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Analysis of Nuclear-Quadrupole-Resonance Spectra in Antiferromagnetic Single Crystals*

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The energy-moment method of Brown and Parker for the analysis of electric-quadrupole magnetic-dipole nuclear-resonance spectra in single crystals is applied to systems in the antiferromagnetic state. A perturbation calculation of the energy shifts produced by an external magnetic field is also given.

I. INTRODUCTION

SEVERAL investigators[1-3] have reported the observation of nuclear-quadrupole resonances in single crystals in the antiferromagnetic state. Analysis of such resonances can yield information complementary to and corroborating that obtained from the study of proton resonances. However, analysis of quadrupolar resonances generally is considerably more complicated than the proton analysis. The energy-moment approach reported by Brown and Parker[4] is a useful tool in the analysis of quadrupolar spectra, and in this communication we wish to discuss the special implications of the energy-moment method with regard to antiferromagnetic resonance. We also present a perturbation calculation which explicitly gives the shifts in the energies produced by an externally applied magnetic field in terms of the parameters of the zero-applied-field problem.

II. THE ENERGY-MOMENT METHOD

The Hamiltonian for the interaction of a nucleus of magnetic-dipole moment $\boldsymbol{\mu}$ and nuclear-quadrupole moment tensor $\mathbf{Q}$ with a magnetic field $\mathbf{H}$ and the crystalline electric-field gradient tensor $\nabla\mathbf{E}$ (in dyadic form) can be written as[5]

$$\mathfrak{H}=-\boldsymbol{\mu}\cdot\mathbf{H}-\tfrac{1}{2}\mathbf{Q}:\nabla\mathbf{E}. \tag{1}$$

In the xyz coordinate system which diagonalizes the field-gradient tensor, $-(\nabla\mathbf{E})_{ij}=\phi_{ij}\delta_{ij}$, and with

$$|\phi_{xx}|\leqslant|\phi_{yy}|\leqslant|\phi_{zz}|, \tag{2}$$

(1) can be written as

$$\mathfrak{H}=-h\nu[(\sin\theta\cos\phi)I_x+(\sin\theta\sin\phi)I_y+(\cos\theta)I_z]/\hbar$$
$$+(hc_3/6)[3I_z^2-I^2+\eta(I_x^2-I_y^2)]/\hbar^2, \tag{3}$$

where I_x, I_y, I_z, and I^2 are angular-momentum operators, where

$$\nu=\mu H/Ih, \tag{4}$$

$$c_3=3eQ\phi_{zz}/2I(2I-1)h=3e^2Qq/2I(2I-1)h, \tag{5}$$

and η is the field-gradient asymmetry parameter

$$\eta=(\phi_{xx}-\phi_{yy})/\phi_{zz}. \tag{6}$$

The angles θ and ϕ are the polar and azimuthal angles, respectively, of $\mathbf{H}$ in the xyz system; I is the nuclear-spin quantum number; ν is the Larmor frequency of $\boldsymbol{\mu}$ in the field $\mathbf{H}$; and c_3 is the frequency interval between pure quadrupole transition frequencies with $\eta=0$. A necessary condition for quadrupole interaction to be present is that $I\geqslant1$.

Let the $(2I+1)$ eigenvalues in units of frequency of the Hamiltonian (3) be equal to F_n, $n=1, 2, 3, \cdots, (2I+1)$. Also, define the moments of energy

$$S_1=\sum_n F_n, \tag{7}$$

$$S_2=\sum_n F_n^2, \tag{8}$$

$$S_3=\sum_n F_n^3. \tag{9}$$

The first moment S_1 is equal to zero for systems whose representations are traceless. For our Hamiltonian (3) this condition is satisfied. The second and third moments, S_2 and S_3, can be regarded as experimentally determinable quantities if sufficient frequency data are available to construct an energy-level diagram subject to $S_1=0$. This is possible if each of the $(2I+1)$ levels is implicated in at least one observed transition, and if such transitions are properly identified. Brown and Parker[4] show that from (3) it follows without approximation that

$$S_2=p_2c_3^2(1+\tfrac{1}{3}\eta^2)+p_1\nu^2 \tag{10}$$

and

$$S_3=p_3c_3^3(1-\eta^2)+3p_2c_3\nu^2(3\cos^2\theta-1+\eta\sin^2\theta\cos2\phi). \tag{11}$$

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[1] R. D. Spence and V. Nagarajan, Phys. Rev. **149**, 191 (1966).

[2] W. J. O'Sullivan, W. W. Simmons, and W. A. Robinson, Phys. Rev. **140**, A1759 (1965).

[3] A. Narath, Phys. Rev. **140**, A552 (1965).

[4] L. C. Brown and P. M. Parker, Phys. Rev. **100**, 1764 (1955).

