Local Magnetic Fields in some Bismuth Compounds. A Survey of Experimental Evidences *

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The splittings observed in the ^{209}Bi nuclear quadrupole resonances of α-Bi_2O_3, in zero magnetic field, follow the typical pattern of a Zeeman perturbed NQR spectrum. The lineshapes in Bi_3O_4Br also indicate a poorly resolved splitting that points to the presence of an internal magnetic field in the order of 200 G. This exceeds notably the dipole nuclear magnetic fields (about several G), but is orders of magnitude smaller than paramagnetic fields produced by unpaired electron spins.

The results obtained using a SQUID and μSR-technique can also be interpreted as indicative of magnetic properties not conventionally expected in such compounds.

Key words: ^{209}Bi NQR, Internal magnetic field, Lineshape, SQUID, μSR.

Introduction

A previously overlooked [1] resonance in the ^{209}Bi NQR spectrum of α-Bi_2O_3 at a frequency of 39.3 MHz was detected in 1969 [2]. The signal was barely visible until a weak external magnetic field was applied. Later, NQR data were reported [3–5] which gave direct evidence for the existence of internal magnetic fields in α-Bi_2O_3 and Bi_3O_4Br. In this review we wish to summarize the experimental results in favour of such fields in α-Bi_2O_3 and Bi_3O_4Br, obtained using NQR-, SQUID- and μSR-technique. Previously published data as well as new experiments indicative of unusual magnetic properties in these and related compounds are discussed.

Results and Discussion

The Internal Magnetic Fields in α-Bi_2O_3 as Evidence by NQR

Clear evidence for internal magnetic fields in α-Bi_2O_3 was given by the splitting in the absence of an external zero magnetic field observed for all ^{209}Bi NQR lines [3]. The recording made on ≈ 0.5 cm^3 single crystals (Fig. 1), presenting typical patterns of Zeeman perturbed NQR, rules out the crystallographic inequivalence of the Bi-sites as the origin of the splitting.

Table 1 lists the parameters of the local magnetic fields calculated from the NQR spectra. The results are in general agreement with those published previously [5].

^{209}Bi Lineshapes of Polycrystalline α-Bi_2O_3 in External Magnetic Field

In the hope of obtaining further evidence for the existence of local magnetic fields (H_{loc}) in α-Bi_2O_3 we extended the preliminary NQR study [6] of the ^{209}Bi lineshapes in static magnetic fields ($0 < H_{ext} < 500$ G) and calculated the expected lineshapes. Fields of various strength were applied perpendicular to the radio-frequency field (H_{rf}), and the series of successive changes in the lineshape was recorded for all the transitions. The calculation [7] of ^{209}Bi NQR lineshapes was made under the assumption that they were influenced by a static magnetic field, taken as the sum of H_{loc} (found from the zero-field NQR experiment) and H_{ext} ($0 < H_{ext} < 8\ H_{loc}$).

Many investigators have calculated Zeeman perturbed NQR powder lineshapes of systems with vari-

