

A SIMPLE METHOD OF FINDING THE PRINCIPAL IONIC SUSCEPTIBILITIES OF CRYSTALS

J. K. GHOSE

DEPARTMENT OF PHYSICS, ST. JOHN'S COLLEGE, AGRA

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ABSTRACT. It is shown that the principal ionic anisotropies in triclinic as well as other crystals can be calculated from just the values of magnetic anisotropy in any two planes and X-ray data regarding the angular orientation of the ions. Slightly less accurate values may be obtained from measurements of anisotropy and the direction of maximum susceptibility in a single plane of the crystal. In case of uniaxial symmetry of the ions, the principal ionic anisotropy can be calculated from a single measurement of magnetic anisotropy in any one plane of the crystal. Additional observation of maximum susceptibility in only one plane, is sufficient for calculating the principal ionic susceptibilities. The probable errors are reduced by choosing a plane of large anisotropy.

INTRODUCTION

Magnetic susceptibility tensor of a crystal is the resultant of the ionic or molecular susceptibility tensors of the magnetic ions or molecules in the unit cell of the crystal. The ultimate quantity of interest is the ionic or molecular susceptibility tensor because of its use in the investigation of ligand fields. The usual procedure is to first determine the crystalline magnetic susceptibility tensor. Satisfactory methods could not be found easily for triclinic crystals. Krishnan and Mookherjee (1936, 1938) had used a trial and error method of calculation requiring a large number of measurements of anisotropy in different planes. Ghosh and Bagchi (1962) had proposed a method requiring the measurements of both maximum susceptibility and anisotropy in five different planes in addition to the average susceptibility of the crystal. The author (Ghose, 1964) had discussed several alternative methods of calculating the principal susceptibilities and directions of the principal axes using the transformation laws for covariant and contravariant tensor matrices in oblique coordinates. Each method requires just six observations and imposes no restrictions as to the planes of measurement. One of them, in contrast with the method of Ghosh and Bagchi (1962), requires only the values of maximum susceptibility and anisotropy in three different planes. Several other methods designed for greater accuracy of results are being published elsewhere (Ghose, 1966 a, b).

Ghosh and Mitra (1964) pointed out that instead of first determining the susceptibility tensor for the crystal, it is possible to calculate the ionic susceptibility tensor directly from the magnetic measurements and the X-ray data regarding the angular orientations of the magnetic ions or molecules. This brings in a great

economy in the labours of numerical calculation. In most cases the principal ionic susceptibilities can be calculated by solving just one set of simultaneous linear equations.

This elegant method of calculation has two rather subtle drawbacks. Firstly it requires more than the minimum number of observations necessary in principle. The sum of the maximum and the minimum susceptibilities in a plane of the crystal was considered as a single piece of information. Actually it requires the measurements of both maximum susceptibility and anisotropy. Thus for uniaxial symmetry of ions, since only the axial principal susceptibility K_{\parallel} and the lateral principal susceptibility K_{\perp} of the ion have to be calculated, just two observations in addition to the data regarding the orientations of the ions should be sufficient. The method of Ghosh and Mitra requires the determination of anisotropy and maximum susceptibility in one plane of the crystal, as well as the average susceptibility of the crystal. The second drawback is a considerable loss of accuracy due to the use of two susceptibility values in the calculations. This is not immediately self-evident from the equations but will be proved here and the cause of this inaccuracy will be traced so that it may be avoided.

An alternative method of calculating the ionic susceptibilities directly from the observations will be presented here. It will be shown that the principal ionic anisotropy ($K_{\parallel} - K_{\perp}$), for axially symmetrical ions can be obtained from only one measurement of magnetic anisotropy in a specified plane, together with X-ray data. In the absence of symmetry the principal ionic anisotropies may be calculated from two anisotropy measurements. In addition to these observations, just one measurement of either maximum susceptibility in a plane or the average susceptibility of the crystal is sufficient for calculating the principal ionic susceptibilities. Not only for triclinic, but for all crystals, this method demands fewer observations and simplifies calculations. Apart from the errors in the measurement of magnetic anisotropy in one case and also absolute susceptibility in the other, the major source of error in the proposed method is the inaccuracy of the X-ray data used. In due course it has been proved that the latter error may be minimised by choosing a plane of measurement such that the observed anisotropy is large. The final error is then expected to be no more than that with the lengthy indirect methods and smaller in some cases.

