If, furthermore, all values of n_j are the same, it may be shown along the lines of Sayre's (1952) derivation that it now follows that

$$U(\mathbf{h}) = N\overline{U(\mathbf{h}')U(\mathbf{h}-\mathbf{h}')}\ . \qquad (6)$$

The average is over all values of h' less than H. This establishes the limits within which Krogh-Moe's result is valid in the equal-atom case, as (12–K.-M.) then reduces to (6). To show that (12–K.-M.) is incorrect when the atoms are unequal, we consider a structure in which $N-2$ atoms are equal, but the remaining two at $\pm r_0$ are m times heavier.

Then

$$\left.\begin{aligned} U(\mathbf{h}) &= 2\sum_{j=1}^{\frac{1}{2}N-1} n\cos 2\pi\mathbf{h}.\mathbf{r}_j + 2mn\cos 2\pi\mathbf{h}.\mathbf{r}_0 \\ &\text{and} \\ G(\mathbf{h}) &= 2\sum_{j=1}^{\frac{1}{2}N-1} g(h)\cos 2\pi\mathbf{h}.\mathbf{r}_j + 2m^2 g(h)\cos 2\pi\mathbf{h}.\mathbf{r}_0\ . \end{aligned}\right\} \qquad (7)$$

Now if

$$\left.\begin{aligned} &|m\cos 2\pi\mathbf{h}.\mathbf{r}_0| < |\sum_{j=1}^{\frac{1}{2}N-1}\cos 2\pi\mathbf{h}.\mathbf{r}_j| \\ &\text{but} \\ &|m^2\cos 2\pi\mathbf{h}.\mathbf{r}_0| > |\sum_{j=1}^{\frac{1}{2}N-1}\cos 2\pi\mathbf{h}.\mathbf{r}_j| \\ &\text{while} \\ &\cos 2\pi\mathbf{h}.\mathbf{r}_0 \text{ and } \sum_{j=1}^{\frac{1}{2}N-1}\cos 2\pi\mathbf{h}.\mathbf{r}_j \end{aligned}\right\} \qquad (8)$$

are opposite in sign it is clear that $U(\mathbf{h})$ and $G(\mathbf{h})$ are opposite in sign, or, using (4),

$$S\{U(\mathbf{h})\} = -S\{\sum_{h'<H} U(\mathbf{h}')U(\mathbf{h}-\mathbf{h}')\}\ ,$$

for the particular values of $\mathbf{h}$ for which conditions (8) happen to be satisfied. $S\{U\}$ is used to denote the sign of U. In these circumstances the two sides of equation (12–K.-M.) are of opposite sign! The only step not rigorously established in Krogh-Moe's derivation is (6–K.-M.), which must therefore be incorrect, except in the equal-atom case.

In the notation used here, Zachariasen's equation (11–Z.) is

$$S\{U(\mathbf{h})\} = S\{\overline{S\{U(\mathbf{h}')\}S\{U(\mathbf{h}-\mathbf{h}')\}}\}\ . \qquad (9)$$

Since Zachariasen stipulated that only large unitary structure factors are to be involved in the averaging process, and since these U's will be approximately equal in magnitude, we may write (11–Z.) as

$$S\{U(\mathbf{h})\} = S\{\overline{U(\mathbf{h}')U(\mathbf{h}-\mathbf{h}')}\}\ . \qquad (10)$$

This result is incorrect when conditions (8) are satisfied, so that (11–Z.) cannot be generally valid. Why then was Zachariasen able to apply it so successfully in practice? The explanation is that while

$$S\{G(\mathbf{h})\} = S\{\overline{U(\mathbf{h}')U(\mathbf{h}'-\mathbf{h})}\} \qquad (11)$$

is rigorously true when the average is over all unitary structure factors within a limiting sphere, the result is still true when only the larger U's appear on the right-hand side of (11). Taking these U's to be equal in magnitude, we obtain

$$S\{G(\mathbf{h})\} = S\{\overline{S\{U(\mathbf{h}')\}S\{U(\mathbf{h}'-\mathbf{h})\}}\}\ . \qquad (12)$$

Comparison of (9) with (12) shows that Zachariasen's procedure really gives the sign of $G(\mathbf{h})$, not of $U(\mathbf{h})$. When the atoms are equal, or nearly so, $S\{U\} = S\{G\}$ (see equations (5)), and even when they are very unequal this will usually be true for the larger structure factors (see equations (7)). In such circumstances (11–Z.) is correct, but, as we have shown, exceptions may in principle occur.

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The unit cell and space group of ethyl nitrolic acid.

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(*Received* 6 *July* 1953 *and in revised form* 3 *August* 1953)

Ethyl nitrolic acid ($C_2N_2O_3H_4$) was prepared by the action of potassium hydroxide and sodium nitrite on nitroethane (Meyer & Constam, 1882). The crystals were pale yellow, orthorhombic, and two habits were observed, both of which gradually decomposed with the evolution of nitrous fumes. Recrystallization from chloroform, ether or water gave needles elongated along [c], and exhibiting the forms {100}, {010}, {001}, {110} and {210}, while small plates exhibiting {011} and {100} were obtained by slow evaporation of a chloroform solution. Both habits were consistent with the 222 class.

From rotation photographs taken with Cu $K\alpha$ radiation, and from an optical examination, the crystal was found to be orthorhombic with axial lengths

$$[a] = 11{\cdot}28,\ [b] = 8{\cdot}06,\ [c] = 4{\cdot}85\ \text{Å}\ .$$

Reflexions were indexed on oscillation photographs and the only systematic absences were ($h00$), ($0k0$) and ($00l$) for h, k and l odd respectively. The space group is therefore D_4^2–$P2_12_12_1$.

The density measured by flotation was 1·555 g.cm.$^{-3}$. This agrees with a calculated value of 1·567 g.cm.$^{-3}$ for four molecules in the unit cell.

Reference

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