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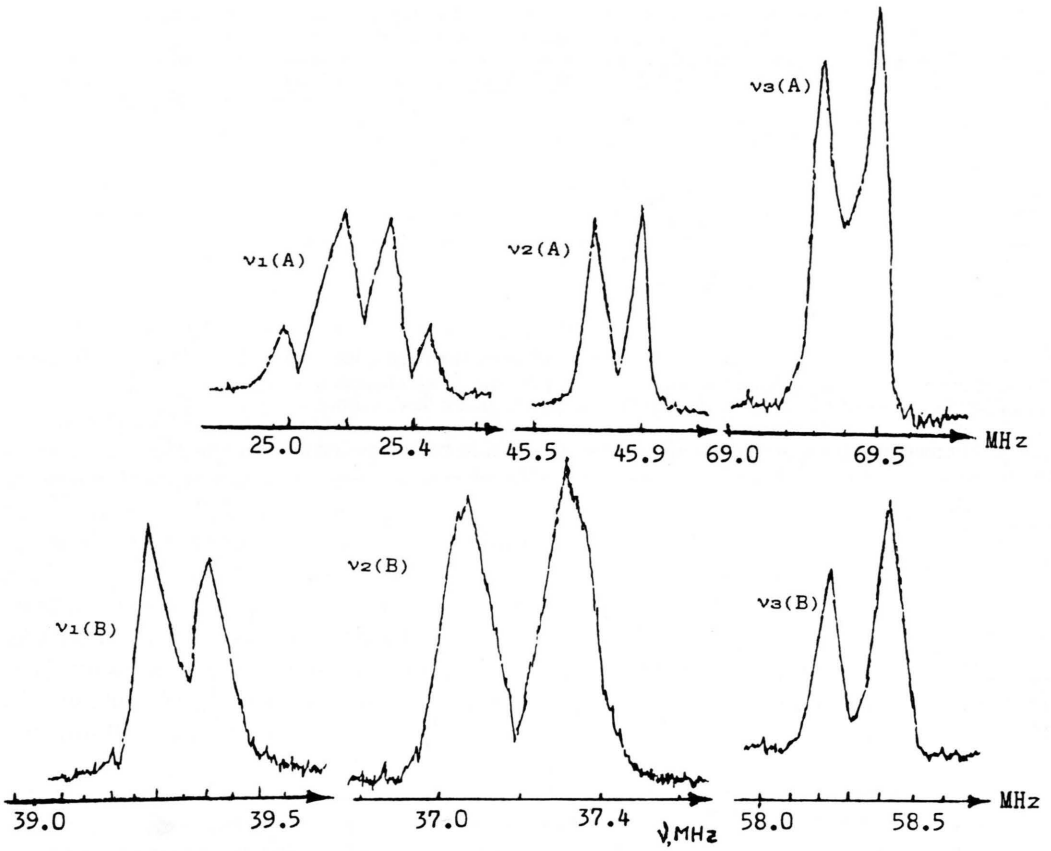

Fig. 1. Recording of selected ^{209}Bi NQR lines in α-Bi_2O_3 in zero magnetic field at 77 K. The upper row shows the lines assigned to the A sites ($e^2Qq/h \approx 556.7$ MHz, $\eta \approx 0.10$ [2]). The lower row shows the lines assigned to the B sites ($e^2Qq/h \approx 482.6$ MHz, $\eta \approx 0.40$ [2]).

Table 1. Parameters of H_{loc} calculated from NQR data at 77 K.

Bi-sites	H_{loc}, G	θ_0	φ_0	$H\parallel$, G	$H\perp$, G	Ref.
A	171	38°	0	134	105	[7]
B	136	0	–	136	0	
A	162±10	22±6°	4±90°			[5]
B	139± 9	0±2°				

ous nuclear spins and EFG asymmetry parameters, [8, 9] and refs. therein. Considerable difficulty has been experienced in obtaining adequate experimental results due to the NQR linewidths being not free from undesirable contributions masking the effect of interest. That the sample of α-Bi_2O_3 used in our experiment was magnetically inhomogeneous, although consisting of single crystals ($\approx \{3 \times 4 \times 7\}$ mm^3), is illustrated by Fig. 2, which shows the line ν_3 (A) recorded under high resolution operating conditions.

The lineshape simulation [7] was made using various empirical parameters σ, which denoted the initial linewidth. Its most reasonable value could be chosen by comparison of the simulation results with experiment.

Figure 3 shows the main steps in the lineshape evolution as found in the experiment for a representative example as function of the strength of H_{ext}. In [7] it is compared to the computer simulation.

One can see that the separations between the split components decrease at weak H_{ext}. The line components coalesce at $H_{ext} < H_{loc}$, a trend also qualitatively seen in the simulations. With the field further increasing the line splitting reoccurs.

