

ANISOTROPY OF ELECTRONIC DENSITY IN BISMUTH OXIDES AND ITS ANALYSIS THROUGH NQR SPECTRA

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Abstract: This article investigates the magnetic properties of bismuth oxide α -Bi₂O₃ and related bismuth oxide and oxyhalide compounds using nuclear quadrupole resonance (NQR). Although these materials exhibit diamagnetic behavior, ordered local magnetic fields—reaching up to 250 Gs—were detected through the NQR response of the ²⁰⁹Bi nucleus. Quadrupole splitting induced by the electric field gradient, along with Zeeman effects observed under external magnetic fields, enables the identification of nonequivalent atomic positions within the crystal lattice. Spectral lines obtained from single-crystal and powdered samples were processed through mathematical analysis and computer modeling, allowing for the determination of the magnitude and orientation of internal magnetic fields. The results provide deep insight into the electronic structure of bismuth-containing compounds, the anisotropy of the electric field gradient, and the mechanisms underlying the formation of local magnetic fields, thereby forming a significant scientific basis for the physics of functional materials.

Keywords: Bismuth oxide; nuclear quadrupole resonance; ²⁰⁹Bi nucleus; electric field gradient; Zeeman effect; local magnetic field.

INTRODUCTION

Bismuth oxide (α -Bi₂O₃) and its related compounds are widely used as primary raw materials in the synthesis of high-temperature superconductors and ferroelectric materials. In addition, these substances contain functional materials that exhibit notable optical, electro-optical, piezoelectric, and electrochemical properties. However, despite the high level of scientific interest, the magnetic properties of this class of compounds have not yet been sufficiently investigated.

At present, bismuth oxide-based compounds are being extensively studied as key functional components for advanced technological devices such as superconductors, piezoelectric sensors, electro-optic modulators, ion-conducting materials, and radiation detectors. Many of their technical characteristics are determined precisely by the local electric and magnetic fields within the crystal lattice. From this perspective, the quadrupole interactions and Zeeman splittings recorded through the ²⁰⁹Bi nucleus provide unique information about the fundamental microstructure of the material.

Although these compounds are diamagnetic, the emergence of ordered magnetic fields in NMR measurements remains one of the unresolved issues in modern science. Such peculiar phenomena may indicate the existence of new quantum states of electromagnetic nature, unconventional distributions of electron density, or distortions of crystallographic symmetry. Therefore, a precise analysis of the magnetic properties of bismuth oxide compounds is essential not only from the standpoint of fundamental physics but also for practical materials science applications.

Studies of nuclear quadrupole resonance (NQR) involving the ²⁰⁹Bi nucleus have shown that in compounds such as α -Bi₂O₃, BiOBr, Bi₄AlO₉, Bi₄Ge₃O₁₂, BiB₃O₆, and BiSbO₄, there are no magnetic carriers—i.e., no free electrons—and the atoms are diamagnetic in the conventional



sense. Nevertheless, ordered local magnetic fields have been detected within these materials, with magnitudes reaching up to 250 Gs. This phenomenon is explained by the presence of pronounced line splittings in the NQR spectra, which are observed even in the absence of strong external magnetic fields.

During the experiments, it was found that in some cases, the NQR spectra exhibited significant line splitting, while in others, such splittings were completely absent. This result indicates that the interaction between valence electrons and local magnetic fields is weak, estimated to be below approximately 500 Gs. The variability of these properties points to the unique electronic structure of the studied compounds. Notably, the observed decrease in NQR intensity of the ^{209}Bi nuclei under the influence of an external magnetic field suggests that the internal magnetic structure of these materials is highly complex. Such behavior does not fully conform to the conclusions derived from the classical Zeeman theory, implying that additional quantum or structural factors influence the local magnetic ordering in bismuth-based compounds.

Nuclear quadrupole resonance (NQR) spectroscopy is one of the most direct, precise, and effective methods for detecting and studying nuclear quadrupole interactions. This is because the quadrupole Hamiltonian is determined by the interaction between the nuclear electric quadrupole moment (Q) and the electric field gradient (EFG) generated by the crystal lattice. All nuclei with a spin quantum number $I > 1/2$ possess an electric quadrupole moment, and their interaction with the EFG leads to characteristic line splittings and resonance features observed in NQR spectra.

$$q_{ij} = \frac{\partial E_i}{\partial j} = - \frac{\partial^2 U}{\partial ij}$$

Here, E_i represents the strength of the electric field, while U denotes the potential of this field at the point where the nucleus is located. The indices $i, j = x, y, z$ correspond to the spatial axes. The main experimentally measurable quantity in NQR studies is the nuclear quadrupole interaction constant, which characterizes the strength of the interaction between the nuclear quadrupole moment and the electric field gradient at the nucleus.

