

## Study of the Errors in Calculated Molecular Susceptibilities in Orthorhombic Crystals\*

BY M.A. LASHEEN AND S.TADROS

Physics Department, Faculty of Science, Alexandria University, Alexandria, U.A.R.

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Expressions are obtained for the variances and the relative uncertainties of the molecular magnetic susceptibilities and anisotropies in the case of orthorhombic crystals. It is deduced that when the ratios of the crystal magnetic susceptibilities are nearly equal to the corresponding ratios of the squares of the direction cosines of one of the molecular principal axes, the relative molecular susceptibility uncertainties along the other two molecular principal axes will be relatively large.

It has been recently noticed (Lasheen, 1968), following a suggestion by Prof. Dame K. Lonsdale, that small experimental errors in the measurement of crystal magnetic anisotropies may sometimes lead to relatively large uncertainties in the calculated molecular susceptibilities and anisotropies. It is the aim of this work to discuss some conditions concerning the values of the molecular direction cosines which might lead to such cases for orthorhombic crystals.

The study of the magnetic properties of orthorhombic crystals by the method given by Krishnan & Banerjee (1935) consists in the determination of two different values of the crystal anisotropies when the crystal is suspended along two different principal axes; thus

$$\chi_a - \chi_b = A \text{ say (crystal suspended along } c \text{ axis)} \quad (1)$$

and

$$\chi_a - \chi_c = B \text{ (crystal suspended along } b \text{ axis),} \quad (2)$$

and making use of the relation

$$\chi_a + \chi_b + \chi_c = C, \quad (3)$$

where  $C/3 = \chi_M$ , the crystal gram-molecular susceptibility measured by any of the familiar powder methods, the values of  $\chi_a, \chi_b, \chi_c$  are thus deduced from the following equations:

$$\left. \begin{aligned} \chi_a &= \frac{1}{3}A + \frac{1}{3}B + \frac{1}{3}C \\ \chi_b &= -\frac{2}{3}A + \frac{1}{3}B + \frac{1}{3}C \\ \chi_c &= \frac{1}{3}A - \frac{2}{3}B + \frac{1}{3}C. \end{aligned} \right\} \quad (4)$$

The corresponding variances are hence given by

$$\left. \begin{aligned} \sigma^2 \chi_a &= \frac{1}{9} \sigma^2 A + \frac{1}{9} \sigma^2 B + \frac{1}{9} \sigma^2 C \\ \sigma^2 \chi_b &= \frac{4}{9} \sigma^2 A + \frac{1}{9} \sigma^2 B + \frac{1}{9} \sigma^2 C \\ \sigma^2 \chi_c &= \frac{1}{9} \sigma^2 A + \frac{4}{9} \sigma^2 B + \frac{1}{9} \sigma^2 C, \end{aligned} \right\} \quad (5)$$

\* In the course of this work, a copy of an unpublished paper by Mr D. Walley, in which he had studied the same errors for the case of monoclinic crystals, was kindly sent to us by Prof. Lonsdale.

where  $\sigma^2 A$  and  $\sigma^2 B$  are the experimental variances of the anisotropies  $A$  and  $B$  and  $\sigma^2 C$  that in  $3\chi_M$ . Equations (5) show that accurate measurements of  $A, B$  and  $\chi_M$  assure sufficient accuracy in the values of the crystal susceptibilities  $\chi_a, \chi_b$  and  $\chi_c$ .

The molecular susceptibilities  $K_L, K_M$  and  $K_N$  are next deduced, making use of the relations given by Lonsdale & Krishnan (1936), namely:

$$\begin{pmatrix} \chi_a \\ \chi_b \\ \chi_c \end{pmatrix} = \begin{pmatrix} \alpha_1^2 & \alpha_2^2 & \alpha_3^2 \\ \beta_1^2 & \beta_2^2 & \beta_3^2 \\ \gamma_1^2 & \gamma_2^2 & \gamma_3^2 \end{pmatrix} \begin{pmatrix} K_L \\ K_M \\ K_N \end{pmatrix} \quad (6)$$

where

$$\begin{aligned} \alpha_1^2 &= \Sigma \alpha_1^2; & \alpha_2^2 &= \Sigma \alpha_2^2; & \alpha_3^2 &= \Sigma \alpha_3^2; \\ \beta_1^2 &= \Sigma \beta_1^2; & \beta_2^2 &= \Sigma \beta_2^2; & \beta_3^2 &= \Sigma \beta_3^2; \\ \gamma_1^2 &= \Sigma \gamma_1^2; & \gamma_2^2 &= \Sigma \gamma_2^2; & \gamma_3^2 &= \Sigma \gamma_3^2. \end{aligned}$$