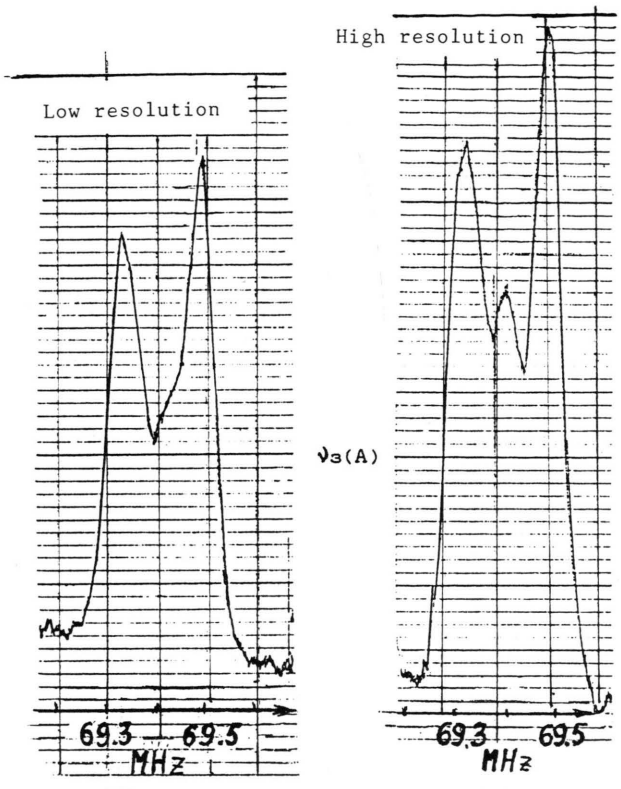

Fig. 2. ^{209}Bi ν_3 (A) resonance in α-Bi_2O_3 recorded at 77 K at lower (left) and higher (right) resolution (see text).

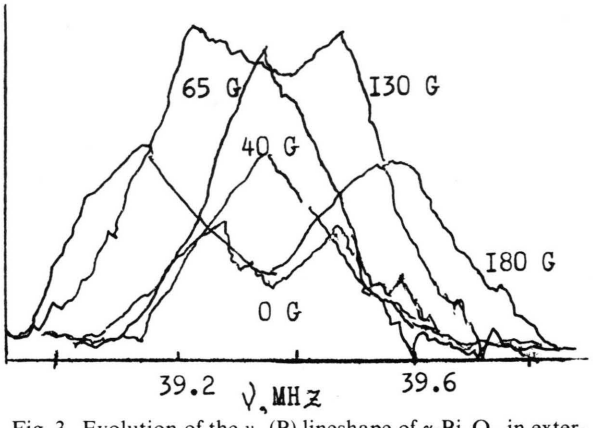

Fig. 3. Evolution of the ν_1 (B) lineshape of α-Bi_2O_3 in external magnetic fields as observed in the experiment.

^{209}Bi NQR Spectra of Powdered Bi_3O_4Br in External Magnetic Field

The asymmetrical ^{209}Bi NQR lineshapes in powdered Bi_3O_4Br also give evidence for an internal magnetic field. We can estimate H_{loc} for bismuth at the B sites [7] (Table 2). The lineshapes assigned to the A sites are, however, less distinctly distorted. In addition, the appropriate low-frequency resonances are too weak to allow the estimation of H_{loc}, if any, with reasonable accuracy. The NQR spectrum of this compound in a weak external magnetic field exhibits a very unusual property. A rise of the resonance intensity similar to that seen in α-Bi_2O_3 (Fig. 3) was observed for the lines assigned to the B sites but on a much larger scale (Figure 4). The lower-transition lines are more strongly influenced by the external field than the upper resonances. This observation is in agreement with the expectation of greater importance of magnetic contributions to the lower-transition resonances [10]. Lines assigned to the A site bismuth atoms are much weaker influenced by the field applied than those assigned to the B site.

Table 2. ^{209}Bi NQR spectrum of Bi_3O_4Br (MHz) at 77 K and parameters of H_{loc} at B site.