[5] M. H. Cohen and F. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.

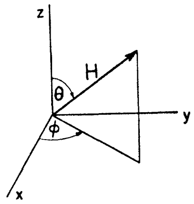

FIG. 1. Orientation of magnetic fields with respect to the principal axes of the crystalline electric field-gradient tensor.

The quantities p_1, p_2, and p_3 are polynomials in I as follows:

$$p_1=2I(I+1)(2I+1)/3!, \tag{12}$$

$$p_2=2I(I+1)(2I-1)(2I+1)(2I+3)/3(5!), \tag{13}$$

$$p_3=2I(I+1)(2I-3)(2I-1) \times(2I+1)(2I+3)(2I+5)/3(7!). \tag{14}$$

The result that S_2 is independent of the orientation of **H** is useful as a check on the frequency assignments, since it may be expected that only under correct assignments will S_2 remain orientation independent. Use of (10) and (11) allows determination of e^2qQ and η, and study of the angular dependence of S_3 allows determination of the principal directions of the field-gradient tensor.

III. APPLICATION TO ANTIFERROMAGNETIC RESONANCE

For single crystals in the antiferromagnetic state, the magnetic field **H** at the site of the nucleus is, in general, the sum of the internal field $\mathbf{H}_i$ and an externally applied field $\mathbf{H}_a$ which typically is much smaller than the internal field. In this section we calculate the change in moments S_2 and S_3 when a constant, uniform, external field $\mathbf{H}_a$ is applied to the crystal. (S_1 remains zero.)

Let the total field be **H** and have direction (θ, ϕ) with respect to the principal directions x, y, and z of the field-gradient tensor, as in Fig. 1. Similarly, let the internal field $\mathbf{H}_i$ have direction (θ_i, ϕ_i), and let the applied field $\mathbf{H}_a$ have direction (θ_a, ϕ_a), again with respect to the principal directions x, y, and z of the field-gradient tensor. Furthermore, let the angle α, $0\leqslant\alpha\leqslant\pi$, be the angle between $\mathbf{H}_i$ and $\mathbf{H}_a$, as in Fig. 2. Also define

$$\nu=\mu H/Ih, \qquad \nu_i=\mu H_i/Ih, \qquad \nu_a=\mu H_a/Ih. \tag{15}$$

From Fig. 2 we have that

$$H^2=H_i^2+H_a^2+2H_iH_a\cos\alpha, \tag{16}$$

and thus, because of (15),

$$\nu^2=\nu_i^2+\nu_a^2+2\nu_i\nu_a\cos\alpha. \tag{17}$$

Now, taking x, y, and z-components of $\mathbf{H}=\mathbf{H}_i+\mathbf{H}_a$ and using (15) gives after some manipulation

$$\nu\cos\theta=\nu_i\cos\theta_i+\nu_a\cos\theta_a, \tag{18}$$

and

$$\nu^2\sin^2\theta\cos2\phi=\nu_i^2\sin^2\theta_i\cos2\phi_i+\nu_a^2\sin^2\theta_a\cos2\phi_a +2\nu_i\nu_a\sin\theta_i\sin\theta_a\cos(\phi_i+\phi_a). \tag{19}$$

Now, let $S_2(t)$ be the value of the second moment S_2 in the presence of the total field $\mathbf{H}=\mathbf{H}_i+\mathbf{H}_a$, and let $S_2(i)$ be the value of S_2 for zero applied field, $\mathbf{H}=\mathbf{H}_i+\mathbf{0}$. Then we find by using (10) and (17) that

$$S_2(t)-S_2(i)=2p_1\nu_i\nu_a\cos\alpha+p_1\nu_a^2. \tag{20}$$

Use of this result readily establishes α, the angle between $\mathbf{H}_i$ and $\mathbf{H}_a$. The second term on the right-hand side will ordinarily be negligible since in most situations $\nu_a\ll\nu_i$. Carrying through a similar procedure for S_3, we find with the aid of (11), (17), (18), and (19) that

$$S_3(t)-S_3(i)=3p_2c_3\{2\nu_i\nu_a[3\cos\theta_i\cos\theta_a-\cos\alpha +\eta\sin\theta_i\sin\theta_a\cos(\phi_i+\phi_a)] +\nu_a^2[3\cos^2\theta_a-1+\eta\sin^2\theta_a\cos2\phi_a]\}, \tag{21}$$

which is the exact result. For $\nu_a\ll\nu_i$, the term quadratic in ν_a may be neglected. Study of the angular dependence of (21) allows determination of the direction of the internal field relative to the field-gradient tensor, and determination of the field-gradient tensor relative to the crystal.

IV. TEMPERATURE DEPENDENCE IN ZERO APPLIED FIELD

Variation of the temperature of the crystal below the Néel point results in a change of the internal field $\mathbf{H}_i$. This phenomenon can be made the basis for another way of using the moment Eqs. (10) and (11).