Their values are directly dependent on the distribution of electron density surrounding the nucleus under investigation. Therefore, even minor distortions in the electron cloud produce detectable changes in the NQR spectra. The NQR method can be applied to study a wide range of physical phenomena associated with variations in the electric field at the location of the resonant nucleus. For this reason, in the present research, this method was chosen as the primary analytical tool.

The results of the study demonstrate that methods based on the measurement of nuclear quadrupole interactions possess high sensitivity in detecting magnetic fields present within a material. As discussed in this review, the experiments conducted by the authors involved examining the shape of the ^{209}Bi NQR lines in crystalline powders and single crystals both in the absence of an external field and under the influence of applied magnetic fields (H_n) oriented differently relative to the sample. In addition, the degree of line splitting in the quadrupole spin echo signals was also analyzed, providing further insight into the nature of the local electric and magnetic environments in bismuth-containing compounds.

The spectra obtained from single-crystal samples made it possible to identify very fine splittings of the recorded lines and to analyze modulated quadrupole spin echo (QSE) signals. By applying mathematical-spectral analysis and computer modeling, the parameters of these splittings or QSE shapes corresponding to Zeeman splitting were calculated. This allowed for the quantitative characterization of local magnetic fields within the crystal, providing precise information on the field strength and its orientation.

The conducted analyses revealed that, in most of the compounds examined in this study, the ^{209}Bi nuclei exhibit Zeeman NQR spectra in the form of multiplets. This observation confirms that the



positional states of bismuth atoms within the crystal lattice are magnetically nonequivalent, indicating subtle local variations in the magnetic environment of these nuclei.

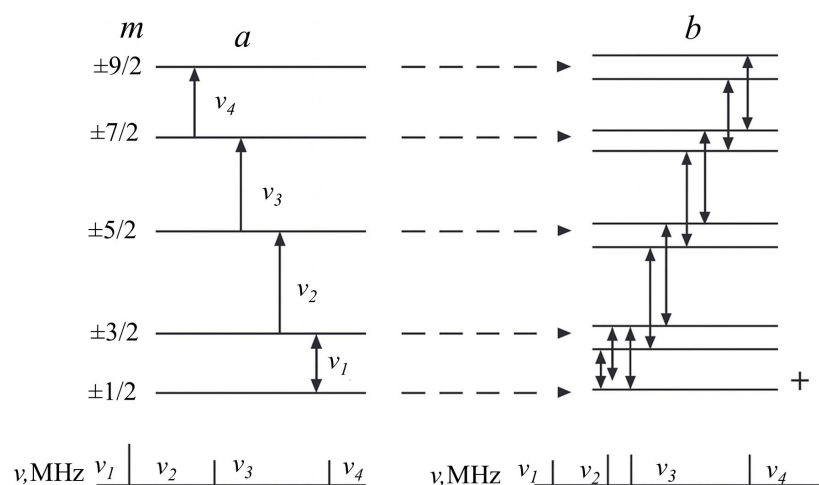


Figure 1. Quadrupole energy levels of the ^{209}Bi nucleus and the transitions between them: (a) in the absence of an external magnetic field, (b) under the influence of an external magnetic field of the Zeeman type.

In the above figure (Figure 1), the quadrupole energy levels of the ^{209}Bi nucleus and the allowed transitions between them are shown, and the diagram includes two cases. In part (a) of the figure, the quadrupole splitting scheme under conditions with no external magnetic field is presented. Here, the energy levels are formed solely under the influence of the electric field gradient, and the transition frequencies are denoted by specific values ν_1 , ν_2 , ν_3 , and ν_4 . The symmetric arrangement of the energy levels follows from the nuclear spin value $I = 9/2$.

In part (b) of the figure, the additional splitting that occurs when an external Zeeman magnetic field is applied is shown. Under the influence of the magnetic field, the energy levels are further split into finer sublevels in accordance with the Zeeman effect, and the number of allowed transitions increases. As a result, numerous additional lines appear in the NQR spectrum, making it a sensitive indicator of the local magnetic environment. The variation in the spacing between the transition lines depends on the symmetry of the electric field gradient in the crystal lattice and on the orientation of the external magnetic field.

