Nuclear quadrupole coupling of 115In in NH 4 In (SO 4) 2 · 12 H 2 O

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factor of Eq. (1) is expanded as:

$$(3 \cos^2\psi_{ij} - 1) = 2P_2(\cos\psi_{ij})$$
$$= \tfrac{8}{5}\pi \sum_{m=-2}^{+2} y_2^{m*}(\theta, \phi) \cdot y_2^m(\theta_{ij}, \phi_{ij}), \quad (2)$$

where θ, ϕ and θ_{ij}, ϕ_{ij} are, respectively, the polar angles of the magnetic field and interprotonic vectors in an arbitrary coordinates system fixed with respect to the crystal and:

$$\left\langle \frac{3 \cos^2\psi_{ij} - 1}{r_{ij}^3} \right\rangle_m^2 = (\tfrac{8}{5}\pi)^2$$
$$\times \left| \sum_{m=-2}^{2} y_2^{m*}(\theta, \phi) \cdot \left\langle \frac{y_2^m(\theta_{ij} \cdot \phi_{ij})}{r_{ij}^3} \right\rangle_m \right|^2. \quad (3)$$

For a powder specimen, the orientation of the magnetic field with respect to the individual monocrystal is random and the second moment is found by averaging $y_2^m(\theta, \phi)$ over the various values of θ and ϕ. From the orthogonality properties of spherical harmonics, Eq. (3) is reduced to a sum of squared terms:

$$\langle \langle 3 \cos^2\psi_{ij} - 1/r_{ij}^3 \rangle_m^2 \rangle_p = \tfrac{1}{5}[\langle 3 \cos^2\theta_{ij} - 1/r_{ij}^3 \rangle_m^2$$
$$+ 12 \, |\langle \sin\theta_{ij} \cos\theta_{ij} \exp(i\phi_{ij})/r_{ij}^3 \rangle_m|^2$$
$$+ 3 \, |\langle \sin^2\theta_{ij} \exp(2i\phi_{ij})/r_{ij}^3 \rangle_m|^2] \quad (4)$$

and

$$S_{2m,p} = \frac{K}{N} \sum_i^N \sum_j \tfrac{1}{5}(A^2 + 12B^2 + 3C^2). \quad (5)$$

Equation (5) provides a general and easy way to calculate the second moment reduction factors. $F = S_{mp}/S_p$. Two simple cases will be presented here.

The intrapair contribution to the second moment for a solid in which the nuclear pairs take one orientation characterized by the polar angles $\theta = 0$ and $\phi = 0$ with a probability p and another orientation characterized by $\theta = \gamma$ and $\phi = 0$ with a probability $(1-p)$ can be easily calculated. In this case the average values appearing in Eq. (5) are simply the weighted mean values between two equilibrium positions:

$$S_{m,p} = (K/5r^6)\{[p(3 \cos^2\gamma - 1) + (1-p)^2]^2$$
$$+ 12(p \sin\gamma \cos\gamma)^2 + 3(p \sin^2\gamma)^2\} \quad (6)$$

which shows a reduction factor

$$F = S_{m,p}/S_p = 1 - 3p(1-p) \sin^2\gamma. \quad (7)$$

S_p being here the second moment for a rigid lattice: $K(4/5)r^{-6}$. The limited case of $p = 1/2$ has already been discussed by Andrew[3] in his study on solid cyclobutane.

The intrapair contribution to the second moment for a solid in which proton pairs are rotating freely about a reference z axis is given by

$$S_{m,p} = \frac{K}{N} \frac{1}{5} \sum_i^N \left[\left(\frac{3 \cos^2\theta_i - 1}{r_i^3} \right)^2 + 12 \frac{\sin^2\theta_i \cos^2\theta_i}{r_i^3} \right.$$
$$\left. \times \langle \exp(i\phi_i) \rangle_\phi^2 + 3 \frac{\sin^4\theta_i}{r_i^3} \langle \exp(2i\phi_i) \rangle_\phi^2 \right], \quad (8)$$

where the summation $\sum_i$ is extended over the non-equivalent proton pairs in the unit cell and where $\langle \ \rangle_\phi$ denotes the average value over ϕ_i, which varies continuously from 0 to 2π, θ_i having here a constant value and being the angle between the axis of rotation and r_i. In order to conform to general usage we denote this angle by γ_i. Compared to the rigid lattice second moment given by $S_p = (4/5)(1/N)\sum_i r_i^{-6}$ this expression shows a reduction factor:

$$F = S_{m,p}/S_p = \tfrac{1}{5} \sum_i (3 \cos^2\gamma_i - 1)^2 r_i^{-6}/\tfrac{4}{5} \sum_i r_i^{-6}, \quad (9)$$

which reduces to $F = (1/4)(3 \cos^2\gamma - 1)^2$ when all γ_i are equal. For the special case in which the rotational axis is perpendicular to all internuclear vectors Eq. (9) gives the well known[1] reduction factor $F = 1/4$.

