

This furnishes

$$(\mathbf{a} \cdot \mathbf{b} \times \mathbf{c})^2 = V^2 = \begin{vmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ab \cos \gamma & b^2 & bc \cos \alpha \\ ac \cos \beta & bc \cos \alpha & c^2 \end{vmatrix} \\ = a^2 b^2 c^2 [1 + 2 \cos \alpha \cos \beta \cos \gamma - \cos^2 \alpha \\ - \cos^2 \beta - \cos^2 \gamma].$$

More details are contained in a text by Buerger (1942, pp. 349–351). The corresponding expression for V^{*2} may be obtained in the same way. Application of (7) to the evaluation of $(\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}) (\mathbf{a}^* \cdot \mathbf{b}^* \times \mathbf{c}^*)$ yields

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

and leads at once to the identity $V V^* = 1$.

An expression for V that contains both direct and reciprocal lattice quantities may be obtained by starting with

$$a = |\mathbf{b}^* \times \mathbf{c}^*| / V^* = b^* c^* \sin \alpha^* / V^*. \quad (9)$$

When b^* and c^* are expressed by direct lattice quantities this becomes

$$a = (c a \sin \beta / V) (a b \sin \gamma / V) (\sin \alpha^* / V^*). \quad (10)$$

Solving for V , and using $V V^* = 1$ leads to the final result,

$$V = a b c \sin \alpha^* \sin \beta \sin \gamma. \quad (11)$$

which remains valid when the star is switched to other angles, as in

$$V = a b c \sin \alpha \sin \beta^* \sin \gamma. \quad (12)$$

Therefore also,

$$(\sin \alpha / \sin \alpha^*) = (\sin \beta / \sin \beta^*) = (\sin \gamma / \sin \gamma^*), \quad (13)$$

which is the equivalent of the sine law of spherical trigonometry:

$$\sin r / \sin R = \sin s / \sin S = \sin t / \sin T. \quad (14)$$

Relationships reciprocal to (11) and (12), of the form

$$V^* = a^* b^* c^* \sin \alpha \sin \beta^* \sin \gamma^* \quad (15)$$

are, of course, correct also.

Another expression for V follows from solving $a^* = b c \sin \alpha / V$ for V :

$$V = b c \sin \alpha / a^*. \quad (16)$$

Cyclic variation yields two additional formulas, and analogous expressions exist for V^* .

Combining (12) and (16) yields

$$a a^* \sin \beta^* \sin \gamma = 1, \quad (17)$$

which invites comparison with $\mathbf{a} \cdot \mathbf{a}^* = 1$, that is,

$$a a^* \cos (\mathbf{a}, \mathbf{a}^*) = 1. \quad (18)$$

It follows that

$$\cos (\mathbf{a}, \mathbf{a}^*) = \sin \beta^* \sin \gamma = \sin \beta \sin \gamma^*, \quad (19)$$

where (13) has also been used. The argument of the cosine is the angle between the zone direction [100] and the normal to the (100) plane. An expression for $\cos (\mathbf{a}, \mathbf{a}^*)$ containing direct lattice quantities only follows from solving equation (12) for $\sin \beta^* \sin \gamma$ and insertion into (19),

$$\cos (\mathbf{a}, \mathbf{a}^*) = V / a b c \sin \alpha. \quad (20)$$

Likewise, in reciprocal space quantities,

$$\cos (\mathbf{a}, \mathbf{a}^*) = V^* / a^* b^* c^* \sin \alpha^*. \quad (21)$$

Expressions analogous to (19), (20), and (21) follow by cyclic permutation.

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Possibility of 'Bijvoet differences' in the non-centrosymmetric structures of the elements. By K. S. CHANDRASEKARAN, *Physics Department, Madurai University, Madurai-2, India*

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It is proposed that it would be interesting to look for and measure Bijvoet differences in the noncentrosymmetric structures of the elements like α -manganese and the hexagonal, isomorphous tellurium and selenium. This would check directly the validity of some of the usual assumptions regarding temperature factors in X-ray diffraction.

The purpose of this communication is to point out the possibility of directly checking the usual assumptions on the temperature factors in X-ray diffraction in cases where the anomalous scattering is appreciable, through experiments on the non-centrosymmetric structures of some elements.