$(\alpha_1, \beta_1, \gamma_1)$ ,  $(\alpha_2, \beta_2, \gamma_2)$  and  $(\alpha_3, \beta_3, \gamma_3)$  are the direction cosines of the molecular principal axes with respect to the crystal axes, the summation being taken over the independently oriented molecules in the unit cell.

From equation (6) the molecular susceptibilities are then given by:

$$K_L = D_1/A; \quad K_M = D_2/A; \quad K_N = D_3/A, \quad (7)$$

where  $A$  is the direction cosine determinant which is given by

$$A = \begin{vmatrix} \alpha_1^2 & \alpha_2^2 & \alpha_3^2 \\ \beta_1^2 & \beta_2^2 & \beta_3^2 \\ \gamma_1^2 & \gamma_2^2 & \gamma_3^2 \end{vmatrix}, \quad (8)$$

while the determinants  $D_1, D_2$  and  $D_3$  are respectively given by:

$$D_1 = \begin{vmatrix} \chi_a & \alpha_2^2 & \alpha_3^2 \\ \chi_b & \beta_2^2 & \beta_3^2 \\ \chi_c & \gamma_2^2 & \gamma_3^2 \end{vmatrix}; \quad D_2 = \begin{vmatrix} \alpha_1^2 & \chi_a & \alpha_3^2 \\ \beta_1^2 & \chi_b & \beta_3^2 \\ \gamma_1^2 & \chi_c & \gamma_3^2 \end{vmatrix}; \quad D_3 = \begin{vmatrix} \alpha_1^2 & \alpha_2^2 & \chi_a \\ \beta_1^2 & \beta_2^2 & \chi_b \\ \gamma_1^2 & \gamma_2^2 & \chi_c \end{vmatrix}. \quad (9)$$

Substituting for  $\chi_a, \chi_b$  and  $\chi_c$  the values given in equation (4), we have

$$\left. \begin{aligned} K_L &= \frac{1}{3A} [(a_1 - 2b_1 + c_1)A \\ &\quad + (a_1 + b_1 - 2c_1)B + (a_1 + b_1 + c_1)C] \\ K_M &= \frac{1}{3A} [(a_2 - 2b_2 + c_2)A \\ &\quad + (a_2 + b_2 - 2c_2)B + (a_2 + b_2 + c_2)C] \\ K_N &= \frac{1}{3A} [(a_3 - 2b_3 + c_3)A \\ &\quad + (a_3 + b_3 - 2c_3)B + (a_3 + b_3 + c_3)C], \end{aligned} \right\} (10)$$

where

$$\begin{aligned} a_1 &= \beta_2^2 \gamma_3^2 - \gamma_2^2 \beta_3^2, & b_1 &= \gamma_2^2 \alpha_3^2 - \alpha_2^2 \gamma_3^2, & c_1 &= \alpha_2^2 \beta_3^2 - \beta_2^2 \alpha_3^2, \\ a_2 &= \beta_3^2 \gamma_1^2 - \gamma_3^2 \beta_1^2, & b_2 &= \gamma_3^2 \alpha_1^2 - \alpha_3^2 \gamma_1^2, & c_2 &= \alpha_3^2 \beta_1^2 - \beta_3^2 \alpha_1^2, \\ a_3 &= \beta_1^2 \gamma_2^2 - \gamma_1^2 \beta_2^2, & b_3 &= \gamma_1^2 \alpha_2^2 - \alpha_1^2 \gamma_2^2, & c_3 &= \alpha_1^2 \beta_2^2 - \beta_1^2 \alpha_2^2. \end{aligned}$$

