Knight shifts and linewidths in antimony*

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Nuclear quadrupole resonance by nuclear induction was performed at room temperature on annealed 25-μm antimony powder. A static magnetic field of about 360 G was applied and four transitions were observed, corresponding to the two stable isotopes of antimony and the two ($1/2 \leftrightarrow 3/2$) transitions of the quadrupole regime which have singularities in their powder pattern spectra. A theory and method was derived to analyze these data, giving the final values for the isotropic and anisotropic Knight shifts of $(1.8 \pm 0.3)\%$ and $(-2.6 \pm 0.5)\%$, respectively. The half-intensity linewidths were measured as 22.7 ± 1.8 kHz and 12.5 ± 1.2 kHz for ^{121}Sb and ^{123}Sb, respectively. Finally, the likelihood of Van Vleck orbital paramagnetism being the dominant contributor to the Knight shifts is discussed with a theoretical order-of-magnitude estimate yielding 1.9% for the isotropic Knight shift. The linewidths are interpreted as being magnetic in origin.

I. INTRODUCTION

Solid antimony is a semimetal composed of two stable isotopes, ^{121}Sb and ^{123}Sb, of roughly equal amounts, 57.25% ^{121}Sb and 42.75% ^{123}Sb.[1] The nuclear spins of ^{121}Sb and ^{123}Sb are $\frac{5}{2}$ and $\frac{7}{2}$, with nuclear electric quadrupole moments[2] of $(-0.69 \pm 0.3) \times 10^{-24}$ and $(-0.68 \pm 0.10) \times 10^{-24}$ cm^2. The corresponding nuclear magnetic moments are 3.3415 and 2.5334 nuclear magnetons.[3]

The crystalline structure is rhombohedral and of the arsenic A_7 group.[4] Electric field gradients are present in the crystal with threefold rotation symmetry along the [111] direction, and the electric field gradient is along this principal axis.

The nuclear quadrupole resonance (NQR) was first performed on antimony by Hewitt and Williams using Zeeman modulation by pure quadrupole resonance.[5] They reported the quadrupole interaction e^2qQ of both isotopes over a range of temperatures; at 4.2 °K they were $e^2qQ = 76.867 \pm 0.001$ MHz (^{121}Sb) and $e^2qQ = 97.999 \pm 0.001$ MHz (^{123}Sb). The corresponding intrinsic linewidths were 30.1 ± 0.4 z and 19.6 ± 0.7 kHz at 4.2 °K. The measurements reported here are at room temperature (300 °K).

Hygh and Das estimated the isotropic and anisotropic Knight shifts as 0.07% and −0.05%, respectively, including spin-orbital interactions.[6] However, they indicated that Van Vleck orbital paramagnetism could yield an order-of-magnitude increase in these effects.

Our efforts to measure the Knight shifts in antimony have been complicated by the quadrupole interaction being much greater than the nuclear magnetic interaction so that the resonance is still in the quadrupole regime, even for static magnetic fields of 20 kG.

The method used was nuclear quadrupole resonance by nuclear induction and applying small magnetic fields as a perturbation.[7,8] The technique is similar to that used by Itoh and Kusaka and by Segel and Barnes[9] for observing magnetic shifts that are relatively independent of the quadrupole interaction on the $m = (-\frac{1}{2} \leftrightarrow \frac{1}{2})$ transitions. Here the Knight shifts were obtained by observing the $(\frac{1}{2} \leftrightarrow \frac{3}{2})$ transitions. The resultant Larmor perturbation was $\frac{1}{30}$th the size of the quadrupole interaction.

Since these measurements were done on a powder of random crystallite orientation, the analysis has been done for a powder-pattern average of all angles between the principal [111] axis and the applied magnetic field.

