^{209}Bi NQR Powder Spectra Influenced by Local and Applied Magnetic Fields*

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Several experimental techniques have shown evidence for the existence of internal magnetic fields of the order of 200 G in α-Bi_2O_3 [1]. The asymmetrical ^{209}Bi NQR lineshapes in Bi_3O_4Br also point to a source of poorly resolved splitting present in this compound.

In order to obtain further insight into the origin of the local magnetic fields in these compounds the ^{209}Bi NQR lineshapes of polycrystalline α-Bi_2O_3 and Bi_3O_4Br were recorded in weak (below 500 G) static magnetic fields. A calculation of the expected powder lineshapes in α-Bi_2O_3 under the influence of the internal and applied magnetic fields up to 1 kG was made. The results of the computer simulation are compared with the lineshapes recorded. From the ^{209}Bi lineshapes observed in the experiment, the local magnetic field at one of the two Bi-sites in Bi_3O_4Br was estimated.

Key words: ^{209}Bi NQR, Internal magnetic field, Lineshape, Applied magnetic field, Computer simulation.

Introduction

The lineshapes of NQR spectra perturbed by the applied Zeeman field (H_{ext}) for nuclei with spin $I = 3/2$ have been extensively studied in connection with the problem of determining the EFG asymmetry parameters in solids (including powders) [2–10]. NQR spectra under the influence of internal magnetic fields (H_{loc}) are also of considerable interest, since they allow to determine the strength and orientation of the local magnetic field with respect to the EFG axes [11–12].

The splitting, in zero magnetic field, of ^{209}Bi resonances observed in the NQR spectrum of α-Bi_2O_3 [13] conforms to the Zeeman patterns produced by internal magnetic fields of definite strength and orientation relative to the EFG axes at the Bi-sites.

In parallel with measurements of magnetic susceptibilities of those compounds [14] and the study of local magnetic fields using the μSR-technique [15], we extended the preliminary work [16] on the observation of ^{209}Bi NQR lineshapes in α-Bi_2O_3 and Bi_3O_4Br in weak (below 500 G) static magnetic fields. We hoped to obtain further insight into the origin of the local magnetic fields in these compounds by correlating the results with the calculated lineshapes.

A calculation of all the ^{209}Bi NQR powder lineshapes in α-Bi_2O_3 was made. The approach developed by Toyama [2] and later reconsidered by Bryant and Hacobian [9] was extended to the spin $\frac{9}{2}$ system influenced simultaneously by the internal and static external magnetic fields up to 1 kG. The computer simulation of the lineshapes was performed by the histogram method of van Meerwall et al. [17]. The results are compared to the lineshapes observed in the experiment.

Calculations

Theory

When the spin system of a quadrupolar nucleus is perturbed simultaneously by a local ($H_{loc}(\theta', \varphi')$), radio-frequency ($H_{rf}(\theta_1, \varphi_1)$) and external ($H_{ext}(\theta_0, \varphi_0)$) magnetic field ($\theta$ and φ are polar coordinates in the principal axes system of the EFG), its entire Hamiltonian is

$$H = H_Q + H_M + H_{rf}, \quad (1)$$

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where

$$H_Q = e^2 Q q_{zz} h^{-1}/\{4I(2I-1)\}\,[3I_z^2 - I^2 + \eta(I_x^2 - I_y^2)]\,, \tag{2}$$

$$H_M = H_{loc} + H_{rf}\,, \tag{3}$$

$$H_{loc} = -\gamma H_{loc} \cdot (I_x \sin\theta' \cos\varphi' + I_y \sin\theta' \sin\varphi' + I_z \cos\theta')\,, \tag{4}$$

$$H_{ext} = -\gamma H_{ext} \cdot (I_x \sin\theta_0 \cos\varphi_0 + I_y \sin\theta_0 \sin\varphi_0 + I_z \cos\theta_0)\,, \tag{5}$$

$$H_{rf} = -2\gamma H_{rf}(I_x \sin\theta_1 \cos\varphi_1 + I_y \sin\theta_1 \sin\varphi_1 + I_z \cos\theta_1 \cos\omega t)\,. \tag{6}$$

