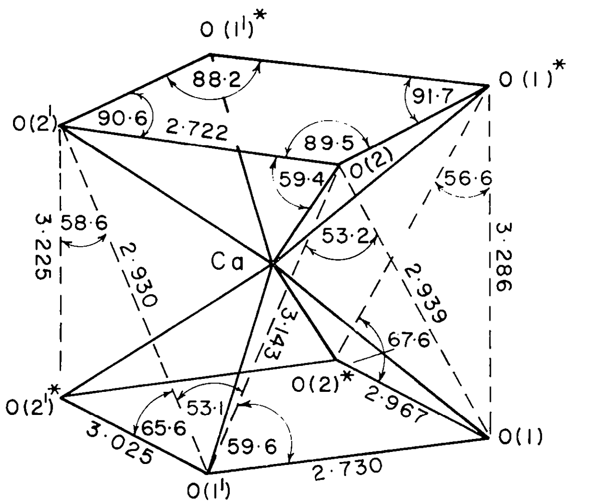

Fig. 3. Perspective view of a ($Ca-O_8$) coordination unit. Unstarred labels with the same indices (one primed) refer to oxygen atoms belonging to a single diacetamide molecule. An asterisk indicates an oxygen atom related by the two-fold axis to the oxygen atom with the same index.

coordination units. The average Br–N separation is 3·28 Å. The N–Br–N angle is 176°.

Discussion

This structure differs from the structures of the diacetamide complexes of the alkali halides (Roux & Boeyens, 1969*a,b*) in that there is no nearest-neighbour interaction between cation and anion. In this respect it corresponds with the ionic thiourea complexes (Boeyens & Herbstein, 1967) where complete segregation of anions and cations occurs. Unlike the alkali halide complexes of diacetamide, but like the thiourea complexes (Boeyens & Gafner, 1968), the $CaBr_2$. 4(diacetamide) thus appears to be a simple ion-dipole complex. Whether or not the NH-Br contact of 3·28 Å should be interpreted as a hydrogen bond as suggested by the infrared study of Gentile & Shankoff (1965), is not clear.

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References

Boeyens, J. C. A. & Gafner, G. (1968). *J. Chem. Phys.* **49**, 2435.
Boeyens, J. C. A. & Herbstein, F. H. (1967). *Inorg. Chem.* **6**, 1408.
Dunning, A. J. & Vand, V. (1969). *Acta Cryst.* A**25**, 489.
Gentile, P. S. & Shankoff, T. A. (1965). *J. Inorg. Nucl. Chem.* **27**, 2301.
Hoppe (1969). In the discussion on a paper by Kheiker, D. M. (1969). *Acta Cryst.* A**25**, 82.
International Tables for X-ray Crystallography (1965). 2nd ed., Vol. I, p. 101. Birmingham: Kynoch Press.
Roux, J. P. & Boeyens, J. C. A. (1969*a*). *Acta Cryst.* B**25**, 1700.
Roux, J. P. & Boeyens, J. C. A. (1969*b*). *Acta Cryst.* B**25**, 2395.

Acta Cryst. (1970). B**26**, 531

The Squared-Tangent Formula*

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In the noncentrosymmetric space groups, the values of the squares of the tangents of a basic set of phases determine the values of the squares of the tangents of others, provided that the crystal structure consists of identical atoms. In selected, noncentrosymmetric space groups, *e.g.* $P2_12_12_1$, the square of the tangent of any phase is uniquely determined by the magnitudes alone of the structure factors. Hence, in the latter space groups, it is expected that the formulas derived here will supplement the older tangent formula and will facilitate the early determination of the values of certain phases.

1. Introduction

It has long been known that, for structures consisting of N identical atoms in the unit cell, a number of relationships among the structure factors exist. One of these is the so-called tangent formula (Karle & Hauptman, 1956),

$$\tan \varphi_{\mathbf{h}} = \frac{\langle |E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}| \sin (\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}}\rangle_{\mathbf{k}}}{\langle |E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}| \cos (\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}})\rangle_{\mathbf{k}}}, \quad (1·1)$$

in which φ denotes the phase of the normalized structure factor E, the vector $\mathbf{h}$ is fixed, and the averages are extended over the same set of vectors $\mathbf{k}$. Equation (1·1)

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is used to determine the values of new phases once preliminary values of a basic set of phases have been obtained. It is useful because it retains its validity even if the vectors **k** are restricted so that the $|E_{\mathbf{k}}|$ and $|E_{\mathbf{h}-\mathbf{k}}|$ are large, *e.g.* greater than unity.

