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Questions about the existence of the spin reorientations in $HoFe_{10-x}Co_xMo_2$

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Abstract

The magnetization curves of single-crystal and powder samples of $HoFe_{10-x}Co_xMo_2$ ($0 \leqslant x \leqslant 8$) have been studied. It has been shown that the easy magnetization direction in these compounds is parallel to the *c* axis in the temperature interval 4.2–300 K. Peculiarities observed in the temperature dependences of the initial susceptibility and the magnetic moment are shown not to be connected with spin reorientations.

1. Introduction

Interest in the magnetic properties of iron-rich rare earth $RFe_{12-y}M_y$ compounds ($M \equiv Ti$, V, Cr, Si, Mo, W; $1 \leqslant y \leqslant 3$) with the tetragonal $ThMn_{12}$ structure has been stimulated by the prospect of using some of them (for instance, the Sm alloys) as permanent magnetic materials. Many reports have been devoted to the study of the magnetocrystalline anisotropy of such compounds, and, in particular, the spin reorientation.

In ref. 1 we investigated the temperature variation of the orientation of the easy magnetization direction for the $RFe_{10}Mo_2$ series with the help of a rotational anisometer. At room temperature the easy magnetization direction for all the compounds, except those where $R \equiv Nd$ and Pr, was found to be parallel to the *c* axis; with decreasing temperature the deviation of the easy magnetization direction from the *c* axis by a certain angle was observed for the alloys with $R \equiv Tb$, Dy and Er. For the rest of the compounds, including $HoFe_{10}Mo_2$, the easy magnetization direction was parallel to the *c* axis up to 4.2 K. Such temperature variation of the magnetocrystalline anisotropy behaviour is typical of the $RFe_{12-y}M_y$ series with the other M. The only exception is the $HoFe_{12-y}M_y$ compounds, for which there are contradictory data in the literature. There are several reports on the absence of the spin reorientation in $HoFe_{11}T$ [2, 3], $HoFe_{10}V_2$ [2, 4] and on its presence: $HoFe_{11}Ti$ [5, 6], $HoFe_{10}V_2$ and $HoFe_{10}Mo_2$ [2, 4], $HoFe_{10}Si_2$ [8], $HoFe_{10}Cr_2$ [9].

Additional investigation of the temperature behaviour of the magnetocrystalline anisotropy when using a single crystal has been carried out to clarify the question about the existence of the spin reorientation in $HoFe_{10}Mo_2$. The effect of the substitution of cobalt for iron also has been studied in the $HoFe_{10-x}Co_xMo_2$ alloys ($0 \leqslant x \leqslant 8$).

2. Experimental

The alloys were prepared by induction melting followed by annealing at 1200 °C for 4 h. Standard powder X-ray diffraction and thermomagnetic analyses were used for the phase identification. The orientation of the easy magnetization direction was found from the line intensities on diffractograms of magnetically oriented powders at room temperature.

The magnetic moment was measured for powder samples with a vibrating sample magnetometer in fields up to 2 T in an electromagnet or with the 9 T extraction magnetometer in a superconducting magnet. A single crystal in the shape of a sphere about 1.5 mm in diameter was prepared from a large-grain ingot of $HoFe_{10}Mo_2$ compound. The type of magnetocrystalline anisotropy was determined from the shape of the magnetization curves $\sigma(H)$ measured along different crystallographic axes. The a.c. susceptibility was measured with a standard mutual inductance technique, using a driving field less than 1 mT at a frequency of 80 Hz.

3. Results and discussion

X-ray diffraction showed that the easy magnetization direction of the $HoFe_{10-x}Co_xMo_2$ compounds coincided with the *c* axis at room temperature. The *c* axes of the powders were magnetically aligned at 300 K and

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fixed with epoxy resin. The magnetization curves measured on free powders, with field parallel ($\sigma_{\parallel}(H)$) and perpendicular ($\sigma_{\perp}(H)$) to the c axes for the alloys with different x values at 4.2 K, are represented in Fig. 1. For $x=0$, the $\sigma(H)$ dependences are measured on a single crystal.

