Arsenic-75 NMR: Knight shifts in arsenic metal

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Abstract. A ^{75}As NMR study of rhombohedral metallic arsenic has yielded values for the isotropic and axial components of the Knight shift of $K_{iso} = 1.5$ (± 0.07) $\times 10^{-3}$ and $K_{ax} = 3.2(\pm 0.3) \times 10^{-5}$.

1. Introduction

NMR investigations of the rhombohedral semi-metals arsenic and antimony are severely constrained by a large quadrupole interaction which leads to considerably frequency-dispersed linewidths which make spectroscopic investigation difficult. In fact nuclear resonance was first observed for ^{75}As in metallic arsenic [1] and ^{121,123}Sb in metallic antimony [2] by NQR. Since the latter is a zero field technique it yields only the nuclear quadrupole interaction, and no information is obtained about the isotropic or axial Knight shifts (K_{iso} and K_{ax}). However Knight shift measurements have been reported for ^{121,123}Sb [3] and ^{75}As [4], based on a Zeeman-perturbed NQR technique, using a static magnetic field of order 0.03 T.

The values reported for Sb are

$$K_{iso} = 1.8 \pm 0.3 \times 10^{-2}, \text{ and } K_{ax} = -2.6 \pm 0.5 \times 10^{-2}$$

and for As (preliminary data)

$$K_{total} = 0.7 \times 10^{-2}.$$

These values considerably exceed the theoretical predictions for Sb (by several orders of magnitude) by Hygh and Das [5] who suggested, however, that the inclusion of Van Vleck orbital paramagnetism in the calculation of the orbital component of the Knight shift might increase their theoretical values by an order of magnitude. An order of magnitude calculation in [3] along these lines supported this suggestion.

A rough estimate of K_{iso} for ^{75}As in metallic arsenic can be made from measurements of the nuclear spin-lattice relaxation time T_1 as a function of temperature [6] which follow a Korringa-like relation,

$$T_1 T \approx \text{constant} = (0.68)^{-1} \text{ s K}. \tag{1}$$

For free electrons the Korringa relation [7] is

$$K_{iso}^2 T_1 T = (\gamma_e/\gamma_n)^2 (h/8\pi^2 k_B) = 8.9 \times 10^{-6} \text{ (for } ^{75}\text{As)} \tag{2}$$

where γ_e and γ_n are the electronic and nuclear gyromagnetic ratios. Substituting (1) into (2) gives the free electron estimate of $K_{iso,FE} = 2.5 \times 10^{-3}$.

The work reported here is a measurement of K_{iso} and K_{ax} for arsenic metal via direct observation of the high field NMR spectrum of a polycrystalline As specimen.

2. Experiment

The NMR spectra were acquired at 296 K with a Bruker MSL 400 spectrometer at a nominal field of 9.395 T, using the broadband low-power transmitter over a frequency range of 57.05 to 80.36 MHz with a two-pulse echo sequence using 10 μs pulses with a repetition period of 0.1 s. The lineshapes were defined by frequency-stepping the spectrometer and recording the amplitude of the Fourier-transformed echo at the observation frequency, which was then plotted as a function of frequency. Each data point in figures 1 and 2 represents 5000 acquisitions. The NQR lineshape was obtained at a frequency near 22.575 MHz from a Fourier-transformed echo, using two 5 μs pulses (short enough for the pulse power spectrum to easily cover the linewidth), with the probe removed from the supercon solenoid and well away from significant stray field. The high purity As specimen was from the same source as that used in two previous investigations [1, 8]. A standard NMR reference frequency was provided by a powdered specimen of high purity (device grade) GaAs in which the As has exact tetrahedral point symmetry, ensuring zero electric field gradient at the As site and a sharp static NMR linewidth ($\Delta \nu_{1/2} = 2.2$ kHz). The Larmor frequency for ^{75}As in GaAs in the magnetic field used here was 68.504 MHz.

