Investigation of bismuth oxide α-Bi_2O_3 by the muon method

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The muon method has been used for the first time to investigate bismuth oxide α-Bi_2O_3. It was shown that the observed fast ($\sim 10\ \mu s^{-1}$) and slow ($\sim 0.1\ \mu s^{-1}$) muon-spin relaxations are not successive stages of the same relaxation process, but rather they are associated with muons localized in two different sites of the crystal lattice. It is shown that the muons diffuse through the α-Bi_2O_3 crystal by a tunnelling process. No indications of a magnetically ordered state of α-Bi_2O_3 were observed in the temperature range $T=10$–300 K.

1. INTRODUCTION

The muon method is widely used to investigate oxides of different metals. The oxides MnO, Fe_2O_3, Fe_3O_4, V_2O_3, Al_2O_3 and some others have been investigated in detail. The localization of the muon (μ^+) and muonium (μ^+e^-) and their interactions in the crystal, the parameters of the quasi-free impurity muonium atom, and the diffusion of a muon through the crystal have been determined. The muon method is used to study the magnetic properties of transition-metal oxides. The experiments have shown that the interactions of muons in metal-oxide crystals are complicated and diverse, and further investigation of this class of substances by the muon method is required. Specifically, it is of interest to investigate nonmagnetic metal oxides in detail.

In the present work the muon method is used for the first time to study bismuth oxide α-Bi_2O_3, a diamagnetic dielectric. However, to interpret the experimental nuclear quadrupole resonance (NQR) spectrum, it was necessary to assume that local intracrystalline magnetic fields $H_0 \simeq 150$ G exist at the bismuth nuclei.[1] The muon method makes it possible to measure the internal magnetic fields on the muon, which are directed associated with the magnetic structure of the α-Bi_2O_3 crystal. The measurements were performed in the temperature range T=10–300 K in magnetic fields which were oriented perpendicular and parallel to the direction of the initial polarization of the muon spin as well as in the absence of a magnetic field. Preliminary results were published in Ref. 2. The experiment was performed on the phasotron in Dubna.

2. EXPERIMENT

The experimental α-Bi_2O_3 sample consisted of 7 cm^3 of fine-grain powder of analytically pure grade. The experimental time dependence of the polarization $P(t)$ of the muon spin in the transverse (TF), longitudinal (LF), and zero (ZF) magnetic fields are displayed in Figs. 1 and 2. According to these figures, the relaxation of the muon spin in the α-Bi_2O_3 crystal is a sum of fast ($\sim 10\ \mu s^{-1}$) and slow ($\sim 0.1\ \mu s^{-1}$) relaxation processes, whose amplitudes at $T \simeq 140$ K are $\sim 40\%$ and $\sim 60\%$, respectively. We shall examine below in detail the parameters of the function $P(t)$ in a α-Bi_2O_3 crystal as a function of the temperature and external magnetic fields.

2.1. Transverse-field experiment

The relaxation and precession of the muon spin, shown in Fig. 1, in a transverse magnetic field $H_\perp$ can be represented in the form

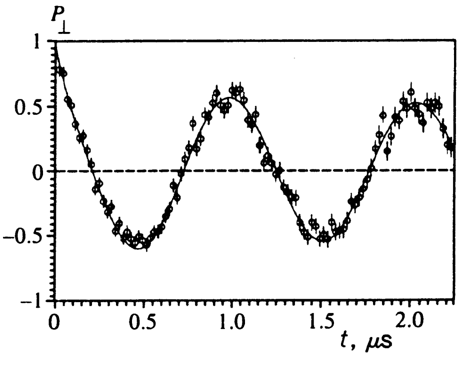

FIG. 1. Relaxation and precession of muon spin in α-Bi_2O_3 in a transverse magnetic field $H_\perp = 70$ Oe at $T = 140$ K. The solid curve represents the function (1) $P_\perp(t)$.

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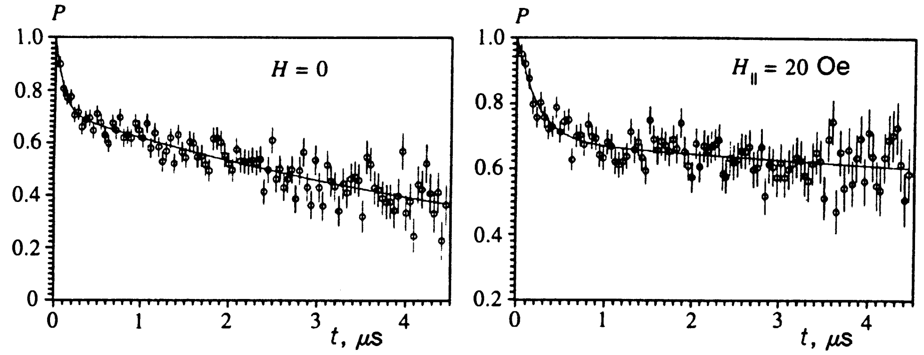