For $HoFe_{10}Mo_2$, the curves of $\sigma_{\parallel}(H)$ and $\sigma(H)$ along the easy magnetization direction (free crystal) practically coincide. This indicates that the easy magnetization direction is parallel to the c axis at 4.2 K. At this temperature the sample has a noticeable coercivity ($H_c=0.4$ T). The magnetization curves of the thermally demagnetized sample indicate that pinning of domain walls is the governing coercive force mechanism. The $\sigma_{\perp}(H)$ plot in fields of about 2 T is close to a straight line; it is a typical magnetization curve of a uniaxial crystal along the hard magnetization direction. An anomalous increase of the magnetization is also observed in the field range 2–4 T. This discontinuity indicates a first-order magnetization process (type I) with a large hysteresis.

The hysteresis loops for oriented powder samples of $HoFe_{10}Mo_2$ in fields up to 2 T at different temperatures are shown in Fig. 2. In the interval 167–300 K, the $\sigma_{\parallel}(H)$ and $\sigma_{\perp}(H)$ magnetization curves are similar to those at 167 K. It is seen from the $\sigma(H)$ plots that the easy magnetization direction for the compound is parallel to the c axis at all temperatures between 4.2 and 300 K. As the temperature rises, the critical fields of the field-induced phase transition decrease (the peculiarities on $\sigma_{\perp}(H)$ at 40, 65 and 88 K).

The magnetization curves for the alloys containing cobalt are similar to those of $HoFe_{10}Mo_2$: $\sigma_{\parallel}(H)$ and $\sigma(H)$ along the easy axis for free powder particles coincide in comparatively small fields, and magnetizing powders in the direction perpendicular to the c axis is difficult. Therefore, one can suppose that the easy magnetization direction for $HoFe_{10-x}Co_xMo_2$ ($x \leqslant 8$) is parallel to the c axis at 4.2 K. For the alloys with $x \geqslant 6$, the curves $\sigma_{\perp}(H)$ and $\sigma(H)$ for free powders lie above $\sigma_{\parallel}(H)$ in large fields. In both cases the magnetic moment increases linearly with increasing field, while on the $\sigma_{\parallel}(H)$ curves the state close to saturation is observed.

As x increases, the magnetic moment determined from the $\sigma_{\parallel}(H)$ curves in a field of 9 T decreases from 36 $Am^2\ kg^{-1}$ when $x=0$ to 10 $Am^2\ kg^{-1}$ when $x=8$. Since these compounds are ferrimagnetic materials with antiparallel coupling of the magnetic moments of the holmium and 3d metal sublattices, the decrease in the

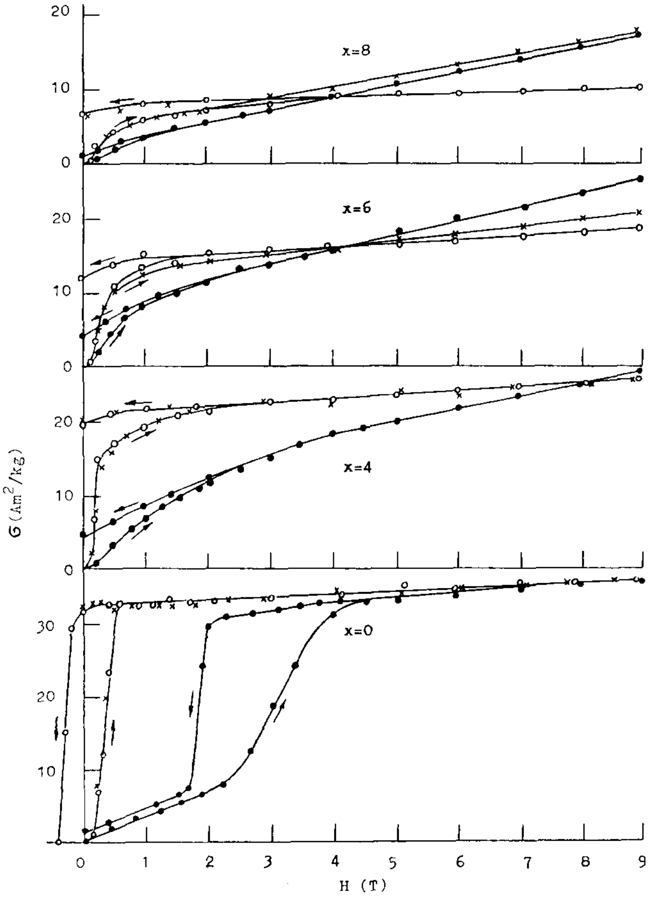

Fig. 1. Magnetization curves for $HoFe_{10-x}Co_xMo_2$ at 4.2 K: ×, H is parallel to the easy axis (free crystal or powders); ○, H is parallel to the c axis; ●, H is perpendicular to the c axis.

