in Q, whereas an incorrectly chosen axis of librational motion should lead to a value of Ω not significantly different from zero.

Example 1: *Lithium purpurate dihydrate*

In this crystal structure analysis (Bürgi, Djuric, Dobler & Dunitz, 1972) the rigid-body treatment of the complex anion (Fig. 2) gave $\langle \Delta U_{ij}^2 \rangle^{1/2} = 0{\cdot}0022$ Å^2 compared with $\sigma(U_{ij}) \sim 0{\cdot}0015$ Å^2. Since the possibility of internal motions involving libration about the central N–C bonds had been raised, we decided to estimate the magnitudes of these two motions by the procedure described above. Our model permitted C(5), C(7), C(8), N(4), N(5), O(4), O(5), O(6) to librate about N(3)–C(6) and C(1), C(2), C(3), N(1), N(2), O(1), O(2), O(3) to librate about N(3)–C(4) and led to values of Ω that were zero within one standard deviation! As an alternative model we considered motion of the oxygen atoms perpendicular to the planes of the heterocyclic rings (such out-of-plane motions can be simulated as librations about a bond adjacent to the C–O bond in question, *i.e.* O(1) librates about N(1)–C(1), O(2) about N(2)–O(2), *etc.*). This model yielded values of Ω in the range 3–8°, significantly different from zero, and reduced $\langle \Delta U_{ij}^2 \rangle^{1/2}$ from 0·0022 to 0·0017 Å^2. We can conclude that the internal motions of largest amplitude in this molecule involve out-of-plane vibrations of the oxygen atoms rather than torsional vibrations about the central C–N bonds, as first supposed.

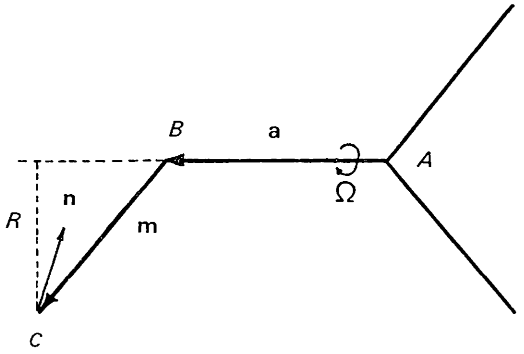

Fig. 1. Atom *C* is supposed to librate about the bond *AB*.

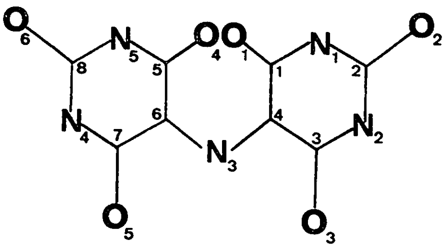

Fig. 2. Numbering of atoms in purpurate anion.

Example 2: *s-Trinitrobenzene in the* 1:1 *complex of s-trinitrobenzene and s-triaminobenzene* (*Iwasaki & Saito,* 1970)

Rigid-body analysis of the published thermal parameters gave $\langle \Delta U_{ij}^2 \rangle^{1/2} = 0{\cdot}0063$ Å^2. For this molecule the obvious intramolecular libration axes $\mathbf{a}_j$ are the three C–N bonds. which are crystallographically independent. Introduction of internal motions for the oxygen atoms gave Ω values of 14, 11 and 9° about the three C–N bonds and reduced $\langle \Delta U_{ij}^2 \rangle^{1/2}$ to 0·0048 Å^2.

Although there are certain pitfalls we believe that this kind of treatment, when applied with discretion, can yield useful semiquantitative descriptions of the more important internal motions of non-rigid molecules. A Fortran computer program for rigid-body thermal-motion analysis, incorporating this treatment as an option, is available on application to D.N.J.W.

One of us (D.N.J.W.) is indebted to the Royal Society for the award of an European Fellowship.

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Debye–Waller factors for magnesium oxide.

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The Debye–Waller factors for magnesium oxide have been measured from X-ray diffraction data and have been found to be 0·30 ± 0·01 Å^2 and 0·34 ± 0·02 Å^2 for the magnesium and oxygen ions respectively.