Another interpretation of (1·1) is that the sines and cosines of some phases determine the values of the sines and cosines of others (assuming, of course, that the magnitudes of the normalized structure factors, $|E|$, are known). It is therefore natural to ask whether less information, *e.g.* knowledge of only the squares of the tangents of some phases, might not similarly lead to the values of the squares of the tangents of others. The chief aim in the present paper is to give an affirmative answer to this question. (It is of course well known that the value of the square of any trigonometric function of the angle φ uniquely determines the value of the square of any other trigonometric function of φ, as well, incidentally, as the cosine of 2φ.)

Only the space groups $P1$ and $P2_12_12_1$ are treated in detail here since they illustrate the two kinds of formulas which arise. However, analogous formulas exist for all the noncentrosymmetric space groups. It is assumed throughout that the crystal structure consists of N identical atoms in the unit cell.

2. Space group $P1$

In the space group $P1$ the normalized structure factor is defined by means of

$$E_{\mathbf{k}}=|E_{\mathbf{k}}| \exp (i\varphi_{\mathbf{k}})=\frac{1}{N^{1/2}}\sum_{j=1}^{N}\cos 2\pi\mathbf{k}\,.\,\mathbf{r}_j + \frac{i}{N^{1/2}}\sum_{j=1}^{N}\sin 2\pi\mathbf{k}\,.\,\mathbf{r}_j\,, \quad (2·1)$$

where $\mathbf{r}_j$ is the position vector of the atom labelled j. Then

$$|E_{\mathbf{k}}| \cos \varphi_{\mathbf{k}}=\frac{1}{N^{1/2}}\sum_{j=1}^{N}\cos 2\pi\mathbf{k}\,.\,\mathbf{r}_j\,, \quad (2·2)$$

$$|E_{\mathbf{k}}|^2 \cos^2 \varphi_{\mathbf{k}}=\frac{1}{N}\sum_{j=1}^{N}\cos^2 2\pi\mathbf{k}\,.\,\mathbf{r}_j + \frac{1}{N}\sum_{\substack{j\neq j'\\1}}^{N}\cos 2\pi\mathbf{k}\,.\,\mathbf{r}_j\cos 2\pi\mathbf{k}\,.\,\mathbf{r}_{j'}\,, \quad (2·3)$$

$$|E_{\mathbf{k}}|^2 \cos^2 \varphi_{\mathbf{k}}-\frac{1}{2}=\frac{1}{2N}\sum_{j=1}^{N}\cos 4\pi\mathbf{k}\,.\,\mathbf{r}_j + \frac{1}{N}\sum_{\substack{j\neq j'\\1}}^{N}\cos 2\pi\mathbf{k}\,.\,\mathbf{r}_j\cos 2\pi\mathbf{k}\,.\,\mathbf{r}_{j'}\,. \quad (2·4)$$

In a similar way,

$$|E_{\mathbf{k}}|^2 \sin^2 \varphi_{\mathbf{k}}-\frac{1}{2}=-\frac{1}{2N}\sum_{j=1}^{N}\cos 4\pi\mathbf{k}\,.\,\mathbf{r}_j + \frac{1}{N}\sum_{\substack{j\neq j'\\1}}^{N}\sin 2\pi\mathbf{k}\,.\,\mathbf{r}_j\sin 2\pi\mathbf{k}\,.\,\mathbf{r}_{j'}\,. \quad (2·5)$$

Equations (2·4) and (2·5) lead directly to

$$\langle|E_{\mathbf{k}}|^2 \cos^2 \varphi_{\mathbf{k}}\rangle_{\mathbf{k}}=\langle|E_{\mathbf{k}}|^2 \sin^2 \varphi_{\mathbf{k}}\rangle_{\mathbf{k}}=\tfrac{1}{2}\,, \quad (2·6)$$

in which the averages are taken over all vectors **k** in reciprocal space. (It should perhaps be emphasized that (2·6) is no longer valid if the vectors **k** are restricted, for example, so that the $|E_{\mathbf{k}}|$ are greater than unity.)