II. THEORY

The eigenvectors were calculated to second order and the eigenvalues calculated to third order in magnetic interaction ν_L using degenerate perturbation theory.[10] These functions were labeled by the component of nuclear spin along the principal axis m, so that the perturbed wave functions would reduce to their corresponding degenerate spin-state solutions for a zero static magnetic field. Since the $m = \pm\frac{1}{2}$ states were mixed by the Larmor perturbation, the added criteria that the $m = \pm\frac{1}{2}$ zero-order states reduce to their degenerate solutions $|I, \pm\frac{1}{2}\rangle$ for a magnetic field parallel to the principal axis was necessary.[11] The isotropic and anisotropic Knight shifts were derived to first order in energy level only.

This yields four transition frequencies corresponding to the $m = (\frac{1}{2} \leftrightarrow \frac{3}{2})$ transitions. The results are, for general nuclear spin I,

$$\nu_{I,\pm\pm} \equiv \nu(I, m = \pm\tfrac{1}{2} \leftrightarrow \pm\tfrac{3}{2}) = \nu_{Q,I} \mp \tfrac{1}{2}\,\nu_{L,I}(1 + K_{\rm iso} + 2K_{\rm aniso})\cos\theta[3 - f_I(\theta)] \mp \tfrac{3}{2}\,\nu_{L,I} K_{\rm aniso}\tan^2\theta\,\frac{\cos\theta}{f_I(\theta)}(I+\tfrac{1}{2})^2$$
$$+\frac{3\nu_{K,I}^2}{8\nu_{Q,I}}\sin^2\theta(I^2+I+\tfrac{1}{4}) \pm \frac{\nu_{K}^3{}_{,I}}{32\nu_{Q}^2{}_{,I}}\sin^2\theta\cos\theta[15(I^2+I-1.35) - 4(I^2+I-0.75)f_I(\theta)] \quad (1)$$

and

$$\nu_{I,\pm\mp} \equiv \nu(I, m = \pm\tfrac{1}{2} \leftrightarrow \mp\tfrac{3}{2}) = \nu_{Q,I} \pm \tfrac{1}{2}\,\nu_{L,I}(1 + K_{\rm iso} + 2K_{\rm aniso})\cos\theta[3 + f_I(\theta)] \mp \tfrac{3}{2}\,\nu_{L,I} K_{\rm aniso}\tan^2\theta\,\frac{\cos\theta}{f_I(\theta)}(I+\tfrac{1}{2})^2$$
$$+\frac{3\nu_{K}^2{}_{,I}}{8\nu_{Q,I}}\sin^2\theta(I^2+I+\tfrac{1}{4}) \mp \frac{\nu_{K}^3{}_{,I}}{32\nu_{Q,I}^2}\sin^2\theta\cos\theta[15(I^2+I-1.35) + 4(I^2+I-0.75)f_I(\theta)], \quad (2)$$

where $\nu_{Q,I} = 3e^2qQ/2I(2I-1)$; θ is the angle between the principal coordinate and the external static magnetic field H; $\nu_{L,I} = (\gamma_n/2\pi)\,H$; $K_{\rm iso}$ and $K_{\rm aniso}$ are the isotropic and anisotropic Knight shifts, respectively; $\nu_{K,I} = (1+K_{\rm iso})\,\nu_{L,I}$; and $f_I(\theta) = [1 + (I+\frac{1}{2})^2\tan^2\theta]^{1/2}$.

Singularities in the powder-pattern powder distribution occur whenever $d\nu/d(\cos\theta) = 0$.[12] It can be shown that $d\nu_{I,\pm\pm}/d(\cos\theta) \neq 0$ for $\nu_{L,I} \neq 0$, so that these transitions are flattened out by the magnetic field and were never observed (see Sec. III). The $\nu_{I\pm\mp}$ lines, however, do have such singularities, which to first order in $\nu_{L,I}$ are given by[13]

$$\cos\theta_s = \frac{(2I+1)}{[(2I-1)(2I+3)]^{1/2}} \times \left(1 + \frac{(2I-1)(2I+3)}{36}\right)^{-1/2}. \quad (3)$$

For ^{121}Sb, $\cos\theta_s = 0.7717$, and for ^{123}Sb, $\cos\theta_s = 0.6325$. The angle varies somewhat when higher-order terms [using Eq. (2)] are incorporated, but no analytical expression for $\cos\theta_s$ was obtained. $\cos\theta_s$ was calculated as needed using Newton's method.

