

An expression for ε was derived by Karle & Hauptman (1956) in rather a complicated form, and the physical meaning of the ε value was discussed by Wilson (1950). This paper shows that ε is equal to the ratio of the number of symmetry-equivalent positions in a unit cell to the number of point-group equivalent reflexions without Friedel's law.

Let the s th equivalent position \mathbf{r}_s of a given position \mathbf{r} be generated by operating a 3×3 rotation matrix \mathbf{R}_s to \mathbf{r} and then by adding a translation vector \mathbf{t}_s :

$$\mathbf{r}_s = \mathbf{R}_s \mathbf{r} + \mathbf{t}_s.$$

We consider a structure composed of many similar isotropic atoms randomly distributed in an asymmetric unit. The structure factor can be written in the form:

$$F(\mathbf{h}) = \sum_{j=1}^{N/M} \sum_{s=1}^M f_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_{js}) \\ = \sum_{j=1}^{N/M} f_j \left[\sum_{s=1}^M \exp(2\pi i \mathbf{h}_s \cdot \mathbf{r}_j) \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_s) \right], \quad (1)$$

where the subscript j runs through the atoms in an asymmetric unit, $\mathbf{h}_s \equiv \mathbf{h} \mathbf{R}_s$ is the s th equivalent index for \mathbf{h} (Waser, 1955) and M is the number of equivalent positions in a unit cell.

First let us assume that the cell is primitive and each component of \mathbf{t}_s is $0 \pmod{1}$ for all s . The equation (1) then reduces to the form:

$$F(\mathbf{h}) = \sum_{j=1}^{N/M} f_j \left[\sum_{s=1}^M \exp(2\pi i \mathbf{h}_s \cdot \mathbf{r}_j) \right]. \quad (2)$$

For a general index \mathbf{h} there are M different indices $\mathbf{h}_1, \dots, \mathbf{h}_M$, corresponding to M independent \mathbf{R} matrices, and the number of equivalent reflexions, m , is equal to M . For a certain kind of special index m may be less than M , and M/m terms in the square bracket of equation (2) have a common index \mathbf{h}_s . In general we obtain

$$F(\mathbf{h}) = \sum_{j=1}^{N/M} f_j (M/m) \sum_{s=1}^m \exp(2\pi i \mathbf{h}_s \cdot \mathbf{r}_j),$$

and this expression immediately leads to the mean square structure factors as

$$\langle |F(\mathbf{h})|^2 \rangle \sim \sum_{j=1}^{N/M} (M^2/m) f_j^2 = (M/m) \sum_{n=1}^N f_n^2. \quad (3)$$

The above result is valid also for a case in which some \mathbf{t}_s 's are different from lattice vectors. Even in such a case, exponential factors $\exp(2\pi i \mathbf{h} \cdot \mathbf{t}_s)$ in equation (1) present no new problems for most kinds of indices, and the relation (3) can

be obtained from (1) in a similar way as from (2). The special kinds of indices to be considered are those which are associated with the space-group absences. As far as non-vanishing reflexions are concerned, however, relation (3) is valid because for these reflexions we always have, by selecting a proper origin of the unit cell,

$$\exp(2\pi i \mathbf{h} \cdot \mathbf{t}_s) = 1. \quad (4)$$

This can be seen, for example, by considering a screw axis p_q along the b axis. The index \mathbf{h} we are concerned with is $0k0$ with $k = pn$. Since the relevant \mathbf{t}_s has the form $(t_1, nq/p, t_3)$, relation (4) is obviously satisfied. A similar situation can also be found for glide planes. A strict proof of relation (4) for a non-vanishing reflexion will be given elsewhere (Iwasaki, 1977).

If the cell is non-primitive, the same index \mathbf{h}_s always appears L times in the square bracket of (1). Here L is the multiplicity of the compound lattice: 2 for a body or base-centred cell, 3 for a hexagonal-rhombohedral and 4 for a face-centred. A similar calculation leads again to the same result as (3) for a non-vanishing reflexion, provided that N is the number of atoms in the compound unit cell and M is the number of equivalent positions in the *same* unit cell.

Therefore, we always have

$$\varepsilon(\mathbf{h}) = M/m(\mathbf{h}), \quad (5)$$

i.e. the quantity ε for a given index \mathbf{h} is equal to the ratio of the number of space-group equivalent positions in the unit cell to the number of point-group equivalent reflexions for that reflexion. It must be noted that m is not the number of Laue-group equivalent reflexions which is known as the multiplicity of a plane in powder diffractometry: reflexions hkl and $\bar{h}\bar{k}\bar{l}$ are not equivalent for non-centrosymmetric structures.

The ε values based on the table of equivalent reflexions (Iwasaki, 1971) are listed in Table 1.

References

- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 350–351. Birmingham: Kynoch Press.
 IWASAKI, H. (1971). *Rep. Inst. Phys. Chem. Res.* **47**, 61–80.
 IWASAKI, H. (1977). *Sci. Papers Inst. Phys. Chem. Res.* To be published.
 KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635–651.
 STEWART, J. M. & KARLE, J. (1976). *Acta Cryst.* **A32**, 1005–1007.
 WASER, J. (1955). *Acta Cryst.* **8**, 595.
 WILSON, A. J. C. (1950). *Acta Cryst.* **3**, 258–261.

Acta Cryst. (1977). **A33**, 229–230

Dispersion corrections for X-ray atomic scattering factors. By M. J. COOPER, *Materials Physics Division, AERE Harwell, Oxfordshire, OX11 0RA, England*

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Recently tabulated values of dispersion corrections for X-ray atomic scattering factors are misleading since they imply an unrealistically high reliability and do not take into account their variation with $\sin \theta/\lambda$, which can in general be quite significant.

