

# Quadrupole spin-echo envelopes for $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ single crystals doped with atoms of transition and rare earth elements

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Influence of weak (below 50 Oe) constant magnetic field on quadrupole spin-echo envelope was studied for non-doped single crystal  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ , in which local magnetic fields of the order of 20–30 G were earlier found, as well as for single crystals  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  doped with atoms of transition and rare earth elements. In all the cases, the spin-echo envelopes were strongly influenced. A considerable increase in the nuclear spin-spin relaxation time  $T_2$  was observed for the non-doped sample upon switching weak external magnetic fields. For the doped samples, the spin-echo envelope decay became much slower already in zero field. The external magnetic fields exhibited markedly weaker influence on the spin-echo envelope for the doped samples.

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Unique magnetic properties were found by studying nuclear quadrupole interactions (NQI) in compounds of type  $\text{Bi}_k\text{Al}_l\text{O}_m\text{X}_n$  ( $A = \text{Al}, \text{B}, \text{Ge}, \text{Ba}$ ;  $X = \text{Cl}, \text{Br}$ ) which comprise no atoms of  $d$ - or  $f$ -elements: the existence of internal (local) magnetic fields ( $H_{\text{loc}}$ ) of the strength up to 250 G and strong increase in intensity of the NQR lines in weak (below 500 Oe) external constant magnetic fields ([1] and refs. therein). By SQUID-measurements, the anisotropic paramagnetism which depends on the magnetic prehistory of the sample was found in  $\alpha\text{-Bi}_2\text{O}_3$  single crystal. The magnetoelectric effect linear in magnetic field was also observed in this crystal [2].

The  $^{209}\text{Bi}$  NQR experiments which involved a study of the zero-field line shape, analysis of the Zeeman-perturbed patterns in the fields below 500 Oe and examination of the spin-echo envelope (SEE) in zero field indicated the existence of internal source of magnetic splittings of the lines in the crystal  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  [1, 3]. By a computer modeling of the Zeeman patterns [1, 3] and modulations of the SEE in zero field [4],  $H_{\text{loc}}$  in this compound was estimated to be 20–30 G. An examination of nuclear spin-lattice relaxation in the  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  single crystal showed a noticeable contribution of the magnetic mechanism at low temperatures [5].

Here, we report the results of a study of external magnetic field ( $H_{\text{ext}}$ ) influence on the SEE for the  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  single crystal whose  $^{209}\text{Bi}$  NQR spectrum exhibited a strong increase in the line intensity upon

switching  $H_{\text{ext}}$ . In pulsed NQR experiments, only homogeneous line broadening contributes to the spin echo amplitude [6], and the character of the SEE decay brings an information on the spin-spin relaxation time ( $T_2$ ) of the compound. An influence of magnetic dopants on the SEE for such a compound is also of current interest, and we prepared and studied the  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  single crystals doped with the Cr (0.015 mol%), Gd (0.2 mol%), Pr (0.2 mol%) and Nd (0.5 mol%) atoms.

A pulsed NQR spectrometer operating in a two-pulse mode ( $90-\tau-180-\tau$ -echo) was used for the experiments carried out at room temperature. As the  $^{209}\text{Bi}$  NQR spectra showed, the doping resulted only in non-homogeneous broadening of the resonances, the values of the quadrupole coupling constant and EFG asymmetry parameter  $\eta$  remaining unchanged. Modulations of the SEE in constant magnetic field are determined by interference due to the mixing of the states  $|+1/2\rangle$ ,  $| -1/2\rangle$  and  $|+m\rangle$ ,  $| -m\rangle$  ( $m \geq 3/2$ ) if the EFG is not axially symmetric ( $\eta \neq 0$ ). If  $\eta = 0$ , the modulations of the SEE for the transitions  $\pm m \leftrightarrow \pm(m+1)$  are absent [7].