Here $e^2 Q q_{zz}/h$ is the quadrupole coupling constant, η the asymmetry parameter of the EFG, γ the gyromagnetic ratio, and ω the frequency of H_{rf}. By defining b as the ratio of the fields,

$$b = H_{ext}/H_{loc}\,, \tag{7}$$

the Hamiltonian that describes the magnetic interaction is given as

$$H_M = -\gamma H_{loc}[I_x(\sin\theta' \cos\varphi' + b \sin\theta_0 \cos\varphi_0) + I_y(\sin\theta' \sin\varphi' + b \sin\theta_0 \cos\varphi_0) + I_z(\cos\theta' + b \cos\theta_0)]\,. \tag{8}$$

The formula for the transition probability between the states E' and E'' (provided $e^2 Q q_{zz}/h \gg \gamma H_{loc}, \gamma H_{ext}$) is known to be

$$W = T^2(E', E'')\, g(\nu)/h^2\,, \tag{9}$$

where $g(\nu)$ is the spectral distribution function, and the energy levels E' and E'' are the eigenstates of the Hamiltonian (1). The square transition moment $T^2(E', E'')$ may be written in terms of the radio-frequency field components as

$$T^2(E', E'') = \gamma^2 |\langle E''| I H_{rf} |E'\rangle|^2 = \gamma^2 \sum H_{ri} H_{rj} J_{ij}(E', E'')\,, \; i,j = x,y,z \tag{10}$$

Here $J_{i,j}$ are the intensity parameters

$$J_{ij}(E', E'') = 1/2[\langle E''|I_i|E'\rangle\langle E'|I_j|E''\rangle + \langle E''|I_j|E'\rangle\langle E'|I_i|E''\rangle]\,. \tag{11}$$

The NQR lineshapes of polycrystalline samples in a weak applied magnetic field were simulated for half integral spin nuclei including $I = 9/2$ by Bryant et al. [9]. In zero applied magnetic field the polycrystalline material may be considered as single crystal with respect to the internal magnetic field H_{loc}, whose strength and orientation with respect to the EFG is fixed within a representative microcrystalline. On the other hand, the directions of the EFG principal axes at the ^{209}Bi site are randomly oriented with respect to the direction of H_{rf}. The transition moment should therefore be averaged over the polar angles θ_1 and φ_1 as follows:

$$\overline{T^2}(E', E'') = \tfrac{1}{4}\pi \int_0^{\pi} \sin\theta_1 \,\mathrm{d}\theta_1 \int_0^{2\pi} \mathrm{d}\varphi_1 \; T^2(E', E'') = \gamma^2 H_r^2/3[J_{xx}(E', E'') + J_{yy}(E', E'') + J_{zz}(E', E'')]\,, \tag{12}$$

where the intensity parameters for the $\Delta|m| = 1$ transition are

$$J_{xx}(\pm) = (1/2)(I_x^2)_{m',m''}\{1 \pm F_{m',m''}[(I_x)_{m',m'}(I_x)_{m'',m''} H_x^2 + (I_y)_{m',m'}(I_y)_{m'',m''} H_y^2 + (I_z)_{m',m'}(I_z)_{m'',m''} H_z^2]\}\,, \tag{13}$$

$$J_{yy}(\pm) = (1/2)(I_y^2)_{m',m''}\{1 \pm F_{m',m''}[-(I_x)_{m',m'}(I_x)_{m'',m''} H_x^2 - (I_y)_{m',m'}(I_y)_{m'',m''} H_y^2 + (I_z)_{m',m'}(I_z)_{m'',m''} H_z^2]\}\,, \tag{14}$$

$$J_{zz}(\pm) = (1/2)(I_z^2)_{m',m''}\{1 \pm F_{m',m''}[-(I_x)_{m',m'}(I_x)_{m'',m''} H_x^2 + (I_y)_{m',m'}(I_y)_{m'',m''} H_y^2 - (I_z)_{m',m'}(I_z)_{m'',m''} H_z^2]\}\,, \tag{15}$$

and

$$J_{ij}(\pm) \equiv J_{ij}(m'M, \pm m''M) = J_{ij}(-m'M, \mp m''M); m'' = m' + 1\,.$$

Here the symbol F is given as

$$F_{m',m''} = 1/[E_M(m')\, E_M(m'')]\,, \tag{16}$$

where

$$E_M(m) = \pm[(I_x)_{m,m}^2 H_x^2 + (I_y)_{m,m}^2 H_y^2 + (I_z)_{m,m}^2 H_z^2]^{1/2}\,. \tag{17}$$