3. Results and discussion

The powder lineshape $\theta = \pi/2$ singularity for the ^{75}As satellite $(1/2, 3/2)$ and $(-1/2, -3/2)$ and the central $(1/2, -1/2)$ transition for polycrystalline metallic arsenic are displayed in figure 1(a) and (b) and figure 2 respectively. The frequencies of the singular points and edges in the spectrum are gathered, along with the ^{75}As GaAs NMR reference and arsenic metal ^{75}As NQR frequency, in table 1.

Table 1. Frequencies of singular spectral features for ^{75}As in metallic arsenic.

| Feature	Frequency (MHz)
Low frequency $(1/2, 3/2)$ satellite edge	57.35 ($\pm$0.01)
High frequency $(-1/2, -3/2)$ satellite edge	79.86 ($\pm$0.01)
Low frequency $(1/2, -1/2)$ edge ν_6	$68.507 - 2.380$ ($\pm$0.01)[a]
High frequency $(-1/2, 1/2)$ edge ν_1	$68.507 + 1.520$ ($\pm$0.01)[a]
Intermediate step ν_4	68.507 ($\pm$0.01)
NQR $(\pm1/2, \pm3/2)$ line	22.757 ($\pm$0.005)
Ga^{75}As reference	68.504 ($\pm$0.002)

[a] The spectrometer operating frequency was 68.507 MHz.

Note that the edges of the satellite spectra displayed in figures 1(a) and (b) are sharply defined (bearing in mind that these are separated by 22.6 MHz), as required by the three-fold rotation axis at the As site in the rhombohedral structure. The low frequency satellite has smaller intensity compared to its high frequency partner; the (arbitrary) intensity scale in figures 1(a) and (b) is the same for both satellites. The observed intensity ratio is due to the different signal to noise ratios ($\sim \nu^{3/2}$) that obtain at the two widely differing frequencies, and the fact that a different probe specimen coil was used to observe each satellite.

It is important also to note the ratio of the quadrupolar and Zeeman contributions to the hyperfine interaction at the nucleus. This is given by ν_q/ν_L, where $\nu_q = e^2qQ/2I(2I - 1)h$ and ν_L is the Larmor resonance frequency for a nucleus with spin I, quadrupole moment $|e|Q$ at a site with electric field gradient eq. For metallic arsenic in a field of 9.4 T, $\nu_L \approx 3\nu_q$, so that it is pertinent to question the accuracy of first (and second) order perturbation theory in
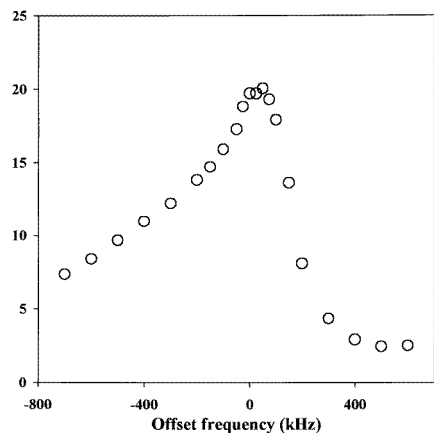
(a)
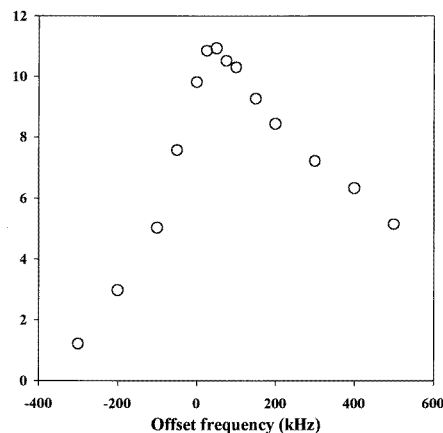
(b)

Figure 1. The $\theta = \pi/2$ edge singularities of the ^{75}As NMR lineshape for polycrystalline metallic arsenic: (a) $(1/2, 3/2)$ with the zero offset corresponding to a spectrometer operating frequency of 79.76 MHz, and (b) $(-1/2, -3/2)$ with the zero offset corresponding to a spectrometer operating frequency of 57.35 MHz.

