Influence of Dimensional Effects on the Curie Temperature of Dy and Ho Thin Films

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Abstract—The role of size effects in the formation of the magnetic structure of Dy and Ho thin films in absence of epitaxial strain is studied in this work. It was found that, for Dy in the temperature range between the Néel temperature and the Curie temperature of bulk Dy and, for Ho, in the temperature range between the Néel temperature and the temperature of phase transition into the conic phase, the temperature dependences of the period of magnetic helicoid in the bulk and film metals are similar. The character of the transition into the ferromagnetic phase in the Dy films changes at lower temperatures, and the transition into the commensurable conic phase in the Ho films is suppressed. This is explained exclusively by the influence of dimensional effects.

Keywords: rare-earth metals, dysprosium, holmium, neutron reflectometry, X-ray diffraction analysis, magnetic ordering

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INTRODUCTION

Heavy rare-earth metals, which demonstrate complex types of magnetic orders, have been an area of active research for many decades [1]. Magnetic nanostructures containing rare-earth metals have attracted particular attention in recent years, which is motivated both by high values of magnetic moments of rare-earth atoms and the complexity of their magnetic phase diagrams in temperature and applied magnetic field.

Among the rare-earth magnets with a complex magnetic structure, metallic Dy and Ho can be selected. Bulk Dy and Ho crystallize with the formation of hcp (hexagonal close-packed) structure with the lattice parameters $a = 0.35903$ and $c = 0.6475$ nm and $a = 0.35773$ and $c = 0.56158$ nm, respectively [2]. In the case of bulk Dy, the long-period helical magnetic structure forms in the temperature range between the Curie ($T_C = 85$ K) and Néel ($T_N = 178$ K) temperatures; magnetic moments of Dy are within the basal plane, and the helicoid period is incommensurate with the crystal lattice parameter of Dy. In applied magnetic field, the helical magnetic order can transform into helifan, fan, or ferromagnetic orders [3, 4]. In bulk Ho, the long-period incommensurate helical magnetic order is observed between $T_N = 132$ K and $T_C = 18$ K; in this case, the magnetic moments also are within the basal plane. Below $T = 19$ K, the helicoid period in Ho becomes commensurate with the crystal lattice parameter and temperature-independent; magnetic moments partially deviate from the basal plane to form the commensurate conic magnetic structure [5–7].

There has been growing interest in the study of rare-earth nanostructures, which was initiated by finding a number of novel effects, such as the giant magnetocaloric effect [8]. Such effects are determined by the magnetic properties of nanostructures and their variations with temperature or magnetic field. Some types of magnetic order which forms in thin films and multilayered nanostructures based on rare-earth helimagnets, such as Dy and Ho, result from the mutual influence of size effects and epitaxial strains and are not observed in bulk materials.

The influence of dimensional effects manifests itself in changing the Néel temperature of helimagnets as the thickness of rare-earth film changes. In particular, it was found that the Néel temperature in thin film Ho decreases as the film thickness decreases. The
Dy and Ho films upon their growth in the kinetic ensure the complete relaxation of the crystal lattice of that epitaxial strains caused by mismatch of the crystal [001]Nb || RE (RE = Y, Dy, Gd, Ho). Al₂O₃ || [011]Nb || [0001]RE, Al₂O₃ || fer and rare-earth layers were also determined; these epitaxial relationships between the substrate and buf- a thermodynamically equilibrium mode [15, 16]. The influence of adjacent layers, lead to a shift of the Curie temperature [11]. For many rare-earth superlattices, in particular, for Dy/Y [12] and Dy/Gd [13], in which the influence of both epitaxial strains and size effect takes place, the helical to ferromagnetic phase transition is completely suppressed.