The calculations were performed on the differences, using $\cos\theta_s$, $\nu_{121} \equiv \nu_{5/2,+-} - \nu_{5/2,-+}$, and $\nu_{123} \equiv \nu_{7/2,+-} - \nu_{7/2,-+}$, so that any hexadecapole terms that may be present were canceled identically. The quadrupole term canceled identically to first order in $\nu_{L,I}$, and almost canceled to second order in $\nu_{L,I}$. (The second-order term did not completely cancel since the exact angle $\cos\theta_s$ and $\nu_{L,I}$ were slightly different for the two lines $\nu_{I,+-}$ and $\nu_{I,-+}$.) The net result was that a deviation of 1 kHz in $\nu_{Q,I}$ caused a deviation of less than 10^{-6} in $K_{\rm iso}$ or $K_{\rm aniso}$ so that the experiment is very insensitive to $\nu_{Q,I}$.

The approximate behavior of these lines is given by substituting $\cos\theta_s$ into Eq. (2), giving

$$\nu_{121} = 4.46H(1 + K_{\rm iso} + 0.786K_{\rm aniso}), \quad (4)$$

$$\nu_{123} = 2.80H(1 + K_{\rm iso} + 0.200K_{\rm aniso}), \quad (5)$$

where H is in gauss and ν_{121} and ν_{123} in kHz. Equations (4) and (5) correspond to frequency spreads of 1600 and 1000 kHz, respectively, at 360 G, and would be exact through second order in $\nu_{L,I}$ if the angles and magnetic field measurements were all identical; the third-order (in $\nu_{L,I}$) results were used for the final calculations, their systematic error being 0.4 and 0.2 kHz for ν_{121} and ν_{123}, respectively.

Finally, a line-shape analysis had to be performed for each of the four transitions in order to determine the position of the singularity frequencies from the observed derivative absorptive line. This quantity is given by[13]

$$\frac{dP_{I,\pm\mp}}{d\nu}(\nu)\alpha - \frac{2}{\sigma^2}\int_{\cos\theta=0}^{1}(1+\cos^2\theta)\,\nu_{I,\pm\mp} \times \left|\langle \mp\tfrac{3}{2}\left|\hat{I}\pm\right|\pm\tfrac{1}{2}\rangle\right|^2(\nu - \nu_{I,\pm\mp}) \times \exp\left(-\frac{(\nu-\nu_{I,\pm\mp})^2}{\sigma^2}\right) d(\cos\theta), \quad (6)$$

where ν is the spectrometer frequency. The wave functions $|\mp\frac{3}{2}\rangle$ and $|\pm\frac{1}{2}\rangle$ are to second order in $\nu_{L,I}$. The half-intensity half-width is σ.

In Eq. (6), the Gaussian is from the intrinsic broadening mechanisms between the nuclei[13], the factor $1+\cos^2\theta$ is because of averaging of the orientations of the radio-frequency field,[14] and the frequency dependence of the power absorption is linear because of the difficulty of maintaining a resonance and impedance match in the spectrometer over a wide frequency band.[15] The assumption of a Gaussian distribution is discussed in Sec. III. Table I lists the matrix elements for all four transitions and general nuclear spin I, where $\cos^2\alpha$ is $[f_I(\theta)-1]/2f_I(\theta)$ and $\sin^2\alpha$ is $[f_I(\theta)+1]/2f_I(\theta)$.

There is the possibility of eddy-current mixing of the dispersive mode into the absorptive mode as discussed by Chapman *et al.*[16] The upper limit on the mean equivalent diameter of the antimony powder is 25 μm.[17] The characteristic parameter of eddy-current mixing, p, is about $\frac{1}{4}$ at 12 MHz; and, using Chapman's results, this gives a negligible 0.0006 for the amount of dispersive mode mixed into the absorptive mode. Equation (6) was evaluated using Simpson's rule with a resultant accuracy of 10^{-7}.