Next, let the vector **h** be fixed. Multiplying (2·4) by the like equation obtained by replacing **k** by **h**−**k** in (2·4), averaging over all vectors **k**, and employing also (2·4), one is led to

$$\left\langle\left(|E_{\mathbf{k}}|^2 \cos^2 \varphi_{\mathbf{k}}-\frac{1}{2}\right)\left(|E_{\mathbf{h}-\mathbf{k}}|^2 \cos^2 \varphi_{\mathbf{h}-\mathbf{k}}-\frac{1}{2}\right)\right\rangle_{\mathbf{k}} =\frac{1}{2N}\left(|E_{\mathbf{h}}|^2\cos^2\varphi_{\mathbf{h}}-\frac{1}{2}\right) - \frac{1}{8N^2}\sum_{j=1}^{N}\cos 4\pi\mathbf{h}\,.\,\mathbf{r}_j\,. \quad (2·7)$$

Finally, in view of (2·2) and (2·6),

$$\left\langle|E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|^2 \cos^2 \varphi_{\mathbf{k}}\cos^2 \varphi_{\mathbf{h}-\mathbf{k}}-\frac{1}{4}\right\rangle_{\mathbf{k}} =\frac{1}{2N}\left(|E_{\mathbf{h}}|^2\cos^2\varphi_{\mathbf{h}}-\frac{1}{2}\right) - \frac{1}{8N^{3/2}}|E_{2\mathbf{h}}|\cos\varphi_{2\mathbf{h}}\,. \quad (2·8)$$

In a similar way, using (2·5) and the equation obtained from (2·4) by replacing **k** by **h**−**k**, one obtains

$$\left\langle|E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|^2 \sin^2 \varphi_{\mathbf{k}}\cos^2 \varphi_{\mathbf{h}-\mathbf{k}}-\frac{1}{4}\right\rangle_{\mathbf{k}} =\frac{1}{2N}\left(|E_{\mathbf{h}}|^2\sin^2\varphi_{\mathbf{h}}-\frac{1}{2}\right) + \frac{1}{8N^{3/2}}|E_{2\mathbf{h}}|\cos\varphi_{2\mathbf{h}}\,. \quad (2·9)$$

Ignoring terms of order $\frac{1}{N^{3/2}}$ in (2·8) and (2·9), which is permissible if N is sufficiently large, these equations lead directly to

$$\frac{|E_{\mathbf{h}}|^2 \sin^2\varphi_{\mathbf{h}}-\frac{1}{2}}{|E_{\mathbf{h}}|^2\cos^2\varphi_{\mathbf{h}}-\frac{1}{2}} \approx \frac{\left\langle|E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|^2 \sin^2 \varphi_{\mathbf{k}}\cos^2 \varphi_{\mathbf{h}-\mathbf{k}}-\frac{1}{4}\right\rangle_{\mathbf{k}}}{\left\langle|E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|^2 \cos^2 \varphi_{\mathbf{k}}\cos^2 \varphi_{\mathbf{h}-\mathbf{k}}-\frac{1}{4}\right\rangle_{\mathbf{k}}} \quad (2·10)$$

and finally, after a straightforward but tedious computation, to

$$\tan^2\varphi_{\mathbf{h}} \simeq \frac{\left\langle \left(|E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|^2 \sin^2\varphi_{\mathbf{k}} \cos^2\varphi_{\mathbf{h}-\mathbf{k}} - \frac{1}{4}\right) + \frac{1}{2|E_{\mathbf{h}}|^2} |E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|^2 \cos 2\varphi_{\mathbf{k}} \cos^2\varphi_{\mathbf{h}-\mathbf{k}} \right\rangle_{\mathbf{k}}}{\left\langle \left(|E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|^2 \cos^2\varphi_{\mathbf{k}} \cos^2\varphi_{\mathbf{h}-\mathbf{k}} - \frac{1}{4}\right) - \frac{1}{2|E_{\mathbf{h}}|^2} |E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|^2 \cos 2\varphi_{\mathbf{k}} \cos^2\varphi_{\mathbf{h}-\mathbf{k}} \right\rangle_{\mathbf{k}}} \quad (2\cdot11)$$

the squared-tangent formula in the space group $P1$.

3. Space group $P2_12_12_1$

3·1. *Two preliminary formulas*

Assume that h, k, and l are even integers. Then the normalized structure factor is given by (*International Tables for X-ray Crystallography*, 1952)

$$E_{hkl} = \frac{N^{1/2}}{4} \left\{ \sum_{j=1}^{N/4} (\cos 2\pi hx_j \cos 2\pi ky_j \cos 2\pi lz_j - i \sin 2\pi hx_j \sin 2\pi ky_j \sin 2\pi lz_j) \right\}. \quad (3\cdot1)$$