Bi-sites	Resonance Frequencies (Δm)				e^2Qq/h	η
	(1/2–3/2)	(3/2–5/2)	(5/2–7/2)	(7/2–9/2)		
A	21.62	25.13	39.59	53.34	322.6	0.311
B	58.04	43.30	62.92	86.63	536.9	0.617

$H_{loc} = 250 \pm 10$, G $\quad \theta_0 = 52 \pm 2^\circ \quad \varphi_0 = 6 \pm 2^\circ$

The mechanism of the intensity increase observed for Bi_3O_4Br in H_{ext} involves, however, no effective increase of the transverse relaxation times (T_2) [10]. Figure 5 shows the behavior of the Bi_3O_4Br spin echo envelope in an external magnetic field compared to that typical for compounds showing an effective lengthening of spin echo decay as source of line narrowing. The external magnetic field seems to have no observable effect on the characteristic ^{209}Bi spin echo decay in Bi_3O_4Br. A similar behavior, although on a reduced scale, was observed for α-Bi_2O_3. These observations do not support the earlier conclusion [3] about the increase in amplitude of α-Bi_2O_3 lower-transition signals in external magnetic fields due to prevailing contribution of magnetic interactions to the transverse relaxation time. The mechanism of the NQR line intensity growth in external magnetic fields is yet to be clarified.

Results of Magnetic Susceptibility Measurements

The direct measurement of the unusual magnetic properties of these compounds as revealed by NQR was imperative.

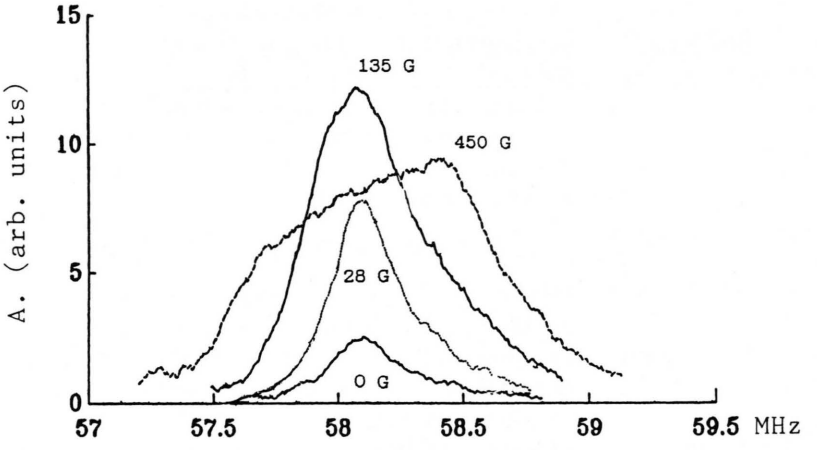

Fig. 4. Recording of a selected ^{209}Bi NQR line, ν_1 (B), in Bi_3O_4Br (Table 2) in external magnetic fields at 77 K.

