

## NUCLEAR QUADRUPOLE RESONANCE AS A NON-DESTRUCTIVE TESTING TOOL

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### INTRODUCTION

Nuclear pure quadrupole resonance (NQR) is a resonance technique that provides distinctly different information from that provided by nuclear magnetic resonance (NMR). In NMR the splitting of the energy levels, and therefore the frequency observed, occurs because of the interaction of the nuclear magnetic moment with an *external* magnetic field. Information about the system under study comes from perturbations on this magnetic interaction. These perturbations lead to a broadening of the line, or to relaxation effects on the interchange of energy between the spins and the lattice, and among the spins. In NQR the primary interaction is between the electric quadrupole moment of a nucleus and the electric field gradient at that nucleus. The field gradient is provided by *internal* interactions in the sample itself, arising from the chemical bonds, rather than by an external field. Anything that changes the bonding environment, such as tensile stress, will cause shifts in the quadrupole resonance frequency. All nuclei with spin greater than 1/2 have a nuclear quadrupole moment, in addition to their magnetic moment. The nucleus used as an example in this paper is  $^{75}\text{As}$ , which has spin 3/2.

The field gradient at a nucleus is provided by the chemical bonds attached to the atom under study, so that NQR provides detailed information about the local environment of that atom. If the bonding is symmetric, such as tetrahedral, no field gradient will exist, and no NQR resonance can be observed. The interaction of the field gradient with the quadrupole moment splits the energy levels in a different fashion than in NMR, as seen in Fig. 1. Nevertheless the observational techniques are very similar to NMR, except that no external magnetic field is needed. This makes the experiments intrinsically simpler to perform. The experiments that we discuss here were performed using a pulsed NMR spectrometer of fairly standard design [1]. The observation is the intensity of the spin echo.

The experiments described are intended to show the utility of the technique in determining the environment of the atom under study, not as a specific example of non-destructive evaluation (NDE). We have studied the  $^{75}\text{As}$  NQR in semiconducting

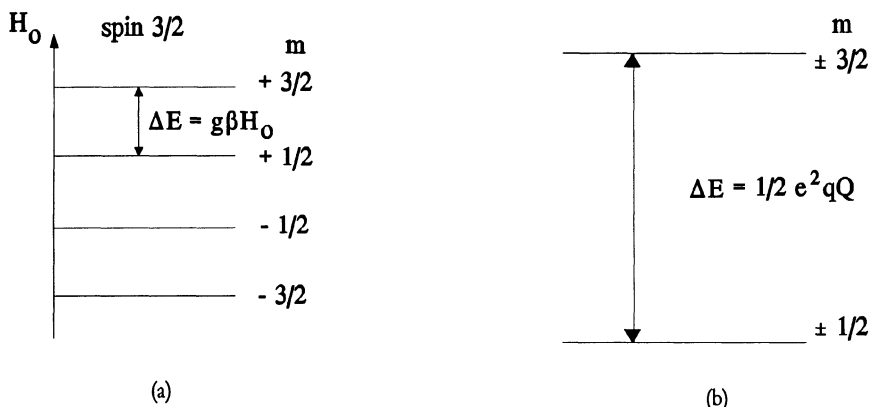


Fig. 1. (a) Energy levels for NMR in an external field where  $\beta$  is the nuclear magneton,  $g$  the magnetic moment,  $H_0$  the external field. (b) Energy levels for NQR where  $e$  is the electron charge,  $Q$  the quadrupole moment of the nucleus and  $q$  the principle component of the electric field gradient tensor.