TABLE I. Matrix elements $|\langle a|\hat{I}\pm|b\rangle|^2$ to third order, general nuclear spin I.

Transition	Value
$\pm\frac{1}{2}\leftrightarrow\pm\frac{3}{2}$ $\lvert\langle\pm\frac{3}{2}\rvert\hat{I}\pm\rvert\pm\frac{1}{2}\rangle\rvert^2$ $\Delta m=\pm1$	$\left(\frac{(2I-1)(2I+3)}{4}+\frac{(2I-1)}{64\nu_{Q,I}^2}(2I+3)(2I-3)(2I+5)\,\nu_{K,I}^2\sin^2\theta\right)\sin^2\alpha$ $+\frac{(2I-1)(2I+3)}{64}(2I+1)^2\left(1\pm\frac{3\nu_{K,I}}{\nu_{Q,I}}\cos\theta\right)\frac{3\nu_{K,I}^2}{\nu_{Q,I}^2}\cos^2\alpha\sin^2\theta$ $\mp\frac{(2I-1)}{128\nu_{Q,I}^3}(2I+3)(2I-3)(2I+5)\nu_{K,I}^3\sin^2\theta\sin^2\alpha\cos\theta(f+\frac{3}{2})$
$\pm\frac{1}{2}\leftrightarrow\mp\frac{3}{2}$ $\lvert\langle\mp\frac{3}{2}\rvert\hat{I}\pm\rvert\pm\frac{1}{2}\rangle\rvert^2$ $\Delta m=\mp1$	$\left(\frac{(2I-1)}{4}(2I+3)+\frac{(2I-1)}{64\nu_{Q,I}^2}(2I+3)(2I-3)(2I+5)\nu_{K,I}^2\sin^2\theta\right)\cos^2\alpha$ $+\frac{(2I-1)}{4}(2I+3)(2I+1)^2\;1\mp\frac{3\nu_{K,I}}{\nu_{Q,I}}\cos\theta\;\;\frac{\nu_{K,I}^2}{\nu_{Q,I}^2}\sin^2\alpha\sin^2\theta$ $\mp\frac{(2I-1)}{128\nu_{Q,I}^3}(2I+3)(2I-3)(2I+5)\nu_{K,I}^3\sin^2\theta\cos^2\alpha\cos\theta(f-\frac{3}{2})$

Figure 1 is an example theoretical power-absorption derivative curve for the ^{123}Sb $\nu_{7/2,+-}$ transition. There are two extrema: the maximum occurring at higher frequency than the minimum, with the maximum height about twice the minimum height. This was typical behavior for the (+ −) lines. However, with the (− +)-type lines, the maximum was a lower frequency than the minimum, otherwise the curves were similar.

The final results are summarized below, where ν_A are the maxima and ν_B the minima:

^{121}Sb, $\nu_{5/2,+-}$ transition, $\nu_A>\nu_B$, $\delta\equiv\nu_A-\nu_B$:

$$\nu_{5/2,+-}=\nu_A-C\delta, \tag{7}$$

$$C=0.240+(3.14\times10^{-4}\delta)\pm0.0015, \tag{8}$$

$$\sigma/\delta=0.615\pm(0.592\times10^{-4}\delta)\pm0.002; \tag{9}$$

^{121}Sb, $\nu_{5/2,-+}$ transition, $\nu_A<\nu_B$, $\delta\equiv\nu_B-\nu_A$:

$$\nu_{5/2,-+}=\nu_A+C\delta, \tag{10}$$

$$C=0.237+(4.73\times10^{-4}\delta)\pm0.003, \tag{11}$$

$$\sigma/\delta=0.61+(4.1\times10^{-4}\delta)\pm0.01; \tag{12}$$

^{123}Sb, $\nu_{7/2,+-}$ transition, $\nu_A>\nu_B$, $\delta=\nu_A-\nu_B$:

