

Computation of the Principal Components of an Asymmetric \mathfrak{g} Tensor from Paramagnetic Resonance Data*

J. E. GEUSIC† AND L. CARLTON BROWN

Department of Physics and Astronomy, The Ohio State University, Columbus, Ohio

(Received June 5, 1958)

A straightforward method is developed for obtaining the principal components of the asymmetric tensor \mathfrak{g} and its orientation in a crystal system. The necessary paramagnetic resonance data involve three crystal rotations about arbitrary orthogonal axes. Although the spin Hamiltonian is probably not applicable except for $S = \frac{1}{2}$, the development, which is based upon a calculation of the second moment of the energy levels about their mean, is quite general.

INTRODUCTION

FOR the case of a paramagnetic ion having no nuclear spin and having $S = \frac{1}{2}$, the paramagnetic resonance properties of the ion in a crystal can be predicted from the spin Hamiltonian

$$\mathcal{H} = \beta \mathbf{S} \cdot \mathfrak{g} \cdot \mathbf{H} = \beta \sum_i \sum_j S_i g_{ij} H_j, \quad (1)$$

where \mathbf{H} and \mathbf{S} are vectors and \mathfrak{g} is a symmetric second-order tensor. In the principal coordinate system of the tensor \mathfrak{g} the Hamiltonian takes the simpler form

$$\mathcal{H} = \beta (g_{x'} S_{x'} H_{x'} + g_{y'} S_{y'} H_{y'} + g_{z'} S_{z'} H_{z'}). \quad (2)$$

The constants $g_{x'}$, $g_{y'}$, and $g_{z'}$ as well as the orientation of the principal axes relative to the crystal axes must be determined from experimental data.

If the direction of the principal coordinates relative to the crystal axes can be inferred from the symmetry properties of the crystal, the determination of the constants $g_{x'}$, $g_{y'}$, and $g_{z'}$ is indeed simple. However, in many cases the orientation of the principal coordinate system is not suggested by the crystal symmetry and an analysis of the data becomes correspondingly more troublesome. In the following procedure¹ paramagnetic resonance measurements, obtained from three crystal rotations about arbitrarily chosen orthogonal reference axes, are used to obtain numerical values for the components $(\mathfrak{g}^2)_{ij}$ of the symmetric tensor (\mathfrak{g}^2) . This tensor is then diagonalized to provide values for the principal components of (\mathfrak{g}^2) and of (\mathfrak{g}) as well as the orientation of the principal axes relative to the reference axes.

PROCEDURE

Although the spin Hamiltonian (1) is probably not applicable except for the case $S = \frac{1}{2}$, a general derivation for any S can be given and is preferable to a more restricted treatment. If Eq. (1) is rewritten as

$$\mathcal{H} = \beta \mathbf{S} \cdot (\mathfrak{g}\mathbf{H}), \quad \mathcal{H} = \beta \mathbf{S} \cdot \mathbf{H}', \quad (3)$$

* Work supported in part by the Office of Scientific Research, Air Research and Development Command.

† Now at Bell Telephone Laboratories, Murray Hill, New Jersey.

¹ J. E. Geusic and L. Carlton Brown, Bull. Am. Phys. Soc. Ser. II, 3, 8 (1958).

where \mathbf{H}' represents a transformation of \mathbf{H} by \mathfrak{g} , then it follows that the resulting energy levels will be equally spaced for any fixed relative orientation of \mathfrak{g} and \mathbf{H} . Thus, with Z taken along the direction of \mathbf{H}' ,

$$(m - m') h\nu = E_m - E_{m'}, \quad (4)$$

where E_m and $E_{m'}$ are any two levels and $h\nu$ is the spacing between adjacent levels. A reorientation of \mathfrak{g} with respect to \mathbf{H} (rotation of the crystal) will modify the magnitude and direction of \mathbf{H}' and thus change $h\nu$, but will not affect the validity of Eq. (4).

