

Magnetic structure of the surface and interior of Ba hexaferrites

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The magnetic structure of the surface layer of single crystals of Ba hexaferrites has been studied in direct comparison with the magnetic structure of the interior of the sample by a method involving simultaneous γ , x-ray, and electron Mössbauer spectroscopy. Within the experimental error of ~ 10 nm, the results do not reveal a surface transition layer in which the orientation of the magnetic moments changes smoothly from the direction observed on the surface to the direction in the interior. In antiferromagnets, on the other hand, the thickness of this transition surface layer is hundreds of nanometers. © 1995 American Institute of Physics.

The magnetic properties of surfaces have attracted large research interest. One reason is the need to reach an understanding of fundamental phenomena that occur in surface layers. Another is the need to determine the role played by surfaces in shaping the properties of materials. It is also necessary to determine how the properties of surfaces are interrelated with those of the interior of a crystal. Such studies are now important for applications, because an understanding of the nature of the onset of a noncollinear magnetic structure in a surface layer (as in, for example, Ba hexaferrites) will make it possible to develop magnetic data storage media with high and ultrahigh storage densities.

The first studies of the magnetic properties of the surfaces^{1,2} of macroscopic crystals led to the conclusion that the antiferromagnetism vector in the surface layer of α -Fe₂O₃ deviates from the basal plane at (100) and (111) faces. It was suggested in Ref. 1, on the basis of the results which were found, that at the surface of hematite there is a “transition” layer in which the orientation of the magnetic moments changes smoothly from a direction in the interior to a direction at the surface. A phenomenological theory was derived in Ref. 2, and the thickness of this transition layer was calculated for hematite.

Studies of the surface properties with the help of thin powders of γ -Fe₂O₃ (Refs. 3 and 4), CrFe₂O₄ (Ref. 5), and NiFe₂O₄ (Ref. 6), and CrO₂ (Ref. 7) showed that the magnetic moments of the ions in a thin surface layer are not collinear with the moments of ions in the interior of the sample.

A surface transition layer was observed in studies of macroscopic crystals of

FeBO₃ (Refs. 8 and 9), ErFeO₃ (Ref. 10), and TbFeO₃ (Ref. 11). The experimental results showed that the thickness of the surface layer in which the properties differ from the bulk properties is⁸ ~500 nm. The theory of surface magnetism derived in Ref. 2 was used in Ref. 9 to calculate the thickness of the transition layer for FeBO₃. The thickness which was found turned out to agree well with the estimates made in Ref. 8 on the basis of experimental data.

Direct experimental proof of the existence of a transition layer at the surface of a macroscopic crystal was reported in Ref. 12. Those results were found by a new method, proposed in Ref. 13, which involves simultaneous γ , x-ray, and electron Mössbauer spectroscopy. That composite method makes it possible to find information of the surface layer and the interior of the crystal simultaneously. It was shown¹² as a result that there exists a layer ~400 nm thick at the surface of a bulk antiferromagnetic crystal of Fe₃BO₆ (which, like FeBO₃, belongs to the family of borates), in which the orientation of the magnetic moments differs from that in the interior of the sample. A layer-by-layer study of the transition layer revealed that this difference increases toward the surface.¹²

That a transition layer exists was thus demonstrated convincingly. However, all those measurements were carried out on crystals with an antiferromagnetic order. In light of the discussion above, we undertook a study of the magnetic structure of the surface layer of crystals of hexagonal ferrites of type M.

For the measurements we used the method proposed in Ref. 13. In that method, one simultaneously records Mössbauer spectra with various types of radiation, which differ in their range in the material: γ rays, characteristic x radiation, and secondary (conversion and Auger) electrons. These types of radiation carry information on the properties of the interior, of surface layers a few microns thick, and of surface layers 300 nm thick, respectively, of a bulk crystal. The energy of an electron leaving the sample is smaller, the deeper the atom in which this electron was formed. Accordingly, an energy selection of the secondary electrons is carried out in the composite method in order to study the properties of surface layers with a thickness of less than 300 nm (Ref. 15).

For the present experiments we selected single crystals of a Ba hexaferrite in the form of wafers ~150 μ m thick. The C crystallographic axis was perpendicular to the plane of the wafers. For the surface studies, the crystals were subjected to chemical polishing by boiling in orthophosphoric acid. The Mössbauer spectra were processed on a computer. The parameters of the hyperfine interactions, the intensities, and the linewidths of the Zeeman sextuplets were determined.

This composite method was used to obtain experimental spectra over the temperature range from 300 to 700 K. Figure 1 shows some spectra obtained during the recording of γ rays and secondary electrons in the case in which the wave vector of the γ rays was parallel to the C crystallographic axis. We see that the spectral lines corresponding to different sublattices are resolved well. It is thus possible to determine the orientation of the magnetic moments of each sublattice highly accurately.