Ionic and crystalline susceptibilities

Let the cosines of the angles between the principal ionic axes K_1, K_2, K_3 of any magnetic ion and any set of orthogonal axes x, y, z , fixed in the crystal, be as follows :

	x	y	z
K_1	α_1	β_1	γ_1
K_2	α_2	β_2	γ_2
K_3	α_3	β_3	γ_3

The direction cosines $\cos \phi_i^a$, $\cos \phi_i^b$, $\cos \phi_i^c$, of each ionic axis K_i , with respect to the crystallographic axes a, b, c , are known from the X-ray data. Hence α_i, β_i and γ_i may be easily calculated. It has been shown by Ghoso (1965) that if the orthogonal axes are so chosen that the z axis coincides with the c axis and the x axis lies in the $a-c$ plane and close to the a axis, then α_i, β_i and γ_i can be calculated without any ambiguity by the following matrix equation.

$$[\alpha_i, \beta_i, \gamma_i] = [\cos \phi_i^a \cos \phi_i^b \cos \phi_i^c] \begin{bmatrix} \frac{1}{\sin \beta} & \frac{\cos \alpha \cos \beta - \cos \gamma}{M \sin \beta} & 0 \\ 0 & \frac{\sin \beta}{M} & \\ \frac{\cos \beta}{\sin \beta} & \frac{\cos \beta \cos \gamma - \cos \alpha}{M \sin \beta} & \end{bmatrix} \quad (1)$$

where α, β, γ are the triclinic angles and M is the positive square root of $(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)$. There is no ambiguity. Similar matrix relations may be obtained if any other set of orthogonal axes is selected.

In most of the actual problems it would be necessary to calculate the values of only γ_i . A shorter method of calculating it for different directions of z axis will be discussed later.

If in the unit cell there are n ions of a particular type with different orientations, then the susceptibility matrix for the crystal is $1/n$ times the sum of the susceptibility matrices for the n ions. Thus in the x, y, z coordinate system, the susceptibility matrix is

$$\begin{bmatrix} \chi_{11} & \chi_{12} & \chi_{13} \\ \chi_{12} & \chi_{22} & \chi_{23} \\ \chi_{13} & \chi_{23} & \chi_{33} \end{bmatrix} = \frac{1}{n} \sum \begin{bmatrix} \alpha_1 & \alpha_2 & \alpha_3 \\ \beta_1 & \beta_2 & \beta_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{bmatrix} \begin{bmatrix} K_1 \\ K_2 \\ K_3 \end{bmatrix} \begin{bmatrix} \alpha_1 & \beta_1 & \gamma_1 \\ \alpha_2 & \beta_2 & \gamma_2 \\ \alpha_3 & \beta_3 & \gamma_3 \end{bmatrix} \quad \dots \quad (2)$$

Probable errors of existing methods

The observed values of anisotropy, maximum susceptibility and average susceptibility are subject to errors of the order of 0.1%. The estimated error is smallest for anisotropy and is 0.1% (Krishnan and Banerji, 1935; Datta, 1953, 1954). The error in the values of maximum susceptibility may be about 0.2% (Dutta Roy, 1955) or slightly less (Das, 1963). The error in measuring average susceptibility for powdered samples may be larger still. Thus the estimated errors in the last two quantities is never less than 0.1%.

For uniaxial symmetry of the magnetic ion, i.e., $K_1 = K_2 = K_{\perp}$ and $K_3 = K_{\parallel}$, Ghosh and Mitra proved that

$$K_{\parallel} \left(1 - \frac{1}{n} \sum \alpha_i^2 \right) + K_{\perp} \left(1 + \frac{1}{n} \sum \alpha_i^2 \right) = 2\chi_{max} - A \quad (3)$$

where χ_{max} and A are the maximum susceptibility and anisotropy in the $y-z$ plane. Also for the mean susceptibility, we have

$$\bar{\chi} = \frac{1}{3}(2K_{\perp} + K_{\parallel}) \quad \dots (4)$$

Solving equations (3) and (4), we get

$$(K_{\parallel} - K_{\perp}) = \frac{2\chi_{max} - A - 2\bar{\chi}}{\Sigma\alpha_3^2} \quad \dots (5)$$

This is an exact relation without any approximation. If the magnitude of the errors in the values of χ_{max} , A and $\bar{\chi}$ be $\partial\chi_{max}$, ∂A and $\partial\bar{\chi}$, then the magnitude of the error in the calculated value of ionic anisotropy is given by

$$\partial(K_{\parallel} - K_{\perp}) = \frac{2\partial\chi_{max} + \partial A + 2\partial\bar{\chi}}{\frac{1}{3} - \frac{\Sigma\alpha_3^2}{n}} + \frac{2\chi_{max} - A - 2\bar{\chi}}{n \cdot \left(\frac{1}{3} - \frac{\Sigma\alpha_3^2}{n}\right)} \partial(\Sigma\alpha_3^2)$$

