Mössbauer study of spin–flip phase transition on the Fe_3BO_6 surface

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The spin–flip phase transition in the skin layer of an antiferromagnetic Fe_3BO_6 bulk crystal with a weak ferromagnetic moment was investigated. The measurements were performed by a Mössbauer method which makes it possible to study simultaneously the surface and volume properties of bulk material. The following features were observed: 1) The first-order spin–flip phase transition observed in the volume of the crystal is accompanied by continuous reversal of spins at the crystal surface and this continuity increases toward the surface; 2) outside the region of the spin–flip phase transition the surface magnetic moments are not directed in the same direction as the moments in the bulk of the crystal. The experimental data agree with the phenomenological theory.

Surface phase transitions are now attracting a great deal of attention. Most of these studies involve transitions at the Curie point.[1] Spin–flip phase transitions (SFPT) in a surface layer have been studied significantly less.

In the first studies of surface magnetism[2,3] it was concluded that the antiferromagnetism vector in the surface layer of α-Fe_2O_3 tilts away from the basal plane on the (100) and (111) faces at temperatures above the SFPT of the Morin type. In $ErFeO_3$ (Ref. 4) and $TbFeO_3$ (Ref. 5) the spin–flip temperature in the surface layer was found to be up to 40° higher than in the volume of the crystal. Mössbauer studies of α-Fe_2O_3 (Ref. 6) have shown that the SFPT is shifted by several degrees in the surface layer, while in Ref. 7 no difference was observed, within the limits of the measurement error (± 5 K), in the SFPT temperatures on the surface and in the volume of α-Fe_2O_3. Spin reversal of the type $G_xF_z \leftrightarrow G_zF_x$ in the volume of $TbFeO_3$ (Refs. 8 and 9) becomes in the surface layer a transition of the Morin type[5] $G_xF_z \leftrightarrow G_y$. A transitional layer, in which the magnetic properties change, has been observed on a $FeBO_3$ surface[10,11] and on a $TbFeO_3$ surface.[5] Mössbauer studies of the surface layer and volume of a Fe_3BO_6 bulk crystal have shown[12,13] that the SFPTs occur in the same temperature ranges and the spin-flip mechanisms are the same, i.e., a first-order SFPT with formation of an inhomogeneous state is observed in the surface layer, just as in the volume of the crystal.[14]

M. I. Kaganov studied theoretically the problem of an SFPT on a surface.[15] He constructed a phenomenological theory of an SFPT on a surface and showed that transitions in the volume must be accompanied by surface transitions. In addition, the shape of the temperature hysteresis loop must also change (it becomes narrower). The orientation angle of spins on the surface of the crystal was determined as a function of

the first anisotropy constant for different orientations of the easy axis on the surface in the presence of a first-order SFPT in the volume of the magnet.[15]

There are obviously not enough experimental data in order to make comparisons with theoretical results. In addition, the methods enumerated above are used to investigate a thick surface layer, whose properties can apparently be similar to those in the volume of the crystal.

In view of the circumstances mentioned above, we have decided to study the magnetic structure and an SFPT in a thin surface layer of a Fe_3BO_6 bulk crystal.

We employed the method of simultaneous γ-ray, x-ray, and electron Mössbauer spectroscopy proposed in Ref. 13. Later, in Ref. 16, this method was called simultaneous triple radiation Mössbauer spectroscopy (STRMS). The STRMS method enables studying, by recording simultaneously γ rays (GR), characteristic x rays (CXR), and secondary electrons (SE), the properties of the volume and surface layers, several μm and 300 nm thick, respectively, of a bulk crystal. In the present work, however, it was necessary to study surface layers less than 300 nm thick, and for this reason the proportional SE detector, which is described in Ref. 17 and employed in the method of simultaneous detection of these radiations at temperatures from 100 to 750 K, was improved so as to select SE by energy. It is well known that the deeper the layer from which an electron emerges, the lower the energy of the electron is. Thus the improved method made it possible to obtain Mössbauer spectra of a $\sim$40-nm thick layer located about 300 nm from the surface by recording SE from different energy groups, as well as Mössbauer spectra from the volume of a bulk sample by recording γ rays, and simultaneously under identical experimental conditions.

Surface studies were conducted on crystals chemically polished for $\sim$50 h at room temperature in 1:1 mixtures of H_3PO_4 and H_2SO_4 acids.

The experimental Mössbauer spectra obtained at temperatures below and above the SFPT region consist of two sextuplets, corresponding to iron ions in nonequivalent 8*d* and 4*c* positions. The spectra obtained in the SFPT region by recording γ rays and secondary electrons are shown in Fig. 1. The solid and dashed lines are the Zeeman lines corresponding to different phases. The line corresponding to 8*d* iron ions are two times stronger than the lines of the 4*c* iron ions. As is evident from Fig. 1, the experimental spectra in the SFPT region consist of a superposition of spectra observed at temperatures below and above the SFPT region. The positions of the lines corresponding to different phases are well resolved (Fig. 1), which makes it possible to investigate the behavior of the magnetic moments of each phase.

Analysis of the spectra showed that in the SFPT region the lines of the phase observed below the SFPT become weaker as the temperature increases, and at some temperature these lines vanish. In the SFPT region the line of the phase observed above the SFPT increases in strength, from zero to the maximum value, with increasing temperature.

