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

N. E. Ainbinder, G. A. Volgina, E. A. Kravchenko, A. N. Osipenko, A. A. Gippius, Suan Hai Fam, and A. A. Bush

1 Radiospectroscopy Laboratory, Perm University, Perm 614005, Russia.
2 Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow 117907, Russia.
3 Moscow State University, Department of Physics, Moscow 117234, Russia

**Z. Naturforsch.** 49a, 425–432 (1994); received December 15, 1993

Several experimental techniques have shown evidence for the existence of internal magnetic fields of the order of 200 G in z-Bi$_2$O$_3$ [1]. The asymmetrical 209Bi NQR lineshapes in Bi$_3$O$_4$Br 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 209Bi NQR lineshapes of polycrystalline z-Bi$_2$O$_3$ and Bi$_3$O$_4$Br were recorded in weak (below 500 G) static magnetic fields. A calculation of the expected powder lineshapes in z-Bi$_2$O$_3$ 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 209Bi lineshapes observed in the experiment, the local magnetic field at one of the two Bi-sites in Bi$_3$O$_4$Br was estimated.

**Key words:** 209Bi NQR, Internal magnetic field, Lineshape, Applied magnetic field, Computer simulation.

---

**Introduction**

The lineshapes of NQR spectra perturbed by the applied Zeeman field ($H_{\text{ext}}$) 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 ($H_{\text{int}}$) are 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 209Bi resonances observed in the NQR spectrum of z-Bi$_2$O$_3$ [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 209Bi NQR lineshapes in z-Bi$_2$O$_3$ and Bi$_3$O$_4$Br 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 209Bi NQR powder lineshapes in z-Bi$_2$O$_3$ was made. The approach developed by Toyama [2] and later reconsidered by Bryant and Hacobian [9] was extended to the spin $3/2$ 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 ($H_{\text{loc}}(\theta, \phi')$), radio-frequency ($H_{\text{rf}}(\theta_1, \phi_1)$) and external ($H_{\text{ext}}(\theta_2, \phi_2)$) magnetic field ($\theta$ and $\phi$ are polar coordinates in the principal axes system of the EFG), its entire Hamiltonian is

$$H = H_Q + H_M + H_{\text{rf}},$$

where $H_Q$, $H_M$, and $H_{\text{rf}}$ are the nuclear Hamiltonians for the quadrupole, spin and rf terms, respectively.

---

* Presented at the XIIth International Symposium on Nuclear Quadrupole Resonance, Zürich, July 19–23, 1993.

Reprint requests to Prof. Dr. E. A. Kravchenko, Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow 117907, Russia.

0932-0784 / 94 / 0100-0425 $01.30/0. – Please order a reprint rather than making your own copy.
where

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

\[ H_M = H_{\text{loc}} + H_{\text{rf}}, \]

\[ H_{\text{loc}} = -\gamma H_{\text{loc}} \]

\begin{align*}
&\cdot (I_x \sin \theta \cos \phi' + I_y \sin \theta \sin \phi' + I_z \cos \theta'), \\
&H_{\text{ext}} = -\gamma H_{\text{ext}} \\
&\cdot (I_x \sin \theta_0 \cos \phi_0 + I_y \sin \theta_0 \sin \phi_0 + I_z \cos \theta_0), \\
&H_{\text{rf}} = -2\gamma H_{\text{rf}} (I_x \sin \theta_1 \cos \phi_1 + I_y \sin \theta_1 \sin \phi_1 \\
&+ I_z \cos \theta_1 \cos \omega t).
\end{align*}

Here \( e^2 Q q_{zz} / h \) is the quadrupole coupling constant, \( \gamma \) the asymmetry parameter of the EFG, \( \gamma \) the gyromagnetic ratio, and \( \omega \) the frequency of \( H_{\text{rf}} \). By defining \( b \) as the ratio of the fields,

\[ b = H_{\text{ext}} / H_{\text{loc}}, \]

the Hamiltonian that describes the magnetic interaction is given as

\[ H_M = -\gamma H_{\text{loc}} I_x (\sin \theta \cos \phi' + b \sin \theta_0 \cos \phi_0) + I_y (\sin \theta \sin \phi' + b \sin \theta_0 \cos \phi_0) + I_z (\cos \theta + b \cos \theta_0). \]

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

\[ W = T^2(E', E'') g(v)/h^2, \]

where \( g(v) \) 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 frequency field components as

\[ T^2(E', E'') = \gamma^2 \left| \langle E' | I H_{\text{rf}} | E'' \rangle \right|^2 \]

\[ = \gamma^2 \sum J_{ij} (E', E''), \quad i, j = x, y, z \]

Here \( J_{ij} \) are the intensity parameters

\[ J_{ij}(E', E'') = 1/2 \left( \langle E'' | I_j | E' \rangle \langle E' | I_i | E'' \rangle \right) \]

\[ + \left( \langle E' | I_j | E'' \rangle \langle E'' | I_i | E' \rangle \right). \]