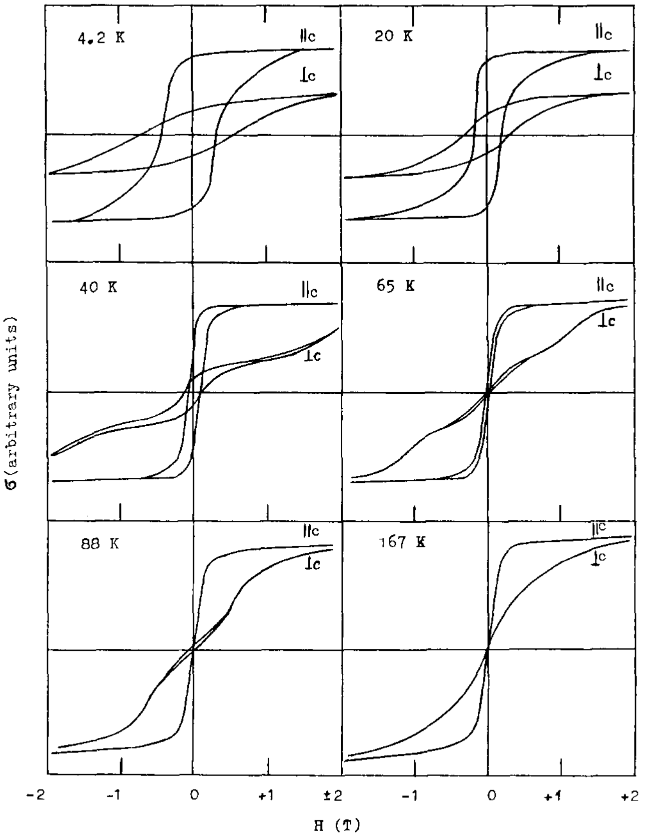

Fig. 2. Hysteresis loops for $HoFe_{10}Mo_2$ at different temperatures.

3d sublattice magnetization with increasing x leads to almost complete compensation of the two sublattice moments. For this reason, the main contribution to the magnetization in the basal plane originates from a change in the absolute value of the spontaneous moment, as a result of the formation of a non-collinear structure of the sublattice moments, rather than from its rotation. Free powders also behave similarly to antiferromagnets. They orient their easy axes perpendicular to the magnetic field and the sublattice moments bend from the easy axis towards the applied field direction. The $\sigma(H)$ curves in large fields reflect such a behaviour.

Coercivity is observed at all concentrations of cobalt: it rises with increasing x and is equal to 1 T when $x=8$. The decrease in the magnetic moment value of the compounds might be one of the reasons for the H_c increase. It should be noted that the existence of H_c at 4.2 K in $HoFe_{10-x}Co_xMo_2$ can be regarded as a manifestation of the uniaxial anisotropy of the compounds.

The substitution of cobalt for iron leads to the disappearance of the field-induced phase transition in the $\sigma_\perp(H)$ plots (it is already absent when $x=1$).

In most of the reports the conclusion about the presence of the spin reorientation in $RFe_{12-y}M_y$ has been made on the basis of the temperature variations of the initial susceptibility and the magnetic moment. The $\chi(T)$ and $M(T)$ dependences measured in a magnetic field parallel or perpendicular to the c axis on a powder sample of the $HoFe_{10}Mo_2$ alloy are shown in Figs. 3 and 4. Similar curves are obtained for the compounds with cobalt. At low temperatures the susceptibility is small but at $T=60$–90 K it sharply rises both along and perpendicular to the c axis. Analogous $\chi(T)$ curves on the polycrystalline samples have been obtained for $HoFe_{11}Ti$ [6] and $HoFe_{10}Cr_2$ [9]. The authors of these papers suppose that the deviation of the easy magnetization direction from the c axis is responsible for the sharp growth of χ.