Under the simultaneous action of both internal and external magnetic fields, H_x^2, H_y^2, and H_z^2 become

$$H_x^2 = \gamma^2 H_{loc}^2 (\sin\theta' \cos\varphi' + b \sin\theta_0 \cos\varphi_0)^2\,,$$
$$H_y^2 = \gamma^2 H_{loc}^2 (\sin\theta' \sin\varphi' + b \sin\theta_0 \sin\varphi_0)^2\,, \tag{18}$$
$$H_z^2 = \gamma^2 H_{loc}^2 (\cos\theta' + b \cos\theta_0)^2\,.$$

The matrix elements of the components of nuclear spins (transition moments) I_x, I_y, and I_z in (13)–(17) were used in the representation of the quadrupole Hamiltonian (2). For the nuclei with half integral spins $I > 3/2$ and arbitrary value of asymmetry parameter η they can be derived from the tables of Cohen [18]. For

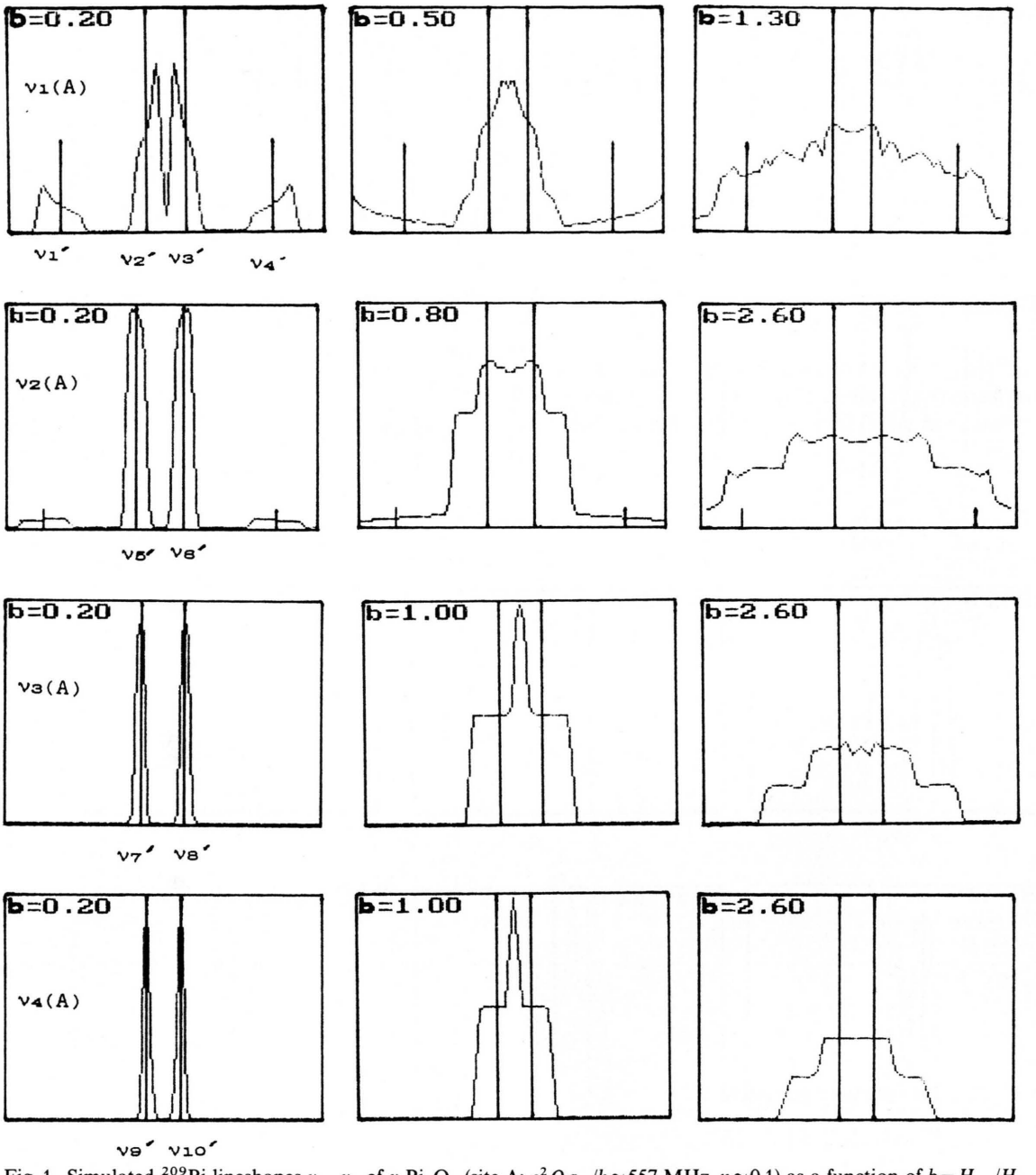

Fig. 1. Simulated ^{209}Bi lineshapes $\nu_1 - \nu_4$ of α-Bi_2O_3 (site A: $e^2 Q q_{zz}/h \approx 557$ MHz, $\eta \approx 0.1$) as a function of $b = H_{ext}/H_{loc}$ (see text).

nuclei with $I = 3/2$ one can calculate them using the analytical expressions reported in [2], [19]. If the magnetic and quadrupole interaction energies are of arbitrary strengths, one can refer to the procedure described in [7].

Computer Simulation of α-Bi_2O_3 Lineshapes

The calculation of the powder NQR lineshapes in zero field and applied magnetic field was made by the histogram method [17]. The Gauss spectral distribu-