For $\mathbf{H}_a=0$, let us denote the ratio of the magnitudes of the internal field at two temperatures T' and T by r,

$$r=H_i(T')/H_i(T). \tag{22}$$

Then also

$$\nu_i(T')/\nu_i(T)=r. \tag{23}$$

By using (10) to write down the second moment $S_2(i)$ in the absence of an applied field at the two tempera-

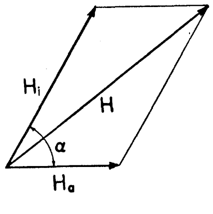

FIG. 2. The total magnetic field H as the sum of the internal field H_i and the externally applied field H_a.

tures, we obtain

$$\nu_i^2(T)=[S_2(i,\,T')-S_2(i,\,T)]/p_1(r^2-1),\quad(24)$$

and

$$c_3^2(1+\tfrac{1}{3}\eta^2)=[r^2S_2(i,\,T)-S_2(i,\,T')]/p_2(r^2-1),\quad(25)$$

where it has been assumed that η and c_3 are temperature-independent in the temperature range considered, and that the direction of the internal field at the site of the nucleus also remains unaffected by the temperature change.

Proceeding in a similar manner with (11), one secures

$$c_3^3(1-\eta^2)=[r^2S_3(i,\,T)-S_3(i,\,T')]/p_3(r^2-1),\quad(26)$$

which, however, cannot be used when $I=\frac{3}{2}$, since in that case $p_3=0$. For $I\neq\frac{3}{2}$, (25) and (26) can be used to give c_3 and η, and (24) gives ν_i as a function of temperature. The ratio r may be obtained by measuring the ratio of internal fields at the proton sites.[1] Equations (24) and (25) have recently been used in our laboratory to good advantage in the analysis of the chlorine resonance in $MnCl_2\cdot 4H_2O$.

V. ENERGY SHIFTS INDUCED BY EXTERNAL FIELD

We now derive an expression for the energy shifts ΔF_n, $n=1,\,2,\,3,\,\cdots,\,(2I+1)$, produced by the application of the external field $\mathbf{H}_a$. The energy eigenvalues of the system in the absence of the external field F_n are here regarded as known quantities. We start with (3) in a representation for which

$$I^2\,|\,m\rangle=I(I+1)\hbar^2\,|\,m\rangle,\quad(27)$$

$$I_z\,|\,m\rangle=m\hbar\,|\,m\rangle,\quad(28)$$

with $m=I,\,I-1,\,\cdots,\,-I$. The eigenvectors $|\,n\rangle$ of (3) for $\mathbf{H}=\mathbf{H}_i$ are expressible as linear combinations of $|\,m\rangle$,

$$|\,n\rangle=N_n^{-1}\sum_m A_n^{(m)}\,|\,m\rangle\quad(29)$$

with the coefficients $A_n^{(m)}$ determined from the diagonalization procedure, and with N_n chosen such that $|\,n\rangle$ is normalized.

Application of an external field gives rise to an additional term in the Hamiltonian which, in units of frequency, is

$$-\boldsymbol{\mu}\cdot\mathbf{H}_a$$
$$=-\nu_a[(\sin\theta_a\,\cos\phi_a)I_x+(\sin\theta_a\,\sin\phi_a)I_y+(\cos\theta_a)I_z]/\hbar.\quad(30)$$

In first order, the energy shifts produced by this term are given by the diagonal matrix elements of the perturbation in the eigenvectors of the unperturbed problem:

$$\Delta F_n=\langle n\,|\,-\boldsymbol{\mu}\cdot\mathbf{H}_a\,|\,n\rangle.\quad(31)$$

Introducing $I_\pm=I_x\pm iI_y$, and using (29) gives

$$\Delta F_n=-(\nu_a/\hbar\,|\,N_n\,|^2)\Big(\sin\theta_a\sum_m\sum_{m'}\tfrac{1}{2}A_n^{(m')*}A_n^{(m)}$$
$$\times\langle m'\,|\,I_+\exp(-i\phi_a)+I_-\exp(i\phi)\,|\,m\rangle$$
$$+\cos\theta_a\sum_m\sum_{m'}A_n^{(m')*}A_n^{(m)}\langle m'\,|\,I_z\,|\,m\rangle\Big).\quad(32)$$

