ and $x = 0\cdot4960$ Å after applying libration corrections to the values from Pawley & Rinaldi (1972). The molecule is finally rotated from the coordinate system of Fig. 1 to its position in the crystal by the matrix A,

$$A = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

(ii) *Symmetry of the eigenvectors*

The eigenvectors e_i with non-zero eigenvalues belong to the representations

$$\Gamma = 2A_1 + B_1 + B_2 + 2E_1 + 3E_2 + 2E_3.$$

The transformation properties of the eigenvectors under the symmetry operations of the molecular site must be considered. Those belonging to the B_2 representation are antisymmetric under the 2_z operation and can be discarded for the following reason. The operation 2_z is a crystalline symmetry, and therefore any distortion of the molecule in the crystal must obey this symmetry operation. Consequently no distortion breaking this symmetry is allowed.

The A_1 modes are symmetric with respect to all the operations in the symmetry group of the molecule. There will clearly be some distortion corresponding to this symmetry, and this will simply affect the values of r and x. This is distortion which it is not possible to measure by crystal-structure analysis whereas it is possible, as Pawley & Rinaldi (1972) show, to measure the distortion from the symmetrical state. We can therefore compare the measured distortion with the calculated effect of $B_1 + 2E_1 + 3E_2 + 2E_3$ representations.

(iii) *Calculation of the forces and displacements*

As a first approximation for the intermolecular forces **f** we used the atomic positions for symmetric molecules in the crystal. Using these in equation (11) a first approximation to the distortion vector **u** was got. The procedure was then repeated with the distorted molecule and iterations were made until the difference between successive results for **u** became negligible.

Before each iteration cycle the crystal potential was minimized in the way as done in the lattice statics study of Rinaldi & Pawley (1973). Small changes in the cell parameters a, b and c and in the parameters z and θ for the molecule position had to be made to attain a true potential minimum. The total amounts of these shifts were $\Delta a = -0\cdot008$, $\Delta b = 0\cdot162$, $\Delta c = 0\cdot257$, $\Delta z = 0\cdot077$ Å and $\Delta\theta = -1\cdot9°$.

After the calculation we were able to correct the molecular parameters r and x as measured by crystal-structure analysis for the effect of the A_1 distortion, giving the structure of the free-state molecule. These corrections are $\Delta r = -0\cdot0022$ and $\Delta x = 0\cdot0037$ Å.

The calculated values of the distortion parameters α_i are given in Table 1, together with the corresponding frequencies and representation symbols. One of the lowest frequency modes, E_2, contributes considerably more than any of the others.

Table 1. *Coefficient (last column) of the amplitude of distortion in the various representation occurrences, due account being taken of degeneracy*

The largest distortion is listed first, and the frequencies of the corresponding modes of vibration are given.

Represen- tation	Frequency cm^{-1}	Degen- eracy n	$\dfrac{(\sum\alpha_i^2)^{1/2}}{n}$ Å
E_2	86	2	0·02444
A_1	218	1	0·01147
E_1	191	2	0·01112
E_2	152	2	0·00831
A_1	475	1	0·00440
B_1	411	1	0·00310
E_3	248	2	0·00308
E_1	471	2	0·00221
E_2	475	2	0·00066
E_3	437	2	0·00045

The distortion vector **u** is presented in Table 2 and in Fig. 1. This is compared with the differences in coordinates which were got by Pawley & Rinaldi (1972) in their refinement with and without using the symmetry-shape constraint. The shifts we now calculate are in the same general directions but are systematically somewhat small. The comparison can be seen in Fig. 1 where the stippled arrows are the result of the structure refinement.

Table 2. *Molecular-distortion vectors in the coordinate frame of Fig. 1, where the Z axis is coincident with the crystal z axis*

The atoms are numbered as in Abrahams (1955), and the measured molecular distortion comes from the constrained refinement of Pawley & Rinaldi (1972). As this cannot include the A_1 distortion, the calculated A_1 distortion included in the present calculation is listed separately in the last column.

Atom		Molecular distortion (Å)		
		from constrained refinements	from present calculation	from the A_1 representation
S_1	X	−0·021	−0·011	−0·004
	Y	0·009	0·005	0·001
	Z	−0·006	−0·002	−0·002
S_2	X	0·022	0·008	−0·004
	Y	−0·011	−0·001	0·002
	Z	−0·019	−0·012	0·001
S_3	X	−0·031	−0·017	0·004
	Y	−0·012	−0·002	0·002
	Z	0·011	0·003	−0·001
S_4	X	0·030	0·029	−0·004
	Y	0·018	0·010	0·001
	Z	0·017	0·011	0·002

Conclusion

The calculated static distortion of the S_8 molecule agrees well with the experimental observations. However the amount of distortion deduced from experiments seems to be somewhat bigger than that calculated. This observation is consistent with the preliminary comparison of the calculated and observed phonon dispersion data of Rinaldi (1973), suggesting that the potential used is somewhat too soft and the forces correspondingly too weak.

The calculation shows that the crystal forces are strong enough to cause definitely observable distortions in the molecules. The degree of distortion of S_8 is however somewhat exceptional because of the very soft E_2 internal mode which corresponds to roughly half of the distortion. Other molecules lacking such low-frequency modes would have correspondingly smaller distortions under forces of equal strength.

The energy involved in the molecular distortion, $\frac{1}{2}u\varphi u^T$, is calculated to be 0·0837 kcal/mole (5·81 × 10^{-22} joule/molecule) compared with the sublimation energy of about -25 kcal/mole (-1740×10^{-22} joule/molecule). If the intermolecular forces are constant over the small displacement u, the total crystal potential would drop by $\frac{1}{2}u\varphi u^T$ as the intermolecular potential contribution would be lowered by $u\varphi u^T$. As these forces vary slightly, the latter is reduced by a somewhat greater amount, 0·1834 kcal/mole ($12\cdot7 \times 10^{-22}$ joule/molecule).

We anticipate little change in our main result when the accurate X-ray and neutron structural studies which are now in progress become available. Therefore the symmetrical molecule from Pawley & Rinaldi (1972), corrected for the effect of libration and A_1 distortion is probably the most accurate measure we have of octasulphur in the free state.

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Twinning in Cr-Doped VO₂

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Twinning has been studied in several samples of VO₂ containing in substitution solid solution 0·5 and 2·5 at.% Cr. The twinning is by reticular pseudo-merohedry and it is controlled by the tetragonal pseudo-symmetry of a superlattice obtained from the original monoclinic cell ($a \simeq 9\cdot1$, $b \simeq 5\cdot8$, $c \simeq 4\cdot5$ Å, $\beta \simeq 90°$) by means of the transformation 100/002/0$\bar{1}$0. More than one twin law is found in every sample studied. All the theoretically possible twin laws, except one, have been observed. The possibility of twinning simulating a lattice and a space group different from the true ones has been pointed out and methods for detecting twins in these cases are given.

Introduction

In general, the structural changes occurring in metal–insulator transitions can be described in terms of small distortions of the crystal structure of one of the two phases involved in the transformation. When the distortions result in a final phase having a symmetry lower than that of the initial phase, the transition is usually associated with twin formation. The presence of twinned individuals in a sample complicates the interpretation of the diffraction patterns and, if not detected, might result in erroneous structural determinations. Therefore, a detailed analysis of twinning is always necessary in order to determine the true crystallographic parameters.

Cr-doped VO₂ undergoes a metal–insulator transi-