$$\nu_{7/2,+-}=\nu_A-C\delta, \tag{13}$$

$$C=0.241+(1.37\times10^{-4}\delta)\pm0.002, \tag{14}$$

$$\sigma/\delta=0.619-(1.82\times10^{-4}\delta)\pm0.007; \tag{15}$$

^{123}Sb, $\nu_{7/2,-+}$ transition, $\nu_A<\nu_B$, $\delta=\nu_B-\nu_A$:

$$\nu_{7/2,-+}=\nu_A+C\delta, \tag{16}$$

$$C=0.240+(3.32\times10^{-4}\delta)\pm0.001, \tag{17}$$

$$\sigma/\delta=0.614+(0.902\times10^{-4}\delta)\pm0.001. \tag{18}$$

The results are very close to those obtained by the earlier work in the Zeeman regime.[12]

III. RESULTS

The experiment was performed on 325-mesh antimony powder, supplied by the Consolidated Mining and Smelting Co. of Canada. The sample was annealed for 2 h in a carbon boat at a vapor pressure of 10^{-5} Torr and at a temperature of 583 ± 4 °C.

The annealed sample was sifted through a 25-μm sieve producing 12 g of material for use in a Varian V4210A broadband cross-coil system. The method used to observe the four antimony lines was nuclear quadrupole resonance by nuclear induction.[8] The frequency was measured to ±10 Hz by a Hewlett Packard 5245L frequency meter and the magnet used to obtain the static fields of about 360 G was a 12-in. pole diameter magnet using a rotating-coil system for field control. A proton standard was used before and after each run with a total standard deviation in the magnet field measurements of less than 0.05 G, and a corresponding error in K_{iso} and K_{aniso} of 0.000 13 and 0.000 02, respectively.

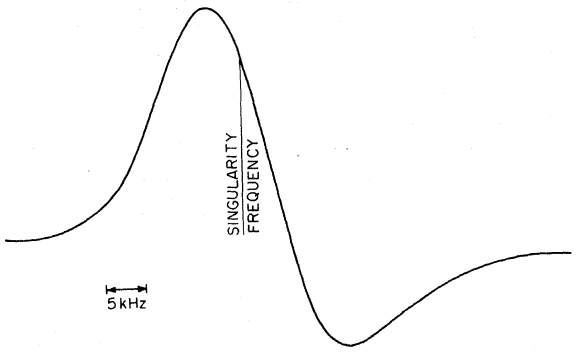

FIG. 1. Example theoretical power-absorption derivative for the ^{123}Sb $\nu_{7/2,+-}$ transition.

The splittings of the $(\frac{1}{2} \leftrightarrow \frac{3}{2})$ transitions were traced over a static magnetic field of 0–360 G and were found to fit Eqs. (4) and (5) for each isotope. Finally, at 360 G each line was measured, corresponding to $\nu_{L,I}/\nu_{Q,I} \sim \frac{1}{30}$ for either isotope. The four transitions were measured on four different days so that four magnetic field measurements had to be made. Figure 2 is a reproduction of one of the ^{123}Sb $\nu_{1/2,+-}$ recorded traces.

The type of intrinsic line-broadening mechanism was determined by observing the zero static magnetic field [pure nuclear quadrupole resonance (NQR)] resonance of the ^{123}Sb isotope. The modulation field was 3.6 G and the line was recorded twice. Both a Gaussian and a Lorentzian curve were fitted to one of the recorded traces with the result that the Gaussian was the best fit; this is illustrated in Fig. 3. Since $M_4^{1/4}/M_2^{1/2} = 1.32$, 1.40, 1.158, and 1.29 for a Gaussian (infinite limits), [11] Lorentzian (truncated at ±34 kHz), rectangular curve (infinite limits), [11] and Gaussian (truncated at ±34 kHz), a Gaussian curve was the best function to use in Eq. (6) as $M_4^{1/4}/M_2^{1/2} = \frac{1}{28} \pm 0.04$ for the recorded pure NQR curves.

