Magnetic Properties of the Bismuth Oxide $\alpha - \text{Bi}_2\text{O}_3$ *

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A very unusual magnetic behaviour of $\alpha - \text{Bi}_2\text{O}_3$ was observed in a wide range of temperatures and magnetic fields. A longitudinal magnetoelectric effect was found at 4.2 K. The existence of an antiferroelectrically ordered subsystem of electric dipoles in $\alpha - \text{Bi}_2\text{O}_3$ is proposed. The mechanism of spin-orbit coupling is regarded as the physical origin for the occurrence of the ordered magnetic moments in $\alpha - \text{Bi}_2\text{O}_3$.

Key words: ^{209}Bi NQR, Magnetisation of $\alpha - \text{Bi}_2\text{O}_3$, Magnetoelectric effect, Antiferroelectric, spin-orbit interaction.

The bismuth oxide $\alpha - \text{Bi}_2\text{O}_3$ is traditionally classified as a diamagnetic substance. But the splitting of all ^{209}Bi NQR lines observed on a powder sample and on a set of single crystals [1–3] pointed to the existence of internal magnetic fields in $\alpha - \text{Bi}_2\text{O}_3$. A SQUID magnetometer with the sensitivity of about $10^{-7} \text{ G} \cdot \text{cm}^3$ was used. The experimental results are shown in Figures 1 and 2. In the investigated region of magnetic fields and temperatures the magnetisation of the $\alpha - \text{Bi}_2\text{O}_3$ single crystal differs significantly from the theoretical diamagnetic magnetisation $M_{\text{dia}} = \chi_{\text{dia}} \cdot H$, where $\chi_{\text{dia}} = -1.85 \cdot 10^{-7} \text{ cm}^3/\text{g}$ was estimated using the reference data [4].

Some peculiarities of the magnetisation of $\alpha - \text{Bi}_2\text{O}_3$ follow from Figures 1 and 2: the paramagnetic sign and nonlinearity of the magnetic moment at $T = 4.2 \text{ K}$; the presence of a residual magnetic moment in vanishingly small external fields; a change of the sign of the magnetisation at certain temperatures, and independence of the magnetisation of temperature at $T > 20 \text{ K}$.

In order to gain insight into the features of magnetic behaviour of $\alpha - \text{Bi}_2\text{O}_3$ it is necessary to consider the

contributions of the three magnetic subsystems: 1) the diamagnetic subsystems of the cores of atoms, 2) the paramagnetic contribution, and 3) the presumably antiferromagnetically ordered subsystem of magnetic moments.

The longitudinal magnetoelectric effect on a single crystal was also observed at 4.2 K. In fields below 50 kOe the polarization increased linearly, whereas in higher fields it tended to saturation. The effect evidenced the occurrence of an antiferroelectrically ordered subsystem of electric dipoles in $\alpha - \text{Bi}_2\text{O}_3$. Thus ordered magnetic moments can be induced in $\alpha - \text{Bi}_2\text{O}_3$ due to the mechanism of spin-orbit interaction [5].

The preliminary NQR experiments carried out at elevated temperatures showed that the splitting of ^{209}Bi NQR lines disappeared in the vicinity of 450 K. So we suggest that the antiferroelectric ordering in $\alpha - \text{Bi}_2\text{O}_3$ breaks down at this temperature.

The magnetisation data and the observation of the magnetoelectric effect have clearly demonstrated that both the electric and magnetic properties of $\alpha - \text{Bi}_2\text{O}_3$ are more complicated than they are conventionally thought to be.

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Fig. 1.
Temperature dependencies
of magnetisation of $\alpha - \text{Bi}_2\text{O}_3$.
 $\Delta - H \parallel c, H = 1000 \text{ Oe}$;
 $\blacktriangle - H \parallel c, H = 124 \text{ Oe}$;
 $\square - H \parallel a, H = 4850 \text{ Oe}$;
 $\bullet - \text{powder sample}, H = 500 \text{ Oe}$.

Fig. 2.
Magnetisation of single
crystal of $\alpha - \text{Bi}_2\text{O}_3$.
Experimental data:
 $\Delta - T = 4.2 \text{ K}, H \parallel a$;
 $\diamond - T = 4.2 \text{ K}, H \parallel b$;
 $\blacktriangle - T = 4.2 \text{ K}, H \parallel c$;
 $\square - T = 77 \text{ K}, H \parallel a$;
 $\blacksquare - T = 77 \text{ K}, H \parallel c$;
 $\circ - T = 200 \text{ K}, H \parallel c$.
Dashed line – M_{dia} (see text).
In the insert the initial parts
of some curves are shown.

- [1] A. A. Boguslavskii and G. K. Semin, *Zh. Fiz. Khim.* **53**, 33 (1979).
- [2] E. A. Kravchenko *et al.*, XI Intern. Symp. NQR, Abstracts of Papers, London 1991, p. 1–37.
- [3] E. A. Kravchenko and V. G. Orlov, *Z. Naturforsch.* **49a**, 418 (1994).
- [4] P. W. Selwood, *Magnetochemistry*, 2nd ed., Interscience, New York 1956.
- [5] G. T. Rado, *Phys. Rev. Lett.* **6**, 609 (1961).