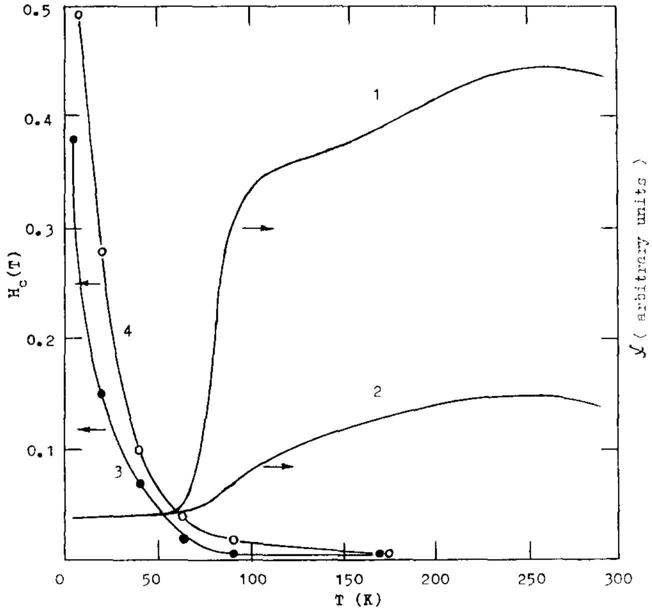

Fig. 3. Temperature variations of susceptibility (curves 1, 2) and coercivity (curves 3, 4) for $HoFe_{10}Mo_2$: 1, 3, H is parallel to the c axis; 2, 4, H is perpendicular to the c axis.

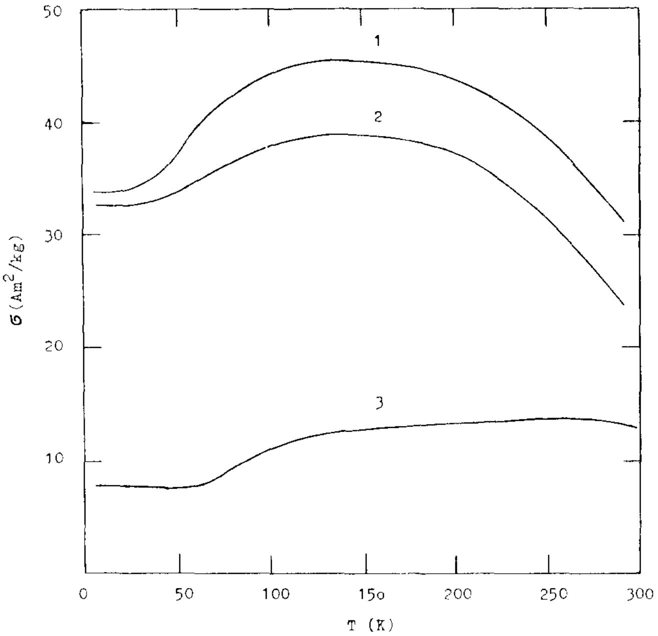

Fig. 4. Temperature variations of the magnetic moment for $HoFe_{10}Mo_2$ in fields of 1 T (curve 1) and 0.2 T (curves 2, 3): 1, 2, H is parallel to the c axis; 3, H is perpendicular to the c axis.

The temperature variation of the powder coercivity, which in this case is determined by pinning of domain walls, is also presented in Fig. 3. At low temperatures, the amplitude of the a.c. magnetic field during the measurement of χ is essentially less than the field required for domain walls movement. This results in a small value of χ. In our opinion, the growth of χ with increasing temperature in this case is caused by the decrease in H_c rather than by a spin reorientation.

Curve 1 in Fig. 4 reflects the temperature variation of the saturation magnetization of the compound. Its shape with the presence of maximum is typical of those for ferrimagnetic materials. Curves 2 and 3, measured in a field of 0.2 T parallel and perpendicular to the c axis, have the same shape. Thus the peculiarities observed in $\sigma(T)$ also are not connected with a spin reorientation.