The final results for the half-intensity half-widths σ were

$$\sigma(^{121}\text{Sb}) = 22.7 \pm 1.8 \text{ kHz}, \tag{19}$$

$$\sigma(^{123}\text{Sb}) = 12.5 \pm 1.2 \text{ kHz}; \tag{20}$$

and for the Knight shifts,

$$K_{\text{iso}} = (1.8 \pm 0.3)\%, \tag{21}$$

$$K_{\text{aniso}} = (-2.6 \pm 0.5)\%. \tag{22}$$

IV. CONCLUSIONS

Of the final results, the most interesting are those observed for the Knight shifts since Hygh and Das estimated the Knight shifts due to the conduction electrons as 0.07 and -0.05% for K_{iso} and K_{aniso}, respectively. [6] This means some other mechanism must be responsible for their large observed values.

Hygh has calculated that Landau diamagnetism and correlation and exchange effects among the

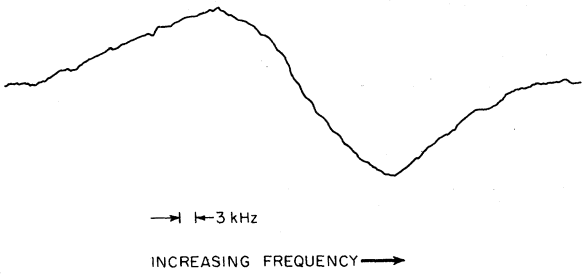

FIG. 2. Reproduction of the ^{123}Sb $\nu_{7/2,+-}$ transition.

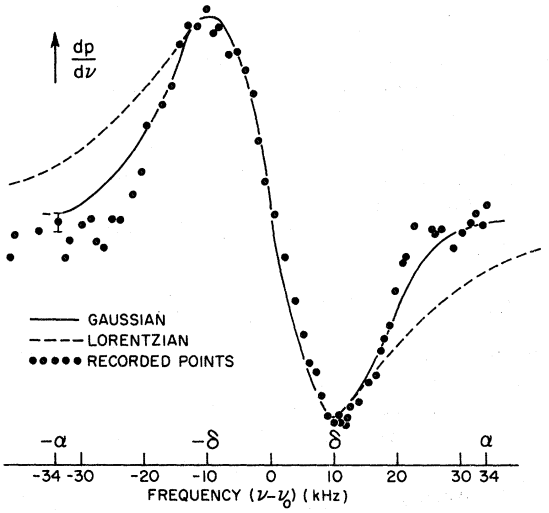

FIG. 3. Recorded pure-NQR derivative curve fitted to a Gaussian distribution and a Lorentzian distribution (for $|\nu - \nu_0| < \delta$, all the curves coincide).

conduction electrons would produce approximately a 17% enhancement of the Knight shifts. [6] Recent theories of correlation and exchange effects indicate that this effect could be larger, perhaps by as much as 100%. [18,19] This effect is still small compared to the observed enhancement of the Knight shifts.

Core polarization is another possibility that has been shown to be an important contributor to the isotropic Knight shifts of lithium, [20] beryllium [21] (Landau diamagnetism was invoked to explain the vanishingly small [22] K_{iso} of beryllium), and aluminum metals. [23] In all these cases, however, the effect was 20% or less of the direct contact term; this is not too surprising as the exchange interaction is usually very small. [24] Since this maxium 20% enhancement of the Knight shifts given by Hygh and Das would not approach the observed values, it appears reasonable to ignore this effect.