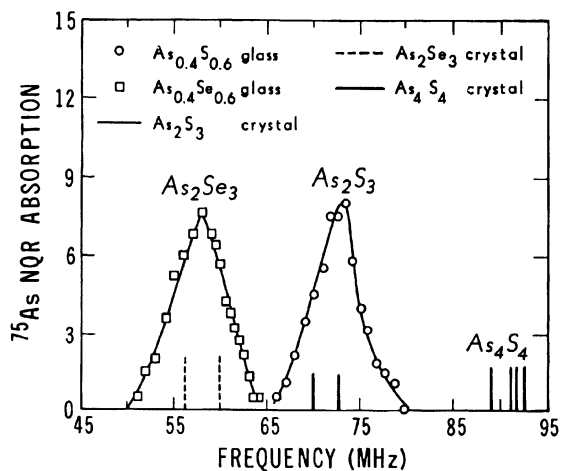


Fig. 2. Summary of  $^{75}\text{As}$  NQR frequencies of glassy and crystalline compositions discussed in this paper.

samples of glassy arsenic triselenide, arsenic trisulfide, and these materials with varying amounts of copper added [2]. These materials are called chalcogenide glasses because S and Se are chalcogens.

## EXPERIMENTS

Figure 2 shows the  $^{75}\text{As}$  NQR line shape for several samples of arsenic chalcogenides. There is a distribution of resonance frequencies in these samples because the amorphous structure of the glassy sample provides a range of

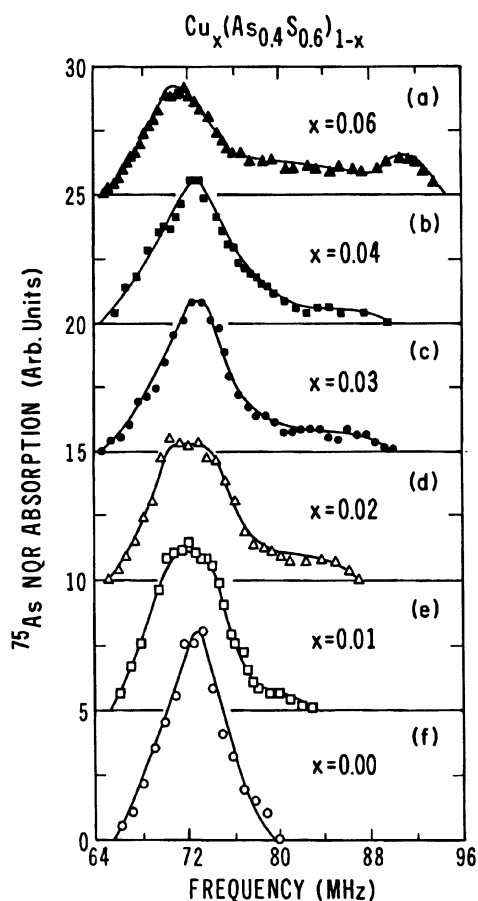


Fig. 3.  $^{75}\text{As}$  NQR lineshapes for the various copper concentrations  $x$  in the  $\text{Cu}_x(\text{As}_{0.4}\text{S}_{0.6})_{1-x}$  normalized to the same area. The labels (a)-(f) correspond to the  $x$  values of 0.06, 0.04, 0.03, 0.02, 0.01 and 0.00, respectively. Lines are aids to the eye.

environments for the As nuclei, in contrast to the situation for crystalline samples. The variations in bond angles that cause these line breadths (variation in resonant frequency) is less than  $1^\circ$ . The quadrupole resonance frequency is thus a very sensitive measure of the bonding configuration and environment of the atom containing the nucleus being studied. The resonant frequencies for crystalline materials of the same composition as the amorphous samples are shown as vertical lines in the figure.

It is known that when elements such as copper and silver are added to these materials that they are fourfold coordinated. The addition of copper thus forces changes in the bonding of the arsenic and the chalcogen nuclei. These experiments were conducted in the belief that as more copper was added, a certain number of As-As bonds would be created for certain compositions in this system. The quadrupole frequency for As-As bonds can be estimated from measurements on  $\text{As}_4\text{S}_4$ , where each As site contains one As-As bond, to be near 90 MHz. This is also shown in Fig. 2. So an increase in signal intensity near 90 MHz would be a symptom of the formation of As-As bonds.