In a recent paper Cromer (1976) has given the results of new calculations for the values of the dispersion corrections $\Delta f'$ and $\Delta f''$ for Co $K\alpha_1$ radiation which were made in response to numerous requests. Previous values for the dispersion

corrections for Co $K\alpha$ radiation were in fact published (Cooper, 1963) as a function of both atomic number and $\sin \theta/\lambda$. Comparison of these two sets of values shows quite large differences for some elements, but although the new

values are clearly more reliable it is doubtful if their accuracy is in general as good as is implied by their tabulation to two decimal places without further indication of their reliability, particularly for values close to absorption edges.

Dispersion corrections for other characteristic X-radiations have been calculated by Cromer & Liberman (1970) and these have also been tabulated in *International Tables for X-ray Crystallography* (1974). Although, as stated therein, it is difficult to assess the accuracy of these corrections, values have been given to three decimal places which must certainly imply a quite unrealistic accuracy. No variation with θ is given since it is stated that in general this variation is probably less than the uncertainty in the calculated values. However, reference to previously tabulated values (e.g. *International Tables for X-ray Crystallography*, 1962; Cooper, 1963) and to recent results given by Hazell (1975) shows that in general the values of Af' and Af'' vary by at least 5 to 10% over the possible range of $\sin \theta/\lambda$ and in many cases by several times this factor. Since X-ray atomic scattering factors decrease so rapidly with $\sin \theta/\lambda$ this change in the dispersion corrections may become quite important.

The tabulation of dispersion corrections to two or three

decimal places, without indication of either their reliability or their variation with $\sin \theta/\lambda$, is therefore misleading for two reasons. It implies that the tabulated values have an unrealistic accuracy and that their dependence on $\sin \theta/\lambda$ is negligible. However, it is suggested that, although the values may be unreliable, their variation with $\sin \theta/\lambda$ is nevertheless a systematic effect which is in many cases sufficiently significant to merit being taken into account.

References

- COOPER, M. J. (1963). *Acta Cryst.* **16**, 1067–1069.
 CROMER, D. T. (1976). *Acta Cryst.* **A32**, 339.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 HAZELL, A. C. (1975). *Anomalous Scattering*, edited by S. RAMASESHAN & S. C. ABRAHAMS, pp. 41–51. Copenhagen: Munksgaard.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Acta Cryst. (1977). **A33**, 230–232

Could acetic acid crystallize as dimers? By J. L. DERISSEN and P. H. SMIT, *Department of Chemistry, Structural Chemistry Group, State University of Utrecht, Padualaan 8, Utrecht, The Netherlands*

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It is shown that hypothetical acetic acid crystal structures can be constructed which are built from dimers and which have a lattice energy equivalent to that of the experimental chain structure. The lattice energy was calculated by the atom-atom potential method with a modified Lippincott-Schroeder potential for the hydrogen bonds.

As far as is known, monocarboxylic acids in the gaseous state occur as monomers or as hydrogen-bonded cyclic dimers, the degree of association depending on the temperature and vapour pressure. These dimers have also been observed for most monocarboxylic acids in the crystalline state. But there are a few exceptions: formic and acetic acid form hydrogen-bonded chains (Nahringbauer, 1970), and in one of its modifications chloroacetic acid is found to be tetrameric (Kanters & Roelofs, 1976). These exceptions require an explanation, and we wondered whether a molecular-packing analysis might shed some light on this problem.

In principle therefore, we have to study the free energy as a function of the crystal structure. The structure corresponding to the minimal free energy at a given temperature is the stable one. But, as Kitaigorodsky (1970) argued, one may confine oneself to the calculation of minima in the lattice energy. In that case all the structures belonging to the lowest minima with comparable depths have to be considered. The stable structure will be governed by the delicate balance of lattice-energy and entropy terms yielding the minimal free energy.

But even such a lattice-energy analysis may be a hopeless task, as one has to look at all possible space groups and cell dimensions for each structure proposed.

Yet, acetic acid seemed to be suited for tractable calculations. Its crystal structure has been accurately determined (Nahringbauer, 1970), and an expected space group and a set of cell parameters for a hypothetical crystal of dimers could be derived by assuming a structural analogy with fluoro-

acetic acid (Kanters & Kroon, 1972) and with propionic acid (Strieter, Templeton, Scheurman & Sass, 1962), which have the usual dimer structures (Table 1). The molecular structure of the centrosymmetric crystalline acetic acid dimer was assumed from analogies between the crystal structures of β -oxalic acid (Derissen & Smit, 1974) and acetic acid, and is given in Table 2.

We then performed a lattice-energy analysis for hypothetical acetic acid dimer crystal structures with two centrosymmetric dimers per cell in $P2_1/c$ and with the cell dimensions of Table 1. For this purpose 2275 independent structures were generated by rotation of the dimer in steps of 15° around three perpendicular axes through the centre of

Table 1. *Space group and cell constants of acetic acid dimer crystal from analogy with fluoroacetic acid and with propionic acid*

	Propionic acid	Fluoro-acetic acid	Acetic acid dimer	Acetic acid chains
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$Pna2_1$
Z	4	4	4	4
d (g cm^{-3})	1.22	1.60	1.27	1.266
a (\AA)	4.04	4.30	4.1	13.32
b (\AA)	9.06	7.55	7.7	4.08
c (\AA)	11.00	9.98	10.0	5.77
β ($^\circ$)	91	85.2	90	