Following the derivation of equations (2·4) and (2·5), one is led in a similar way to

$$\sum_{\substack{j\neq j'\\1}}^{N/4} \cos 2\pi hx_j \cos 2\pi hx_{j'} \cos 2\pi ky_j \cos 2\pi ky_{j'} \times \cos 2\pi lz_j \cos 2\pi lz_{j'} = \frac{N}{16}\left(|E_{hkl}|^2 \cos^2\varphi_{hkl} - \frac{1}{2}\right) - \frac{N^{1/2}}{32}\left((E_{2h00} + E_{02k0} + E_{002l} + E_{2h2k0} + E_{02k2l} + E_{2h02l} + |E_{2h2k2l}| \cos\varphi_{2h2k2l}\right), \quad (3.2)$$

$$\sum_{\substack{j\neq j'\\1}}^{N/4} \sin 2\pi hx_j \sin 2\pi hx_{j'} \sin 2\pi ky_j \sin 2\pi ky_j \sin 2\pi lz_j \times \sin 2\pi lz_{j'} = \frac{N}{16}\left(|E_{hkl}|^2 \sin^2\varphi_{hkl} \;\; \frac{1}{2}\right) + \frac{N^{1/2}}{32}\left(E_{2h00} + E_{02k0} + E_{002l} - E_{2h2k0} - E_{02k2l} - E_{2h02l} + |E_{2h2k2l}| \cos\varphi_{2h2k2l}\right). \quad (3\cdot3)$$

3·2. *The squared-cosine formula*

Assume that h, k, l, and h_1 are even integers. Then the two-dimensional structure factor E_{h_1k0} (or one-dimensional if h_1 or k happens to be zero) is given by

$$E_{h_1k0} = \frac{4}{N^{1/2}} \sum_{j=1}^{N/4} \cos 2\pi h_1x_j \cos 2\pi ky_j . \quad (3\cdot4)$$

As in the derivation of (2·4), (3·4) leads to

$$|E_{h_1k0}|^2 - 1 = \frac{4}{N} \sum_{j=1}^{N/4} (\cos 4\pi h_1x_j + \cos 4\pi ky_j + \cos 4\pi h_1x_j \cos 4\pi ky_j) + \frac{16}{N} \sum_{\substack{j\neq j\\1}}^{N/4} \cos 2\pi h_1x_j \times \cos 2\pi h_1x_{j'} \cos 2\pi ky_j \cos 2\pi ky_{j'} . \quad (3\cdot5)$$

Similarly,

$$|E_{h-h_10l}|^2 - 1 = \frac{4}{N} \sum_{j=1}^{N/4} [\cos 4\pi(h-h_1)x_j + \cos 4\pi lz_j + \cos 4\pi(h-h_1)x_j \cos 4\pi lz_j] + \frac{16}{N} \sum_{\substack{j\neq j'\\1}}^{N/4} \cos 2\pi(h-h_1)x_j \cos 2\pi(h-h_1)x_{j'} \cos 2\pi lz_j \times \cos 2\pi lz_{j'} . \quad (3\cdot6)$$

Fixing the even integers h and l and multiplying (3·5) and (3·6), one finds, after some simplification, that

$$\langle(|E_{h_1k0}|^2 - 1)(|E_{h-h_10l}|^2 - 1)\rangle_{h_1} = \frac{16}{N^2} \sum_{j=1}^{N/4} \left(\frac{1}{2} \cos 4\pi hx_j + \frac{1}{2} \cos 4\pi hx_j \cos 4\pi lz_j + \cos 4\pi ky_j \cos 4\pi lz_j + \frac{1}{2} \cos 4\pi hx_j \cos 4\pi ky_j + \frac{1}{2} \cos 4\pi hx_j \cos 4\pi ky_j \cos 4\pi lz_j\right) + \frac{128}{N^2} \sum_{\substack{j\neq j'\\1}}^{N/4} \cos 2\pi hx_j \cos 2\pi hx_{j'} \cos 2\pi ky_j \times \cos 2\pi ky_{j'} \cos 2\pi lz_j \cos 2\pi lz_{j'} \quad (3\cdot7)$$

in which the average is extended over all even integers h_1.

Next, let the (three-dimensional) vector $\mathbf{h}$, with even components h,k,l, be fixed. Let $\mathbf{k}$ be a two-dimensional vector, having even components, with the property that $\mathbf{h}-\mathbf{k}$ is also two-dimensional. Then clearly the components of $\mathbf{h}-\mathbf{k}$ are also even. For example, if $\mathbf{k}=(h_1k0)$, where h_1 and k are even, then $\mathbf{h}-\mathbf{k}=(h-h_10l)$ is two-dimensional and its components are also even. The formula (3·7) corresponds to this choice for $\mathbf{k}$. Two other formulas like (3·7) exist. One corresponds to the choice $\mathbf{k}=(0k_1l)$, whence $\mathbf{h}-\mathbf{k}=(hk-k_10)$, where k_1 is even so that $k-k_1$ is also even. The other corresponds to the choice $\mathbf{k}=(h0l_1)$, whence