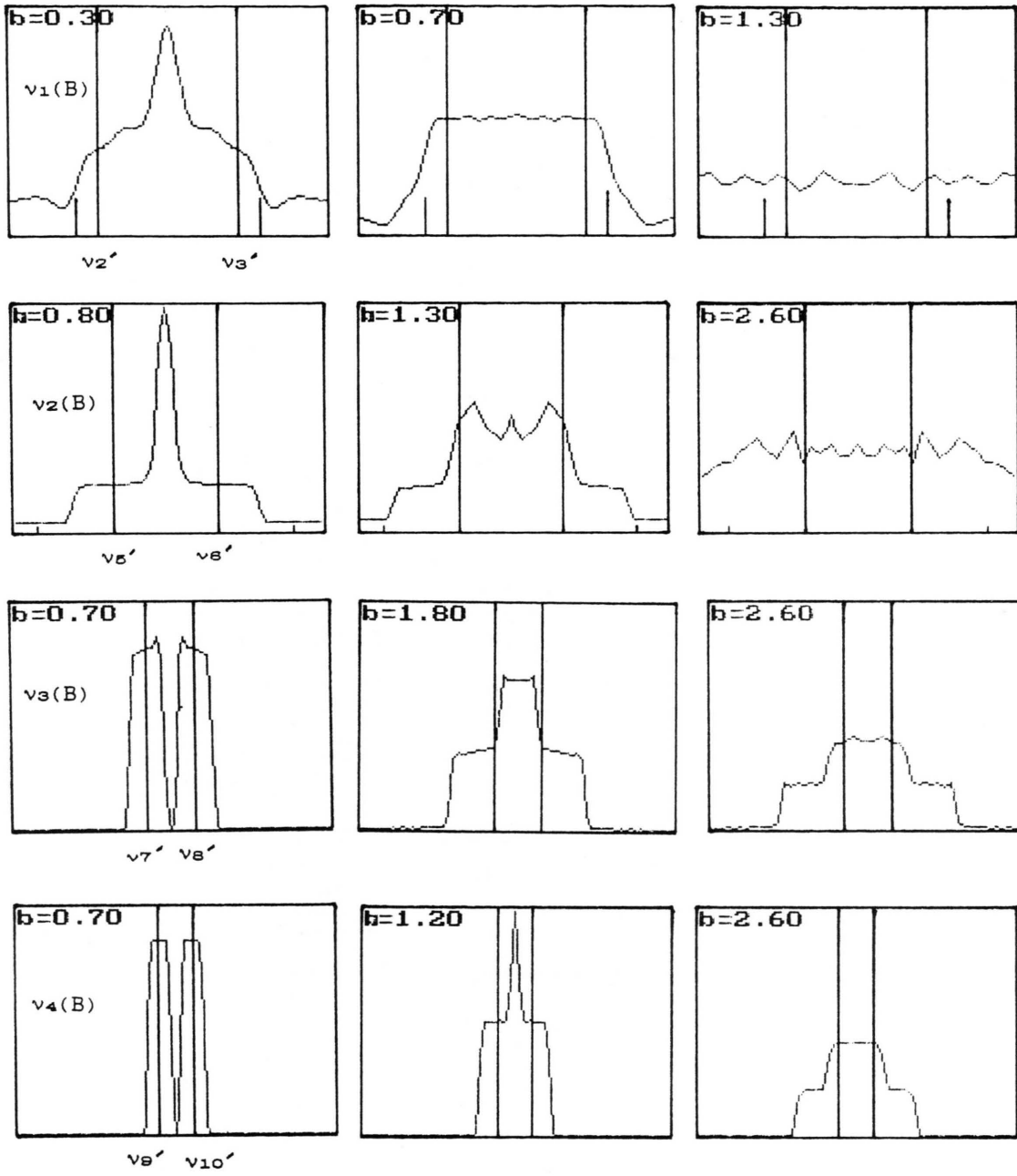

Fig. 2. Simulated ^{209}Bi lineshapes $\nu_1-\nu_4$ of α-Bi_2O_3 (site B: $e^2Qq_{zz}/h\approx 483$ MHz, $\eta\approx 0.4$) as a function of $b=H_{ext}/H_{loc}$.

tion function was used,

$$g_i(\nu)=a_i\exp[(\nu-\nu_{0i})^2/\sigma_i^2], \tag{19}$$

which took into account the initial line broadenings (σ_i) and central resonance frequencies (ν_{0i}), generally different for various line components.

The main steps of the simulated powder lineshape evolution in the external magnetic field are shown in Figs. 1, 2 for all the transitions assigned to the two Bi-sites in α-Bi_2O_3. The vertical lines in the figures mark the positions of the component centers of the ^{209}Bi resonance lines in zero external field ($b=0$) and

make up the scale in accordance with Table 1. The table lists the frequencies of these components (ν_i'), which are consecutively numbered, and the splittings between them ($\delta\nu_i$). The parameters of the quadrupole interaction ($e^2 Q q_{zz}$ and η), and the local field characteristics (H_{loc}, θ, φ, $\nu_0 = (\gamma/2\pi) H_{loc}$) are also given. The labelling suggests that the NQR lines assigned to the $\Delta m = 1/2 - 3/2$ transitions involve the components from ν_1' to ν_4', those assigned to the $\Delta m = 3/2 - 5/2$ transitions, the ν_5' and ν_6' components, and so on. This means that $\delta\nu_1 = \nu_2' - \nu_1'$, ... $\delta\nu_4 = \nu_6' - \nu_5'$, etc.