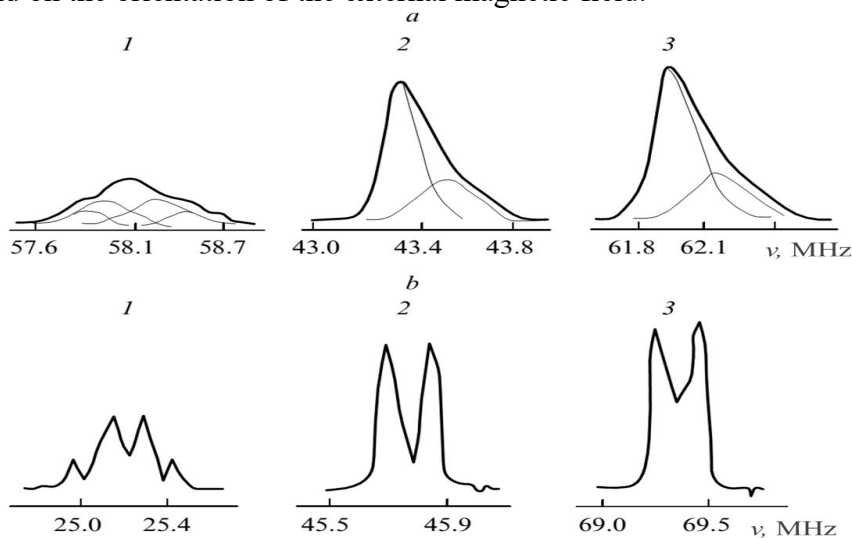


Figure 2. NQR spectral lines of the ^{209}Bi nucleus recorded in $\text{Bi}_5\text{O}_4\text{Br}$ (a) and $\alpha\text{-Bi}_2\text{O}_3$ (b) samples in the absence of an external magnetic field: lines corresponding to the ν_1 (1), ν_2 (2), and ν_3 (3) transitions (Table 1).

$\text{Bi}_5\text{O}_4\text{Br}$ sample (a): In this compound, the NQR lines are well defined, and the degree of spectral line broadening is small. This indicates a relatively well-ordered symmetry of the electric field gradient (EFG) in the crystal lattice, while the local magnetic fields are weak or nearly absent. The regular proportional arrangement of the ν_1 , ν_2 , and ν_3 transition frequencies further свидетельствует о высокой кристаллографической симметрии.

$\alpha\text{-Bi}_2\text{O}_3$ sample (b): In this compound, the spectral pattern is more complex; some lines exhibit broader dispersion and differing amplitudes. Such features indicate that the ^{209}Bi nuclei occupy different crystallographic positions and that the local electric field gradients in the lattice differ significantly. As a result, noticeable shifts in the transition frequencies occur, reflecting the anisotropy of the electric field gradient within the $\alpha\text{-Bi}_2\text{O}_3$ crystal structure.

Table 1. NQR spectra of the ^{209}Bi nucleus and values of the internal magnetic field H_{loc} : measured in bismuth oxide compounds under conditions of zero external magnetic field $H_0=0$ (the frequency values are averaged over the atomic lattice sites).

Compound	T, K	Transition frequencies, MHz				eqQ/h, MHz	η , %	H_{loc} ,Gs
		ν_1	ν_2	ν_3	ν_4			
$\alpha\text{-Bi}_2\text{O}_3$								
Bi(1)	77	25.2	45.8	69.4	92.8	556.7	0.13	171
Bi(2)		39.2	37.2	58.3	79.4	482.6	0.40	136
$\text{Bi}_5\text{O}_4\text{Br}$								
Bi(1)	77	21.6	25.1	39.6	53.3	322.6	0.31	-
Bi(2)		58	43.4	61.9	86.6	536.9	0.62	250
$\text{Bi}_4\text{Al}_4\text{O}_9$	77	33.15	50.5	78	104.1	626.4	0.19	150
$\text{Bi}_4\text{Ge}_3\text{O}_{12}$	300	20.4	40.9	61.3	81.7	490.3	0	25
	300	25.25	50.5	75.7	101	605.9	0	-
$\text{Bi}_2\text{Ge}_3\text{O}_9$	77	25.7	51.6	77.35	103.2	618.8	0	60

CONCLUSION

In this study, nuclear quadrupole resonance spectroscopy of the ^{209}Bi nucleus was successfully applied to investigate the local electric and magnetic environments in bismuth oxide and bismuth oxyhalide compounds. The obtained results demonstrate that, despite the diamagnetic nature of these materials, well-defined internal magnetic fields exist and can reach values of several hundred gauss. These fields manifest themselves through characteristic line splittings and multiplet structures in the NQR spectra, even in the absence of an external magnetic field.

The analysis of quadrupole energy levels and allowed transitions confirms that the electric field gradient plays a dominant role in shaping the NQR spectra, while the application of an external magnetic field leads to additional Zeeman splitting and a significant increase in the number of observable transitions. Comparative studies of $\text{Bi}_5\text{O}_4\text{Br}$ and $\alpha\text{-Bi}_2\text{O}_3$ reveal that higher crystallographic symmetry is associated with narrower and more regularly spaced spectral lines, whereas structural complexity and multiple nonequivalent bismuth positions result in broadened spectra and pronounced frequency shifts.



Overall, the results provide clear evidence of anisotropy in the electric field gradient and magnetic nonequivalence of atomic positions in bismuth-containing compounds. This work highlights the high sensitivity of the NQR method for probing subtle features of electronic structure and local magnetic ordering, and it establishes a reliable experimental basis for further fundamental studies and practical applications of functional bismuth-based materials.

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