The second moment² of the energy levels about their mean can be calculated from Eq. (4) as follows:

$$\sum_m \sum_{m'} (m - m')^2 (h\nu)^2 = \sum_m \sum_{m'} (E_m - E_{m'})^2,$$

from which

$$\frac{1}{3} S(S+1)(2S+1)(h\nu)^2 = \sum_m E_m^2 = \text{Tr}(\mathcal{H}^2). \quad (5)$$

The trace of \mathcal{H}^2 can be obtained from Eq. (3) by writing

$$\begin{aligned} \text{Tr}(\mathcal{H}^2) &= \text{Tr} \sum_i \beta S_i (\mathfrak{g}\mathbf{H})_i \sum_j \beta S_j (\mathfrak{g}\mathbf{H})_j \\ &= \sum_i \sum_j \beta^2 (\mathfrak{g}\mathbf{H})_i (\mathfrak{g}\mathbf{H})_j \text{Tr}(S_i S_j) \\ &= \frac{1}{3} S(S+1)(2S+1) \beta^2 \sum_i \sum_j (\mathfrak{g}\mathbf{H})_i (\mathfrak{g}\mathbf{H})_j \delta_{ij} \\ &= \frac{1}{3} S(S+1)(2S+1) \beta^2 (\mathfrak{g}\mathbf{H})^2. \end{aligned} \quad (6)$$

The subscripts i and j range over x , y , and z in any arbitrarily oriented system. Finally from Eqs. (5) and (6),

$$\begin{aligned} (h\nu)^2 &= \beta^2 (\mathfrak{g}\mathbf{H})^2 \\ &= \beta^2 \sum_i \sum_j \sum_k g_{ij} H_j g_{ik} H_k \\ &= \beta^2 \sum_j \sum_k (\sum_i g_{ij} g_{ik}) H_j H_k \\ &= \beta^2 \sum_j \sum_k (\mathfrak{g}^2)_{jk} H_j H_k, \end{aligned} \quad (7)$$

where

$$(\mathfrak{g}^2)_{jk} = \sum_i g_{ij} g_{ik} \quad (8)$$

can be represented by a symmetric matrix (\mathfrak{g}^2) which is the square of the symmetric matrix (\mathfrak{g}) .

Alternatively, it can be seen that Eq. (3) implies that

$$h\nu = \beta |(\mathfrak{g}\mathbf{H})|,$$

from which

$$(h\nu)^2 = \beta^2 |(\mathfrak{g}\mathbf{H})|^2. \quad (9)$$

² L. Carlton Brown and Paul M. Parker, Phys. Rev. 100, 1764 (1955); J. Chem. Phys. 27, 1108 (1957).

Equation (9) can then be reinterpreted to obtain

$$(h\nu)^2 = \beta^2 (\mathfrak{g}\mathbf{H})^2,$$

again leading to Eq. (7).

In a practical application some convenient crystal-fixed xyz coordinate system is chosen and the crystal is rotated in the magnetic field about each of the three axes in succession. The effective value of g , defined as

$$g_e = h\nu/\beta H_0, \quad (10)$$

is measured at a number of orientations in each rotation. Consider a rotation about the x axis such that

$$\begin{aligned} H_x &= 0, \\ H_y &= H_0 \cos\phi_x, \\ H_z &= H_0 \sin\phi_x. \end{aligned} \quad (11)$$

For this case Eq. (7) reduces to

$$\begin{aligned} g_e^2 &= (\mathfrak{g}^2)_{yy} \cos^2\phi_x + (\mathfrak{g}^2)_{zz} \sin^2\phi_x \\ &\quad + 2(\mathfrak{g}^2)_{yz} \cos\phi_x \sin\phi_x. \end{aligned} \quad (12)$$

Similarly, for a rotation about y

$$\begin{aligned} g_e^2 &= (\mathfrak{g}^2)_{zz} \cos^2\phi_y + (\mathfrak{g}^2)_{xx} \sin^2\phi_y \\ &\quad + 2(\mathfrak{g}^2)_{zx} \cos\phi_y \sin\phi_y, \end{aligned} \quad (13)$$

and about z

$$\begin{aligned} g_e^2 &= (\mathfrak{g}^2)_{xx} \cos^2\phi_z + (\mathfrak{g}^2)_{yy} \sin^2\phi_z \\ &\quad + 2(\mathfrak{g}^2)_{xy} \cos\phi_z \sin\phi_z. \end{aligned} \quad (14)$$

A Fourier analysis of the measured values of g_e^2 as a function of rotation angle thus provides experimental values for the constants $(\mathfrak{g}^2)_{ij}$ which appear in (12), (13), and (14). The corresponding matrix (\mathfrak{g}^2) can then be diagonalized by the usual methods to obtain the principal components of (\mathfrak{g}^2) . The square roots of these components are the principal components of the tensor (\mathfrak{g}) . Furthermore, the transformation which diagonalizes the experimental (\mathfrak{g}^2) gives the correct relationship between the reference xyz system and the principal coordinate system of (\mathfrak{g}) .

ACKNOWLEDGMENTS

The authors wish to thank Professor Dudley Williams and Professor Jan Korrington for their helpful comments.