The local field parameters are in general agreement with the results published previously [13]. As Figs. 1, 2 show, the lineshapes exhibit a gradual decrease in splitting with increasing H_{ext} leading to a coalescence of the components at $H_{ext} < H_{loc}$. The estimated field of coalescence appeared sensitive to the magnitude of the σ-parameter, whose reasonable value (0.1 MHz) has been chosen empirically by the best agreement with the experiment. The results of the simulations show a weaker effect of the external magnetic field on the lineshapes of upper transitions.

Table 1. The ^{209}Bi NQR spectroscopic parameters for α-Bi_2O_3 at 77 K (see text).

Parameters	A-site		B-site	
	exp.	calc.	exp.	calc.
ν_1, MHz	24.92		–	
ν_2, MHz	25.12		39.25	
ν_3, MHz	25.28		39.43	
ν_4, MHz	25.46		–	
ν_5, MHz	45.73		37.09	
ν_6, MHz	45.92		37.35	
ν_7, MHz	69.32		58.20	
ν_8, MHz	69.50		58.40	
ν_9, MHz	92.67		79.32	
ν_{10}, MHz	92.84		79.52	
$\delta\nu_1$, MHz	0.20	0.19	<0.04	0.02
$\delta\nu_2$, MHz	0.16	0.12	0.18	0.16
$\delta\nu_3$, MHz	0.18	0.19	<0.04	0.02
$\delta\nu_4$, MHz	0.19	0.15	0.25	0.25
$\delta\nu_5$, MHz	0.18	0.18	0.20	0.21
$\delta\nu_6$, MHz	0.17	0.19	0.21	0.19
ν_0, MHz		0.117		0.093
H_{loc}, Oe		171		136
θ, degree		38		0
φ, degree		0		
η		0.13		0.40
$\frac{e^2 Q q_{zz}}{h}$ MHz		557		483