determining the nuclear energy levels of a system with a dominant Zeeman and perturbing quadrupole interaction of that relative magnitude. However there exists an exact solution to this problem when the nuclear Hamiltonian consists of just two terms: the Zeeman term H_Z and the quadrupole term H_q [9] of arbitrary strengths, and the principal axis of the electric field gradient tensor is at an angle of $\pi/2$ to the static magnetic field. The theory is summarized here in a form suited to the present discussion. The combined Hamiltonian, written in a representation which diagonalizes I_z, is

$$H_Z + H_q = \nu_0 \begin{bmatrix} -3/2 + \beta & 0 & \sqrt{3}\beta & 0 \\ 0 & -1/2 - \beta & 0 & \sqrt{3}\beta \\ \sqrt{3}\beta & 0 & 1/2 - \beta & 0 \\ 0 & \sqrt{3}\beta & 0 & 3/2 + \beta \end{bmatrix} \tag{3}$$

where $\beta = \nu_q/4\nu_0$, $\nu_q = 3e^2qQ/2I(2I-1)h$, and ν_0 is the (Knight-shifted) Larmor frequency.
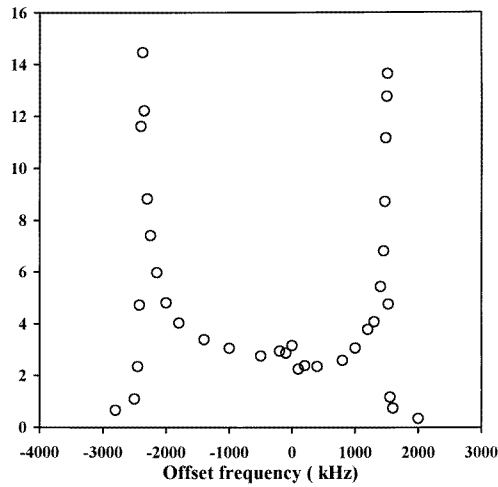
Figure 2. The $(1/2, -1/2)$ ^{75}As NMR lineshape for polycrystalline metallic arsenic.

The eigenvalues of this matrix are given by the roots of the characteristic equation,

$$\varepsilon_{1\pm} = 1/2 \pm (4\beta^2 + 2\beta + 1)^{1/2} \qquad \varepsilon_{2\pm} = -1/2 \pm (4\beta^2 - 2\beta + 1)^{1/2} \qquad (4)$$

with the identifications $|1+\rangle \equiv |3/2\rangle$, $|1-\rangle \equiv |-1/2\rangle$, $|2+\rangle \equiv |+1/2\rangle$, $|2-\rangle \equiv |-3/2\rangle$. Using this solution it can be simply demonstrated that, for arbitrary H_Z and H_q, in the case where the [111] axis of the As crystallite (i.e. the principal axis of the electric field gradient tensor at the As site) makes an angle of $\pi/2$ with the magnetic field, the frequencies of the $(1/2, 3/2)$ and $(-1/2, -3/2)$ transitions are equally spaced about the Knight-shifted Larmor frequency. This Zeeman-state labelling is formally an approximation, since the states between which these transitions take place are in fact admixtures of other m-states, due to the influence of the quadrupolar term. However it can be shown that the spin eigenfunctions in the present case are well described by a single m-state since the admixture coefficient of the $m \pm 2$-state is small; an estimate by first order perturbation theory is $3^{1/2}\nu_q/8\nu_L \approx 0.07$. This result may be directly confirmed by explicitly constructing the spin eigenvectors, after solving for the eigenvalues. The exact expressions for the frequency of the $\theta = \pi/2$ edges of the ^{75}As powder spectrum for the two satellite transitions are

$$\nu_{1/2,3/2} = \nu_0\{1 + \tfrac{1}{2}[(4\beta^2 + 2\beta + 1)^{1/2} - (4\beta^2 - 2\beta + 1)^{1/2}] = \nu_0 + g(\beta) \qquad (5)$$

$$\nu_{-1/2,-3/2} = \nu_0 - g(\beta). \qquad (6)$$

The average of the peak position frequencies of the two observed satellite lineshapes therefore gives the Knight-shifted Larmor frequency. Comparison with a reference frequency from GaAs gives an isotropic Knight shift, $K_{iso} = 1.5(\pm0.07) \times 10^{-3}$. The rough estimate of 2.5×10^{-3}, given above, is therefore tolerably close to the observed value.