Working from the relative intensities of the first and second lines (and also the fifth and sixth lines) of the sextuplets and the formula (Ref. 16, for example)

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

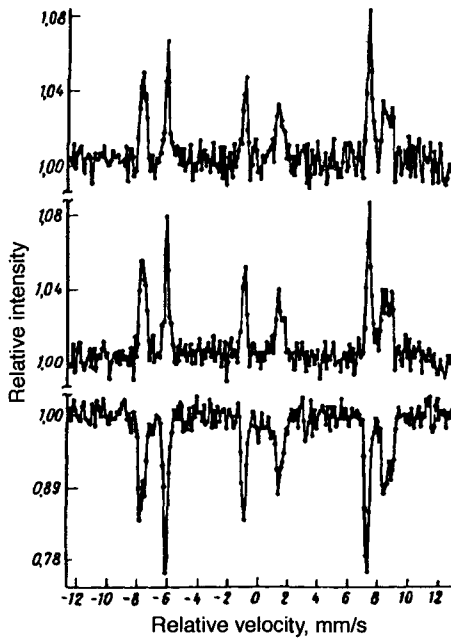


FIG. 1. Mössbauer spectra of a Ba hexaferrite recorded at 293 K. 1—Secondary electrons from surface layers between 0 and 40 nm were detected; 2—secondary electrons from the layer from 50 to 100 nm; 3— γ rays from the interior of the crystal. The γ -ray wave vector was parallel to the C crystallographic axis.

we found the angles θ , which determine the direction of the magnetic moments with respect to the γ -ray wave vector.

Analysis of the spectra found through the detection of γ rays showed that the intensities of the second and fifth lines, which correspond to transitions with $\Delta m = 0$, in the Zeeman sextuplets of each nonequivalent position are zero. This result means that the angle θ is zero, so the magnetic moments of the iron ions at positions in the interior of the crystal are collinear with the γ -ray wave vector and are parallel to the C crystallographic axis. This pattern is observed over the entire temperature range studied. This result agrees well with published data on the bulk properties of these crystals (Ref. 17, for example).

Analysis of the spectra obtained through the detection of secondary electrons shows that the intensities of the second and fifth lines of the sextuplets are zero. This result means that the magnetic moments of the iron ions in the layer between a depth ~ 100 nm and a depth ~ 150 nm, like those in a layer between 0 and 40 nm, are collinear with the γ -ray wave vector and with the C crystallographic axis. This pattern is observed up to 600 K; above this temperature, it becomes difficult to analyze the spectra because of the poor resolution of the lines.

We also carried out some control experiments. The single crystals under study were positioned in such a way that the γ wave vector made an angle θ with the C axis. Figure 2 shows some Mössbauer spectra recorded at $\theta = 10^\circ$. It can be seen from Fig. 2 that the

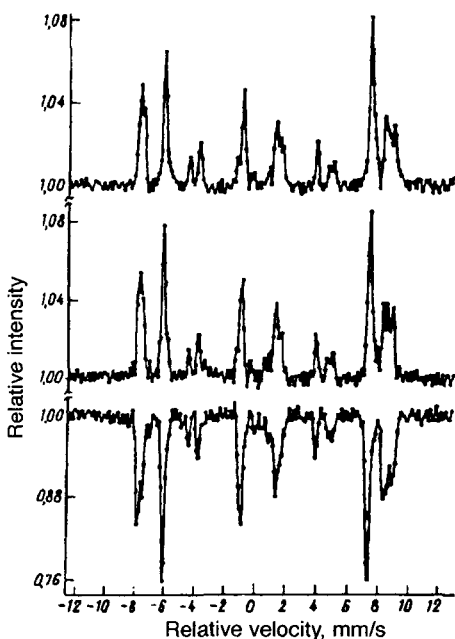


FIG. 2. Mössbauer spectra of a Ba hexaferrite recorded at 293 K. 1—Secondary electrons from a surface layer from 0 to 40 nm were detected; 2—secondary electrons from the layer from 50 to 100 nm; 3— γ rays from the interior. The γ -ray wave vector made an angle of 10° with the C crystallographic axis.

deviation of the magnetic moments from the γ propagation direction gives rise to lines in the Zeeman sextuplets corresponding to transitions with $\Delta m = 0$ in the spectra. The value found for θ from Eq. (1) is 10° , in agreement with the given experimental conditions.

We subsequently modeled the Mössbauer spectra under the assumption that in a transition layer at the surface of the Ba hexaferrites, as in antiferromagnets,^{8,10} the magnetic moments rotate smoothly from the direction normal to the surface to an angle of 25° from this normal, but that the thickness of this layer is ~ 10 nm. Analysis of the model spectra showed that, when Mössbauer spectroscopy is used to study a surface at a depth ~ 40 nm, the accuracy of the method is insufficient for observing a transition layer of this sort with a thickness ~ 10 nm. It follows that more-accurate methods will be necessary in order to determine the orientation of the magnetic moments in a surface layer ~ 10 nm thick.

In summary, it has been demonstrated experimentally, for the first time, that the magnetic moments of iron ions in Ba hexaferrites are oriented parallel to the C crystallographic axis both in the interior of the crystal and in the surface layer. Consequently, a surface transition layer like that which exists in antiferromagnetic crystals^{1,2,8-10} has not been observed in the Ba hexaferrites, within the experimental error ~ 10 nm.

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