Figure 1 shows modulations of the SEE for the transition  $\Delta m = 1/2 - 3/2$  in the  $^{209}\text{Bi}$  NQR spectrum of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  and the SEE for the transition  $\Delta m = 3/2 - 5/2$  in weak external magnetic fields when the Zeeman splittings are still within the line width. The pattern of Fig.1b is quite consistent with the increase in the resonance intensity earlier observed in the Zeeman experiments [1, 3]. It is to be noted that such a behavior of the SEE in magnetic fields has never been observed for

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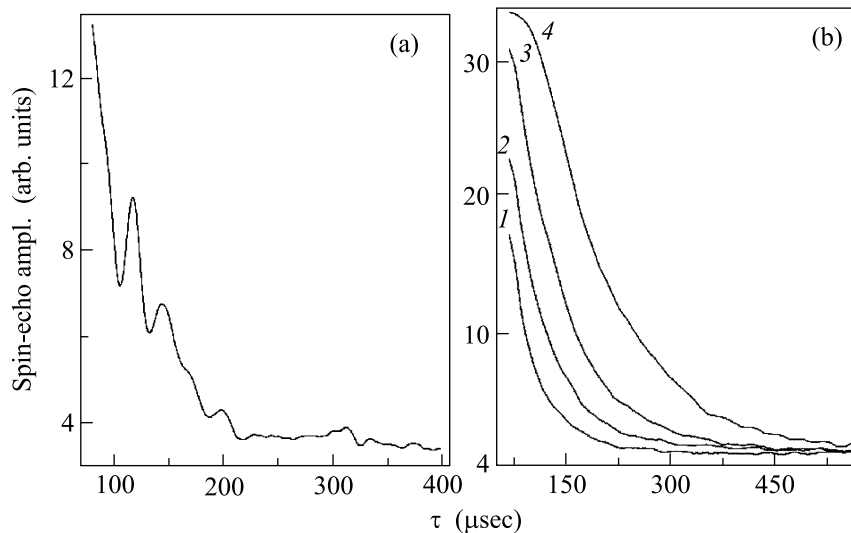


Fig.1. Spin-echo envelopes in the  $^{209}\text{Bi}$  NQR spectrum of non-doped single crystal  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  for the transition  $\Delta m = 1/2 - 3/2$  in zero field (a) and  $\Delta m = 3/2 - 5/2$  in external magnetic fields  $H_{\text{ext}}$  (b):  $H_{\text{ext}} = 0$  (1), 9 (2), 15 (3), 30 Oe (4)