Neglecting ∂A the error in anisotropy and the second term on the right hand side which is due to error in X-ray data, the percentage error in ionic anisotropy is equal to

$$\frac{200(\partial\chi_{max} + \partial\bar{\chi})}{2\chi_{max} - 2\bar{\chi} - A}$$

In any given case this minimum estimated error can be easily calculated because

$\partial\chi_{max} = 0.1\%$ of $\chi_{max} = \frac{\chi_{max}}{1000}$, and $\partial\bar{\chi} = \frac{\bar{\chi}}{1000}$. Since χ_{max} and $\bar{\chi}$ are large quantities, the absolute errors $\partial\chi_{max}$ and $\partial\bar{\chi}$ are quite large; on the other hand the denominator in the above expression for percentage error is very small. So the accuracy of ionic anisotropy calculated by this method will be necessarily small. Substituting the values of χ_{max} , $\bar{\chi}$ etc. given by Ghosh and Mitra (1964), the error in principal ionic anisotropy in the case of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, is found to be about 25%. Similarly for their determination of the principal ionic anisotropy of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, the estimated error is found to range from 20% to 60% for the different sets of observations given by them. Actually the errors must be still larger due to inaccuracies in the X-ray data. The apparently close agreement with previous workers' results, must be due to coincidence. Also the direction cosines of the tetragonal axis of the second copper ion as calculated by them from X-ray data, have an error of about 5%. Proceeding in the same way it can be proved that in the absence of symmetry too, the method of Ghosh and Mitra is likely to give inaccurate results. The only cause of these inaccuracies is the fact that a difference of two large quantities, the maximum susceptibility in a plane and the average

susceptibility, has been used in calculating a small quantity, the principal ionic anisotropy

The same cause may lead to similar large errors in other methods of calculations as well. Thus, following Lonsdale and Krishnan (1936), if χ_a, χ_b, χ_c are the observed susceptibilities along the a, b and c axes of any orthorhombic crystal, then

$$(K_{\perp} - K_{\parallel}) = \frac{\chi_b - \chi_a}{\alpha_a^2 - \beta_a^2}$$

If the quantity $(\chi_b - \chi_a)$ can be measured directly then the percentage error need not be large. On the other hand if χ_b and χ_a are measured independently, then

assuming the X-ray data to be correct, the percentage error is $\frac{100(\partial\chi_b + \partial\chi_a)}{\chi_b - \chi_a}$,

and is considerable. As regards the error due to X-ray data, it will be small if the difference in the magnitudes of α_a and β_a is large

This defect is also common to many methods of determining the magnetic susceptibility tensor for crystals. Ghose (1964, 1966) has shown that if more than one observation of the absolute value of susceptibility have to be used for calculating the elements of the tensor matrix, then large errors are inevitable. Although the percentage error in the value of any of the calculated principal susceptibilities is not much larger than those in the observed values of susceptibilities, the percentage error in the values of the principal anisotropies is much larger and the calculated directions of the principal axes are not accurate. Even if the principal susceptibilities can be directly measured, the error in the calculated principal anisotropies will be large because each is a small difference of two large quantities. On the other hand, the use of several measurements of anisotropy (and also direction cosines of maximum susceptibility in a plane) does not introduce such large errors in the result because the absolute values of the errors are small.

The method of Krishnan and Mookherji (1938) is free of this defect. But the trial and error procedure makes exact calculation so lengthy as to be almost impossible. Moreover, the directions of the M axes and the principal anisotropies are determined more effectively by those planes for which observed anisotropy is small so that probable error is comparatively large.