The magnetocrystalline anisotropy in the $RFe_{12-y}M_y$ compounds consists of two separate contributions originating from the iron and the rare earth sublattices. The anisotropy of the iron sublattice was found to be the easy c axis in the whole magnetic ordering temperature range. Therefore, the anisotropy of the R sublattice, usually described in the crystal field model, is responsible for a deviation of the easy magnetization direction from the *c* axis at low temperatures. For these compounds the second-order crystal field parameter A_2° at the 2a rare earth site is negative and considerably smaller in value than that found for $SmCo_5$ and $R_2Fe_{14}B$. Taking into account only the second-order crystal field term, one can expect a spin reorientation from the *c* axis to a cone or the easy plane at low temperatures for the compounds with negative Stevens' coefficient ($\alpha_j < 0$), *i.e.* for $R \equiv$ Nd, Tb, Dy, Ho, while for $R \equiv$ Sm, Er, Tm ($\alpha_j > 0$) the anisotropy will be uniaxial at all temperatures.

The investigation of the spin reorientation transitions in the $RFe_{12-y}M_y$ compounds supports such a model. However, in some of the compounds 'anomalous' behaviour of the magnetocrystalline anisotropy is observed. These are the compounds with $R \equiv$ Ho and Er. Because of the small value of A_2°, anisotropy resulting from higher order crystal field terms can affect the easy axis orientation in these compounds at low temperatures. In fact, it has been shown in refs. 10 and 11 that it was necessary to include the fourth- and the sixth-order terms to obtain a deviation of the easy magnetization direction from the *c* axis in $ErFe_{10}V_2$ and $ErFe_{11}Ti$.

To explain the absence of a spin reorientation in the compounds with holmium, one can suppose that at low temperatures the uniaxial anisotropy of the iron is large enough to overcome the tendency towards a spin reorientation arising from Ho^{3+}. The calculated energy surface in the (010) plane for $HoFe_{11}Ti$ [7] shows two minima at $\theta = 0°$ and $\theta = 54°$ (where θ is the tilting angle between the easy magnetization direction and the *c* axis) which are almost degenerate. However, at $\theta = 0°$ the energy is slightly lower, *i.e.* the easy axis is parallel to the *c* axis. Then, weakening the transition metal anisotropy, for example, by substituting a few atomic per cent of cobalt for iron [6, 12, 13], could lead to a spin reorientation. Under the assumption of an analogous situation for $HoFe_{10}Mo_2$, one can expect the appearance of a spin reorientation in $HoFe_{10-x}Co_xMo_2$ ($x > 0$) at low temperatures.

It follows from ref. 13, where the magnetocrystalline anisotropy of the 3d sublattice in $YFe_{10-x}Co_xMo_2$ has been studied, that the 3d uniaxial anisotropy decreases with increasing cobalt content. The easy magnetization direction is parallel to the *c* axis when $x \leqslant 6$ and deviates from the *c* axis when $x \geqslant 8$ ($\theta = 53°$ for $x = 10$). The 3d sublattice anisotropy in $HoFe_{10-x}Co_xMo_2$ also is expected to decrease with rising *x*. However, we have not found a spin reorientation in the alloys of this series.

It seems likely that in the ground state the holmium sublattice has uniaxial anisotropy. The effect of higher order crystal field terms could be the reason of such behaviour as in the erbium case. The presence of the first-order magnetization processes on the $\sigma_\perp(H)$ curves (Figs. 1 and 2) is some evidence of an important role of higher order terms.

Unfortunately, the correct calculation of the anisotropy constants for $HoFe_{10}Mo_2$ based on the magnetization curves is difficult because of the following reasons. It has been revealed that the single crystal studied consisted of several fragments with *c* axes disorientations of about 5°. This made it impossible to determine the principal crystallographic directions in the (001) plane. In addition, as has been mentioned above, non-collinear structure of the sublattice magnetic moments arises during magnetizing of the crystals and this complicates a quantitative analysis of $\sigma(H)$.

4. Conclusions

In this research, we have shown the absence of a spin reorientation in $HoFe_{10-x}Co_xMo_2$ ($0 \leqslant x \leqslant 8$) up to 4.2 K. The most probable reason for such behaviour is the uniaxial anisotropy of the holmium sublattice, resulting from the contribution of higher order terms to the anisotropy of Ho^{3+}. It has also been demonstrated that the sharp increase in the initial susceptibility with increasing temperature is not connected with a spin reorientation.

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