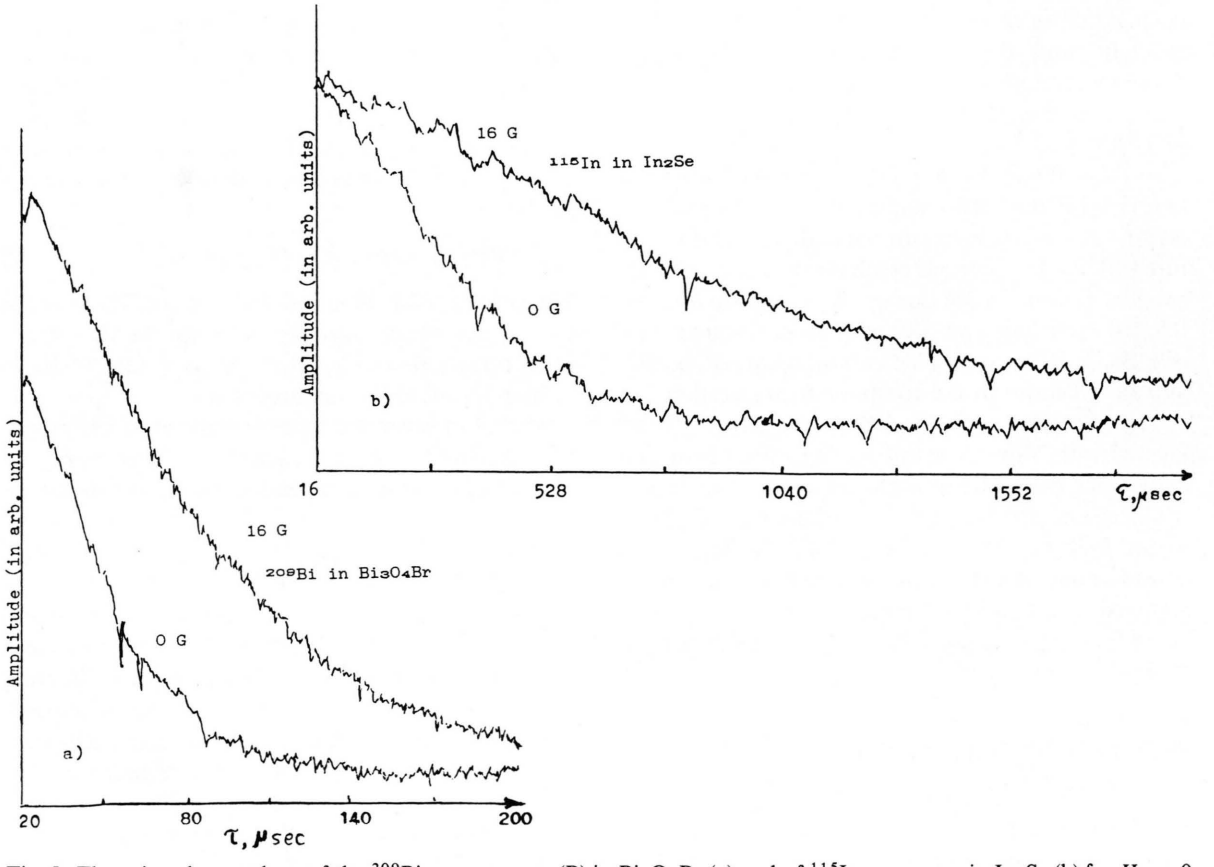

Fig. 5. The spin-echo envelope of the ^{209}Bi resonance ν_1 (B) in Bi_3O_4Br (a) and of ^{115}In resonance in In_2Se (b) for $H_{ext}=0$ and $H_{ext}=16$ G.

The magnetic susceptibility of a nonoriented α-Bi_2O_3 single crystal measured by the Faraday method in $H_{ext}=6$ kG within 4.2 and 300 K appeared to have a temperature independent value of $-7.9\cdot10^{-5}$ emu/mol.

The results found for the magnetic susceptibilities of this compound measured in a weaker magnetic field of 96 G appeared different. The experiment was performed using a SQUID magnetometer [11]. The samples of α-Bi_2O_3 and Bi_3O_4Br were cooled to 15 K in a residual magnetic field of 0.8 G, and then the magnetic field of 96 G was switched on. The magnetic moments were measured on slow heating of the samples up to room temperature.

The total susceptibilities of the compounds were diamagnetic and temperature independent over the whole temperature interval except between 55 and 90 K, where sharp paramagnetic peaks [11] of unknown nature were observed. The molar susceptibilities outside this area, corrected according to Selwood [12], gave paramagnetic contributions to the molar susceptibilities of the order of $6\cdot10^{-5}$ emu/mol for Bi_3O_4Br and $3\cdot10^{-5}$ emu/mol for α-Bi_2O_3 (at $T>50$ K). The latter appears close to that found by Nakamura et al. [13] for $BaBiO_3$ ($3.2\cdot10^{-5}$ emu/mol at 77 K).