Proposed methods

For the orthogonal coordinate system x, y, z , if χ_{max} and A be the observed maximum susceptibility and the anisotropy in x - y plane and ψ be the angle which the direction of maximum susceptibility in this plane makes with the x axis, then the following equations (Ghose, 1964) relating the elements of $[\chi_{mn}]$, the susceptibility tensor matrix can be written down.

$$\chi_{11} = \chi_{max} - A \sin^2\psi \quad \dots (8)$$

$$\chi_{22} = \chi_{max} - A \cos^2 \psi \quad \dots (7)$$

$$\chi_{12} = A \sin \psi \cos \psi \quad \dots (8)$$

Eliminating χ_{max} between equations (6) and (7), we get

$$(\chi_{11} - \chi_{22}) = A \cos 2\psi \quad \dots (9)$$

Substituting the values of χ_{11} etc. from equation (2) in equations (8) and (9), we get

$$(K_2 - K_1)\Sigma\alpha_2\beta_2 + (K_3 - K_1)\Sigma\alpha_3\beta_3 = nA/2 \cdot \sin 2\psi \quad \dots (10)$$

$$(K_2 - K_1)\Sigma(\alpha_2^2 - \beta_2^2) + (K_3 - K_1)\Sigma(\alpha_3^2 - \beta_3^2) = nA \cdot \cos 2\psi \quad \dots (11)$$

The values of α_2 , β_2 , etc. are known from the X-ray data and either equation (1) or some alternative equation. So if A and ψ are measured for the plane $x-y$, then the principal ionic anisotropies, $(K_2 - K_1)$ and $(K_3 - K_1)$ may be found by solving equations (10) and (11). In case of axial symmetry of the ion, a single equation is sufficient.

$$(K_{\parallel} - K_{\perp}) = \frac{nA}{\psi} \cdot \frac{\sin 2\psi}{\Sigma\alpha_3\beta_3} = \frac{nA \cdot \cos 2\psi}{\Sigma(\alpha_3^2 - \beta_3^2)} \quad \dots (12)$$

Thus the principal ionic anisotropies can be calculated from the X-ray data and a single measurement of A and ψ in one plane. If the orthogonal coordinates chosen are those corresponding to equation (1), then A is the anisotropy in a plane perpendicular to the crystallographic c axis and ψ is the angle which the direction of maximum susceptibility in this plane makes with the $a-c$ plane. However it is difficult to determine accurately the value of ψ . But while measuring the anisotropy A , the approximate value of ψ may be easily found for the same plane of observation without requiring any special equipment. Hence the approximate values of the principal ionic anisotropies may be calculated for eliminating ambiguities of results calculated by other methods.

Eliminating ψ between equations (10) and (11) we get

$$\begin{aligned} \{(K_2 - K_1)\Sigma(\alpha_2^2 - \beta_2^2) + (K_3 - K_1)\Sigma(\alpha_3^2 - \beta_3^2)\}^2 + 4\{(K_2 - K_1)\Sigma\alpha_2\beta_2 \\ + (K_3 - K_1)\Sigma\alpha_3\beta_3\}^2 = n^2 A^2 \end{aligned} \quad (13)$$

The summations are for the n ions and A is the anisotropy in $x-y$ plane. For the coordinates corresponding to equation (1), the $x-y$ plane is perpendicular to the c axis and the $x-z$ plane is identical with the crystallographic $a-c$ plane. If \bar{A} be the anisotropy measured in $x-z$ plane, then

$$\begin{aligned} \{(K_2 - K_1)\Sigma(\alpha_2^2 - \gamma_2^2) + (K_3 - K_1)\Sigma(\alpha_3^2 - \gamma_3^2)\}^2 + 4\{(K_2 - K_1)\Sigma\alpha_2\gamma_2 \\ + (K_3 - K_1)\Sigma\alpha_3\gamma_3\}^2 = n^2 \bar{A}^2 \end{aligned} \quad (14)$$

Equations (13) and (14) are simultaneous quadratic equations in $(K_2 - K_1)$ and $(K_3 - K_1)$. Such equations may be solved without difficulty and the numerical values of the principal ionic anisotropies may be calculated. But in general there will be four alternative sets of solutions of which only one is correct. To resolve this ambiguity it will be necessary to note the approximate value of ψ in one of the positions for measuring the anisotropy of the crystal and calculate the approximate values of the principal ionic anisotropies by equations (10) and (11). Of the four alternative sets of solutions previously obtained, the one which is closest to this approximate solution, will be the correct one.

In case of axial symmetry of the ions, equation (13) simplifies to

$$(K_{\parallel} - K_{\perp}) = \frac{\pm nA}{\{(\Sigma\alpha_3^2 - \Sigma\beta_3^2)^2 + 4(\Sigma\alpha_3\beta_3)^2\}^{\frac{1}{2}}} \quad (15)$$

Thus the principal ionic anisotropy can be calculated from a single measurement of anisotropy A in $x-y$ plane, which may be chosen arbitrarily for experimental convenience. To choose the correct sign in equation (15), we note from equation (12) that the positive sign is to be taken if $\Sigma \alpha_n\beta_n$ is positive and at the same time $\sin 2\psi$ is positive, i.e., if the direction of maximum susceptibility in this plane lies between the positive directions of x and y axes.