At present, the cause for such a suppression of the helical to ferromagnetic phase transition for rare-earth thin films and superlattices is not determined. On the one hand, the effect can result from the epitaxial stresses in rare-earth layers; on the other hand, the size and superlattice effects can play an important role. The majority of studies to date related to epitaxial thin rare-earth films and superlattices were performed on samples grown by molecular-beam epitaxy technique according to the protocol [14]. Sapphire single crystals were used as the substrates; a thick Nb buffer layer, an intermediate Y layer, and a rare-earth nanostructure were sequentially grown on the substrates at an elevated temperature. Typical growth rates did not exceed 1 monolayer/min; this favored the epitaxial growth in a thermodynamically equilibrium mode [15, 16]. The epitaxial relationships between the substrate and buffer and rare-earth layers were also determined; these are [1 1 0 2] Al₂O₃ || [011] Nb || [0001] RE, [1 1 0 2] Al₂O₃ || [001] Nb || [1 0 1 0] RE (RE = Y, Dy, Gd, Ho).

The peculiarity of rare-earth films and nanostruc- tures consists in the fact that epitaxial strains, which are due to the mismatch of crystal lattices of substrate, buffer layers, and rare-earth films, are nearly always present in the films. The epitaxial strains almost do not affect the Néel temperature of helimagnets but substantially influence the temperature of helical to ferromagnetic phase transition. In particular, it was shown that epitaxial strains in sufficiently thick Dy (more than 2000 monolayers), which are induced by the effect of adjacent layers, lead to a shift of the Curie temperature [11]. For many rare-earth superlattices, in particular, for Dy/Y [12] and Dy/Gd [13], in which the influence of both epitaxial strains and size effect takes place, the helical to ferromagnetic phase transition is completely suppressed.

The peculiarity of such systems consists in the fact that epitaxial strains caused by mismatch of the crystal lattices of rare-earth film and adjacent buffer layers are induced. As was shown recently [17], it is possible to ensure the complete relaxation of the crystal lattice of Dy and Ho films upon their growth in the kinetic growth mode. For this purpose, Dy and Ho rare-earth films were grown on [1 1 0 2] Al₂O₃ single-crystal substrates by high-vacuum magnetron sputtering using typical growth rates ~1 monolayer/s, which favor the kinetic growth mode of nanostructures. In this case, the epitaxial relationships [1 1 0 2] Al₂O₃ || [1 0 1 0] Nb || [0 0 0 1] RE (RE = Dy, Ho) are realized, which were not observed previously, and epitaxial stresses in the rare-earth films are not induced. In the present study, we investigate the magnetic structure of Dy and Ho films 200 nm thick, which were grown according to the protocol [17]; it is assumed that the effect of epitaxial stresses on the magnetic structure is absent.
tion of soft X-ray radiation at the given energies and interference of signals from magnetic satellites and charge signals from oscillations of the total film thickness. On the other hand, the use of classic neutron diffraction is impossible because of the small amount of scattering material. At the same time, it was shown in [18, 19] that the neutron reflectometry, which allows one to detect the signal from the magnetic satellite (0000)+ at low values of transmitted pulse, can be an efficient method for the study of such systems. The position of this satellite allows us to determine the helicoid period, whereas the integral intensity can serve as the order parameter of the helical phase. Since the neutron scattering does not allow one to detect the magnetic signal from magnetic moments oriented along scattering vector, the deviation of magnetic moments from the basal plane must result in a decrease in the signal from the (0000)+ magnetic satellite. The appearance of a ferromagnetic component must also be accompanied by a decrease in the intensity of this signal. Neutron measurements were performed using a REMUR time-of-flight reflectometer that operates based on an IBR-2M pulse fast reactor available at the Laboratory of Neutron Physics of the Joint Institute for Nuclear Research. Experimental data obtained with the REMUR reflectometer were transformed from the instrumental coordinate system into the reciprocal space coordinate system using Överlåtaren software [20].

RESULTS AND DISCUSSION

Figure 1 shows X-ray diffraction patterns of Dy and Ho films, which were measured in the Θ−2Θ mirror geometry; observed reflections are marked.