Experimental

The ^{209}Bi NQR spectra of α-Bi_2O_3 and Bi_3O_4Br were recorded at 77 K using a pulse NQR spectrometer ISSh-1 operating in the frequency range of 2 to 300 MHz. The α-Bi_2O_3 sample consisted of small single crystals [1], which were grown by a hydrothermal procedure at 573 K in an autoclave under a pressure of 80 MPa. According to the results of X-ray microanalysis (CAMEBAX-301) and those of a neutron diffraction study, kindly communicated to us by Sarin V. A. prior to publication, the composition of the samples may be written as $(Bi_{0.981}Pb_{0.008}Cr_{0.0005}Si_{0.001})_2O_3$, the oxygen content being stoichiometric to the second decimal. The Bi_3O_4Br sample was a powder.

The external magnetic field of variable strength was applied perpendicular to the radio-frequency field, and the series of lineshapes was recorded for all the NQR transitions of both compounds. Because the experiment was time-consuming, we had to choose the operating conditions in such a way as to reach a compromise between the speed of scanning and the extent of accumulation. In order to avoid the night pauses during the recording of the same line the latter was chosen relatively low.

Figure 3 shows the ^{209}Bi lineshapes recorded for α-Bi_2O_3 at 77 K in external magnetic fields of selected strength. Only the curves that reflect the main steps in the lineshape evolution are presented. The lines assigned to the upper transitions were omitted, being least demonstrative. As one can see from the figure, the split lines coalesce at values of $H_{ext} < H_{loc}$ followed by a recurrence of splitting accompanied by line broadening. It is also seen that the lower-transition resonances increase in intensity in H_{ext}, which is most clearly evidenced by the line ν_1 assigned to the B site of bismuth.

As Table 1 shows that the calculated parameters account very well for the splitting measured at $H_{ext} = 0$. It is to be noted that the compounds in question present a complicated system for the calculation of the quadrupole interaction and local magnetic field characteristics. It is well known that the values of $e^2 Q q/h$ and η for the heavy multispin nuclei can be determined only approximately even in the absence of internal magnetic fields. The asymmetry parameters, when calculated from the ratio of neighboring transi-