Some special cases are worth noticing. In orthorhombic crystals, due to the symmetry of orientation of ions in the unit cell, $(\Sigma\alpha_3, \beta_3)$ is equal to zero, while the squares of α and β have the same value for each ion. So equation (15) reduces to the relation given by Lonsdale and Krishnan (1936)

On the other hand if all ions are magnetically equivalent, equation (15) simplifies to

$$(K_{\parallel} - K_{\perp}) = \frac{\pm A}{\alpha_3^2 + \beta_3^2} = \frac{\pm A}{1 - \gamma_3^2} \quad (16)$$

Again in many triclinic crystals like $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, there are only two magnetically inequivalent ions with axial symmetry. If the direction cosines of the second ion be distinguished by a dash suffix, then equation (15) reduces to

$$\begin{aligned} (K_{\parallel} - K_{\perp}) &= \frac{\pm 2A}{\{(\alpha_3^2 - \beta_3^2 + \alpha_3'^2 - \beta_3'^2)^2 + 4(\alpha_3\beta_3 + \alpha_3'\beta_3')^2\}^{\frac{1}{2}}} \\ &= \frac{\pm 2A}{\{(\alpha_3^2 + \beta_3^2 - \alpha_3'^2 - \beta_3'^2)^2 + 4(\alpha_3\alpha_3' + \beta_3\beta_3')^2\}^{\frac{1}{2}}} \\ &= \frac{\pm 2A}{\{(\gamma_3'^2 - \gamma_3^2)^2 + 4(\cos \phi - \gamma_3\gamma_3')^2\}^{\frac{1}{2}}} \end{aligned} \quad (17)$$

where ϕ is the angle between the axes of these two ions.

The quantities γ_3 and γ_3' are the cosines of the angles between the magnetic axes of the ions and the z axis or the normal to the plane in which anisotropy

has been measured. So when using equations (16) and (17), it will be more convenient to calculate γ_3 and γ_3' directly instead of by equation (1) or its equivalent. For this purpose the unit normal may be expressed as a contravariant vector matrix, as will be illustrated in due course. A unit covariant vector in the direction of the axis of an ion may be expressed by the matrix $[\cos \phi_3^a \cos \phi_3^b \cos \phi_3^c]$. So γ_3 is the scalar product of these two vectors and is equal to the product of the two matrices.

Probable errors in the proposed methods

The methods of calculation discussed in the last section, do not involve small differences of large quantities like absolute values of susceptibility. So the percentage errors would be of the same order as in the measurement of anisotropy but for the errors introduced through the X-ray data. The effect of the latter can be reduced by a judicious selection of the plane in which anisotropy is measured.

Consider first the simplest case where all ions in the unit cell are magnetically equivalent, and have axial symmetry. The principal ionic anisotropy is to be calculated by equation (16). If the direction cosine γ_3 be equal to $\cos \theta$, then the maximum percentage error in the calculated value of the principal ionic anisotropy will be

$$\frac{\partial(K_{\parallel} - K_{\perp})}{(K_{\parallel} - K_{\perp})} \cdot 100 = \frac{\partial A}{A} \cdot 100 + 200 \cdot \frac{\cos \theta}{\sin \theta} \cdot \partial \theta \quad \dots (18)$$

The first term on the right hand side of this equation is the percentage error introduced by magnetic measurement and is no more than that in the measurement of anisotropy. The percentage error due to an error of half a degree in the X-ray data is $\frac{200\pi}{360} \cdot \frac{\cos \theta}{\sin \theta}$, or, $\frac{200\pi}{360} \cdot \left(\frac{A_1}{A} - 1\right)^{\frac{1}{2}}$, where A is the observed anisotropy and A_1 is the principal ionic anisotropy, which in this case is the maximum observable anisotropy. This error is very large when the observed anisotropy is nearly zero. On the other hand, when the observed anisotropy is maximum, the error is negligible compared to even the 0.1% error due to anisotropy measurement. When γ_3 is 0.5, the error is near about 1%. So for greater accuracy, the plane of measurement should be so chosen that the observed anisotropy is large.

