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An expression for orientation in cellulose fibres, By V. D. Gupta,* *Physics Department, University of Allahabad, Allahabad, India*

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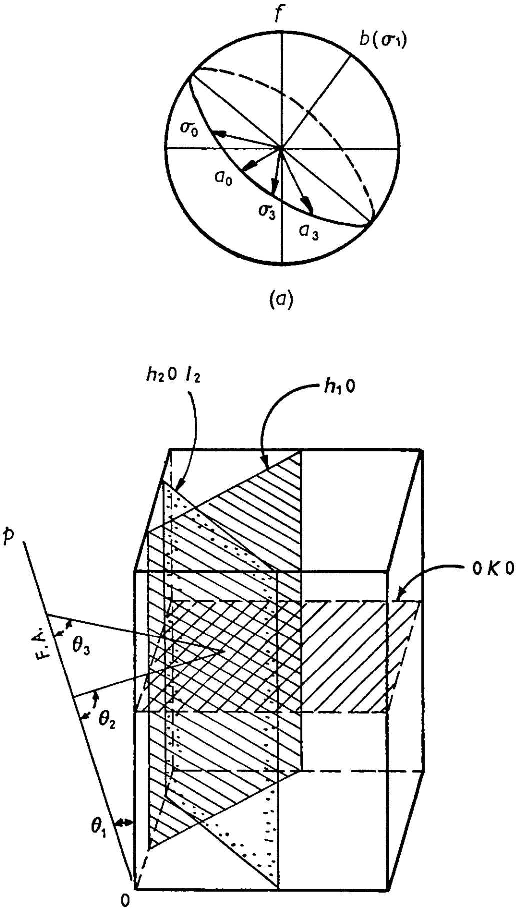
Hermans (1946) orientation factor can be evaluated only when the diatropic and paratropic interferences arise from planes which form an orthogonal set—a condition only approximately satisfied in case of both Cellulose I and Cellulose II. In the present communication an exact expression has been derived which can be evaluated from X-ray measurements, angle between face normals of paratropic interferences and the optical constants.



(a)

(b)

Fig. 1.

In Fig. 1 let one of the axes of the polarization ellipsoid coincide with the crystallographic b axis which represents the direction along the cellulose chains and σ_1, σ_0, σ_3 the three polarizabilities. Further let b denote the normal to the diatropic planes $0k0$ and a_0, a_3 those to h_10l_1 and h_20l_2. The principal axis σ_1 of the polarization ellipsoid coincides with b and σ_0, σ_3 lie in the plane a_0a_3. If δ is the angle $\widehat{\sigma_0\ a_0}$; θ_1 is $\widehat{b\ f}$; ψ_0 is $\widehat{\sigma_0\ f}$; ψ_3 is $\widehat{\sigma_3\ f}$, the polarizability in the direction of the fibre axis resulting from unit electric field in the direction of the fibre axis is

$$\sigma_{||}=\sigma_1\cos^2\theta_1+\sigma_0\cos^2\psi_0+\sigma_3\cos^2\psi_3\,. \tag{1}$$

It is obvious that

$$\begin{aligned}\cos\psi_0&=\operatorname{cosec}\alpha\,[\ \ \sin(\alpha+\delta)\sin\theta_2-\sin\delta\sin\theta_3]\\ \cos\psi_3&=\operatorname{cosec}\alpha\,[-\cos(\alpha+\delta)\sin\theta_2+\cos\delta\sin\theta_3]\end{aligned}$$

where α is the angle $\widehat{a_0\ a_3}$.

Also

$$\overline{\cos^2}\,\theta_1=1-\operatorname{cosec}^2\alpha\,(\overline{\sin^2}\,\theta_2+\overline{\sin^2}\,\theta_3)$$

(see below) where θ_2, θ_3 are the angles which the normals to the two paratropic planes make with the fibre axis and supplements of these are measured from the equator in the X-ray photograph when this relation is satisfied. Making the sesubstitutions in (1) and taking the average we have,

$$\begin{aligned}\sigma_{||}=\sigma_1-\overline{\sin^2}\,\theta_2\,&[(\sigma_1-\sigma_0\sin^2(\alpha+\delta)-\sigma_3\cos^2(\alpha+\delta))]\operatorname{cosec}^2\alpha\\ \overline{\sin^2}\,\theta_3\,&[(\sigma_1-\sigma_0\sin^2\delta-\sigma_3\cos^2\delta)]\operatorname{cosec}^2\alpha\end{aligned}$$

remembering that

$$\overline{\sin\theta_2\sin\theta_3}=0\,.$$

Polarizability perpendicular to the fibre axis is

$$\begin{aligned}\sigma_\perp=\tfrac{1}{2}[\sigma_0+\sigma_3+\{\operatorname{cosec}^2\alpha(\sigma_1-\sigma_0\sin^2(\alpha+\delta)\\ -\sigma_3\cos^2(\alpha+\delta))\}\\ \overline{\sin^2}\,\theta_2+\{\operatorname{cosec}^2\alpha(\sigma_1-\sigma_0\sin^2\delta-\sigma_3\cos^2\delta)\}\,\overline{\sin^2}\,\theta_3]\,.\end{aligned}$$