The expressions (5) and (6) predict (using ν_q from NQR and ν_L from the diamagnetic reference GaAs) positions for the high and low frequency edges of 79.766 and 57.242 MHz respectively, with a separation of 22.524 MHz, which is within the experimental error of the observed separation of 22.51 MHz, but perceptibly different from the value of $\nu_q = 22.757$ MHz given by first order theory. The relatively small difference in the present case (0.81%) appears to reflect the fact that, for the purpose of determining ν_q by taking the difference frequency between high and low frequency satellites, the first order approximation, which places the satellite at $\nu_0 \pm 1/2\nu_q$, is correct also in second order [10]. However it should be

noted that the third order correction [11] to the satellite positions yields a correction to the difference frequency of $(17/32)v_q^3/v_0^2$, which leads to a value 5.9% higher than the experimental (and exact theoretical) result, and that further higher order corrections are required to restore the good agreement of experiment with first order theory.

The Knight shift characterizing a non-cubic nuclear site is a tensor quantity. The elements of this tensor, in a principal axis frame, and in order of increasing magnitude, are K_{11}, K_{22} and K_{33}. Since the arsenic crystal structure is rhombohedral, this tensor will reflect the $3m$ axial symmetry of the As site, so that $K_{11} = K_{22}$. In the following discussion the definitions and theoretical description of Baugher *et al* [12]) are used. The definitions then become

$$K_{iso} = (2K_{11} + K_{33})/3 \qquad K_{ax} = (K_{33} - K_{11})/3. \tag{7}$$

The features that mark the lineshape for the $(1/2, -1/2)$ transition (figure 2), which is perturbed only in second (and higher) order by the quadrupole interaction, are used to obtain K_{ax}. Three features can be identified: the high frequency edge singularity v_1, the low frequency edge singularity v_6 and the intermediate step frequency v_4. It should be noted that the value of v_q obtained from a second order perturbation theory analysis using the $v_{1,6}$ separation, and assuming quadrupole interaction only (using the Bruker program POWDER), gave a value of 22.71 MHz, closely similar to that of 22.757 MHz obtained from NQR. This immediately suggests that K_{ax} is small, since if appreciable it will perturb the lineshape [12]. The strategy adopted here was to use the $v_{1,4}$:$v_{4,6}$ ratio to determine K_{ax} (where $v_{1,4} = v_1 - v_4$ etc). If $K_{ax} = 0$, this ratio is 9/16 (=0.5625); the observed ratio is 0.639. The following expression (which can be derived from [12]) was used to extract K_{ax}:

$$v_{1,4}/v_{4,6} = (3v_q^2/16v_0 + 3K_{ax}v_0)/\{3v_q^2/9v_0 - (4/3)K_{ax}v_0 + (4/3)K_{ax}^2 v_0^3/3v_q^2\}. \tag{8}$$

If K_{ax} is $\sim 10^{-4}$, the term in the denominator quadratic in K_{ax} is $\sim 3 \times 10^{-3}$ times the linear term and thus negligible. Evaluation of K_{ax}, omitting the quadratic term, yields $K_{ax} = 3.2(\pm 0.3) \times 10^{-5}$, and justifies the approximation. Although this result was derived under the approximation of second order perturbation theory, it seems clear from all the data presented here that this approximation is already quite good, so that a more exact treatment of the data will not yield a substantially different value.

Finally it may be noted that the values of K_{iso} and K_{ax} are relatively small for a heavy nucleus like ^{75}As, so is worth briefly justifying them as Knight shifts rather than chemical shifts, as would apply to the the neighbouring isotope ^{77}Se in solid selenium, where the (anisotropic) chemical shift tensor components are of the same order as for arsenic [13]. Arsenic exhibits metallic conductivity and a $T_1 T =$ constant spin–lattice relaxation behaviour [6] indicating a contact interaction, which is consistent with a Knight shift. Selenium, on the other hand, exhibits semiconductor-type electrical transport behaviour and $T_1 T^2 =$ constant, indicating two-phonon (Raman) spin–lattice relaxation [13].

Acknowledgment

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