In case of two ions in the unit cell, an expression for the maximum error can be obtained from equation (17). Putting $(\gamma_3'^2 - \gamma_3^2) = R \cos \omega$; $2(\cos \phi - \gamma_3 \gamma_3') = R \sin \omega$; $\gamma_3 = \cos \theta$ and $\gamma_3' = \cos \theta'$, we get the following expression for fractional error.

$$\begin{aligned} \frac{\partial(K_{\parallel} - K_{\perp})}{(K_{\parallel} - K_{\perp})} &= \frac{\partial A}{A} + \frac{\cos \omega}{R} \{ \mp \sin 2\theta' \partial \theta' + \sin 2\theta \partial \theta \} \\ &+ \frac{2 \sin \omega}{R} \{ \sin \phi \partial \phi \pm \cos \theta \sin \theta' \partial \theta' + \cos \theta' \sin \theta \partial \theta \} \end{aligned}$$

Supposing the maximum errors $\partial\theta$, $\partial\theta'$ and $\partial\phi$ due to errors in X-ray data, to be each half degree or $\pi/360$ radian, the maximum percentage error

$$\begin{aligned}
 &= \frac{\partial A}{A} \cdot 100 + \frac{100\pi}{360 \cdot R} \{ \cos \omega (\sin 2\theta \mp \sin 2\theta') + 2 \sin \omega (\sin \phi + \sin \theta \pm \theta') \} \dots \quad (19) \\
 &\leq \frac{\partial A}{A} \cdot 100 + \frac{100\pi}{360 \cdot R} \{ 2 \cos \omega + 4 \sin \omega \} \\
 &\leq \frac{\partial A}{A} \cdot 100 + \frac{100\pi 2(5)^{\frac{1}{2}}}{360 \cdot R}
 \end{aligned}$$

The second term represents the maximum limiting value of the percentage error due to X-ray data and is equal to $3.9/R$. The value of R , the denominator in equation (17), lies between 0 and 2. If the observed anisotropy A is large, then R is also large and the error is small. The anisotropy A is maximum when the normal to the plane of measurement bisects the larger angle between the magnetic axes of the two ions. Then θ and θ' are equal to $(\pi \pm \phi)/2$ or $\pm \phi/2$, according as ϕ is greater than or less than $\pi/2$. Substituting these values in equation (19), the maximum error when the observed anisotropy is largest, is found to be

$\frac{400\pi \sin \phi}{360(1+3 \cos \phi)}$ %, provided that only the numerical value of $\cos \phi$ be used in this expression. For $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in particular, this error is rather large, namely about 2.3%, because $\cos \phi$ has the low value of 0.1633. On the other hand, if the angle between the magnetic axes of two ions be small, then the error introduced by X-ray data can be made negligibly small.

In case of more than two ions or in the absence of axial symmetry of the ions, it is not possible to get a concise algebraic expression for the percentage error. However, equation (15) indicates that firstly the percentage error introduced by magnetic measurements is equal to that in measuring the anisotropy of the crystal in a plane. Secondly, the error due to X-ray data is minimised if the denominator is large which will be the case if the measured anisotropy is near about the maximum observable value.

Example of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

According to the X-ray data given by Beevers and Lipson (1934), each unit cell of copper sulphate crystal contains two copper ions, each of which is at the centre of an octahedron composed of four oxygen atoms in a plane and belonging to water molecules, and two other oxygen atoms belonging to sulphate groups at the two vertices.

Let the matrix $[\theta_{mn}] = \begin{bmatrix} 1 & \cos \gamma & \cos \beta \\ \cos \gamma & 1 & \cos \alpha \\ \cos \beta & \cos \alpha & 1 \end{bmatrix}$

where α , β and γ are the crystallographic triclinic angles, $82^\circ 16'$, $107^\circ 26'$ and $102^\circ 40'$ respectively. Hence the reciprocal matrix is

$$[\theta_{mn}]^{-1} = \begin{bmatrix} 1.1394 & 0.2076 & 0.3135 \\ 0.2076 & 1.0562 & -0.0799 \\ 0.3135 & -0.0799 & 1.1047 \end{bmatrix}$$

Krishnan and Mookherji (1938) have taken the lines joining the sulphate oxygens at the vertices of the octahedrons, as the magnetic axes of the ions. Taking the crystallographic axes a , b , c , as the coordinate axes, the oblique cartesian coordinate (x, y, z) of any atom is found by multiplying the positions given by Beavers and Lipson, by a , b , c the dimensions of the unit cell. A line joining two atoms in positions (x_1, y_1, z_1) and (x_2, y_2, z_2) may be expressed (Ghose, 1964) as a contravariant vector matrix

$$\begin{bmatrix} (x_2 - x_1) \\ (y_2 - y_1) \\ (z_2 - z_1) \end{bmatrix}$$

or as a covariant matrix $[U_1 U_2 U_3] = [\theta_{mn}] \begin{bmatrix} (x_2 - x_1) \\ (y_2 - y_1) \\ (z_2 - z_1) \end{bmatrix}$