For the matrix elements of $I_\pm$ and I_z, we have[6]

$$\langle m'\,|\,I_\pm\,|\,m\rangle=\hbar(I\mp m)^{1/2}(I\pm m+1)^{1/2}\delta_{m',m\pm1},\quad(33)$$

$$\langle m'\,|\,I_z\,|\,m\rangle=\hbar m\delta_{mm'}.\quad(34)$$

Introducing these into (32) we find that

$$\Delta F_n=-\nu_a(B_n\,\sin\theta_a+C_n\,\cos\theta_a)/\,|\,N_n\,|^2,\quad(35)$$

where

$$B_n=\tfrac{1}{2}\sum_m[A_n^{(m+1)*}A_n^{(m)}(I-m)^{1/2}(I+m+1)^{1/2}$$
$$\times\exp(-i\phi_a)+A_n^{(m-1)*}A_n^{(m)}(I+m)^{1/2}(I-m+1)^{1/2}$$
$$\times\exp(i\phi_a)],\quad(36)$$

$$C_n=\sum_m m\,|\,A_n^{(m)}\,|^2,\quad(37)$$

$$|\,N_n\,|^2=\sum_m|\,A_n^{(m)}\,|^2.\quad(38)$$

The coefficients $A_n^{(m)}$ are independent of the magnitude or polar direction of the applied field. Therefore (35) shows that for given azimuth ϕ_a, the energy shifts ΔF_n depend on θ_a sinusoidally, a fact which is well known from experiment.

VI. ENERGY SHIFTS FOR $I=1$

For $I=1$ we find that

$$B_n=[A_n^{(0)*}A_n^{(1)}+A_n^{(-1)*}A_n^{(0)}]\exp(i\phi_a)/\sqrt{2}$$
$$+\text{complex conjugate},\quad(39)$$

$$C_n=|\,A_n^{(1)}\,|^2-|\,A_n^{(-1)}\,|^2,\quad(40)$$

$$|\,N_n\,|^2=|\,A_n^{(1)}\,|^2+|\,A_n^{(0)}\,|^2+|\,A_n^{(-1)}\,|^2,\qquad n=1,\,2,\,3.\quad(41)$$

The coefficients $A_n^{(m)}$, $n=1,\,2,\,3$; $m=1,\,0,\,-1$, are found as the cofactors of any given row of the secular determinant after substitution of the nth unperturbed eigenvalue F_n, according to standard procedure. Taking the second row for this purpose (since it leads to

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[6] J. L. Powell and B. Crasemann, *Quantum Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1961).

somewhat more symmetrical expressions), we determine that

$$A_n^{(1)} = -(\nu_i \sin\theta_i/\sqrt{2})\begin{bmatrix} e^{-i\phi_i} & \eta c_3/6 \\ e^{i\phi_i} & \nu_i \cos\theta_i + c_3/6 - F_n \end{bmatrix}, \tag{42}$$

$$A_n^{(-1)} = -(\nu_i \sin\theta_i/\sqrt{2})\begin{bmatrix} -\nu_i \cos\theta_i + c_3/6 - F_n & e^{-i\phi_i} \\ \eta c_3/6 & e^{i\phi_i} \end{bmatrix}, \tag{43}$$

$$-A_n^{(0)} = \begin{bmatrix} -\nu_i \cos\theta_i + c_3/6 - F_n & \eta c_3/6 \\ \eta c_3/6 & \nu_i \cos\theta_i + c_3/6 - F_n \end{bmatrix}. \tag{44}$$

Now we let

$$q_3 = c_3/6\nu_i, \tag{45}$$

and define the dimensionless quantity

$$W_n = (F_n/\nu_i) - q_3. \tag{46}$$

With these we calculate that

$$B_n = 2\sin\theta_i\{(W_n \cos^2\theta_i - W_n^3)\cos(\phi_a - \phi_i) + [\eta^3 q_3^3 \cos(\phi_a + \phi_i) + \eta^2 q_3^2 W_n \cos(\phi_a - \phi_i) + \eta q_3(\cos^2\theta_i - W_n^2)\cos(\phi_a + \phi_i)]\}, \tag{47}$$

$$C_n = -2\sin^2\theta_i \cos\theta_i (W_n + \eta q_3 \cos 2\phi_i), \tag{48}$$

$$|N_n|^2 = [W_n^4 - (3\cos^2\theta_i - 1)W_n^2 + \cos^2\theta_i] + [\eta^4 q_3^4 + \eta^2 q_3^2(\cos^2\theta_i + 1 - 2W_n^2) + \eta q_3(2W_n \sin^2\theta_i \cos 2\phi_i)]. \tag{49}$$

A factor of ν_i^4 common to B_n, C_n, and $|N_n|^2$ is omitted since it would just cancel out in (35).

For spins $I > 1$, corresponding expressions for B_n, C_n, and $|N_n|^2$ can be developed. These are, however, quite cumbersome, and in these cases it is preferable to proceed numerically. Presupposing satisfactory analysis of the zero-order problem, the coefficients B_n, C_n, and $|N_n|^2$ can then be found numerically for given ϕ_a for any spin.