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Measurement of Nuclear Magnetic Resonance with Quadrupolar and Dipolar Broadening in Polycrystalline Samples*

J. E. Adams,† B. F Williams,‡ and R. R. Hewitt
University of California, Riverside, California

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The maxima for NMR lines in the presence of quadrupolar broadening in polycrystalline samples are shown to be shifted by the addition of dipolar broadening σ. A quantitative determination of this shift is given for a wide range of σ.

I. INTRODUCTION

RECENT nuclear-magnetic-resonance (NMR) studies in indium[1] and bismuth[2] have indicated the feasibility of measuring the isotropic Knight shift k, the anisotropic Knight shift a and the quadrupolar coupling parameter ν_Q in high-spin, broad-line systems in metal powders. The analysis of the spectrum, given by Jones *et al.*,[3] involves an averaging technique over a magnetic field range to obtain single values for k, a, and ν_Q appropriate to that field range. A detailed analysis of the power-absorption line shape is also given in Ref. 3.

It is possible, by the use of expressions developed in Ref. 3 to determine k, a, and ν_Q at a single field point and, therefore, to investigate the field dependence of these parameters. The technique involves measuring three different transitions at a fixed field and applying iterative methods to the resulting three nonlinear nonhomogeneous simultaneous equations. To accomplish this it is necessary to identify that point on the experimental dipole-broadened derivative trace which corresponds to the original singularity in the unbroadened theoretical expressions in Ref. 3. A study[4] of line shapes in the indium spectrum has revealed that the shape of the line depended on the m value of the transition. Typical experimental curves for the $\frac{1}{2}\leftrightarrow\frac{1}{2}$ and the $\frac{3}{2}\leftrightarrow\frac{1}{2}$ transitions are shown in Fig. 1 and a question of line measurement arises. Neither of these resonances has the theoretically predicted Gaussian-broadened shape[5] although the variance is not large. An empirical method for measurement was developed by Williams[6] and applied to the indium and bismuth spectra. In indium the linewidths are typically 30 kc/sec and the resulting errors change the value of k by 0.02% and shift the value of ν_Q by 6 kc/sec. However, in the complicated and very broad lines of the bismuth spectrum, where the linewidths are 200 G and with correspondingly larger errors in k, a, and ν_Q, there is an actual ambiguity in the line identification without the shift correction. The indium line identification is much easier than that in bismuth because the value of ν_Q has been determined by pure nuclear quadrupolar techniques.[7] The bismuth spectrum has the additional problem of line crossing as a function of magnetic field.[8] We feel that closer attention must be given to line measurement and have developed a quantitative expression for the case of Gaussian-broadened powder samples with large quadrupolar interactions.

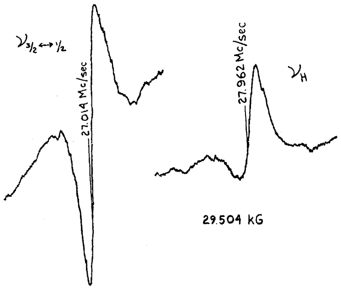

FIG. 1. Resonances in indium metal powder at 4.2°K.

Considerable work in line-shape analysis has been done for various combinations of ν_Q, a, and line width σ. A spin-$\frac{1}{2}$ system is treated by Borsa and Barnes[9] that is complicated by the fact that the broadening function, in β tin, cannot be represented as either pure Gaussian or pure Lorentzian. In the case of indium the dipolar broadened line is 30 G wide and is well represented by Gaussian broadening. Furthermore, in indium the anisotropic Knight shift is very small and the shape of the spectrum is dominated by quadrupole effects.

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† National Science Foundation Graduate Fellow.

‡ Present address: David Sarnoff Research Center, Princeton, New Jersey.

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II. CALCULATION OF THE LINE SHAPE

As has been extensively discussed in the literature,[10] the presence of a quadrupolar interaction introduces a splitting of the normally 2I-fold–degenerate absorption line. Each of these lines is asymmetrically broadened as a result of averaging over angle as required in a powder. This broadening is proportional to the quadrupolar interaction and the m value of the transition. In some cases this effect can broaden the NMR line by several Mc/sec. Following Ref. 3 the resonance frequency of a single crystal whose crystalline axis of symmetry makes an angle θ with the external magnetic field is given by

$$\nu=A+B\mu^2+C\mu^4, \tag{1}$$

where

$$\mu\equiv\cos\theta$$

$$\nu_q\equiv 3eqQ/2I(2I-1)h,$$

and

$$\begin{aligned}A\equiv{}&(1+k-a)\nu_0-(m-\tfrac{1}{2})\nu_q\\&-(\nu_q{}^2/32\nu_0)[6m(m-1)-2I(I+1)+3],\\B\equiv{}&3\nu_0a+\tfrac{3}{2}\nu_q(m-\tfrac{1}{2})\\&+(\nu_q{}^2/32\nu_0)[108m(m-1)-20I(I+1)+42],\\C\equiv{}&(\nu_q{}^2/32\nu_0)[102m(m-1)-18I(I+1)+39].\end{aligned}$$