Along with the reflections corresponding to the substrate, reflections (110) belonging to the Nb buffer layer and (0001) reflections of the hcp structure of Dy and Ho are observed in the X-ray diffraction patterns. A contribution from the other orientations of rare-earth films is also observed; however, it is insignificant. When measurements were performed in the non-mirror geometry, reflections from the [10T0] and [10 T1] planes of rare-earth films were detected, which allowed us to determine their lattice parameters. It was found that, within an experimental error, the lattice parameters of Nb, Ho, and Dy correspond to those of the bulk crystals. Thus, in growing the rare-earth structures on the sapphire substrates with the Nb buffer layer at high rates in the kinematic regime, the epitaxial relationships [1 T0][Al₂O₃]∥[110][Nb]∥[0001][RE], which were earlier observed in [17], are realized, and the complete relaxation of the crystal lattices of Nb and rare-earths occurs. Thus, the prepared structures are model systems, which can be used to study the influence of dimensional effects on the magnetic structure of thin rare-earth films in the absence of epitaxial strains.

Figures 2 and 3 show the temperature dependences of the magnetization of Dy and Ho and literature data for bulk crystals [17, 19]. It should be noted that, above the Curie temperature of Dy and temperature of phase transition to the conic phase of Ho crystals, the behavior of the magnetization of thin films slightly differs from that of bulk crystals, and, in particular, the Néel temperatures are sufficiently close.

On the other hand, the low-temperature behavior of the magnetization in bulk crystals and that in thin films differ substantially. As the temperature decreases over the wide range, the abrupt transition to the ferro-
magnetic phase, which is typical of bulk Dy crystals, in the case of film, changes to the monotonic increase in the magnetization. The transition temperature for the film is lower than that for the bulk crystal. The magnetization of Dy film at low temperatures is half the saturation magnetization. The data given in Fig. 2 allow us to assume that, in contrast to the Dy bulk crystal, the Dy film below the Curie temperature is characterized by the presence of both helical and ferromagnetic components. This is also typical of fan magnetic structure. The abrupt nonmonotonic change of the magnetization, which, with changing temperature, takes place for bulk Ho below the temperature of the phase transition to the conic phase, changes to the monotonic increase for the Ho film. The magnetization of the Ho film at low temperatures is half that for bulk crystals and more than 20 times lower than the saturation magnetization. It is possible to assume the presence of insignificant ferromagnetic component in the Ho film, as it should be observed in applied magnetic field.

The magnetic structure of the films and its changes with temperature were determined by neutron reflectometry and off-specular neutron scattering. As was discussed above, for this purpose, signals from the (0000) magnetic satellite were detected. Figure 4 shows the typical two-dimensional reflectometry patterns taken at different temperatures in applying the magnetic field $H = 1$ kOe along the easy magnetization axes of the Dy and Ho films.

The neutron patterns taken at temperatures above the Néel temperature exhibit only the specular line at $Q_z = 0$ corresponding to the reflectometry curve for the layered structure. Below the Néel temperature, the patterns exhibit the signal ($Q_z = \text{const}$) from the helical magnetic structure; its position along the $Q_z$ axis characterizes the helicoid period and the intensity can serve as the order parameter of the helical phase. The fact that the signal is observed as a line in the patterns is likely to be explained by the existence of lateral

**Fig. 3.** Temperature dependences of the magnetization of (symbols) Ho thin film and (line) Ho crystal [Ho] measured in the magnetic field $H = 1$ kOe applied along the easy magnetization axis.

**Fig. 4.** Typical two-dimensional off-specular neutron scattering patterns for Dy and Ho films measured at different temperatures in the magnetic field $H = 1$ kOe applied along the easy magnetization axis.
domains in the films, which are characterized by the same helicoid period but different directions of magnetic moment rotation in the basal plane (clockwise and anticlockwise). Below the Curie temperature of bulk Dy, the signal from magnetic helicoids in the film is present as before and the signal intensity decreases as the temperature decreases. The signal from the (0000)\(^+\) magnetic satellite for the Ho film arises below the Néel temperature and the signal intensity increases as the temperature decreases.