$\mathbf{h}-\mathbf{k}=(0kl-l_1)$, where l_1 and $l-l_1$ are both even. The variants of (3·7) which are associated with the latter two choices for $\mathbf{k}$ yield expressions for $\langle(|E_{0k_1l}|^2-1)\times(|E_{hk-k_10}|^2-1)\rangle_{k_1}$, averaged over the even integers k_1, and $\langle(|E_{h0l_1}|^2-1)(|E_{0kl-l_1}|^2-1)\rangle_{l_1}$, averaged over the even integers l_1, respectively. Combining these three formulas, one obtains

$$\left\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}-\mathbf{k}}|^2-1)\right\rangle_{\mathbf{k}} = \frac{8}{3N^2}\sum_{j=1}^{N/4}\cos 4\pi hx_j + \cos 4\pi ky_j+\cos 4\pi lz_j+4\cos 4\pi hx_j\cos 4\pi ky_j +4\cos 4\pi ky_j\cos 4\pi lz_j+4\cos 4\pi lz_j\cos 4\pi hx_j +3\cos 4\pi hx_j\cos 4\pi ky_j\cos 4\pi lz_j) + \frac{128}{3N^2}\sum_{\substack{j\neq j'\\1}}^{N/4} \times\cos 2\pi hx_j\cos 2\pi hx_{j'}\cos 2\pi ky_j\cos 2\pi ky_{j'} \times\cos 2\pi lz_j\cos 2\pi lz_{j'}\,, \quad (3·8)$$

where the average is taken over all two-dimensional vectors $\mathbf{k}$ having even components and such that the vectors $\mathbf{h}-\mathbf{k}$ are also two-dimensional (and incidentally also have even components since the components h,k,l of the vector $\mathbf{h}$ are assumed to be even). Employing (3·4) and (3·2), equation (3·8) reduces to

$$\left\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}-\mathbf{k}}|^2-1)\right\rangle_{\mathbf{k}} = \frac{8}{3N}\left(|E_{\mathbf{h}}|^2\cos^2\varphi_{\mathbf{h}} -\frac{1}{2}\right) - \frac{2}{3N^{3/2}}(E_{2h00}+E_{02k0}+E_{002l}-2E_{2h2k0} -2E_{02k2l}-2E_{2h02l}-|E_{2\mathbf{h}}|\cos\varphi_{2\mathbf{h}})\,, \quad (3·9)$$

the so called squared-cosine formula for the space group $P2_12_12_1$. It should be emphasized again that the fixed vector $\mathbf{h}$ has non-zero components h,k,l, all of which are even, and that $\mathbf{k}$ ranges over all two-dimensional vectors, with even components, such that the vectors $\mathbf{h}-\mathbf{k}$ are also two-dimensional.

3·3. *The squared-sine formula*

Assume that the integers h,k,l are even and that h_1 is odd. The two-dimensional structure factor E_{h_1k0} is now given by

$$E_{h_1k0} = \frac{4i}{N^{1/2}}\sum_{j=1}^{N/4}\cos 2\pi h_1x_j\sin 2\pi ky_j\,. \quad (3·10)$$

As in the derivation of (2·4) one now finds

$$|E_{h_1k0}|^2-1=\frac{N}{4}\sum_{j=1}^{N/3}(\cos 4\pi h_1x_j-\cos 4\pi ky_j- \cos 4\pi h_1x_j\cos 4\pi ky_j)+\frac{16}{N}\sum_{\substack{j\neq j'\\1}}^{N/4}\cos 2\pi h_1x_j \cos 2\pi h_1x_{j'}\sin 2\pi ky_j\sin 2\pi ky_{j'}\,, \quad (3·11)$$

and, in a similar way,

$$|E_{h-h_10l}|^2-1=\frac{4}{N}\sum_{j=1}^{N/4}[-\cos 4\pi(h-h_1)x_j-\cos 4\pi lz_j +\cos 4\pi(h-h_1)x_j\cos 4\pi lz_j]+\frac{16}{N}\sum_{\substack{j\neq j'\\1}}^{N/4}\sin 2\pi(h-h_1)x_j \sin 2\pi(h-h_1)x_{j'}\sin 2\pi lz_j\sin 2\pi lz_{j'}\,. \quad (3·12)$$