Thus the variances in the values of the molecular susceptibilities  $K_L$ ,  $K_M$  and  $K_N$  are given by:

$$\left. \begin{aligned} \sigma^2 K_L &= \frac{1}{9A^2} [(a_1 - 2b_1 + c_1)^2 \sigma^2 A \\ &\quad + (a_1 + b_1 - 2c_1)^2 \sigma^2 B + (a_1 + b_1 + c_1)^2 \sigma^2 C] \\ \sigma^2 K_M &= \frac{1}{9A^2} [(a_2 - 2b_2 + c_2)^2 \sigma^2 A \\ &\quad + (a_2 + b_2 - 2c_2)^2 \sigma^2 B + (a_2 + b_2 + c_2)^2 \sigma^2 C] \\ \sigma^2 K_N &= \frac{1}{9A^2} [(a_3 - 2b_3 + c_3)^2 \sigma^2 A \\ &\quad + (a_3 + b_3 - 2c_3)^2 \sigma^2 B + (a_3 + b_3 + c_3)^2 \sigma^2 C], \end{aligned} \right\} (11)$$

while the variance in the molecular magnetic anisotropy

$$\delta K = \frac{K_L + K_M}{2} - K_N$$

is given by

$$\begin{aligned} \sigma^2(\delta K) &= \frac{1}{9A^2} \left\{ \left[ \frac{1}{2}(a_1 - 2b_1 + c_1) + \frac{1}{2}(a_2 - 2b_2 + c_2) \right. \right. \\ &\quad \left. \left. - (a_3 - 2b_3 + c_3) \right]^2 \sigma^2 A + \left[ \frac{1}{2}(a_1 + b_1 - 2c_1) \right. \right. \\ &\quad \left. \left. + \frac{1}{2}(a_2 + b_2 - 2c_2) - (a_3 + b_3 - 2c_3) \right]^2 \sigma^2 B \right. \\ &\quad \left. + \left[ \frac{1}{2}(a_1 + b_1 + c_1) + \frac{1}{2}(a_2 + b_2 + c_2) \right. \right. \\ &\quad \left. \left. - (a_3 + b_3 + c_3) \right]^2 \sigma^2 C \right\}. \quad (12) \end{aligned}$$

One case for which large molecular susceptibility variances occur is when the ratios of the mean moduli of the direction cosines of two of the molecular principal axes are nearly equal; e.g. if  $\alpha_1^2 : \beta_1^2 : \gamma_1^2 \simeq \alpha_2^2 : \beta_2^2 : \gamma_2^2$ , the denominator determinant  $A$  will be very small, and consequently  $\sigma^2 K_L$  and  $\sigma^2 K_M$  will be very large, while  $\sigma^2 K_N$  will be relatively small, since the corresponding numerator is also very small.

Yet, what are really of importance are the relative uncertainties  $\sigma K_L/K_L$ ,  $\sigma K_M/K_M$  and  $\sigma K_N/K_N$ . These are given by:

$$\left. \begin{aligned} \sigma K_L/K_L &= \frac{1}{3D_1} [(a_1 - 2b_1 + c_1)^2 \sigma^2 A \\ &\quad + (a_1 + b_1 - 2c_1)^2 \sigma^2 B + (a_1 + b_1 + c_1)^2 \sigma^2 C]^{\frac{1}{2}} \\ \sigma K_M/K_M &= \frac{1}{3D_2} [(a_2 - 2b_2 + c_2)^2 \sigma^2 A \\ &\quad + (a_2 + b_2 - 2c_2)^2 \sigma^2 B + (a_2 + b_2 + c_2)^2 \sigma^2 C]^{\frac{1}{2}} \\ \sigma K_N/K_N &= \frac{1}{3D_3} [(a_3 - 2b_3 + c_3)^2 \sigma^2 A \\ &\quad + (a_3 + b_3 - 2c_3)^2 \sigma^2 B + (a_3 + b_3 + c_3)^2 \sigma^2 C]^{\frac{1}{2}}. \end{aligned} \right\} (13)$$

If it happens that the ratios of the crystal magnetic susceptibilities are nearly equal to the corresponding ratios of the mean squares of the direction cosines of one of the molecular principal axes, two of the relative molecular susceptibility uncertainties, those along the two other molecular principal axes, will be relatively large. E.g. if  $\chi_a : \chi_b : \chi_c \simeq \alpha_1^2 : \beta_1^2 : \gamma_1^2$ , then, as seen from equation (9), the determinants  $D_2$  and  $D_3$  will be very small, and consequently, from equation (13),  $\sigma K_M/K_M$  and  $\sigma K_N/K_N$  will have rather high values.

#### References

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