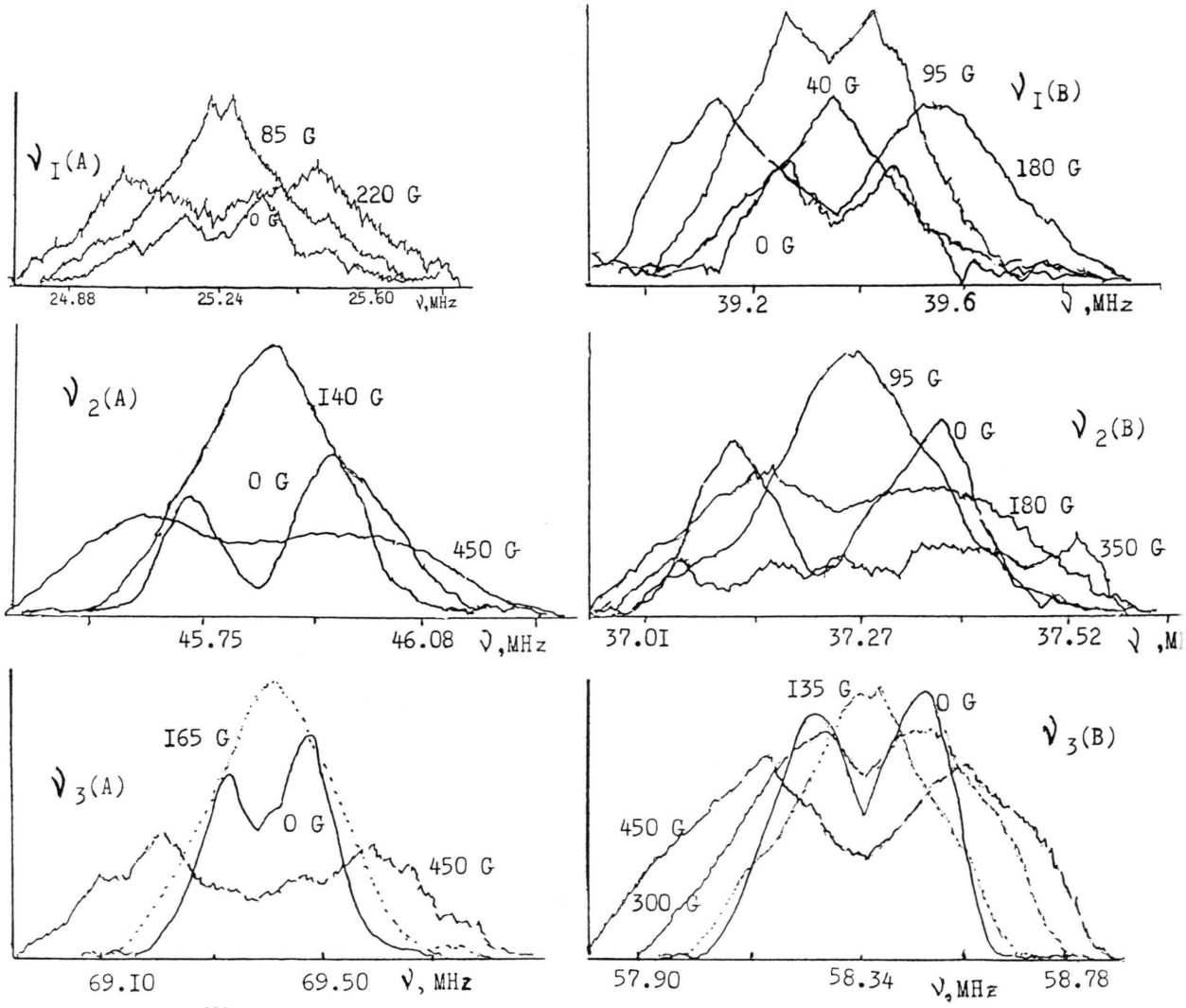

Fig. 3. Evolution of ^{209}Bi lineshapes of α-Bi_2O_3 in external magnetic fields. Left column shows the lines assigned to the A site; right column – those assigned to the B site. The upper-transition lines (ν_4) are omitted (see text).

tion frequencies, may differ by several percent for various pairs of frequencies assigned to the same nucleus site. Among others, the contribution of hexadecapole coupling may be a probable reason for such a difference. The splitting of resonances in internal magnetic field of unknown strength and orientation adds to the complexity of the problem.

The results of our calculation show that the simulated lineshapes are quite sensitive to the values of the asymmetry parameter. As a whole, the calculated lines follow the trend to coalesce at $H_{ext} < H_{loc}$ as exhibited by the measured NQR lines. They also broaden and decrease in intensity in higher external fields. The simulated spectra, however, poorly reflect the recurrence of a line splitting at H_{ext} exceeding the field of coalescence. This feature is seen in Figs. 1, 2 as a weak tendency only. The calculated lineshapes do also not reflect the increase in the integral intensity of the ^{209}Bi resonances in external magnetic fields which was observed for α-Bi_2O_3 and especially for Bi_3O_4Br.

The ^{209}Bi NQR spectrum of Bi_3O_4Br [20] is consistent with the occurrence of two Bi-sites in the crystalline lattice of the compound (Table 2 of [1]). The ^{209}Bi lineshapes assigned to the B-sites are distinctly

