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Nuclear quadrupole resonance studies of ^{209}Bi in $Bi_4(GeO_4)_3$ and $Bi_4(SiO_4)_3$

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Abstract. Nuclear quadrupole resonance (NQR) of ^{209}Bi has been studied in $Bi_4(GeO_4)_3$ and $Bi_4(SiO_4)_3$ using a wide band coherence-controlled superregenerative oscillator-detector. All the four allowed ($\Delta M_I = \pm 1$) transitions are observed. In both cases the electric field gradient (EFG) tensor is axially symmetric ($\eta = 0 \cdot 0$). The quadrupole coupling constant e^2qQ is measured to be $490 \cdot 8 \pm 1$ MHz and $470 \cdot 4 \pm 1$ MHz respectively. It is pointed out that the purely ionic model is inadequate to understand these results. With the available experimental accuracy and the strength of the applied electric field (~ 6 KV/cm), no field-induced effects on the NQR spectrum could be observed in the case of $Bi_4(SiO_4)_3$.

Keywords. Nuclear quadrupole resonance, ^{209}Bi; wide band coherence-control; electric field gradient; covalency effects; electric field-induced effects.

1. Introduction

Extensive literature has been published on the NQR studies (Voronkov and Feshin 1973, Gol'danskii 1964) of the halogen (Cl, Br, I) containing compounds. Due to their strong chemical affinity, the halogens form a vast variety of inorganic and organic chemical compounds. The quadrupole resonances of the halogen nuclei in these compounds are spread in the range of 1 MHz–1000 MHz. On the other hand NQR studies for nuclei such as ^{209}Bi, ^{75}As and the two antimony isotopes ^{121}Sb and ^{123}Sb have been reported in a rather fewer materials. The purpose of this communication is to report the results of our NQR measurements of ^{209}Bi in two crystals $Bi_4(GeO_4)_3$ and $Bi_4(SiO_4)_3$.

2. Experimental

The measurements have been made using a self-quenched superregenerative oscillator-detector. The schemetic diagram of this oscillator is shown in figure 1. This oscillator works satisfactorily in the range of 15 MHz–300 MHz. One has only to replace the inductances L_1 and L_2 for the appropriate range of radio-frequency. No component seems to be critical. The quench rate, and therefore the coherence, can be controlled (manually or mechanically) by varying the voltage to which the grid resistor is returned.

Generally while searching an unknown NQR signal in a material one has to vary the operating frequency of the spectrometer over a wide range. This conse-

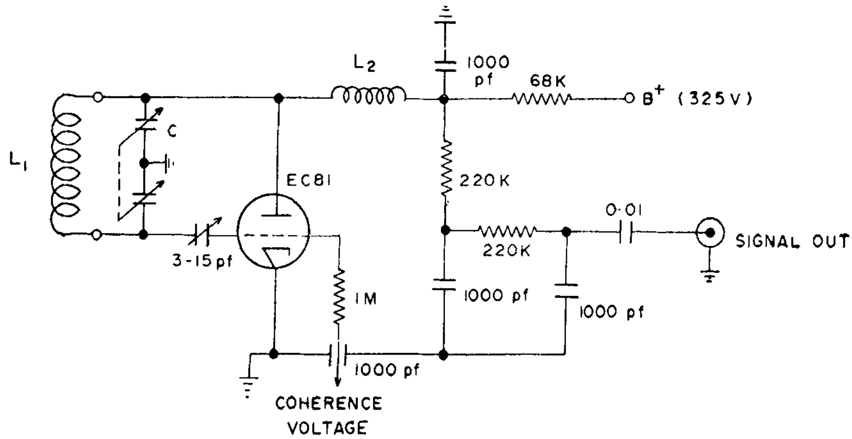

Figure 1 Self-quenched superregenerative oscillator-detector working in the range of 15 MHz—300 MHz.

C = Hammerlund HFD 15 x (3.8–16 pf)
L_1 = Sample Coil
L_2 = Ohmite choke suitable for the desired range of frequency

quently varies the coherence and thereby affects the sensitivity of the spectrometer. During the course of such experiments, it is therefore helpful to control the coherence automatically so that the instrument maintains a uniform sensitivity.

The spectrometer used in these measurements employs a feed-back loop for this purpose. The principle of the automatic wide band coherence control is as follows: Initially the coherence is set at a convenient level. The noise output of the oscillator-detector is rectified and converted into a dc voltage. This dc voltage is then compared with a fixed reference dc potential. Any variation of the coherence due to the change in the operating frequency (while searching an unknown resonance) results in the variation of the noise level which had been set originally. This generates an error signal, which by means of a servo-amplifier, tends to neutralize any variation in the noise level. This kind of instrument had been reported earlier by Peterson and Bridenbaugh (1964). They, however, did not give the details of the servo-amplifier. The complete schematics of the servo-system used in our spectrometer can be had on request from the authors.