Fixing the even integers h and l and multiplying (3·11) and (3·12), one finds, after some simplification, that

$$\langle(|E_{h_1k0}|^2-1)(|E_{h-h_10l}|^2-1)\rangle_{h_1}=\frac{16}{N^2}\sum_{j=1}^{N/4} \left(-\frac{1}{2}\cos 4\pi hx_j+\frac{1}{2}\cos 4\pi hx_j\cos 4\pi lz_j+\cos 4\pi xh_j \times\cos 4\pi lz_j+\frac{1}{2}\cos 4\pi hx_j\cos 4\pi ky_j-\frac{1}{2}\cos 4\pi ky_j \times\cos 4\pi ky_j\cos 4\pi lz_j\right)+\frac{128}{N^2}\sum_{\substack{j\neq j'\\1}}^{N/4}\sin 2\pi hx_j \times\sin 2\pi hx_{j'}\sin 2\pi ky_j\sin 2\pi ky_{j'}\sin 2\pi lz_j\sin 2\pi lz_{j'} \quad (3·13)$$

in which the average is extended over all odd integers h_1.

Next, let the (three-dimensional) vector $\mathbf{h}$, with even components h,k,l, be fixed. Let $\mathbf{k}$ be a two-dimensional vector, having precisely one odd component, with the property that $\mathbf{h}-\mathbf{k}$ is also two-dimensional. Then clearly precisely one component of $\mathbf{h}-\mathbf{k}$ is also odd. Thus $\mathbf{k}=(h_1,k,0)$, $\mathbf{h}-\mathbf{k}=(h-h_1,0,l)$, where h_1 and $h-h_1$ are odd; or $\mathbf{k}=(0,k_1,l)$, $\mathbf{h}-\mathbf{k}=(h,k-k_1,0)$ where k_1 and $k-k_1$ are odd; or $\mathbf{k}=(h,0,l_1)$, $\mathbf{h}-\mathbf{k}=(0,k,l-l_1)$ where l_1 and $l-l_1$ are odd. [The cases $\mathbf{k}=(h_1,0,l)$, $\mathbf{h}-\mathbf{k}=(h-h_1,k,0)$, h_1 and $h-h_1$ odd; $\mathbf{k}=(h,k_1,0)$, $\mathbf{h}-\mathbf{k}=(0,k-k_1,l)$, k_1 and $k-k_1$ odd; $\mathbf{k}=(0,k,l_1)$, $\mathbf{h}-\mathbf{k}=(h,0,l-l_1)$, l_1 and $l-l_1$ odd, give nothing new.] Equation (3·13) corresponds to the first of these choices for $\mathbf{k}$. Corresponding to the second choice for $\mathbf{k}$ is a formula like (3·13) which gives the value of $\langle(|E_{0k_1l}|^2-1)(|E_{hk-k_10}|^2-1)\rangle_{k_1}$ averaged over the odd integers k_1. Finally, there corresponds to the third choice for $\mathbf{k}$ a formula similar to (3·13) which yields an expression for $\langle(|E_{h0l_1}|^2-1)(|E_{0kl-l_1}|^2-1)\rangle_{l_1}$ averaged over the odd integers l_1. These three formulas are combined to give

$$\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}-\mathbf{k}}|^2-1)\rangle_{\mathbf{k}}=\frac{8}{3N^2}\sum_{j=1}^{N/4}(-\cos 4\pi hx_j -\cos 4\pi ky_j-\cos 4\pi lz_j+4\cos 4\pi hx_j\cos 4\pi ky_j +4\cos 4\pi ky_j\cos 4\pi lz_j+4\cos 4\pi lz_j\cos 4\pi hx_j -3\cos 4\pi hx_j\cos 4\pi ky_j\cos 4\pi lz_j) +\frac{128}{3N^2}\sum_{\substack{j\neq j'\\1}}^{N/4}\sin 2\pi hx_j\sin 2\pi hx_{j'}\sin 2\pi ky_j \times\sin 2\pi ky_{j'}\sin 2\pi lz_j\sin 2\pi lz_{j'} \quad (3·14)$$

where the average is taken over all two-dimensional vectors **k** having precisely one odd component and such that the vectors **h** − **k** are also two-dimensional (and incidentally also have precisely one odd component since the components h,k,l of the vector **h** are assumed to be even). Employing (3·10) and (3·3), equation (3·14) reduces to

$$\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}-\mathbf{k}}|^2-1)\rangle_{\mathbf{k}}=\frac{8}{3N}\left(|E_{hkl}|^2\sin^2\varphi_{hkl}-\frac{1}{2}\right)+\frac{2}{3N^{3/2}}(E_{2h00}+E_{02k0}+E_{002l}+2E_{2h2k0}+2E_{02k2l}+2E_{2h02l}-|E_{2h2k2l}|\cos\varphi_{2h2k2l}),\quad(3\cdot15)$$

the so-called squared-sine formula for the space group $P2_12_12_1$. It should be emphasized again that the fixed vector **h** has non-zero components h,k,l, all of which are even, and that **k** ranges over all two-dimensional vectors, with precisely one odd component, such that the vectors **h** − **k** are also two-dimensional.