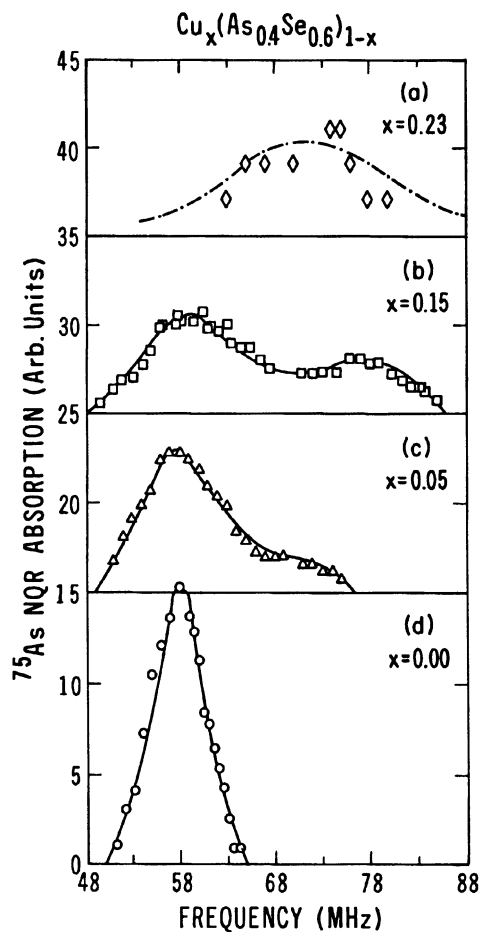


Fig. 4.  $^{75}\text{As}$  NQR lineshapes for various copper concentrations in  $\text{Cu}_x(\text{As}_{0.4}\text{Se}_{0.6})_{1-x}$  normalized to the same area. The labels (a)-(d) correspond to the  $x$  values 0.23, 0.15, 0.05 and 0.00, respectively. Lines are aids to the eye. Signal to noise is poor in (a) because the sample becomes quite conductive.

Figure 3 shows the NQR line shape for  $\text{As}_2\text{S}_3$  as copper is added to the system. Figure 4 shows the NQR line shape for  $\text{As}_2\text{Se}_3$  as copper is added. The range of composition for the glassy phase is 0-15% Cu for the selenide and 0-6% Cu for the sulfide. Clearly, as copper is added, the bonding configuration has changed. We believe that what has happened is the formation of As-As bonds. Note that the change in frequency is large. We are not looking at small changes, but major shifts in the resonant frequencies. The importance of this result from the point of view of semiconductors, is that we have changed the structure from a "soft" structure to a more rigid fourfold coordinated structure. This is discussed elsewhere [2,3].

Two other measurements that can be made in quadrupolar samples, as well as in NMR, are the *relaxation times*. There are two, the spin-lattice and the spin-spin

