Mössbauer study of surface magnetic properties of the antiferromagnet Fe_3BO_6 near the Néel temperature

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The behavior of the magnetic system of antiferromagnetic Fe_3BO_6 crystal was investigated in surface layers of the bulk crystal near the Néel temperature. The experimental method, based on the Mössbauer effect, made it possible to study simultaneously the surface and volume properties of bulk material. On the basis of the experimental results it is assumed that there exists a surface layer of "critical" thickness, within which the transition temperature $T_N(L)$ increases with the distance from the surface and reaches at the lower (from the surface) boundary of the "critical" layer the value of T_N corresponding to the volume of the crystal. It was found that the transition to the paramagnetic phase is accompanied by relaxation of the spin magnetic moments. These relaxation processes are observed in the bulk in a very narrow temperature range, but as the surface is approached, this range increases significantly within the "critical" layer.

There is now a great deal of interest in surface phase transitions, because the lowering of the symmetry of the surface can induce new magnetic structures and interesting magnetic phenomena. Most investigations at the Curie point (of the order-disorder type)[1] have been performed on ultrathin films. However, in order to understand surface phenomena so as to determine how surface and volume effects are related to each other, it is necessary to investigate the surface of bulk crystals, as well as the profiles of the properties (layer by layer analysis) of the surface layer. As was shown in Ref. 2, the Mössbauer effect is very useful in each case.

In this letter we describe the results of comprehensive studies of the surface and volume magnetic properties of bulk Fe_3BO_6 crystals near the Néel temperature. We employed the method developed in Refs. 3 and 4 and improved so as to conduct layer-by-layer analysis of the surface layer within a 300-nm interval, recording the Mössbauer spectra of secondary electrons in different energy groups. This method has the advantage that it makes it possible to study simultaneously the properties of a surface layer only 50 nm thick at any depth within 300 nm from the surface and the properties in the volume of a bulk sample under identical experimental conditions.

The compound Fe_3BO_6 belongs to the orthorhombic system. The magnetic structure of Fe_3BO_6 at temperatures below $T_N=508$ K for a bulk crystal consists of four magnetic sublattices of iron ions, occupying two nonequivalent positions $8d$ and $4c$. These four sublattices form two antiferromagnetic (AFM) sublattices $8d$ and $4c$. The existence of two AFM sublattices complicates the shape of the experimental spectra, which reduces the accuracy with which the effective magnetic fields are determined.

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The following factors were employed in order to improve the resolution of the lines: 1) the number of iron ions at the 8*d* and 8*c* sites and therefore the intensities of these lines are in the ratio 2:1; 2) the 8*d* and 4*c* iron ions occupy octahedral sites, but because the number of magnetic bonds is different, the effective magnetic fields at the nuclei of ions in the 8*d* and 4*c* sites are different from one another and because of the quadrupole splittings, the lines in the sextuplets are shifted significantly in opposite directions; 3) when the wave vector of the γ rays is oriented in the direction of the effective magnetic fields in the crystal, the number of lines in the experimental spectrum decreased, since the second and fifth lines of the Zeeman sextuplets are absent in this case.

Single crystals with the following characteristics were used in the experiments: 1) untreated surface (measurements were performed at the natural mirror-smooth boundary); 2) mechanically polished, using light chemical etchants; and, 3) chemically polished in a 1:1 mixture of H_3PO_4 and H_4SO_4 acids for ~ 50 h at room temperature. The experiments showed that reproducible results are obtained in surface studies only if the crystal is treated by using the last method.

The experimental Mössbauer spectra obtained by recording γ rays and secondary electrons are shown in Fig. 1. The effective magnetic fields obtained from the experimental spectra are shown in Fig. 2. It is obvious that as the temperature increases, the effective magnetic fields in the surface layer decrease more rapidly than in the volume of the crystal. The paramagnetic transition temperatures were determined by the methods employed in Mössbauer spectroscopy, and all methods gave the same value of $T_N(L)$ for the layer lying at a depth L from the surface of the crystal.

Analysis of the experimental spectra of Fe_3BO_6 showed that they can be divided into four characteristic groups: Γ_M, Γ_W, Γ_S, and Γ_P (Fig. 3). The Γ_M spectra consist of a superposition of two Zeeman sextuplets which correspond 8*d* and 4*c* iron ions. In the region Γ_P the experimental spectra of Fe_3BO_6 consist of two quadrupole doublets of 8*d* and 4*c* iron ions. This means that the material in the Γ_P region is in the paramagnetic state.