As was found by a powder neutron diffraction analysis [14], the latter compound has the formulation $BaBi^{3+}Bi^{5+}O_3$. It forms an ordered perovskite structure with the Bi^{3+} cations octahedrally coordinated to oxygen. Neither NQR nor crystal structure analyses [15, 16], including a powder neutron diffraction study of α-Bi_2O_3 [17], gave an indication of coexisting Bi^{3+} and Bi^{5+} cations in the compounds in question.

The structures of both, α-Bi_2O_3 and Bi_3O_4Br are layered with bismuth atoms having stereochemically active lone pairs of electrons. They contain voids.

Coexisting Sb^{3+} and Sb^{5+} cations were found in α- and β-Sb_2O_4 ($Sb^{3+}Sb^{5+}O_4$). This is reflected by a considerable decrease of the ^{121}Sb e^2Qq/h value assigned to the Sb^{5+} -site with respect to that measured for the Sb^{3+}: 145.9 MHz against 497.8 MHz in β-Sb_2O_4 [18].

Results of μSR-Study of α-Bi_2O_3

An attempt was made to obtain information on local magnetic fields in interstitials of the α-Bi_2O_3 lattice using polarized positive muons (μSR-method) [19]. The results of μSR-experiments performed in zero (ZF), transverse (TF) and longitudinal (LF) external magnetic fields existing in powdered α-Bi_2O_3 sample.

The results of the TF-experiment in $H_{ext}\approx400$ G in the temperature interval from 4.2 to 300 K show that over this whole interval the time dependence of the muon polarization was

$$P_{TF}(t)=a_{TF}\exp(-\lambda_{TF}t)\cos(\omega t+\varphi)\,. \tag{1}$$

Here $\omega=\gamma_\mu H_{ext}$ is the precession frequency of the muon spin in the external field and γ_μ is the muon gyromagnetic ratio ($\gamma_\mu/2\pi=13.55$ kHz/Oe). At any temperature $P_{TF}(0)$ appeared to be smaller than unity. This indicates that at least part of the muons undergo a fast depolarization, i.e. they are influenced by a high magnetic field as compared to the dipole field of nuclear magnetic moments. The unusual temperature dependence of $P_{TF}(0)$ was found to decrease as the temperature fell, to pass through a minimum at ≈130 K, and to increase again with further temperature decrease.

A fast depolarization resulting from relatively high magnetic fields that act on the muon spin was distinctly observed for short time intervals in the ZF- and LF-experiments (Figure 6). The spectra of both experiments were best described by the sum of exponents corresponding to fast (λ_f) and slow (λ_s) rates of depolarization,

$$P(t)=a_s\exp(-\lambda_s t)+a_f\exp(-\lambda_f t)\,. \tag{2}$$

The sum (a_s+a_f) coincided with the coefficient of the total experimental asymmetry a_Σ. In the ZF-experiment an increase of λ_f from $\approx5\ \mu s^{-1}$ (at 300 K) to $\approx30\ \mu s^{-1}$ (at 70 K) was observed.

The LF-measurements were made at 135 K, where the amplitude of λ_f reached its maximum. At $H_{ext}>1$ kOe the field dependence of λ_f was described by the Lorentzian

$$\lambda_f=2[(\gamma_\mu\delta)^2\tau]/[1+(\gamma_\mu H_{ext})^2\tau^2]\,, \tag{3}$$

where τ is a correlation time characterizing a fluctuation process. δ^2 is the static Van Vleck second moment reflecting a distribution over the sample of internal magnetic fields acting at the sites of muon localization. The values of δ and τ found from the experiment were (325 ± 1) G and $(6.0\pm0.6)\times10^{-9}$ s, respectively. An additional experiment was performed to rule out the existence of a weakly coupled muonium (μ^+e^-) state in α-Bi_2O_3 as a possible reason for the fast muon depolarization. The strength of the local magnetic