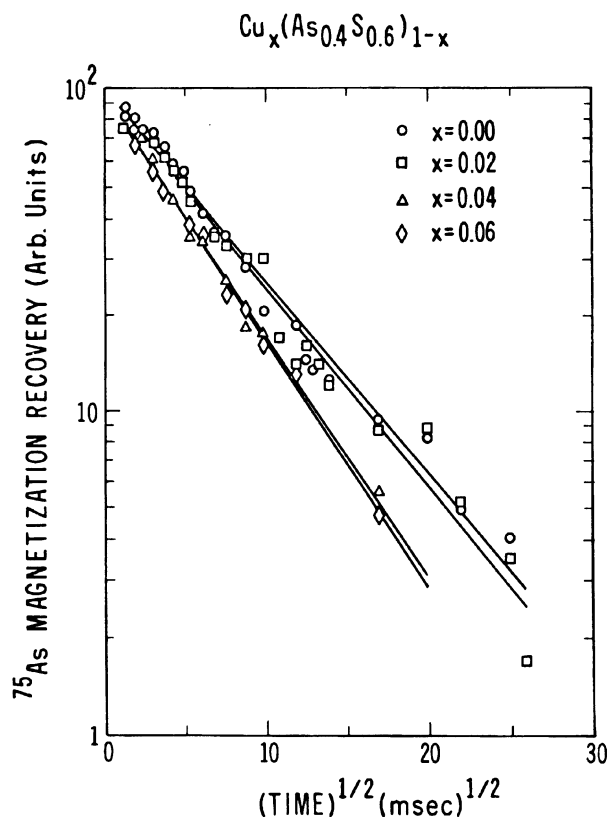


Fig. 5.  $^{75}\text{As}$  NQR relaxation recovery vs. the square root of time ( $t^{1/2}$ ) obtained at 77 K in the  $\text{Cu}_x(\text{As}_{0.4}\text{S}_{0.6})_{1-x}$  for different copper concentrations  $x$ :  $x = 0.00$  ( $\circ$ ),  $x = 0.02$  ( $\square$ ),  $x = 0.4$  ( $\triangle$ ),  $x = 0.06$  ( $\diamond$ ). All data obtained at 58 MHz.

relaxation times. Here we discuss only the spin lattice relaxation time, usually called  $T_1$ . This is a measure of the rate of energy exchange between the spin system and the lattice. Essentially it is the rate of energy exchange between the spins and the outside world. For most systems the energy exchange is measured as an exponential recovery of the equilibrium population of spins in the various energy states. This is observed as an exponential growth in the measured signal after the system has been perturbed.

$$S(t) = S(0) \left[ 1 - \text{EXP} \left( -\frac{t}{T_1} \right) \right] \quad (1)$$

Here  $t$  is the time since the disturbance of the equilibrium population, and  $S(0)$  is the undisturbed signal intensity.

For these glassy systems the relaxation mechanisms are such that the better way to describe the relaxation is with a "stretched exponential".

$$S(t) = S(0) \left[ 1 - \text{EXP} \left( - \left\{ \frac{t}{T_1} \right\}^{1/2} \right) \right] \quad (2)$$

The fit to this form for the  $^{75}\text{As}$  resonance at 77 K is shown in Fig. 5. The model is one of random "relaxation centers," which are therefore at various distances from each of the nuclei. This produces different rates of relaxation, depending on distance to the nearest relaxation center [4].

## IMAGING

The basic idea of imaging is to label the nuclei in some way so that the measured signals can be related to the position of the nuclei in the sample. In magnetic resonance imaging (MRI) this is done by using a gradient in the magnetic field, so that nuclei in different parts of the sample have different resonant frequencies. This cannot be done for NQR, because the interaction causing the quadrupole splitting is not easily accessible experimentally. (However, hydrostatic pressure and external electric fields have been used to change the quadrupole frequencies[5,6]). Therefore some other scheme must be used in an NQR imaging experiment. At least two methods of NQR imaging have been proposed [7,8]. We suggest here another, which is related to the idea of Matsui, but may have some experimental advantages, particularly when the line width is broad, because then the echo is narrow and more easily observed. This section is of the nature of speculation along these lines.

It is well known that the presence of small magnetic fields dramatically affects the amplitude of the quadrupole spin echo signal. Figure 6 shows the measured echo amplitude for  $^{75}\text{As}$  in a sample of  $\alpha\text{-As}_2\text{Se}_3$  as a function of the external magnetic field. The field was produced by a Helmholtz pair. The functional dependence is complex, and is discussed in Ref. 1, p 77-80. In most cases it will probably be easier to measure the dependence, as in Fig. 6, for each sample, rather than calculate.

If we arrange for the magnetic field to vary over a sample, then the amplitude of the echo will be different for different parts of the sample. The measured amplitude is the sum of the amplitudes from all parts of the sample. If the amplitude of the echo is measured with varying magnetic fields and field gradients on the sample, the amplitude of the line from each geometric part of the sample can be calculated using standard techniques. The essential idea is a least squares fit of the data, given the constraint of the external field and field variation. We need to know the value of the field at each part of the sample, and the functional relationship between the echo intensity and external field, which is shown in Fig. 6. The experiment is repeated as many times as possible, with different distributions of magnetic field on the sample. It is not necessary for the magnetic field to be zero in any part of the sample.