The angles θ determining the direction of the magnetic moments with respect to the wave vector of the γ rays were found from the ratios of the intensities of the first and second (fifth and sixth) lines of the Zeeman sextuplets using the formula (see, for example, Ref. 18):

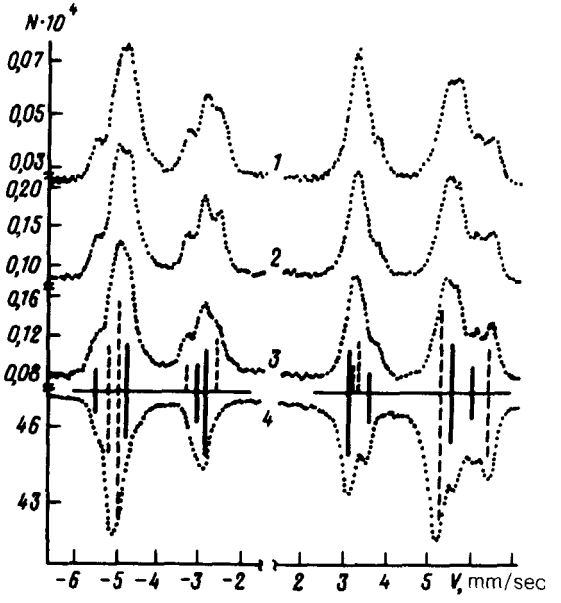

FIG. 1. Fe_3BO_6 Mössbauer spectra obtained near the spin–flip phase transition temperature by recording secondary electrons (1, 2, 3) and γ rays (4), i.e., from surface layers located at 0–40 nm, 50–90 nm, and 150–200 nm and from the volume of the crystal, respectively.

$$A_{1,6}/A_{2,5}=3(1+\cos^2\theta)/(4\sin^2\theta).$$

The temperature dependences of the angles θ in the surface layer studied and in the volume of the crystal are shown in Fig. 2. It is evident that the angle θ, determined for

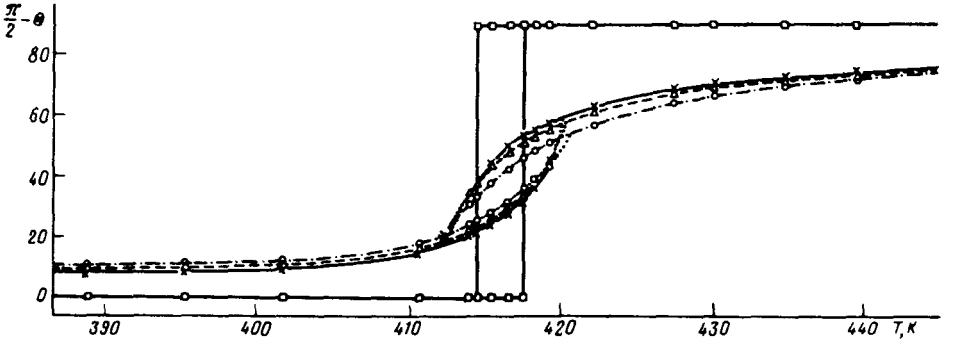

FIG. 2. Temperature dependences of the tilt angle θ of the spin magnetic moments. The dependences were obtained from the Fe_3BO_6 spectra presented in Fig. 1: 0, △, ×— for surface layers and □ — for the volume of the crystal.

the volume of the crystal, assumes only two values: 0 and $\pi/2$. This is clearly seen in the γ-ray spectrum (Fig. 1, bottom spectrum), in which the second and fifth lines in the region of the SFPT consist of components belonging to the phase observed below the SFPT, while the second and fifth lines of the sextuplets, corresponding to the phase observed above the SFPT, are absent. This means that below the SFPT temperature the magnetic moments in the volume of the crystal are oriented along the c axis and above the SFPT temperature they are oriented along the a axis. In the SFPT temperature range these two phases coexist. These results prove convincingly that spin flip in the volume of an Fe_3BO_6 crystal occurs as a first-order phase transition in which an inhomogeneous state is formed in the temperature range from T_1 up to T_2, consistent with the data obtained in preceding studies.[14]

As one can see from Fig. 2, the angles θ in layers located at a depth less than 200 nm from the surface are different from the values obtained for the volume of the crystal. At temperatures above 300 K, but outside the region of the SFPT, the magnetic moments in the surface layers (Fig. 2) tilt away from the directions along which the moments are oriented in the volume of the crystal. This is observed at temperatures significantly below T_1, at which the reorientation $G_xF_z \leftrightarrow G_zF_x$ starts in the volume of the crystal. The tilt angle θ increases as the surface or the SFPT region is approached.

In the SFPT region, in a surface layer less than 200 nm thick, the angle varies continuously from one value to another (Fig. 2). Thus reversal of magnetic moments occurs by a continuous rotation from one direction to another. The closer the observed layer is to the surface of the crystal, the smoother the spin-reversal process. This is clearly seen in Fig. 1 by simply comparing the line intensities for different phases. In addition, in contrast with the γ-ray spectra, the second and fifth lines of the Zeeman sextuplets of both phases are always present in the SE spectra.

At the completion of the phase transition the magnetic moments in the surface layer are oriented not along the crystallographic c axis (as are the magnetic moments in the volume of the crystal), but rather at a small angle with respect to this axis. At temperatures above the SFPT, the farther away from the crystal surface the layer studied is, the smaller this tilt angle. The tilting of the magnetic moments from the c axis decreases as the temperature increases from the SFPT point.

Comparing the experimental data with the theoretical results reveals that the experimental data are similar to the case described in Ref. 15, in which the easy axis at the surface does not lie along the normal to the surface or in the plane of the surface of the crystal.

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