The Γ_W spectra are similar to the Γ_M spectra except that at the temperatures $T_W(L)$ the widths of the outer lines of the sextuplets increase. This broadening increases with the temperature up to $T_N(L)$. The widths of the inner lines of the sextuplets do not change in the temperature range between $T_W(L)$ and $T_N(L)$. The experimental spectra observed in the Γ_C region consist of a superposition of lines of the paramagnetic doublets of the Γ_P phase on the spectra of the Γ_Y phase. We call such spectra mixed. As the temperature increases from $T_C(L)$ to $T_N(L)$, the outer lines of the sextuplets converge and their intensities decrease. At $T_N(L)$ these lines vanish, while the intensity of the paramagnetic lines increases.

The diagram obtained from the experimental spectra is shown in Fig. 3. The position of the boundary $T_C(L)$ was determined by extrapolating to zero the temperature dependences of the intensities of the paramagnetic lines in the spectra. The position of the boundary $T_W(L)$ was found from the temperature dependences of the widths of the outer lines.

As one can see from Fig. 3, near T_N the crystal exhibits a state in which the matter in the bulk is magnetically ordered, while the matter at the surface is para-

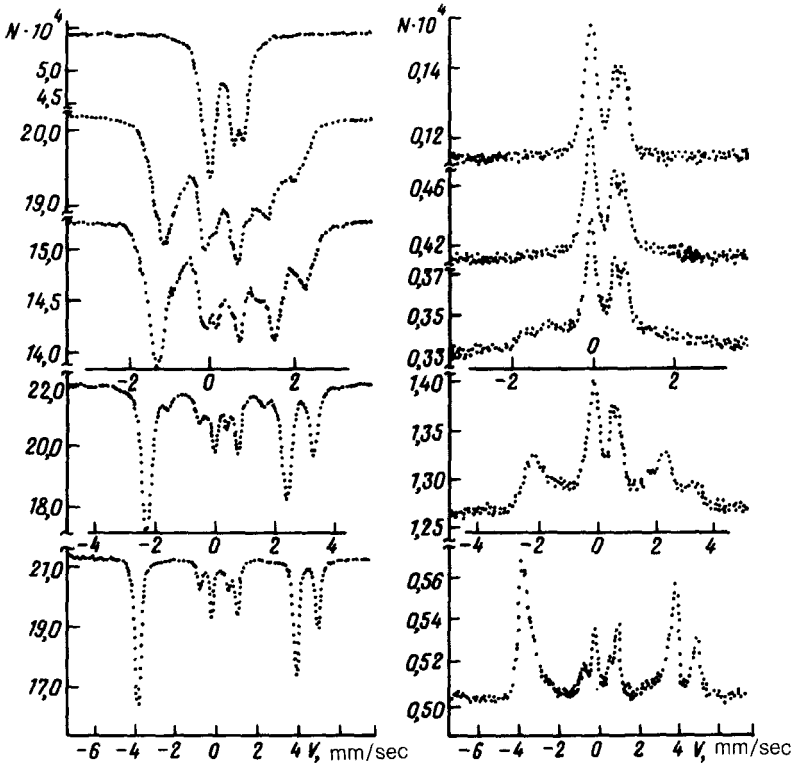

FIG. 1. Fe_3BO_6 Mössbauer spectra obtained near the Néel temperature from the volume of the crystal (by recording γ rays; left side) and from a 200-nm-thick surface layer (by recording secondary electrons; right side) at temperatures (bottom to top) of 471.2 K, 498.7 K, 503.7 K, 504.7 K, and 509 K.

magnetic. The paramagnetic and magnetically ordered phases are separated by the regions Γ_W and Γ_S. The experimental Mössbauer spectra in these regions have a complicated structure. The secondary-electron Mössbauer spectra discussed in this letter were obtained by recording electrons emerging from a $\sim$40-nm-thick layer. This thickness is apparently too large to justify just one magnetic ordering temperature for such a layer. This is clearly seen in Fig. 3 for the $T_N(L)$ line which separates the Γ_S and Γ_p regions. Thus the experimental spectra are a superposition of the spectra of secondary electrons arising in layers thinner than 40 nm. This is convincingly proved by the results of the analysis of such spectra.