The orientation factor f is defined as the ratio between the actual double refraction of the crystalline material and that at complete orientation. Hence

$$\begin{aligned}f=1&\\ &-\tfrac{3}{2}\left[\frac{\operatorname{cosec}^2\alpha\{\sigma_1-\sigma_0\sin^2(\alpha+\delta)-\sigma_3\cos^2(\alpha+\delta)\}}{\{\sigma_1-\frac{1}{2}(\sigma_0+\sigma_3)\}}\right]\overline{\sin^2}\,\theta_2\\ &-\tfrac{3}{2}\left[\frac{\operatorname{cosec}^2\alpha\{\sigma_1-\sigma_0\sin^2\delta-\sigma_3\cos^2\delta\}}{\{\sigma_1-\frac{1}{2}(\sigma_0+\sigma_3)\}}\right]\overline{\sin^2}\,\theta_3\,,\end{aligned}$$

which is the general expression.

If we assume $\sigma_0=\sigma_3$ as is true for most of the cellulose fibres,

$$f=1-\tfrac{3}{2}\,(\overline{\sin^2}\,\theta_2+\overline{\sin^2}\,\theta_3)\operatorname{cosec}^2\alpha\,.$$

It now remains to calculate the relation between θ_1, θ_2 and θ_3. Let the normals to the three planes shown in Fig. 1(b) represent the three axes fixed in space and OP the direction of the fibre axis. If $\mathbf{1}$ be a vector along the fibre axis and a_1, a_2 and a_3 its components, we can write,

$$\mathbf{1}.\mathbf{1}=a_1^2+a_2^2+a_3^2+2a_1a_2\mathbf{i}.\mathbf{j}+2a_2a_3\mathbf{j}.\mathbf{k}+2a_1a_3\mathbf{i}.\mathbf{k}=1\,.$$

Again we have

$$\begin{aligned}\cos\theta_1&=a_1&&+a_2\mathbf{i}.\mathbf{j}&&+a_3\mathbf{i}.\mathbf{k}\\ \cos\theta_2&=a_1\mathbf{j}.\mathbf{i}&&+a_2&&+a_3\mathbf{j}.\mathbf{k}\\ \cos\theta_3&=a_1\mathbf{k}.\mathbf{i}&&+a_2\mathbf{k}.\mathbf{j}&&+a_3\,.\end{aligned}$$

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Solving these equations for a monoclinic system and putting $\mathbf{j}\,.\,\mathbf{k}=\cos\alpha$ (say) we get,

$$\begin{aligned} a_1 &= \cos\theta_1 \\ a_2 &= (\cos\theta_2-\cos\alpha\cos\theta_3)/\sin^2\alpha \\ a_3 &= (\cos\theta_3-\cos\alpha\cos\theta_2)/\sin^2\alpha\,. \end{aligned}$$

Substituting these values in the last equation we get

$$\begin{aligned} &\sin^2\theta_1 \\ &=\operatorname{cosec}^2\alpha\,(\cos^2\theta_2+\cos^2\theta_3)-2\operatorname{cosec}\alpha\cot\alpha\cos\theta_2\cos\theta_3. \end{aligned}$$

If, however, the angles θ_2 and θ_3 are defined as above and an average value of the angles is taken,

$$\overline{\sin^2}\,\theta_1=\operatorname{cosec}^2\alpha\,(\overline{\sin^2}\,\theta_2+\overline{\sin^2}\,\theta_3)\,.$$

Finally the angle between face normals in a crystallographic system is given by

$$\cos^{-1} T(x,y)/[T(x,x)T(y,y)]^{\frac{1}{2}}\,,$$

where $T(x, y)$ is

$$\begin{aligned} &(\sin^2\alpha/x_1y_1)+(\sin^2\beta/x_2y_2)+(\sin^2\gamma/x_3y_3) \\ &\quad+(\cos\gamma\cos\beta-\cos\alpha)\{(1/x_3y_2)+(1/x_2y_3)\} \\ &\quad+(\cos\gamma\cos\alpha-\cos\beta)\{(1/x_3y_1)+(1/x_1y_3)\} \\ &\quad+(\cos\alpha\cos\beta-\cos\gamma)\{(1/x_1y_2)+(1/x_2y_1)\}\,, \end{aligned}$$

where x_1, x_2, x_3 and y_1, y_2, y_3 are intercepts along the three axes and α, β, γ are the axial angles. For a monoclinic system the angle between two paratropic planes in terms of Miller Indices and axial lengths is given by

$$\cos^{-1}\frac{h_1h_2(bc/a)+l_1l_2ab/c-b\cos\beta(l_1h_2+h_1l_2)}{\begin{aligned}&[(h_1{}^2/a_2+l_1{}^2/c_2-2l_1h_1/ac\cos\beta)\\ &\qquad(h_2{}^2/a^2+l_2{}^2/c_2-2l_2h_2/ac\cos\beta)]^{\frac{1}{2}}\end{aligned}}\,.$$

Here β is the monoclinic angle. Thus the orientation factor can be completely evaluated.