Figures 5 and 6 show the reflectometry curves obtained from the two-dimensional patterns by integration along the \(Q_x\) axis. Let us note the following characteristic peculiarities of the reflectometry patterns.

At \(T = 200\) K (above the Néel temperature), no magnetic signal is observed for the Dy film. As the temperature decreases below the Néel temperature, the (0000)\(^+\) magnetic satellite appears, whose intensity increases as the temperature decreases, and its position shifts to the lower values of \(Q_z\); this reflects the increase in the helicoid period. Below the Curie temperature of bulk Dy, the intensity of magnetic satellite decreases, and the helicoid period continues to increase. The weakly intense satellite still is observed at \(T = 50\) K; it is not detected at lower temperatures. The temperature behavior of the helical magnetic structure agrees on the whole with the magnetometry data given in Fig. 2.

The neutron patterns of Ho films (Fig. 6) show that, below the Néel temperature, the (0000)\(^+\) magnetic satellite is detected. As the temperature decreases, its intensity increases and its position shifts toward lower values of \(Q_z\); this assumes an increase in the helicoid period. The temperature range below the temperature of transition of bulk Ho to the conic phase \((T < 25\) K\) is of particular importance. As is seen from Fig. 6, as the temperature decreases to \(T = 1.5\) K, the intensity of magnetic satellite reflection increases insignificantly and its position slightly shifts to the low values of \(Q_z\). As was discussed above, in the case of formation of conic phase in the Ho film, the intensity of satellite should decrease. Since this is not observed, we conclude that the transition to the conic phase in the Ho film is suppressed.

Figure 7 shows the temperature dependences of the period of helical magnetic structure of the Dy and Ho thin films, which were obtained using data given in Figs. 5 and 6; the literature data for bulk crystals also are given for comparison [3, 23].

The following peculiarities of the obtained results should be noted. The temperature dependences of the
helical magnetic structure period for the Dy thin films and bulk crystals above the Curie temperature and for bulk and thin film Ho above the temperature of the phase transition to the conic phase are similar. For Ho, the difference in the behavior of thin-film and bulk systems is within the experimental error; for Dy, this difference is more substantial. Below the corresponding temperatures for bulk crystals, the complete disappearance of magnetic order does not occur completely and is likely to remain in some crystallites within the film; for film Ho, no phase commensurate with the crystal lattice period of crystalline phase forms [23, 24]. It has traditionally been assumed that the suppression of the transition and the decrease in the temperature of the ferromagnetic to conic phase transition for the layered Dy- and Ho-based nanostructures are due to the crystal lattice distortion because of the disagreement of the lattice parameters of adjacent layers. In our case, according to X-ray diffraction data, no crystal lattice distortion of Dy and Ho takes place. Thus, the decrease in the temperature and changing character of transition to the ferromagnetic phase in the Dy film and the suppression of the transition to the conic phase in the Ho film can only be related to the size effects.

CONCLUSIONS

The influence of size effects on the temperatures of ferromagnetic transition and the magnetic structure of relatively thick Dy and Ho films (200 nm thick) is studied; using of special growth conditions, it turned out possible to attain in the rare-earth films the complete crystal lattice relaxation. The structures prepared in such a way are the model systems for the study of the influence of size effects on the formation of helical magnetic order in these films. It was found that, for Dy in a temperature range between the Néel temperature and the Curie temperature of bulk Dy and for Ho in a temperature range between the Néel temperature and the temperature of the phase transition to the conic phase, the temperature dependences of the magnetic helicoid period for bulk and thin-film materials are analogous. At the lower temperatures, the character of the transition to the ferromagnetic phase for Dy films changes, and, for Ho films, the transition to the commensurate conic phase is suppressed; this is explained by the influence of size effects.

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