Considering such a structure with n atoms in the unit cell, the structure factors of the pair of reflexions, hkl and $\bar{h}\bar{k}\bar{l}$, would be

$$F(hkl)_{\pm} = \sum_1^n (f + \Delta f' + i \Delta f'') (A_j \pm i B_j) \quad (\text{temperature factor})_j, \quad (1)$$

where f is the normal atomic scattering factor, $\Delta f'$ and $\Delta f''$ are the real and imaginary parts of the anomalous scattering, $(A_j \pm iB_j)$, the geometric part of the structure factor for the j th atom for hkl and $\bar{h}\bar{k}\bar{l}$ respectively and (temperature factor) $_j$ is of the anisotropic form for the j th atom in the unit cell. The temperature factors for this pair are usually assumed to be the same since the thermal ellipsoid is centrosymmetric. The intensities of these two inverse reflexions would therefore be equal and 'Bijvoet differences', *i.e.* intensity differences due to anomalous scattering and deviation from Friedel's law, cannot arise in principle in such non-centrosymmetric structures of the elements, even if the anomalous scattering is appreciable. These ideas can also be elegantly visualized on the Argand diagram construction.

However, if it is postulated that (i) the temperature factors can be different for the different atoms in the unit cell and also that (ii) the temperature factors for the normal and anomalous components of the scattering can be appreciably different, then a simple algebraic exercise with the complex quantities in the structure factor expressions in equation (1) would show that Bijvoet differences can occur even in such structures. Physically the assumptions would mean that the ratios between the imaginary and real part of the scattering powers of the atoms become different, which is the condition required for the observation of Bijvoet differences.

The plausibility of these assumptions is difficult to consider theoretically. One could state that in a case like α -manganese ($I43m$), with 58 atoms in the unit cell, the former of the two assumptions is not unrealistic. Regarding (ii), it is well known that the anomalous scattering components depend mainly on the inner electrons only, in contrast to the normal scattering, and for this reason the angular dependences of these scattering factors are markedly different. Their temperature factors are, however, usually assumed to be the same.

It appears to the present author that a direct check is possible and would be desirable, by looking for Bijvoet

differences in single crystals of α -manganese and the hexagonal isomorphous selenium and tellurium (enantiomorphous, $P3_121$ or $P3_221$). If appreciable Bijvoet differences are observed for a good number of reflexions, over and above what can be attributed reasonably to errors of measurement due to absorption and shape effects, then it would be a definite indication that the physical factors in the two above assumptions are operative and detailed work would be of interest in understanding the behaviour of temperature factors in X-ray diffraction, in addition to settling the absolute configuration of the structures. For a control on the experimental measurements, one would of course utilize the fact that the intensities of the pair would still be equal, despite these assumptions, for reflexions where the geometric parts in equation (1) are real – for example, reflexions with h or k or l , zero in α -manganese.

These proposals seem opportune now, since accurate refinements of such structures have recently been carried out: α -manganese (Gazzara, Middleton, Weiss & Hall, 1967) and hexagonal selenium (Cherin & Unger, 1966). It should also be mentioned that Bijvoet differences in such structures had been suggested for electron diffraction (Parthasarathy, 1961), through arguments based on the dynamical theory.

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An apparent variation of structure factors for electrons with the accelerating voltage. An observation through Kikuchi patterns. By DENJIRO WATANABE* and RYOZI UYEDA, *Department of Physics, Nagoya University, Nagoya, Japan*, and MOTOKAZU KOGISO, *Department of General Education, Nagoya University, Nagoya, Japan*

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It is shown that the intensity of the Kikuchi line of the second order reflexion 220 in electron diffraction patterns from a thin single crystal of Fe-20 at.% Al alloy gradually changes with the accelerating voltage for incident electrons and vanishes at about 340 kV. owing to the systematic dynamical interactions combined with the relativistic change of electron mass.

The structure factor for electrons $U_h = (2me/h^2)V_h$ changes with the accelerating voltage because of the relativistic change of electron mass (Fujiwara, 1961):

$$m = m_0 / (1 - \beta^2)^{1/2} = m_0 \{ 1 + eE / (m_0 c^2) \} \quad (1),$$

* On leave from the Department of Physics, Tohoku University, Sendai, Japan.

where V_h is the Fourier coefficient of the crystal potential, E the accelerating voltage, and β , e , h , m_0 and c have their usual meanings. The apparent value of structure factor U'_h , which is determined, for example, directly from the ring intensity on the basis of the current formula, changes more with the accelerating voltage owing to the dynamical many-beam interactions. Under certain conditions, approximate values of U'_h can be calculated by Bethe's second approximation (Bethe, 1928; Miyake, Fujiwara & Suzuki, 1963),