3·4. *The squared-tangent formula*

Let all components of the fixed vector **h** be even and suppose that **k** and **h** − **k** are two-dimensional. If all components of **k** are even then all components of **h** − **k** are also even and, owing to the space group symmetry, $\varphi_{\mathbf{k}}=0$ or π and $\varphi_{\mathbf{h}-\mathbf{k}}=0$ or π. Hence, in any event, $\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}}=0$ or π, $\cos^2(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})=1$ and $\sin^2(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})=0$. If, on the other hand, precisely one component of **k** is odd then precisely one component of **h** − **k** is also odd and, owing to the space group symmetry, either $\varphi_{\mathbf{k}}=0$ or π and $\varphi_{\mathbf{h}-\mathbf{k}}=\pm\pi/2$ or else $\varphi_{\mathbf{k}}=\pm\pi/2$ and $\varphi_{\mathbf{h}-\mathbf{k}}=0$ or π. In any event then, $\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}}=\pm\pi/2$, $\cos^2(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})=0$, and $\sin^2(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})=1$. Neglecting the terms of order $1/N^{3/2}$ in (3·9) and (3·15) which is permissible if N is sufficiently large, equation (3·9) and (3·15) may therefore be written

$$|E_{\mathbf{h}}|^2\cos^2\varphi_{\mathbf{h}}-\frac{1}{2}\simeq\frac{3N}{4}\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}-\mathbf{k}}|^2-1)\cos^2(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})\rangle_{\mathbf{k}}\quad(3\cdot16)$$

$$|E_{\mathbf{h}}|^2\sin^2\varphi_{\mathbf{h}}-\frac{1}{2}\simeq\frac{3N}{4}\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}-\mathbf{k}}|^2-1)\sin^2(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})\rangle_{\mathbf{k}}\quad(3\cdot17)$$

where the averages are extended over all two-dimensional vectors **k** for which the vectors **h** − **k** are also two-dimensional and subject now to no additional restriction on the parity of the components of **k**. (Note, however, that the conditions imposed on **h**, **k**, **h** − **k** rule out the possibility that precisely two components of **k** be odd.)

Equations (3·16) and (3·17) imply

$$\frac{|E_{\mathbf{h}}|^2\sin^2\varphi_{\mathbf{h}}-\frac{1}{2}}{|E_{\mathbf{h}}|^2\cos^2\varphi_{\mathbf{h}}-\frac{1}{2}}\simeq\frac{\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}-\mathbf{k}}|^2-1)\sin^2(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})\rangle_{\mathbf{k}}}{\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}-\mathbf{k}}|^2-1)\cos^2(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})\rangle_{\mathbf{k}}}\quad(3\cdot18)$$

which, after some simplification leads finally to the squared-tangent formula for the space group $P2_12_12_1$,

$$\tan^2\varphi_{\mathbf{k}}\simeq\frac{\left\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}-\mathbf{k}}|^2-1)\left\{\sin^2(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})+\frac{1}{2|E_{\mathbf{h}}|^2}\cos 2(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})\right\}\right\rangle_{\mathbf{k}}}{\left\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}-\mathbf{k}}|^2-1)\left\{\cos^2(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}}-\frac{1}{2|E_{\mathbf{h}}|^2}\cos 2(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})\right\}\right\rangle_{\mathbf{k}}},\quad(3\cdot19)$$

or the equivalent

$$\tan^2\varphi_{\mathbf{h}}\simeq\frac{\left\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}-\mathbf{k}}|^2-1)\left\{(|E_{\mathbf{h}}|^2-1)\sin^2(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})+\frac{1}{2}\right\}\right\rangle_{\mathbf{k}}}{\left\langle(|E_{\mathbf{k}}|^2-1)(|E_{\mathbf{h}-\mathbf{k}}|^2-1)\left\{(|E_{\mathbf{h}}|^2-1\cos^2(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})+\frac{1}{2}\right\}\right\rangle_{\mathbf{k}}},\quad(3\cdot20)$$

where the averages are extended over all two-dimensional vectors **k** such that the vectors **h** − **k** are also two-dimensional. Although (3·19) and (3·20) have been derived on the assumption that the components of the three-dimensional vector **h** are all even, the same kind of proof shows that these equations have unrestricted validity independent of the parity of the components of **h**. However, the proof of these formulas requires that $|E_{\mathbf{h}}|$ exceed unity and even, for improved accuracy in practice, that $|E_{\mathbf{h}}|>2$.