Working of the wide band coherence-control is best illustrated with an example. The NQR signals of the two bromine isotopes, ^{79}Br and ^{81}Br, in $NaBrO_3$ occur at 178·0 MHz and 149·3 MHz respectively (Schawlow 1954) at room temperature. Figure 2 *a* shows the NQR signal of ^{81}Br isotope. Here the servo-system has not been put in operation. It is easily seen that a large variation of the noise level takes place as the frequency of the spectrometer increases; the total variation of the frequency shown in this figure is about 7 MHz. On the other hand, once the servo-system is put in operation, the noise level is maintained at a constant and steady level. The two bromine resonances, which are apart by about 30 MHz are observed with almost constant noise level as shown in figure 2 *b*. This clearly demonstrates the working of our servo-system as well as its utility in the NQR studies.

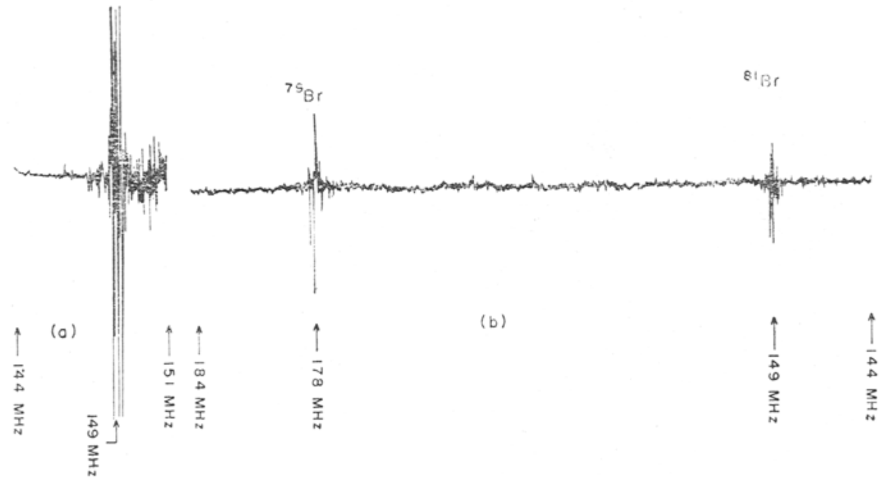

Figure 2. An illustration of the working of the servo amplifier (see text).

The frequencies are measured by introducing radio frequency electromagnetic radiation from an external standard signal generator into the superregenerative oscillator-detector. Due to the interference of the side-band responses with the main resonance, the accuracy to determine the resonance frequencies is rather limited. The crystals used in these measurements were gifted to us by W Rehwald of RCA, Zurich.

3. Results and discussion

The electric quadrupole interaction Hamiltonian H_Q, in the principal frame of reference of the EFG at the site of nucleus of interest, is given by (Abragam 1961)

$$H_Q = A\,[3I_z^2 - I(I+1) + \tfrac{1}{2}\eta\,(I_+^2 + I_-^2)]$$

where as usual $A = e^2 qQ/4I(2I-1)$, η is the asymmetry parameter of the EFG and I is the nuclear spin. Also eq is the magntide of the major principal component of the EFG tensor and eQ is the electric quadrupole moment of the nucleus. In the case of ^{209}Bi-nucleus ($I = 9/2$), one expects four allowed NQR transitions with $\triangle M_I = \pm 1$, namely, $1/2 \to 3/2$, $3/2 \to 5/2$, $5/2 \to 7/2$, $7/2 \to 9/2$. Table 1 summarizes the results of these measurements. Figure 3 shows the resonance line corresponding to the transition $7/2 \to 9/2$ in both the cases. The side-band interference can be seen clearly. It turns out that the frequencies of the four transitions may be expressed as ν_Q, $2\nu_Q$, $3\nu_Q$ and $4\nu_Q$ with $\nu_Q = 3e^2 qQ/2I(2I-1)\,h$. This implies that in H_Q, $\eta = 0$ and thus the EFG at the bismuth nucleus is axially symmetric.

Now the two crystals belong to the cubic space group $I\bar{4}3d$ and have four molecules in a unit cell. All the sixteen bismuth atoms occupy a sixteen-fold special position and are related by the symmetry operations of the crystal structure (Wyckoff 1968). This is why precisely only one set of four NQR transitions is observed. Further the point symmetry at the bismuth site is '3' and thus $\eta = 0$ is consistent with the crystal structure considerations,

Table 1. Frequencies (in MHz) of the four allowed ^{209}Bi NQR transitions in two crystals $Bi_4(GeO_4)_3$ and $Bi_4(SiO_4)_3$.