The power-absorption function is accordingly

$$P(\nu)=\tfrac{1}{2}|d\mu/d\nu|^{-1}, \tag{2}$$

so

$$P(\nu)=\left[8A\left\{\frac{-B\pm[B^2-4A(c-\nu)]^{1/2}}{2A}\right\}^{3/2}+4B\left\{\frac{-B\pm[B^2-4A(c-\nu)]^{1/2}}{2A}\right\}^{1/2}\right]^{-1}. \tag{3}$$

Equation (3) is correct through second-order perturbation terms. The shape of the power absorption is a function of k, a and ν_Q. A typical curve is shown in Fig. 2. In the region of the 90° singularity the curve is well represented by

$$P(\nu)=\tfrac{1}{2}[B(\nu-c)]^{-1/2}. \tag{4}$$

The effects of Lorentzian broadening on (3) have been determined exactly.[11] In this paper we give the results of a numerical calculation of Gaussian broadening on (3). A typical result is shown in Fig. 3. The position of the original singularity must be extracted from this broadened curve. We emphasize that the peak in (3) is shifted away from the discontinuity and a quantitative determination of the magnitude of this shift is necessary for an accurate evaluation of k, a and ν_Q. In this paper we extend the work of Hughes and Rowland[5] to include the treatment of large quadrupolar interaction and to develop an expression for the position of the singularity as a function of measurable properties of the experimental curve. The broadened power-absorption function is given by

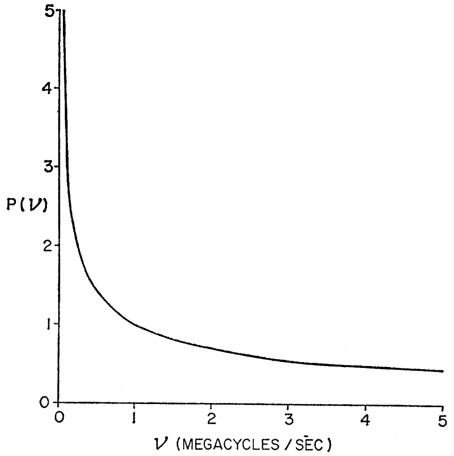

FIG. 2. An unbroadened power absorption function.

$$P(\nu)=\int_0^{5\sigma}\frac{e^{-[(x-\nu)/\sigma]^2}dx}{(Bx)^{1/2}}. \tag{5}$$

The integration is truncated at 5σ to conserve machine time. It was empirically determined that integration beyond this limit had a negligible effect on the results. In the case under consideration σ is small compared to the quadrupolar width of the line and we are interested in $p(\nu)$ only around $\nu=c$. (3) is of a form such that changing σ does not qualitatively affect the shape of (4). The broadened absorption curve is shown in Fig. 4 for two characteristic values of σ. We have shown the derivatives of the absorption curves in Fig. 4 since this is the form in which the data appear. The calculation indicates that the ratio of the extrema, A/B in Fig. 4, is independent of σ and that $A/B=0.46$. The distance D from the singularity to the higher intensity

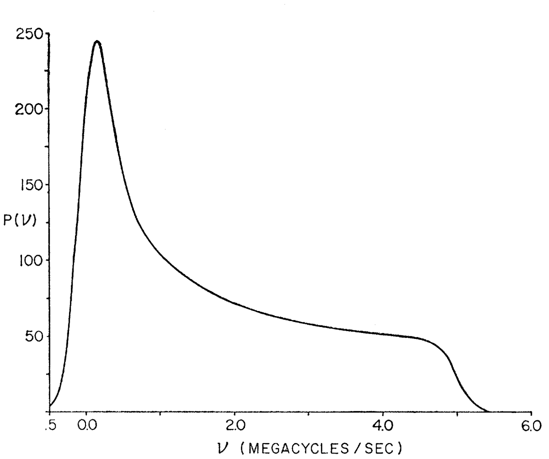

FIG. 3. A Gaussian-broadened power absorption function.