On dividing U_1 , U_2 , U_3 by the length of the vector, i.e., the square root of the product of the covariant and contravariant matrices, we get the direction cosines of this line. The latter form a unit covariant vector matrix $[\cos \phi^a \cos \phi^b \cos \phi^c]$. The calculated values for Z_1 and Z_2 , the axes of the two copper ions agree with those given by Krishnan and Mookherji and are shown in Table 1.

However, the octahedrons are not regular and the water oxygens are closer to the copper ions. So the magnetic axes are likely to be closer to the normals to the planes of water oxygens. The lines joining one of these oxygens with adjacent oxygens may be expressed as before by two contravariant matrices

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} \text{ and } \begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix}.$$

A normal to the plane containing these two lines is given by (Ghose, 1965) by the covariant vector matrix

$$[V_1 V_2 V_3] = [(YZ - ZY) (ZX - XZ) (XY - YZ)]$$

To get the direction cosines, V_1 , V_2 , V_3 are divided by the square root of the matrix product

$$[V_1 V_2 V_3][\theta_{mn}]^{-1} \begin{bmatrix} V_1 \\ V_2 \\ V_3 \end{bmatrix}$$

These values for T_1 and T_2 , the tetragonal axes of the two copper ions are shown in Table I. Those for T_3 differ considerably from the corresponding values calculated by Ghosh and Mitra (1964).

TABLE I

	$\cos \phi^a$	$\cos \phi^b$	$\cos \phi^c$
Z_1	0.2026	-0.6479	0.6179
Z_2	0.3372	0.7489	0.3567
T_1	0.0616	-0.6525	0.6522
T_2	0.3664	0.7104	0.3823

To calculate the ionic anisotropy, equation (17) may be used. The angle between the two ionic axes, either Z_1 and Z_2 , or T_1 and T_2 , is obtained easily by forming the scalar product of the two unit vectors, and is given by

$$\cos \phi = [\cos \phi_1^a \cos \phi_1^b \cos \phi_1^c][\theta_{mn}]^{-1} \begin{bmatrix} \cos \phi_2^a \\ \cos \phi_2^b \\ \cos \phi_2^c \end{bmatrix}$$

The value of $\cos \phi$ is thus found to be -0.1355 for Z_1, Z_2 axes, and -0.1633 for T_1, T_2 axes.

To find the values of γ_3 and γ'_3 , whatever be the plane in which anisotropy is measured, the unit normal to the plane can be expressed as a contravariant vector matrix with respect to the crystallographic axes (Ghose, 1955). If the plane of

measurement be (hkl) , then the normal is a covariant vector $\left[\begin{smallmatrix} h & k & l \\ a & b & c \end{smallmatrix} \right]$ or a contravariant vector $[V^1 \ V^2 \ V^3] = \left[\begin{smallmatrix} h & k & l \\ a & b & c \end{smallmatrix} \right] [\theta_{mn}]^{-1}$. Dividing each element V^1 etc.,

by the magnitude of the vector, i.e., the square root of $[V^1 \ V^2 \ V^3][\theta_{mn}] \begin{bmatrix} V^1 \\ V^2 \\ V^3 \end{bmatrix}$, we

get a unit contravariant vector, say $\begin{bmatrix} v^1 \\ v^2 \\ v^3 \end{bmatrix}$.

Again if the plane of measurement be perpendicular to both the planes (hkl) and $(h'k'l')$ then the normal is a contravariant vector

$$\begin{bmatrix} V^1 \\ V^2 \\ V^3 \end{bmatrix} = \begin{bmatrix} a(kl' - k'l) \\ b(lh' - l'h) \\ c(hk' - h'k) \end{bmatrix}, \text{ which may be changed to}$$

a unit vector as before. If during measurements, one of the crystallographic axes is the normal, then the unit contravariant matrix has a very simple form.

Thus with the c axis normal, it is equal to $\begin{bmatrix} 0 \\ 0 \\ 1 \dots \end{bmatrix}$.