The most likely dominant contribution to both Knight shifts is the Van Vleck orbital paramagnetism [25,26] from the p electron bands of antimony. This mechanism is independent of the amount of conduction electrons at the Fermi surface and depends on the localized nature of the p or d-like electrons. It has been used to successfully describe the isotropic Knight shifts of the transition metals [27,28] and d-band superconductors. [29,30] Additionally, Walstedt and Yafet have recently indicated that this mechanism may be an important contributor to the isotropic Knight shifts in the noble metals where it was previously believed to be insignificant. [31] Also, other authors have speculated about its importance in antimony. [6,32]

Its magnitude may be estimated, in the tight-binding approximation, by the following [27,31]:

$$\chi_{VV} = 2A\,\mu_B^2\,N_o N_u/\Delta, \tag{23}$$

where N_o is the number of occupied p states[33] (≈ 3),[34] N_u is the number of unoccupied p states[33] (≈ 3),[34] A is Avagadro's number (6.02×10^{23} mole^{-1}),[1] μ_B is the Bohr magneton (0.274×10^{-21} ergs/G),[1] Δ is the mean band separation ($\approx 8.6\times10^{-12}$ ergs),[34] and χ_{VV} is the Van Vleck orbital susceptibility.

The contribution to the orbital Knight shift is given by[27]

$$K_{orb} = \beta\chi_{VV} = (2\xi\langle r^{-3}\rangle_{atom}/A)\chi_{VV}, \tag{24}$$

where $\langle r^{-3}\rangle_{atom}$ ($\approx 70.8\times10^{24}$ cm^{-3})[3] is the average over the p-electron wave function and ξ (≈ 0.75) is a phenomenological parameter given by $\xi = \langle r^{-3}\rangle_{metal}/\langle r^{-3}\rangle_{atom}$ since the electron wave functions are expanded in the metal over that of the atom.[27,31]

Substituting these values into Eqs. (23) and (24) yields $\chi_{VV}\approx 1.1\times10^{-4}$ cm^3/mole, $\beta\approx 176$ cm^{-3} mole, and $K_{orb}\approx 1.9\%$, which is close to the observed value for K_{iso}. Since antimony has noncubic symmetry, this mechanism could also explain the large observed value of anisotropic Knight shift.[6] This result is tentative and depends on the localized character of the p-electron wave functions.

The intrinsic line-broadening mechanisms are most likely magnetic in origin since $\sigma(^{121}\mathrm{Sb})/\sigma(^{123}\mathrm{Sb}) = 1.82$ and the respective gyromagnetic ratios are 1.8466. The Gaussian form of the pure-NQR curve also confirms this conclusion.[11]

The method used here is useful in those cases of large quadrupole interactions and half-integral spins: The larger the quadrupole interaction with respect to the Larmor term, the more accurate the procedure will be.

For reference purposes, the expression for K_{iso} and K_{aniso} in terms of the $\nu_{I,\pm\mp}$ lines are shown below to first order for $I=\frac{3}{2}$ through $I=\frac{9}{2}$:

$I=\frac{3}{2}$, $\cos\Theta_s = 1$:

$$\nu_{3/2,+-} - \nu_{3/2,-+} = 4\nu_L(1+K_{iso}+2\,K_{aniso}); \tag{25}$$

$I=\frac{5}{2}$, $\cos\theta_s = 0.7717$:

$$\nu_{5/2,+-} - \nu_{5/2,-+} = 4.373\nu_L(1\times K_{iso} + 0.786K_{aniso}); \tag{26}$$

$I=\frac{7}{2}$, $\cos\theta_s = 0.6325$:

$$\nu_{7/2,+-} - \nu_{7/2,-+} = 5.060\nu_L(1\times K_{iso} + 0.200K_{aniso}); \tag{27}$$

$I=\frac{9}{2}$, $\cos\theta_s = 0.5330$:

$$\nu_{9/2,+-} - \nu_{9/2,-+} = 5.863\nu_L(1\times K_{iso} - 0.148K_{aniso}), \tag{28}$$

where $\nu_L = \gamma n H_{static}/2\pi$. Note that the frequency spread is four to six times the Larmor frequency. If a single-crystal sample is available, other angles may be chosen so that both K_{iso} and K_{aniso} could be obtained from one isotopic species.

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