Reference

Hermans, J. J., Hermans, P. H. & Weidinger, A. (1946). *Rec. trav. chim. Pays-Bas*, **65**, 427.

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Space groups of some coordination compounds of cobalt.

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This is a preliminary report on the unit cell dimensions and space groups of some coordination compounds of cobalt. The cell dimensions were measured from rotation photographs and the space-group absences were determined from the zero- and first-layer Weissenberg photographs taken about the principal axes using Fe $K\alpha$ radiation.

(1) *Sodium salt of cobalt*(III) *ethylene diammine tetra-acetate tetrahydrate*: Na[CoEDTA], 4 H_2O

This crystallizes in long plates and belongs to the orthorhombic system. The axial lengths are

$$a=6{\cdot}45\pm0{\cdot}02,\ b=19{\cdot}28\pm0{\cdot}06,\ c=13{\cdot}70\pm0{\cdot}04\ \text{Å};$$
$$d_o=1{\cdot}760\ \text{g.cm.}^{-3},\ d_c=1{\cdot}733\ \text{g.cm.}^{-3};\ Z=4\,.$$

Systematic absences were found for $h0l$ reflections with h odd and $0kl$ with $k+l$ odd. The space group is therefore $Pna2_1$. The other possible space group $Pnam$ has three sets of four-fold positions (*a*), (*b*) and (*c*). Since there are four formula units of the compound in the unit cell, the cobalt atoms have to occur at one of these positions. The point symmetry at (*a*) and (*b*) is a symmetry centre and at (*c*) a mirror plane of symmetry. The cobalt coordination complex is not likely to have these symmetry elements* and therefore this space group is ruled out.

(2) *Cobalt*(III) *tris glycinate dihydrate* $Co(C_2NO_2H_4)_3$, 2 H_2O

This crystallizes in flat plates which belong to the monoclinic system. The cell dimensions are:

$$a=13{\cdot}50\pm0{\cdot}03,\ b=12{\cdot}87\pm0{\cdot}03,\ c=12{\cdot}71\pm0{\cdot}03\ \text{Å};$$
$$\beta=98^\circ;\ d_o=1{\cdot}754\ \text{g.cm.}^{-3},\ d_c=1{\cdot}730\ \text{g.cm.}^{-3};\ Z=8\,.$$

The systematically absent reflection are $h0l$ with l odd and $0k0$ with k odd. This establishes the space group unequivocally as $P2_1/c$–C_{2h}^5.

(3) *Cobalt*(III) *bis dimethyl glyoximino diammine thiocynate*

This coordination compound was prepared by treating its chloride salt with potassium thiocyanate and was purified by recrystallization from water.

The unit cell of this compound is orthorhombic having

$$a=23{\cdot}20\pm0{\cdot}06,\ b=7{\cdot}05\pm0{\cdot}03,\ c=10{\cdot}44\pm0{\cdot}03\ \text{Å};$$
$$d_o=1{\cdot}54\ \text{g.cm.}^{-3},\ d_c=1{\cdot}45\ \text{g.cm.}^{-3};\ Z=4\,.$$

The systematic absences of the X-ray reflections are $hk0$ for h odd and $0kl$ for $k+l$ odd. This is consistent with the space groups $Pnma$ and $Pn2_1a$.

(4) *Cobalt*(III) *bis dimethyl glyoximino diammine perchlorate*

This compound was prepared by treating the chloride salt of the corresponding complex compound with perchloric acid and was purified by recrystallization through water. It crystallizes in needles which belong to the monoclinic system. The cell dimensions are

$$a=19{\cdot}90\pm0{\cdot}06,\ b=6{\cdot}32\pm0{\cdot}03,\ c=12{\cdot}46\pm0{\cdot}04\ \text{Å};$$
$$\beta=103^\circ;\ d_o=1{\cdot}83\ \text{g.cm.}^{-3},\ d_c=1{\cdot}84\ \text{g.cm.}^{-3};\ Z=4\,.$$

The systematically absent reflections are hkl with $h+k+l$ odd and $h0l$ with l odd. These correspond to the space groups Ic and $I2/c$.

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* See Martell & Calvin (1956). *Chemistry of Metal Chelate Compounds*, Prentice Hall, Inc.