FIG. 2. Relaxation of muon spin in α-Bi_2O_3 in the zero field $H=0$ and in a longitudinal field $H_{\parallel}=20$ Oe at $T=140$ K. The solid curves represent the functions (6) for $P_0(t)$ with $H=0$ and for $P_{\parallel}(t)$ with $H_{\parallel}=20$ Oe.

$$P_{\perp}(t)=\frac{1}{a_0}[a_1P_1(t)+a_2P_2(t)\cos(\omega t+\phi)]$$

$$\text{with } a_1+a_2=a_0=0.150. \tag{1}$$

Here the functions $P_1(t)$ and $P_2(t)$ describe the fast and slow muon spin relaxation processes, respectively; a_1 and a_2 are the corresponding experimental asymmetry coefficients of the angular distribution of the positrons in $\mu^+\to e^+$ decay; ω and ϕ are, respectively, the frequency and phase of the spin precession of a slowly relaxing muon; and a_0 $=0.150$ is the total coefficient for $\mu^+\to e^+$ decay in α -Bi_2O_3, determined from measurements of the time-dependence $P(t)$ in copper.

The expression (1) does not describe the precession of rapidly relaxing muons, since this process is not observed in magnetic fields $H_{\perp}<700$ Oe. The relaxation function P_1(t) fitting the experimental data is virtually temperature-independent and can be written in the form

$$P_1(t)=e^{-\Lambda_1 t}. \tag{2}$$

As the transverse magnetic field $H_{\perp}$ increases, the quantity Λ_1 increases (see Fig. 3) and for $H_{\perp}>300$ Oe the fast muon-spin relaxation process is completed within an unobservably short time $t<20$ ns.

The slow muon spin relaxation in the α-Bi_2O_3 crystal is strongly temperature-dependent and can be explained by muon diffusion through the crystal. The corresponding relaxation function P_2(t) has the form[3]

$$P_2(t)=e^{-2\sigma^2\tau^2\left[e^{-t/\tau}-1+\frac{t}{\tau}\right]}. \tag{3}$$

Here σ is the dipole relaxation rate of the spin of a localized (nondiffusing) muon as a result of interaction with the nuclear magnetic moments and τ is the correlation time of a diffusion hop of a muon into a neighboring interstice. Figure 4 displays the experimentally measured temperature dependence Λ_2(T), following from the expression (3) for $P_2(t)$, of the relaxation rate of the spin of a diffusing muon, defined as $\Lambda_2=1/t_e$, where t_e is the 1/e decay time of the precession amplitude of the muon. The continuous curve in Fig. 4 represents the theoretical function $\Lambda_2^{\rm theor}(T)$, which follows from the expression (3) with the activational temperature dependence[4] $\tau(T)$

$$\frac{1}{\tau}=\nu e^{-Q/T} \tag{4}$$

with the parameters

$$\nu=10^{6.8\pm0.2}\text{s}^{-1}, \quad Q=430\pm70 \text{ K}. \tag{5}$$

which gives the best agreement with experiment. The values (5) of the parameters ν and Q correspond to incoherent tunnelling muon diffusion[4] through the α-Bi_2O_3 crystal. The good agreement, shown in Fig. 4, between the experimental and theoretical temperature dependences $\Lambda_2(T)$ confirms the diffusive nature of the slow relaxation of muon spin in an α-Bi_2O_3 crystal. The rate Λ_2 of the slow muon spin relaxation in the experimental range of fields $H_{\perp}=50-700$ Oe does not depend on the field $H_{\perp}$, as it should in the case of nuclear dipole relaxation of the muon spin. The experimental field dependences $\Lambda_1(H_{\perp})$ and $\Lambda_2(H_{\perp})$ in the α-Bi_2O_3 crystal at $T=140$ K are presented in Fig. 3.