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Nuclear quadrupole coupling of ^{115}In in NH$_4$In(SO$_4$)$_2$ · 12H$_2$O

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The temperature dependence of the nuclear quadrupole coupling constant eqQ/h, has been measured by nuclear magnetic resonance (NMR) techniques for ^{115}In in ammonium indium alum, NH$_4$In(SO$_4$)$_2$·12H$_2$O.

Current interest in this and in other alum compounds lies in the fact that a number of them, particularly when the monovalent ion is NH$_4$ or CH$_3$NH$_3$, are ferroelectric at low temperatures. Their ferroelectric prop-
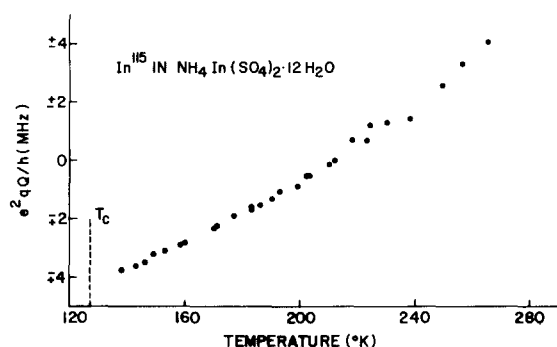
FIG. 1. Temperature dependence of eqQ/h for ^{115}In in $NH_4In(SO_4)_2 \cdot 12H_2O$.

erties have been investigated by Pepinsky and co-workers.[1,2] Ammonium indium alum undergoes a ferroelectric phase transition at $T_c = 127°K$. Attempts to obtain NMR spectra at temperatures below the transition proved fruitless.

A single crystal of ammonium indium alum was obtained from Isomet Corporation. The experimental spectra were collected at "low" temperatures because of a tendency of this particular alum toward decomposition at room temperatures. The splitting of the ^{115}In ($I = 9/2$) NMR line by quadrupolar interaction was measured as a function of crystal orientation and temperature. The specimen was mounted with a (110) direction parallel with the axis of rotation and perpendicular to the static magnetic field H. As a function of orientation ($T = 220°K$) the splitting is proportional to $3\cos^2\theta - 1$, where θ is the angle H makes with a (111) crystal direction. Thus the electric field gradient tensor is axially symmetric with its z-principal axis along a (111) crystal direction. This result is expected from the crystallography[3] and from similar measurements made by Burns[4] for ^{27}Al in a number of alum compounds. In order to measure eqQ/h as a function of temperature, a crystal orientation was chosen so that H was directed

along a (110) crystal direction. At this orientation the resonance spectrum consists of nine components: a central transition flanked on either side by four satellite transitions. The eqQ/h were determined from the measured splittings of the lines. The result is shown in Fig. 1. As can be seen, eqQ/h varies nearly linearly from ±4.1 MHz at 265°K to ±3.8 MHz at 138°K, passing through zero near 213°K. Although observed in other compounds,[5] it is unusual for the alums for eqQ/h to change algebraic sign. Of course the sign was not determined, and thus the symbols $\pm$ and $\mp$ are used in the figure. In other respects the behavior of eqQ/h with temperature is similar to the ^{27}Al results.[4]

A pronounced broadening of the ^{115}In resonance lines occurs on approaching T_c, but no attempt was made to study this effect quantitatively because of difficulties arising from rapid decrease in line intensity. In fact, near T_c the resonance lines could no longer be detected. Qualitatively, this behavior is similar to that observed for the EPR lines for several Cr^{3+} doped alums, including ammonium indium and ammonium aluminum alums, which O'Reilly and Tung Tsang[6] attribute to fluctuations in the fine-structure tensor due to reorientation of the NH_4 ions. It was decided, therefore, to investigate the ^{14}N quadrupolar interaction in the aluminum alum, the results of which will be reported in a later paper.

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Vibrational relaxation of carbon monoxide by helium*

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With the improvement of experimental techniques,[1] which permitted relaxation measurements to increasingly lower temperatures, it became apparent that the Landau–Teller relation,[2] which postulated an exponential behavior of the p_T vs $T^{-1/3}$ function, is not always valid. Vibrational transition probabilities showed a decreasing temperature dependence[3] toward lower

temperatures, and in some instances negative temperature dependence was observed.[4] This phenomena was attributed to the attractive contribution of the interaction potential, which becomes dominant as the relative kinetic energy of the collision decreases.

Theoretical calculations by means of the SSH model[5] fail to take account of the effect of this attraction,