In marked contrast to the tangent formula (1·1), which requires a knowledge of the values of a basic set of phases before additional phases can be determined, the squared-tangent formula (3·19) or (3·20) permits the calculation of the square of the tangent of any three-dimensional phase prior to the determination of the value of any phase, a consequence of the two-dimensional character of **k** and **h** − **k** and of the space group symmetry. Hence (3·20) supplements (1·1) and may find application in the early determination of those phases which can at best be but crudely approximated by (1·1).

4. Concluding remarks

Squared-tangent formulas have been found for the space groups $P1$ and $P2_12_12_1$. Analogous formulas exist for the remaining noncentrosymmetric space groups. It is anticipated that, at least for the space group $P2_12_12_1$ and other, selected, noncentrosymmetric space groups, these formulas will find application in facilitating the early determination of certain phases. The results obtained here raise two questions. First does (3·20) hold also in the space group $P1$? Secondly, does (3·20) retain its validity if the **k** are restricted so that the $|E_{\mathbf{k}}|$ and $|E_{\mathbf{h}-\mathbf{k}}|$ are large, say greater than unity? Although the available evidence indicates strongly that both of these questions are to be answered in the affirmative, rigorous proofs have been elusive so far. With respect to practical applications, the second question is particularly significant since, owing to a reduction of the errors arising from finite sampling, it is better to restrict the vectors **k** so that the $|E_{\mathbf{k}}|$ and $|E_{\mathbf{h}-\mathbf{k}}|$ are large.

References

International Tables for X-ray Crystallography (1952). Vol. I, p. 385. Birmingham: Kynoch Press.
KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635.

Acta Cryst. (1970). **B26**, 536

Neutron and X-ray Diffraction Studies of Hydrazinium Sulfate, $N_2H_6SO_4$*

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Hydrazinium sulfate has been studied by X-ray and neutron diffraction. The crystals are orthorhombic, space group $P2_12_12_1$, with four formula units in a cell of dimensions: $a=8·251$ (5), $b=9·159$ (1), $c=5·532$ (1) Å. Both the X-ray and neutron data were affected by extinction; this effect was very severe in the neutron case. By inclusion of six anisotropic extinction parameters in the least-squares refinement it was possible to obtain a good fit between observed and calculated structure factors. The structure consists of $N_2H_6^{2+}$ ions and SO_4^{2-} ions held together by a three-dimensional system of N–H···O hydrogen bonds. A number of the hydrogen bonds are weak and bifurcated or trifurcated. The $N_2H_6^{2+}$ ion has an almost perfectly staggered conformation. The neutron and X-ray diffraction results are in good agreement with respect to bond lengths involving the non-hydrogen atoms. Although the hydrogen atoms were located with a precision of 0·03 Å in the X-ray study, the mean N–H bond lengths were 0·2 Å shorter than those found from the neutron study, confirming the existence of large systematic errors in the location of hydrogen atoms from X-ray results when a spherical atomic electron distribution is assumed.

Introduction

The crystal structures of a number of hydrazine compounds have been studied; a review of some recent work has been given by Liminga (1968). These compounds often contain a quite complicated arrangement of hydrogen bonds, and an accurate location of the hydrogen atoms is thus essential. Only two hydrazine compounds studied by neutron diffraction bave been reported: lithium hydrazinium sulfate, $LiN_2H_5SO_4$, by Padmanabhan & Balasubramanian (1967) and hydrazinium hydrogenoxalate, $N_2H_5HC_2O_4$, by Nilsson, Liminga & Olovsson (1968).

The present investigation involves the refinement of the hydrazinium sulfate structure by both X-ray and neutron diffraction methods. An X-ray diffraction study of this compound has been carried out by Nitta, Sakurai & Tomiie (1951); the accuracy of this determination was, however, rather low.

Crystal data

Hydrazinium sulfate, $N_2H_6SO_4$, F.W. 130·12. Orthorhombic, $a=8·251(5)$,* $b=9·159(1)$, $c=5·532(1)$ Å. (Nit-

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* Numbers in parentheses here and throughout this paper are estimated standard deviations in the least significant digits.