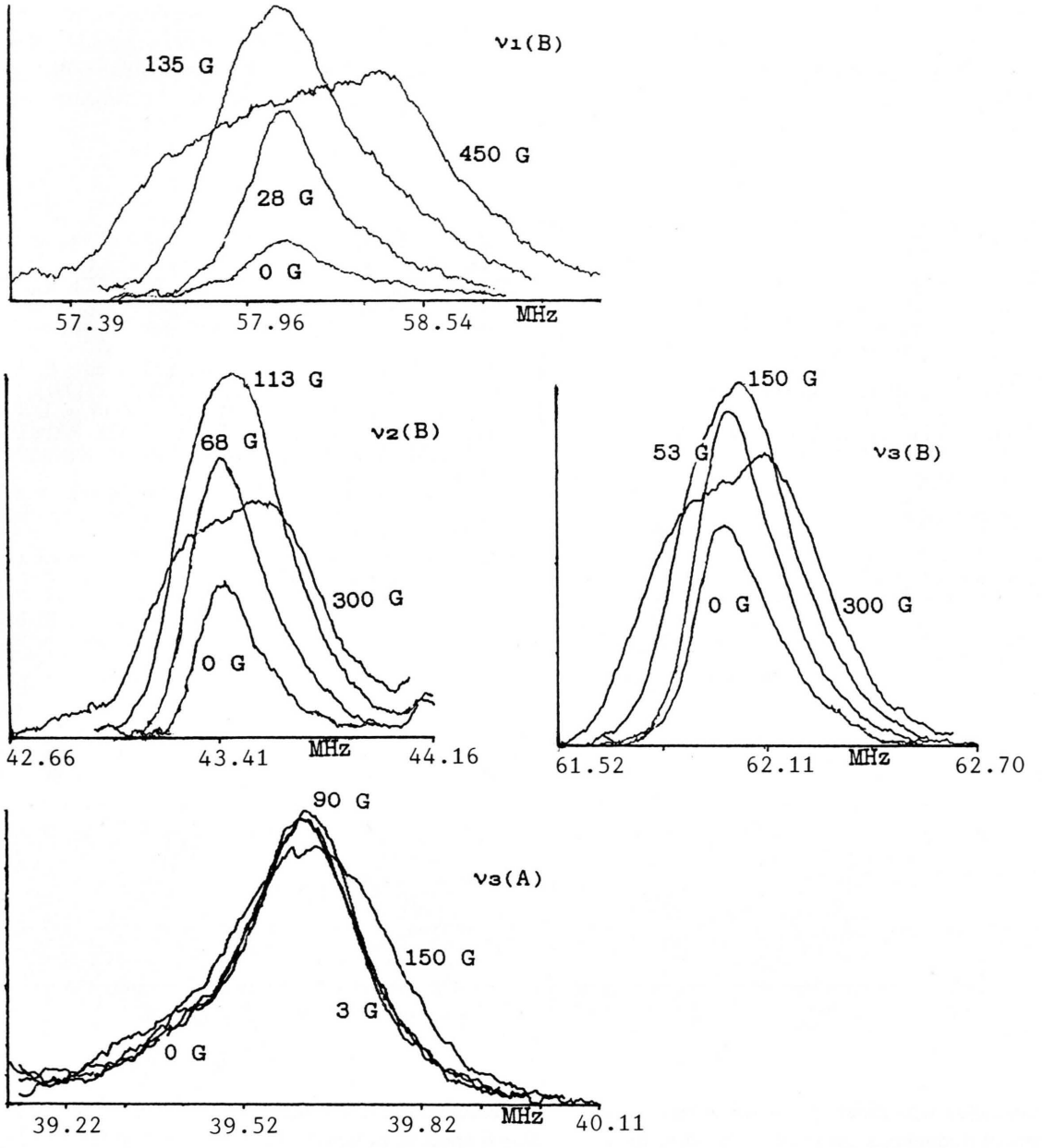

Fig. 4. Recording of selected ^{209}Bi NQR lines in Bi_3O_4Br (see Table 2 of [1]) in external magnetic fields at 77 K.

asymmetric, which enabled us to estimate H_{loc} at the B site: $e^2Qq/h = 536.9$ MHz; $\eta = 61.7\%$; $H_{loc} = 250 \pm 10$ G, $\theta = (152 \pm 2)°$; $\varphi = (6 \pm 2)°$. For the reasons discussed in [1] we could not make any definite conclusions on H_{loc} at the A site of Bi_3O_4Br.

The most interesting feature of the compound is a dramatic rise of intensity of its ^{209}Bi resonances in an external field, particularly strong for the lower-transition line assigned to the B site (Figure 4). As it was noted [1], the external magnetic field had no observable effect on the characteristic time of the ^{209}Bi spin echo decay, i.e. its intensity increase originated not (at least not only) from line narrowing. The true mechanism of this phenomenon is not yet understood.

Conclusions

The ^{209}Bi NQR spectra of α-Bi_2O_3 and Bi_3O_4Br show evidence for internal magnetic fields of about 200 G existing in these compounds.

Calculations of the ^{209}Bi NQR lineshapes under the influence of the internal and external magnetic fields up to 1 kG were performed for polycrystalline α-Bi_2O_3. Only qualitative agreement with the experimental observations was obtained.

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