The investigation of extinction effects in large crystals (Lawrence, 1972) requires a knowledge of the calculated structure factors for the crystal. The values of the Debye–Waller factors for magnesium oxide obtained by Togawa (1965). [B(magnesium) = 0·24 Å^2; B(oxygen) = 0·19 Å^2] from powder samples using copper radiation gave rise to unrealistic extinction effects and it was decided to redetermine the thermal parameters from a single-crystal experiment using molybdenum $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å).

A single crystal was cut from a large block of magnesium oxide and the integrated intensities measured on a Siemens four-circle diffractometer. The counting statistics on all intensities were less than 1% and, with the exception of the *h*00 and *hhh* reflexions, at least six symmetry-equivalent reflexions were measured, the final observed structure factors being taken to be the average over their symmetry equivalents. All reflexions having $\sin\theta < 70°$ were measured for planes of even indices but, for planes of odd indices, only reflexions having $\sin\theta < 54°$ could be measured to the desired accuracy in an acceptable time due to the low reflectivity.

Since magnesium oxide has the rock-salt structure, the thermal parameters for the two ions can be found by simple graphical methods. Only those reflexions having $(\sin\theta)/\lambda > 0{\cdot}35$ were used since the corresponding scattering factors are then almost independent of the state of ionization of the atoms and lower-order reflexions may be suffering from extinction. The scattering factors used were those in *International Tables for X-ray Crystallography* (1968). The temperature factors obtained were:

$$B(\text{magnesium}) = 0{\cdot}30 \pm 0{\cdot}01\ \text{Å}^2$$
$$B(\text{oxygen}) = 0{\cdot}34 \pm 0{\cdot}02\ \text{Å}^2.$$

These values are considerably higher than those obtained by Togawa which were calculated using only those reflexions in the region $(\sin\theta)/\lambda < 0{\cdot}63$, the calculated structure factor in this range being dependent on the state of ionization of the magnesium and oxygen ions.

Table 1 shows the observed and calculated structure factors for magnesium oxide. The R index is 0·0062, showing an agreement between the observed and calculated structure factor comparable with that obtained with similar materials using data measured on the same diffractometer (*e.g.* Killean, Lawrence & Sharma, 1972).

Table 1. *Observed and calculated structure factors*

h	k	l	F_o	F_c
4	4	0	29·22	29·00
6	0	0	16·75	16·70
4	4	2	16·55	16·70
6	2	0	15·54	15·51
6	2	2	14·52	14·34
4	4	4	13·38	13·41
6	4	0	12·68	12·63
6	4	2	11·92	11·89
8	0	0	10·90	10·73
8	2	0	10·25	10·21
6	4	4	10·23	10·21
6	6	0	9·84	9·74
8	2	2	9·79	9·74
6	6	2	9·38	9·36
8	4	0	9·06	8·99
8	4	2	8·61	8·62
6	6	4	8·28	8·29
8	4	4	7·61	7·69
10	0	0	7·30	7·41
8	6	0	7·37	7·41
10	2	0	7·07	7·15
8	6	2	7·14	7·15
10	2	2	6·92	6·91
6	6	6	6·86	6·91
10	4	0	6·49	6·48
8	6	4	6·52	6·48
10	4	2	6·21	6·27
3	3	3	7·19	7·23
5	1	1	7·23	7·23
5	3	1	5·46	5·47
5	3	3	4·15	4·23
7	1	1	3·30	3·33
5	5	1	3·32	3·33
7	3	1	2·68	2·67
5	5	3	2·65	2·67
7	3	3	2·19	2·22
7	5	1	1·94	1·91
5	5	5	1·95	1·91
9	1	1	1·68	1·67
7	5	3	1·64	1·67

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Constrained refinement techniques applied to the structure of ammonium hydrogen sulphate above the ferroelectric transition: errata.

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Corrections are given to *Acta Cryst.* (1972), **A28**, 445–454.

Three printing errors have been found in Nelmes (1972). The corrections are as follows:

(1) In Table 6, for atom O(1)⁻ Z should be 2·435 and not 2·345.

(2) In Table 6, for atom O(7) U_{31} should be −0·0171 and not −0·171.

(3) In the heading of Table 7, after the colon on the third line, the correct form is '**T** parameters (in order T_{11}, T_{22}, T_{33}, T_{23}, T_{31}, T_{12}) . . .', *i.e.* T_{33} and T_{23} have been interchanged.

Reference

Nelmes, R. J. (1972). *Acta Cryst.* **A28**, 445-454.