Now γ, γ' , are the matrix products of the contravariant unit matrices in the direction of the normal to the plane of measurement and the covariant unit matrices in the directions of the magnetic axes of the two ions.

Krishnan and Mookherji (1938) have given the observed values of anisotropy in eight different planes of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystal. These are shown in Table II. The principal ionic anisotropy has been calculated in each case. The values obtained by using T_1 and T_2 , the normals to the planes of water oxygens, are shown in the last column, while those obtained by using Z_1 and Z_2 , the directions of octahedron vortices, are shown in the column last but one.

TABLE II

Mode of suspension	Observed Anisotropy	Calculated ionic anisotropy	
		(Z)	(T)
($\bar{1}11$) horiz.	26	180	130
<i>a</i> axis vert.	60	290	303
($\bar{1}10$) horiz.	117	403	412
(100) horiz.	146	435	513
<i>C</i> axis vert.	183	485	421
(110) horiz.	213	572	578
($\bar{1}00$) and ($\bar{1}11$) vert.	263	550	565
($\bar{1}\bar{1}0$) and (111) vert.	204	542	562

It is found that as observed anisotropy increases, the calculated values of ionic anisotropy become more consistent, as was to be expected from the discussion of probable error in the last section. The last three sets indicate a value of 560 with a probable error of magnitude 20, i.e., about 4%. Actually a much higher error should be expected due to the uncertainty regarding the directions of the magnetic axes of the copper ions. From Table I, it is seen that the angle between the direction of the normal to the plane of water oxygens and the direction of the line of the sulphate oxygens at the vertices of the octahedron, is nineteen degrees for the first copper ion and four degrees for the second. Similar variations in the value of ionic anisotropy calculated with the two sets of axes indicate that neither of them may be considered more correct than the other.

Krishnan and Mookherji (1938) obtained a value of 550 for the ionic anisotropy. As a first step they determined the directions of two magnetic axes by trial and error, such that the ratio $A/(\sin \theta \sin \theta')$ is constant where θ and θ' are the angles

between the normal to the plane of measurement and the magnetic axes. However, with the best fit that they could obtain, the ratio varied between 273 and 296 or by about 4% indicating a corresponding maximum error in either the measurements of anisotropy or in the suspensions of the crystal. Consequently, the errors in the last three Sets of values in Table II are no more than the maximum errors due to anisotropy measurement.

More satisfactory results can not be expected for the copper sulphate crystal. Firstly, the oxygen octahedrons surrounding the two copper ions are not exactly similar, so that the magnetic susceptibilities of the two ions are probably different. Secondly, the octahedrons are not regular, so that axial symmetry of the ions is only approximate. And lastly greater accuracy can be expected in those crystals where the ionic axes are not so nearly perpendicular to each other.

Principal ionic susceptibilities

To determine the principal ionic susceptibilities, it is necessary to have one measurement of absolute value of susceptibility, such as the mean susceptibility of the crystal or the maximum susceptibility in one of the coordinate planes. If the average susceptibility $\bar{\chi}$ is accurately known, K_1 may be calculated by the equation

$$3K_1 + (K_2 - K_1) + (K_3 - K_1) = 3\bar{\chi}$$

Alternatively, the maximum susceptibility in a plane of the crystal may be determined with sufficient accuracy. Adding equations (6) and (7), we get the equation

$$\chi_{11} + \chi_{22} = 2\chi_{max} - A$$

Substituting the value of χ_{11} etc. from equation (2), and using the orthogonal properties of α_1, β_1 , etc., we get

$$2K_1 + (K_2 - K_1) \left(1 - \frac{\sum \gamma_2^2}{n} \right) + (K_3 - K_1) \left(1 - \frac{\sum \gamma_3^2}{n} \right) = 2\chi_{max} - A$$

Substituting the calculated values of $(K_2 - K_1)$ and $(K_3 - K_1)$, as well as the observed values of χ_{max} and A , the maximum susceptibility and anisotropy in $x-y$ plane, the value of K_1 may be calculated. In case of axial symmetry of the ions, the same equation reduces to a simpler form,

$$2K_1 + (K_{||} - K_1) \left(1 - \frac{\sum \gamma_3^2}{n} \right) = 2\chi_{max} - A$$

The error in K_1 , or in $K_{||}$ should be of the same order as the error in determining χ_{max} , i.e., 0.2% because the other quantities in the equations are small. The same error will occur in the values of the other principal ionic susceptibilities calculated from the values of principal ionic anisotropies, because the latter quantities being small the absolute magnitudes of their errors will also be small.

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