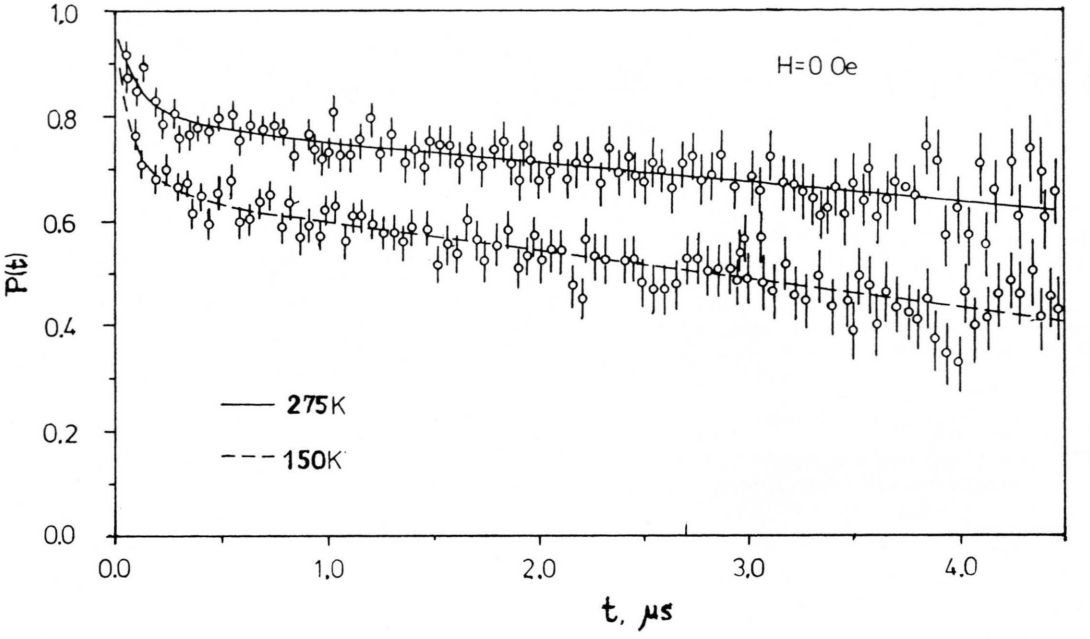

Fig. 6. Time dependence of the muon spin polarization in zero magnetic field.

field in the interstitials of the α-Bi_2O_3 structure found by the μSR-experiment is therefore of the same order of magnitude as that estimated at the Bi-sites from the NQR spectra.

It is known [20, 21] that the magnetism of a system with no d-electrons could have its origin, like in molecular oxygen, in the *p*-orbital degeneracy, provided high local symmetry and exchange interactions are present. In α-Bi_2O_3 all the bismuth and oxygen sites are of *e*-type (of the lowest point symmetry) [17], which makes the suggestion of a *p*-orbital degeneracy nonrealistic.

Conclusions

The results of all the experiments reviewed here show evidence for the unexpectedly complicated magnetic properties of α-Bi_2O_3 and Bi_3O_4Br. No founded model explaining the origin of the internal magnetic field in these compounds can be presented at the moment, and a discussion of various speculations of uncertain reliability seems meaningless.

The area is worthy of further investigations, especially of the magnetic properties in weak external fields. The traditional experiments made in fields of several kG might suppress the phenomenon to be revealed. NQR relaxation studies are also thought of as a powerful tool for clarifying the origin of the fields.

It is to be added that the compounds discussed are hardly rare exceptions. In our opinion, many other antimony and bismuth compounds can be considered as possible candidates to have unusual magnetic properties. For instance, the ^{121,123}Sb lowest-transition NQR signals of SbF_3 are not visible in zero magnetic field. In cubic Sb_2O_3 (senarmontite) the zero-field slow beats on a free induction decay envelope were interpreted [3] as evidence for an internal magnetic field. The study of Bi_3O_4Cl should also be extended using complementary experimental techniques.

Acknowledgement

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