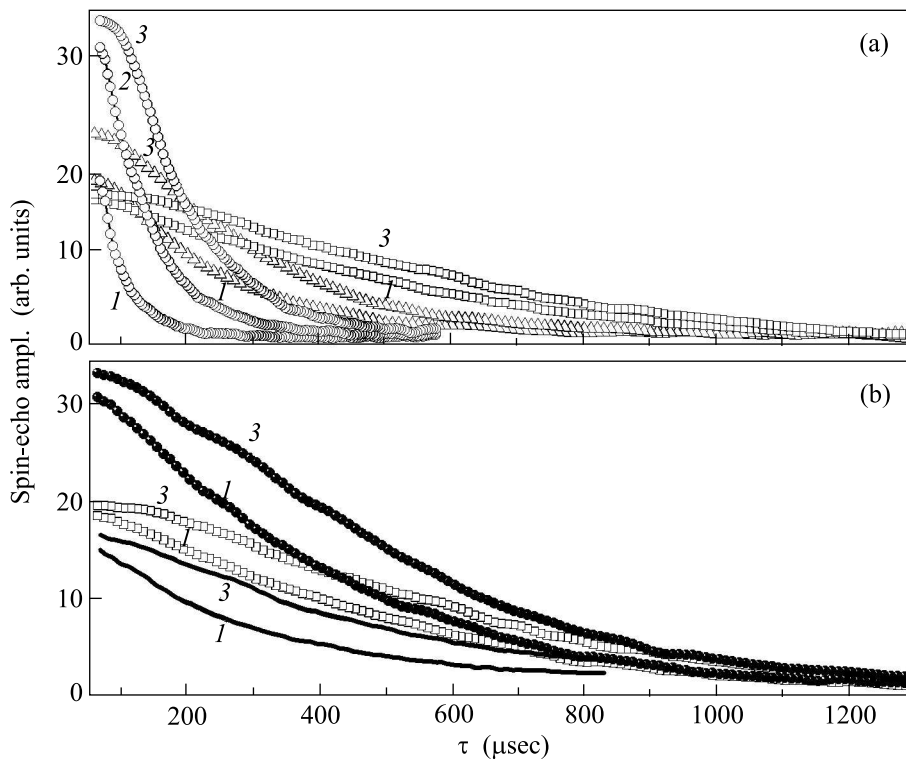


Fig.2. Spin-echo envelopes for the transition  $\Delta m = 3/2 - 5/2$  in the  $^{209}\text{Bi}$  NQR spectrum of the  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  single crystals for non-doped (open circles), doped with praseodymium (solid circles), neodymium (open squares), gadolinium (open triangles), and chromium (solid lines) samples in external magnetic fields  $H_{\text{ext}}$ :  $H_{\text{ext}} = 0$  (1), 15 (2), 30 Oe (3)

compounds exhibiting no anomalies in magnetic properties.

Figure 2 demonstrates considerable effect of doping on the SEE for the transition  $\Delta m = 3/2 - 5/2$ : much slower decay of the SEE (increase in  $T_2$ ) and

weaker influence of external magnetic fields on its character. As was earlier shown by a study of the spin-lattice relaxation for the  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  single crystal, the pre-exponential function contributes considerably to the description of the short-time part of the relaxation curve,

The values of the parameters  $A$  (arb. units) and  $T_2^*$  ( $\mu\text{sec}$ ) used for modeling the observed SEE in Figs.1b and 2. The top line lists the dopant atoms

Sample	Pure	Pure	Pure	Pure	Cr	Cr	Pr	Pr	Nd	Nd	Gd	Gd
$H$ (Oe)	0	9	15	30	0	30	0	30	0	30	0	30
$A$	75	75	75	75	20	20	35	35	23	23	27	30
$T_2^*$	50	60	75	100	300	400	400	500	400	500	220	280

and the effective time of the spin-lattice relaxation may be introduced for each of the four quadrupole transitions ( $1/2 - 3/2, \dots, 7/2 - 9/2$ ) [5].

In a similar way, we attempted to describe phenomenologically the dependence of the quadrupole spin-echo amplitude  $I$  for each of the four NQR transitions on the pulse separation  $\tau$  and conditions of the experiment (the field strength  $H$  and temperature  $T$ ) as a product of two functions:

$$I(\tau, H, T) \sim A(\tau, H, T) \cdot e^{-\tau/T_2^*}, \quad (1)$$

where  $A(\tau, H, T)$  is the pre-exponential function, which shows notable dependence on  $\tau$  only for the transition  $\Delta m = 1/2 - 3/2$  only,  $T_2^*(H, T)$  is the effective time of spin-spin relaxation which also depends on the conditions of the experiment. The expression (1), although simple, describes the experimental data in Figs.1b and 2 fairly well (within the accuracy of 20%). The values of the parameters  $A$  and  $T_2^*$  for all the studied samples of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  are listed in Table.

One can see from Table that for the non-doped crystal  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ , the external magnetic field  $H$  does not influence the value  $A$  of the pre-exponential function, whereas  $T_2^*$  considerably increases as  $H$  grows. The magnetic dopants reduce markedly the values of  $A$  but strongly increase the effective time of spin-spin relaxation  $T_2^*$  as compared to the appropriate parameters for the non-doped crystal.

An unusual influence of weak external magnetic fields on the SEE, observed in the NQR experiments on the  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  single crystal (Fig.1b), as well as a strong

elongation of the spin-spin relaxation time as a result of doping the crystal with paramagnetic atoms (Fig.2) find their explanation if a weakening of fluctuations in the electronic system of bismuth oxy compounds is suggested under the influence of external and local magnetic fields. This conclusion is consistent with the specific features of the electronic structure revealed in the compounds discussed [1].

The data reported in this letter are the first observations of the phenomena which explanation is important for understanding the nuclear spin dynamics in bismuth oxy compounds which are conventionally considered as diamagnets.

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