The best agreement between the experimental and theoretical spectra in the Γ_W region is obtained if the theoretical spectrum is described by a collection of spectra with different Zeeman splittings. From this collection of sextuplets, however, the spectra with the smaller Zeeman splitting can be described only by a model of fluctuations of spin magnetic moments, i.e., by using a relaxation model.[5]

The experimental spectra in the Γ_S region are described satisfactorily by super-

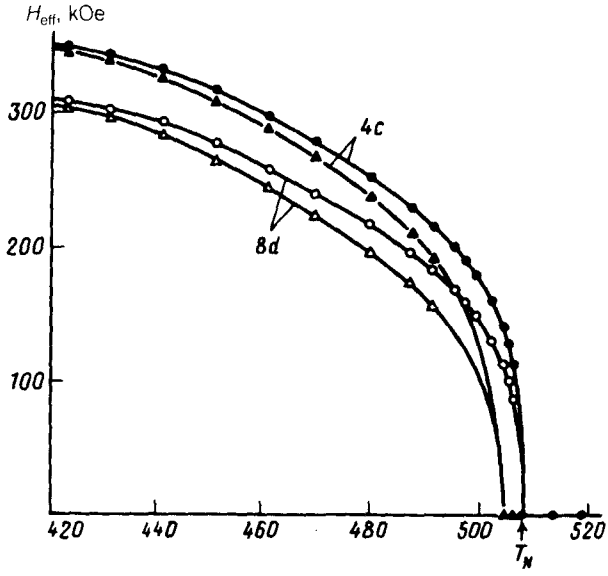

FIG. 2. Temperature dependences of the effective magnetic fields in Fe_3BO_6 at the nuclei of iron ions located in the volume (●, ○) and in a 200-nm-thick surface layer (▲, △) in the same crystal.

posing the paramagnetic lines from the Γ_P region on relaxation spectra from the Γ_W region. The intensities of the lines in the relaxational spectra decrease as the temperature increases, and the lines vanish at the temperature $T_N(L)$. The paramagnetic doublet lines appear at the temperature $T_C(L)$. The intensities of these lines increase

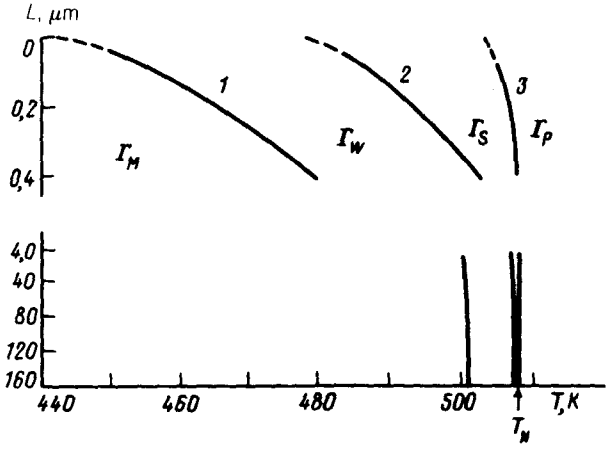

FIG. 3. Fe_3BO_6 phase diagram. *1*—Boundary line $T_y(L)$; *2*—$T_C(L)$; *3*—$T_n(L)$.

with the temperature and at temperatures above $T_N(L)$ the spectra consist only of lines of the paramagnetic phase. It should be noted that the coexistence of lines belonging to the paramagnetic and magnetic phases was observed in Ref. 6 in the Mössbauer diffraction spectra of Fe_3BO_6, which were obtained from surface layers up to the Néel temperature for the bulk sample. Apparently, when the method of Ref. 6 is employed, thick layers are investigated and the observed spectra are a superposition of spectra from a thin surface layer in the paramagnetic state and the volume of the crystal in a magnetically ordered state.

In summary, analysis of the experimental results has shown that as the temperature increases, the relaxation time of the spin magnetic moments of iron atoms located on the surface of the crystal starts to decrease, and in some sections paramagnetic regions arise directly on the surface of the crystal. As the crystal is heated further, the paramagnetic regions on the surface expand and penetrate deeper into the crystal. At a certain temperature, the entire surface becomes paramagnetic, and increasingly deeper layers transform into the paramagnetic phase. At some temperature, the heating destroys the magnetic order simultaneously in the entire remaining volume of the crystal. Thus, there apparently exists a surface layer of "critical" thickness, in which the transition temperature $T_N(L)$ increases with the distance from the surface and reaches the value of T_N of the "critical" field corresponding to the volume of the crystal at the lower boundary.

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