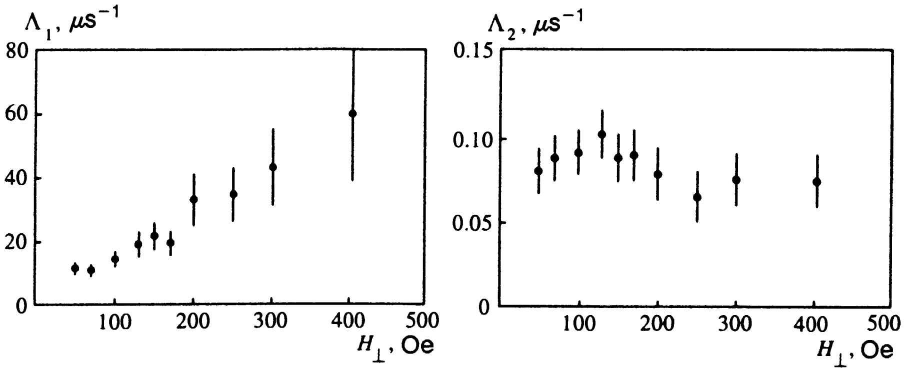

FIG. 3. Fast and slow relaxation rates $\Lambda_1(H_{\perp})$ and $\Lambda_2(H_{\perp})$ of a muon spin in α-Bi_2O_3 at $T=140$ K.

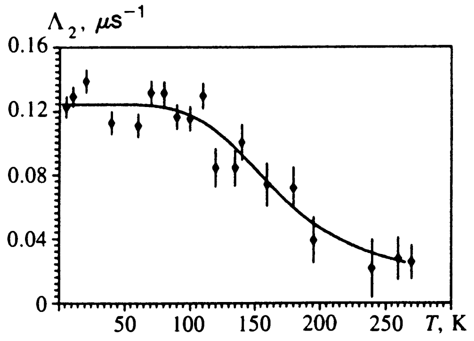

FIG. 4. Temperature dependence of the muon spin relaxation rate $\Lambda_2(T)$ in α-Bi_2O_3 in a transverse magnetic field $H_\perp = 400$ Oe. Solid curve — the theoretical temperature dependence $\Lambda_2^{\text{theor}}(T)$ of the dipole relaxation rate, where $\tau(T)$ is given by the expression (4) (see text).

The temperature dependence $a_2(T)$ of the asymmetry coefficient of the slowly relaxing muons is displayed in Fig. 5. It is obvious from Fig. 5 that this dependence is nonmonotonic. Therefore the temperature dependence $a_1(T) = a_0 - a_2(T)$ is also nonmonotonic.

The field dependence $\omega(H_\perp)$ measured in a transverse magnetic field corresponds to the Larmor precession frequency of a free muon in the entire experimental range of fields $H_\perp < 700$ Oe.

2.2. Zero-field experiment

The results, presented above, of the transverse-field experiments show that external magnetic fields influence the relaxation of the muon spin in the α-Bi_2O_3 crystal (see Fig. 3). At the same time, the characteristic time dependence $P_0(t)$ shown in Fig. 2 for $H = 0$ shows that both the fast and slow relaxations of the muon spin are also observed in the absence of an external magnetic field, which is therefore not the determining factor of these processes. Precession of the muon and muonium spin with $H = 0$ are not observed in α-Bi_2O_3.

Muon spin relaxation in the absence of an external magnetic field was measured for $T > 100$ K. The experimentally determined relaxation function $P_0(t)$ (see Fig. 2) can be represented in the form

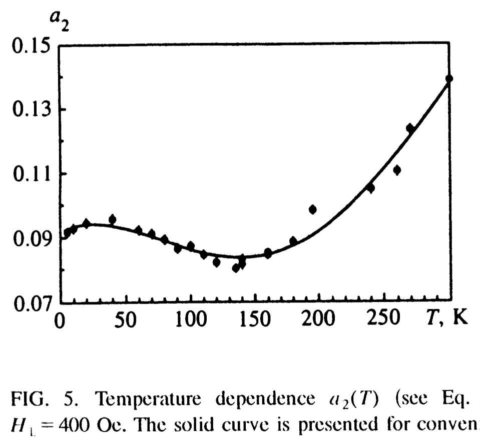

FIG. 5. Temperature dependence $a_2(T)$ (see Eq. (1)) in α-Bi_2O_3 at $H_\perp = 400$ Oe. The solid curve is presented for convenience.