Figure 7 shows a sample divided up into ten parts. The amplitude of the signal from each part of the sample can be calculated as

$$I(i) = N(i)F(i) \quad (3)$$

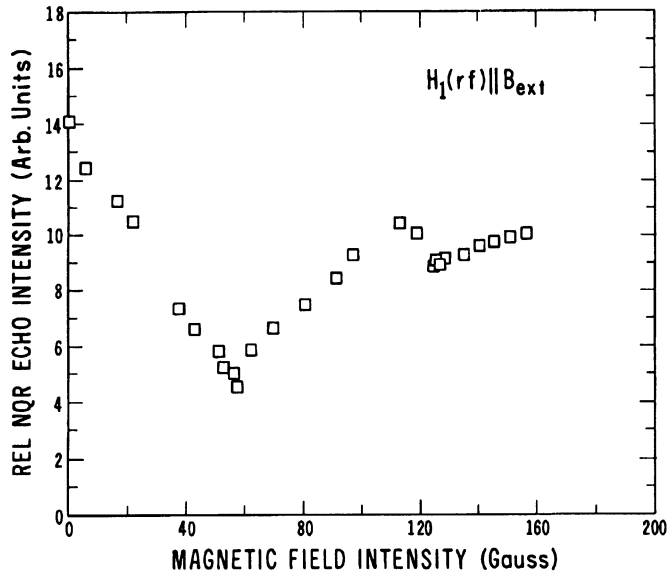


Fig. 6. The NQR echo intensity in a sample of a-As<sub>2</sub>Se<sub>3</sub> As<sub>2</sub>Se<sub>3</sub>, as the magnetic field is varied.

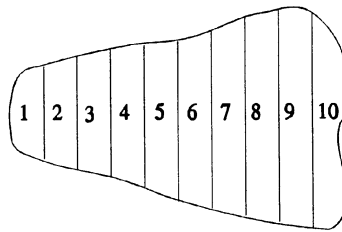


Fig. 7.

where  $N(i)$  is the number of resonant nuclei in part  $i$  at the frequency being measured, and  $F(i)$  is obtained from Fig 6 and the known, imposed field variation.

The amplitude of the total signal for a given measurement is then

$$I_1 = \sum I_1(i) = \sum N(i)F_1(i) \tag{4}$$

Here the subscript 1 indicates experiment number 1. If the experiment is now repeated several times we obtain a array which looks like

$$\begin{aligned} I_1 &= N(1)F_1(1) + N(2)F_1(2)... + N(10)F_1(10) \\ I_2 &= N(1)F_2(1) + N(2)F_2(2)... + N(10)F_2(10) \\ &\dots \\ I_M &= N(1)F_M(1) + N(2)F_M(2)... + N(10)F_M(10) \end{aligned} \tag{5}$$

where the subscript is the number of the experiment, 1...M, and the numbers in

parentheses are the sample positions as in Fig. 7. The functions  $F_1$  to  $F_M$  can be known, and the amplitudes  $I_1$  to  $I_M$  are measured. Standard mathematical techniques can now be applied to calculate the values of the  $N(i)$ , and the errors in these quantities [9].

To do this we create the column matrix  $X_m$  from the experimental measurements  $I_i$ , as

$$X_m = \sum_i F_i(m) I_i \quad (6)$$

and the matrix  $M_{m\ell}$  as

$$M_{m\ell} = \sum_i F_i(m) F_i(\ell) \quad (7)$$

We are assuming that the errors in all measurements are the same to simplify the algebra. [See Ref. 9 for more general formulas.] With these definitions a maximum likelihood determination for the  $N(i)$  leads to the matrix equation:

$$X = M N \quad (8)$$

The  $N$ 's can be found by solving

$$N = M^{-1} X \quad (9)$$

It is interesting to speculate that one could do this experiment in a strained sample, using a frequency away from the center of the line, and thus "map" the strain distribution.

#### ACKNOWLEDGEMENTS

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