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 \( H_{\text{loc}} \), 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 \( ^{209}\text{Bi} \) site are randomly oriented with respect to the direction of \( H_{\text{rf}} \). The transition moment should therefore be averaged over the polar angles \( \theta_1 \) and \( \phi_1 \) as follows:

\[ T^2(E', E'') = \frac{1}{4} \pi \int_0^{\pi} \sin \theta_1 \int_0^{\pi/2} \int_0^{2\pi} d\phi_1 \left( \frac{1}{2} \right)^{10} \left| \langle E' \rangle | I H_{\text{rf}} | E'' \rangle \right|^2 \]

\[ = \gamma^2 H^2 / 3 [J_{xx}(E', E'') + J_{yy}(E', E'') \]

\[ + J_{zz}(E', E'')], \]

where the intensity parameters for the \( \Delta m = 1 \) transition are

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

\[ J_{yy}(\pm) = (1/2) \left( I_y^2 \right)_{m', m''} \left( -\left( I_y \right)_{m', m} \left( I_y \right)_{m, m'} H_x^2 \right) - (I_y)_{m', m} (I_y)_{m, m'} H_y^2 + (I_z)_{m', m} (I_z)_{m, m'} H_z^2 \],

\[ J_{zz}(\pm) = (1/2) \left( I_z^2 \right)_{m', m''} \left( \pm \left( I_z \right)_{m', m} \left( I_z \right)_{m, m'} H_x^2 \right) \]

\[ + (I_y)_{m', m} (I_y)_{m, m'} H_y^2 - (I_z)_{m', m} (I_z)_{m, m'} H_z^2 \],

and

\[ J_{ij}(\pm) = J_{ij}(m'M, m'M) = J_{ij}(m'M, m'M); m'' = m' + 1. \]

Here the symbol \( F \) is given as

\[ F_{m', m''} = 1/\left( E_M(m') E_M(m'') \right), \]

where

\[ E_M(m) = \pm \left| \langle I_{m, m} \rangle H_x^2 + (I_y)_{m, m} H_y^2 + (I_z)_{m, m} H_z^2 \right|^{1/2}. \]

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

\[ H_x^2 = \gamma^2 H_{\text{loc}}^2 (\sin \theta \cos \phi' + b \sin \theta_0 \cos \phi_0)^2, \]

\[ H_y^2 = \gamma^2 H_{\text{loc}}^2 (\sin \theta \sin \phi' + b \sin \theta_0 \sin \phi_0)^2, \]

\[ H_z^2 = \gamma^2 H_{\text{loc}}^2 (\cos \theta' + b \cos \theta_0)^2. \]

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 \( \eta \) they can be derived from the tables of Cohen [18]. For
E. A. Kravchenko et al. ■ 209Bi NQR Powder Spectra Influenced by Local and Applied Magnetic Fields

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 $\alpha$-Bi$_2$O$_3$ 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 $^{209}\text{Bi}$ lineshapes $v_1-v_4$ of $\alpha$-Bi$_2$O$_3$ (site B: $e^2Q_{zz}/\hbar \approx 483$ MHz, $\eta \approx 0.4$) as a function of $b = H_{\text{ext}}/H_{\text{loc}}$.

tion function was used,

$$g_i(v) = a_i \exp\left[\frac{(v-v_{oi})^2}{\sigma_i^2}\right],$$

which took into account the initial line broadenings ($\sigma_i$) and central resonance frequencies ($v_{oi}$), 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 $\alpha$-Bi$_2$O$_3$. The vertical lines in the figures mark the positions of the component centers of the $^{209}\text{Bi}$ resonance lines in zero external field ($b=0$) and
make up the scale in accordance with Table 1. The