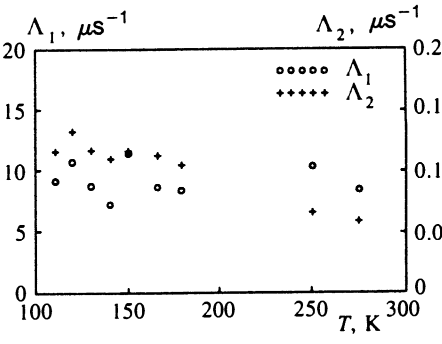

FIG. 6. Temperature dependence of the fast and slow relaxation rates $\Lambda_1(T)$ and $\Lambda_2(T)$ of muon spin in α-Bi_2O_3 in the absence of an external magnetic field.

$$P_0(t) = \frac{1}{a_0}[a_1 e^{-\Lambda_1 t} + a_2 e^{-\Lambda_2 t}], \tag{6}$$

where

$$a_1 + a_2 = a_0 = 0.150.$$

The fast and slow relaxation rates $\Lambda_1(T)$ and $\Lambda_2(T)$ of the muon spin in the absence of a magnetic field are plotted versus temperature in Fig. 6. It is evident from this figure that the fast relaxation rate Λ_1 is approximately 100 times greater than the slow relaxation rate Λ_2 of the muon spin. This ratio of Λ_1 to Λ_2 is an indication that the fast muon spin relaxation in α-Bi_2O_3 could be associated with the formation of muonium. It also follows from Fig. 6 that in α-Bi_2O_3 Λ_1 is independent of the temperature in the range $T = 100 - 300$ K.

2.3. Longitudinal-field experiment

Muon spin relaxation in α-Bi_2O_3 in longitudinal magnetic fields is a complicated function of the field $H_\parallel$. Figure 7 displays the field dependences $\Lambda_1(H_\parallel)$ and $\Lambda_2(H_\parallel)$ of the fast and slow relaxation rates of the muon spin in α-Bi_2O_3. The quantities Λ_1 and Λ_2 presented in this figure were determined by comparing with experiment the two-component relaxation function $P_\parallel(t)$ of the same form as the expression (6) for $P_0(t)$. One can see from Fig. 7 that the functions $\Lambda_1(H_\parallel)$ and $\Lambda_2(H_\parallel)$ have two maxima for the same values of the longitudinal magnetic field $H_\parallel \simeq 100$ Oe and $H_\parallel \simeq 450$ Oe.

3. DISCUSSION

It follows from the transverse-field experiments that more than 60% (up to 90% at $T = 300$ K) of the muons in the experimental α-Bi_2O_3 sample precess with the free-muon frequency. The slow spin relaxation of these muons is explained by the dipole interaction of the magnetic moments of the muons and the nuclei Bi. The longitudinal magnetic fields $H_\parallel \simeq 20$ Oe strongly suppress this slow relaxation. The remaining 40% (up to $\sim 10\%$ at $T \to 300$ K) of the muon-spin polarizations are lost in the process of fast relaxation ($\Lambda_1 \simeq 100\Lambda_2$).

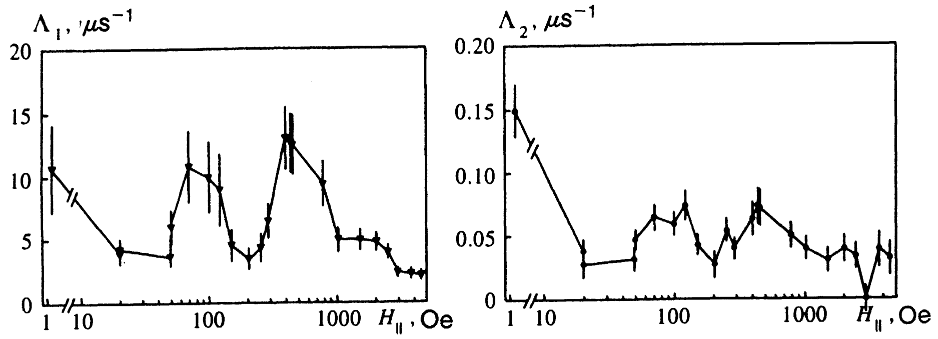

FIG. 7. $\Lambda_1(H_\parallel)$ and $\Lambda_2(H_\parallel)$ in α-Bi_2O_3 at $T=140$ K.

We shall show that the fast and slow muon spin relaxation in α-Bi_2O_3 are not two stages of the same process, for example the process determined by the capture of the initially formed muonium atom in a diamagnetic compound. In the case of such a two-stage process the polarization $P(t)$ of the muon spin can be expressed as a sum of two relaxation functions

$$P(t)=P_{Mu}(t)+P_D(t), \tag{7}$$

where

$$P_{Mu}=e^{-\Lambda t}\cdot e^{-t/\tau_0}$$

is the fraction of the muon polarization in the muonium state (Mu) and

$$P_D(t)=\int_0^t e^{-\Lambda t'}\cdot e^{-\Lambda_2(t-t')}\cdot\frac{1}{\tau_0}\cdot e^{-t'/\tau_0}dt'$$

is the muon polarization in the diamagnetic state. Here Λ is the rate of depolarization of the muon spin in muonium; τ_0 is the time at which the muon enters the diamagnetic compound; Λ_2 is the relaxation rate of the muon spin in the diamagnetic compound ("slow" relaxation). Obviously, $\Lambda_1=\Lambda+1/\tau_0$ is the experimentally observed fast relaxation [see also Eq. (8)]. Equation (7) implies that

$$P(t)=\left[1-\frac{1}{(\Lambda_1-\Lambda_2)\tau_0}\right]\cdot e^{-\Lambda_1 t}+\frac{1}{(\Lambda_1-\Lambda_2)\tau_0}\cdot e^{-\Lambda_2 t}. \tag{8}$$