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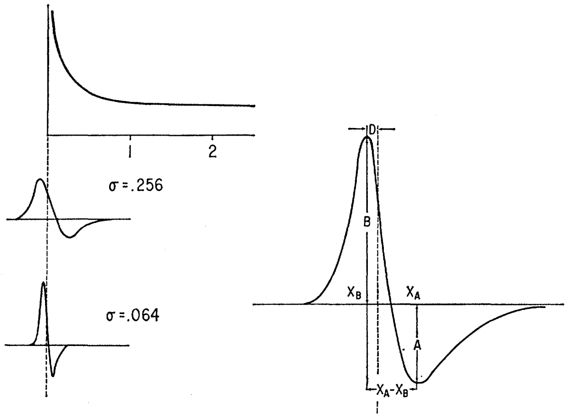

FIG. 4. The effects of Gaussian broadening on the derivative trace for two values of σ.

maximum is given by

$$D=0.241(X_A-X_B). \qquad (6)$$

The position of the singularity as given by (6) is independent of σ. This calculation was done for ten values of σ between 0.0005 and 0.250 Mc/sec and is the same for all a and σ where $\sigma \ll \nu_Q$. This also provides a convenient method for determining σ. For all σ it was found that the distance between the two maxima is given by $\sigma=0.61(X_A-X_B)$. An example is shown in Fig. 5 using $\frac{1}{2}\leftrightarrow\frac{1}{2}$ transition in indium. The correct place to measure the line is identified as C in Fig. 5. If the resonance were measured at the peak an error of 12 kc/sec would result. Another example, shown in Fig. 6, is taken from the $\frac{3}{2}\leftrightarrow\frac{1}{2}$ transition in the bismuth spectrum. The bismuth experiment, Ref. 2, was done at fixed frequency. In this case a measurement at the peak would result in an error of 70 G.

III. DISCUSSION

Equation (6) describes the correct position to measure the resonance when the broadening can be represented by a Gaussian function. There are at least two mechanisms which lead to non-Gaussian broadening. Based on dc conductivity measurements[12] in bulk samples, the classical skin depth of 99.999% indium at 4.2°K and 20 Mc/sec is 0.4 μ. The 2-μ diameter of the particles places an upper limit on the mean free path, and consequently we are not in the anomalous-skin-effect region. The lattice constant in indium is around 3 Å and we calculate that 70% of the nuclei participating in the resonance are located within a distance of 1000 atoms from the surface. Because the quadrupole term is so large compared to the dipolar broadening small changes in the electric field gradient will play as large a role as dipole-dipole effects in line shape determination. For example, a 1% shift in the electric field gradient at the site of a particular nuclei will shift its resonant frequency by 20 kc/sec an amount typical of dipole effects. Although the behavior of the electric-field gradient near the surface of small particles is not known, it is certainly different from the bulk value. Furthermore, a large percentage of the nuclei involved in the resonance are located at noncharacteristic sites in the sample and we do expect an effect on line shape. There is experimental evidence that this is the case from the pure nuclear quadrupole measurement in indium.[13] Here an asymmetry is observed in line shape which increases with increasing m value and vanishes at room temperature. Both of these facts are consistent with surface phenomena. Further investigations in this direction involve a study of the effect on line shapes as sample size is changed.

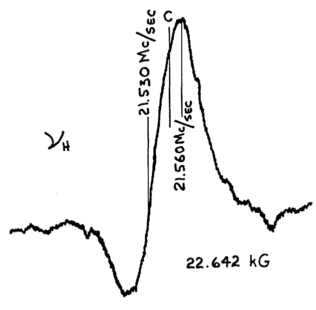

FIG. 5. An example of the measurement problem from the indium spectrum. The line should be measured at c.

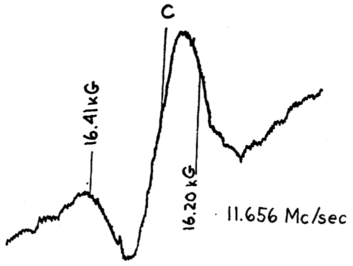

FIG. 6. An example of the measurement problem from the bismuth spectrum. The line should be measured at c.

The second effect involves quantum oscillations in the electronic susceptibility. Recently de Haas–van Alpen oscillations have been observed[14] in the Knight shift in a single crystal of tin. These oscillations are of the order of 5% of the Knight shift and if similar strength oscillations exist in indium a local variance of 4G would result. The mechanism for establishing the basis of different magnetic fields at different sites is just the static dipolar broadening. This is sufficiently large in indium to span about one-half quantum oscillation as these oscillations in indium in the 20-k G region have a period of around 50 G.[15] These effects are small unless the coupling between oscillations in the electronic system and the Knight shift is larger in indium than in tin in which case the effects would be apparent in line shape. A quantitative evaluation can be accomplished by treating the de Haas–van Alphen function as a modulating function on the power-absorption function given by Eq. (5).

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