<table>
<thead>
<tr>
<th>Parameters</th>
<th>A-site</th>
<th>B-site</th>
<th>A-site</th>
<th>B-site</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_1 )</td>
<td>24.92</td>
<td>-</td>
<td>24.92</td>
<td>-</td>
</tr>
<tr>
<td>( \nu_2 )</td>
<td>25.12</td>
<td>39.25</td>
<td>25.12</td>
<td>39.25</td>
</tr>
<tr>
<td>( \nu_3 )</td>
<td>25.28</td>
<td>39.43</td>
<td>25.28</td>
<td>39.43</td>
</tr>
<tr>
<td>( \nu_4 )</td>
<td>25.46</td>
<td>-</td>
<td>25.46</td>
<td>-</td>
</tr>
<tr>
<td>( \nu_5 )</td>
<td>45.73</td>
<td>37.09</td>
<td>45.73</td>
<td>37.09</td>
</tr>
<tr>
<td>( \nu_6 )</td>
<td>45.92</td>
<td>37.35</td>
<td>45.92</td>
<td>37.35</td>
</tr>
<tr>
<td>( \nu_7 )</td>
<td>69.32</td>
<td>58.20</td>
<td>69.32</td>
<td>58.20</td>
</tr>
<tr>
<td>( \nu_8 )</td>
<td>69.50</td>
<td>58.40</td>
<td>69.50</td>
<td>58.40</td>
</tr>
<tr>
<td>( \nu_9 )</td>
<td>92.67</td>
<td>79.32</td>
<td>92.67</td>
<td>79.32</td>
</tr>
<tr>
<td>( \nu_{10} )</td>
<td>92.84</td>
<td>79.52</td>
<td>92.84</td>
<td>79.52</td>
</tr>
<tr>
<td>( \delta \nu_1 )</td>
<td>0.20</td>
<td>0.04</td>
<td>0.20</td>
<td>0.04</td>
</tr>
<tr>
<td>( \delta \nu_2 )</td>
<td>0.16</td>
<td>0.18</td>
<td>0.16</td>
<td>0.18</td>
</tr>
<tr>
<td>( \delta \nu_3 )</td>
<td>0.18</td>
<td>0.04</td>
<td>0.18</td>
<td>0.04</td>
</tr>
<tr>
<td>( \delta \nu_4 )</td>
<td>0.19</td>
<td>0.25</td>
<td>0.19</td>
<td>0.25</td>
</tr>
<tr>
<td>( \delta \nu_5 )</td>
<td>0.18</td>
<td>0.20</td>
<td>0.18</td>
<td>0.20</td>
</tr>
<tr>
<td>( \delta \nu_6 )</td>
<td>0.17</td>
<td>0.19</td>
<td>0.17</td>
<td>0.19</td>
</tr>
<tr>
<td>( \nu_0 )</td>
<td>0.117</td>
<td>0.093</td>
<td>0.117</td>
<td>0.093</td>
</tr>
<tr>
<td>( \theta )</td>
<td>38</td>
<td>0</td>
<td>38</td>
<td>0</td>
</tr>
<tr>
<td>( \phi )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \eta )</td>
<td>0.13</td>
<td>0.40</td>
<td>0.13</td>
<td>0.40</td>
</tr>
<tr>
<td>( e^2 Q q_0 / h ) MHz</td>
<td>557</td>
<td>483</td>
<td>557</td>
<td>483</td>
</tr>
</tbody>
</table>

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 \( H_{\text{ext}} \) leading to a coalescence of the components at \( H_{\text{ext}} < H_{\text{loc}} \). The estimated field of coalescence appeared sensitive to the magnitude of the \( \sigma \)-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.

**Experimental**

The \( ^{209}\text{Bi} \) NQR spectra of \( \alpha-\text{Bi}_2\text{O}_3 \) and \( \text{Bi}_3\text{O}_4\text{Br} \) were recorded at 77 K using a pulse NQR spectrometer ISSh-1 operating in the frequency range of 2 to 300 MHz. The \( \alpha-\text{Bi}_2\text{O}_3 \) 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 \( (\text{Bi}_{0.981}\text{Pb}_{0.008}\text{Cr}_{0.0005}\text{Si}_{0.001})_2\text{O}_3 \), the oxygen content being stoichiometric to the second decimal. The \( \text{Bi}_3\text{O}_4\text{Br} \) 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 \( ^{209}\text{Bi} \) lineshapes recorded for \( \alpha-\text{Bi}_2\text{O}_3 \) 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 \( H_{\text{ext}} < H_{\text{loc}} \) followed by a recurrence of splitting accompanied by line broadening. It is also seen that the lower-transition resonances increase in intensity in \( H_{\text{ext}} \), which is most clearly evidenced by the line \( \nu_1 \) assigned to the B site of bismuth.

As Table 1 shows that the calculated parameters account very well for the splitting measured at \( H_{\text{ext}} = 0 \). 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 \( \eta \) 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-
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 \( H_{\text{ext}} < H_{\text{loc}} \) 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 \( H_{\text{ext}} \) 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 \(^{209}\text{Bi} \) resonances in external magnetic fields which was observed for \( x\)-\( \text{Bi}_2\text{O}_3 \) and especially for \( \text{Bi}_3\text{O}_4\text{Br} \).

The \(^{209}\text{Bi} \) NQR spectrum of \( \text{Bi}_3\text{O}_4\text{Br} \) [20] is consistent with the occurrence of two Bi-sites in the crystalline lattice of the compound (Table 2 of [1]). The \(^{209}\text{Bi} \) lineshapes assigned to the B-sites are distinctly
asymmetric, which enabled us to estimate $H_{\text{loc}}$ at the B site: $e^2 \frac{Q q}{h} = 536.9$ MHz; $\eta = 61.7\%$; $H_{\text{loc}} = 250 \pm 10$ G, $\theta = (152 \pm 2)^\circ$; $\varphi = (6 \pm 2)^\circ$. For the reasons discussed in [1] we could not make any definite conclusions on $H_{\text{loc}}$ at the A site of Bi$_3$O$_4$Br.

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.

Fig. 4. Recording of selected $^{209}$Bi NQR lines in Bi$_3$O$_4$Br (see Table 2 of [1]) in external magnetic fields at 77 K.
Conclusions

The $^{209}\text{Bi}$ NQR spectra of $\alpha$-Bi$_2$O$_3$ and Bi$_3$O$_4$Br show evidence for internal magnetic fields of about 200 G existing in these compounds.

Calculations of the $^{209}\text{Bi}$ NQR lineshapes under the influence of the internal and external magnetic fields up to 1 KG were performed for polycrystalline $\alpha$-Bi$_2$O$_3$. Only qualitative agreement with the experimental observations was obtained.