Sample	$1/2 \rightarrow 3/2$	$3/2 \rightarrow 5/2$	$5/2 \rightarrow 7/2$	$7/2 \rightarrow 9/2$	e^2qQ
$Bi_4(GeO_4)_3$	$20 \cdot 4 \pm 0 \cdot 05$	$40 \cdot 6 \pm 0 \cdot 1$	$61 \cdot 4 \pm 0 \cdot 1$	$81 \cdot 8 \pm 0 \cdot 1$	$490 \cdot 8 \pm 1$
$Bi_4(SiO_4)_3$	$19 \cdot 6 \pm 0 \cdot 05$	$39 \cdot 2 \pm 0 \cdot 1$	$59 \cdot 0 \pm 0 \cdot 1$	$78 \cdot 4 \pm 0 \cdot 1$	$470 \cdot 4 \pm 1$

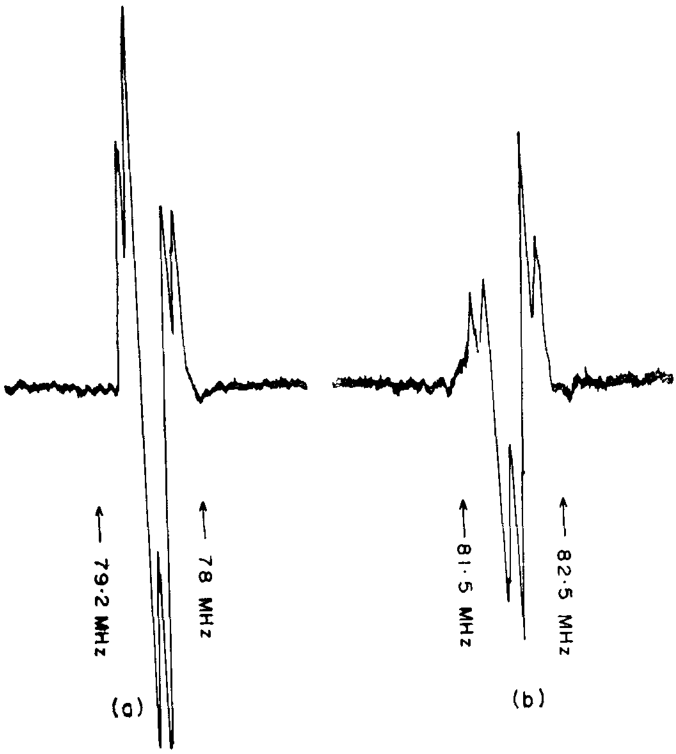

Figure 3. ^{209}Bi-NQR signals of the $7/2 \rightarrow 9/2$ transition in $Bi_4(SiO_4)_3$ and $Bi_4(GeO_4)_3$.

It is to be pointed out that in principle for nuclei with $I \geqslant 2$ the next higher multipole interaction, the hexadecapole interaction, also should be added to H_Q. In literature, evidence has been reported (Wang 1955) as to the observation of the effects, though very small, arising due to this term. In our case, if these interactions did exist, we should have observed the resonances with unequal frequency intervals. However, in these studies, any two neighbouring transitions are separated by ν_Q. The deviations, if any, from this constant frequency separation are within the experimental errors and thus no definite conclusion can be drawn as to the observation of these effects.

Brinkman and Denison (1973) have measured the nuclear quadrupole interaction of ^{209}Bi in these crystals by studying the rotation pattern of NMR spectra, The magnitudes of e^2qQ of ^{209}Bi in the two cases as reported here are in very good agreement with those obtained by them. They have, however, erroneously stated that a naive ionic model can account for the small difference in the values of e^2qQ in these two materials. The lattice constant of the cubic unit cell of $Bi_4(GeO_4)_3$ and $Bi_4(SiO_4)_3$ is, $a = 10 \cdot 527$ Å and $10 \cdot 300$ Å respectively (Wyckoff 1968). Thus according to the ionic model, the silicon compound, with a smaller lattice constant, must have larger value of e^2qQ. This is in striking contrast with experimental observations. In fact, these observations strongly suggest that in these cases a purely ionic model woud be inadequate altogether and therefore no attempt was made to calculate e^2qQ using a point charge model. The results can be understood by realizing that the Si–O distance in $Bi_4(SiO_4)_3$ is $1 \cdot 63$ Å which is to be found in other silicates as well (Pauling 1960). Thus one expects covalency effects in this material of magnitudes similar to those in other silicates. According to Pauling (1960) the effective charge on Si atom in silicates is $+1 \cdot 06e$ which is far from $+4e$ as suggested by purely ionic considerations. This effective charge on germanium may not be the same as that on silicon. This is why the ionic model fails to predict even qualitatively the relative magnitudes of e^2qQ of ^{209}Bi in these two crystals.

These crystals are piezoelectric and do not have a centre of symmetry. Thus it was of considerable interest to see the shift (or the broadening) of the resonance line due to an applied electric field. Gold electrodes were vacuum-deposited on the two opposite (100) faces of the $Bi_4(SiO_4)_3$ crystal. An electric field with strength ~ 6 KV/cm was applied along [100] direction. No measurable effect was observed. Attempts are in progress to generate fields of higher strength in order to observe these effects. The other crystal, $Bi_4(GeO_4)_3$, had an irregular shape and it was not possible to do this experiment.

4. Conclusion

We have reported here the results of our NQR studies on two members of eulytite family, namely, $Bi_4(GeO_4)_3$ and $Bi_4(SiO_4)_3$. It is pointed out that the covalency effects are very important in these cases in so far as the quadrupole interaction of bismuth is concerned. No measurable electric field-induced effects on the NQR spectral lines were observed.

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