For the α-Bi_2O_3 crystal, where $\Lambda_1\simeq 100\Lambda_2$, the expression (8) can be rewritten as

$$P(t)\simeq\left[1-\frac{1}{\Lambda_1\tau_0}\right]\cdot e^{-\Lambda_1 t}+\frac{1}{\Lambda_1\tau_0}\cdot e^{-\Lambda_2 t}. \tag{9}$$

It follows from the expression (8) [or (9)] that in the model of a two-stage process of relaxation of the muon spin the quantities Λ_1 and $a_2\simeq a_0/\Lambda_1\tau_0$ are correlated with one another. It is evident from Fig. 8 that the experimental rates $\Lambda_1(H_\parallel)$ and $a_2(H_\parallel)$ at $T=140$ K are correlated only partially: A nonproportional correlation of Λ_1 and a_2 is observed at $H_\parallel\simeq 450$ Oe and there is no correlation for $H_\parallel<300$ Oe. This result shows that the fast and slow relaxation of the muon spin in α-Bi_2O_3 are determined by unrelated processes. Moreover, for two-stage relaxation of muon spin in α-Bi_2O_3 the quantity $\Lambda_1=\Lambda+1/\tau_0$ cannot be less than $(\Lambda_1)_{min}=1/\tau_0\simeq 6\ \mu s^{-1}$ $(T\simeq 140K)$, which contradicts the experimental values $\Lambda_1\simeq 2\ \mu s^{-1}$ for $H_\parallel\simeq 3000$ Oe. Therefore it must be assumed that the fast and slow muon spin relaxation processes in the α-Bi_2O_3 crystal refer to muons localized in different positions, as is observed in the oxides Fe_2O_3,[5] V_2O_3,[6] and Al_2O_3.[7] It can be conjectured that the two maxima in the functions $\Lambda_1(H_\parallel)$ and $\Lambda_2(H_\parallel)$ (see Fig. 7) correspond to the crossing of the Zeeman and quadrupole levels[8] for two different positions of a muon in the α-Bi_2O_3 crystal.

The large value of the fast muon spin relaxation rate $\Lambda_1\simeq 10\ \mu s^{-1}$ in α-Bi_2O_3 can be explained by the formation of the chemically bound paramagnetic complex Bi-O-μ and the superhyperfine interaction of the muon and bismuth spins in this complex, as happens in the oxides of other metals.[5,7,9,10]

It follows from the results obtained that a magnetically

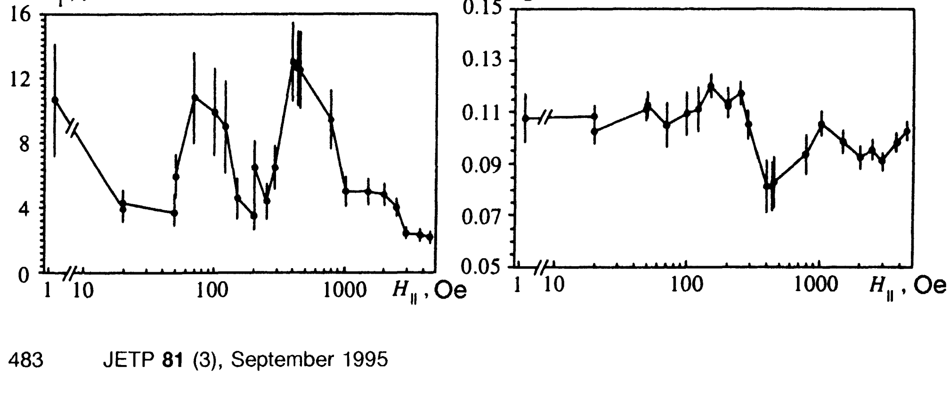

FIG. 8. $\Lambda_1(H_\parallel)$ and $a_2(H_\parallel)$ in α-Bi_2O_3 at $T=140$ K.

ordered state is not observed in the α-Bi_2O_3 crystal at temperatures $T=10-300$ K.

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