Magnetic properties of an erbium single crystal in strong fields

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The magnetization of an erbium single crystal was determined in pulsed magnetic fields up to 250 kOe in the temperature range 4.2–85 °K along various crystallographic directions. A jump of the magnetization along the hexagonal c axis was observed in strong fields. Measurements of the differential susceptibility carried out in the temperature range of this magnetization jump yielded the temperature dependences of the critical fields. The low-temperature anomalies of the magnetization of erbium could be explained by crossing of the ground and excited levels of the Er^{3+} ion under the influence of a magnetic field.

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INTRODUCTION

Erbium has been studied least among heavy rare-earth metals and this is clearly due to its complex magnetic structure.

Neutron diffraction measurements[1-3] have shown that below the magnetic ordering temperature (85 °K) the magnetic moments in erbium are parallel to the c axis and their magnitudes are modulated sinusoidally. Deviation from the simple sinusoidal modulation of the z component of the magnetic moment appear at 53.5 °K and this is accompanied by helicoidal ordering of the transverse component. Finally, below 20 °K the magnetic moments form a conical structure with the axis parallel to the hexagonal axis and the helicoidal order is retained in the basal plane. According to the neutron-diffraction data the cone half-angle is ~29°, whereas NMR measurements give 24° (Refs. 4 and 5).

The magnetization of erbium was investigated experimentally before.[6-8] However, these investigations were carried out mainly in weak fields or above 20 °K and they gave relatively little information on the magnetization processes in the ferromagnetic region.

The present paper reports the results of a study of the magnetization and differential susceptibility of an erbium single crystal along the hexagonal axis and along the b axis in the basal plane. The measurements were carried out in strong magnetic fields and at low temperatures.

SAMPLES. EXPERIMENTAL METHOD

Erbium single crystals were grown by the floating zone method with induction heating in an atmosphere of gaseous helium; this was done at the A. A. Baĭkov Institute of Metallurgy. The composition and homogeneity of the samples were determined by the atomic absorption analysis. Samples selected for the magnetization measurements were spark-machined from bulk single crystals into rectangular rods of 10×1.4×1.2 mm and 5×1×1 mm dimensions, and they were oriented either parallel to the hexagonal axis or parallel to the b axis in the basal plane. Their orientation was checked by the x-ray diffraction method. The orientations were accurate to within 2–3°. Measurements of the magnetization were carried out by an induction method[9] in pulsed magnetic fields up to 250 kOe using pulses of 0.01 sec duration in the temperature range 4.2–85 °K. The error in the determination of the magnetization was 7–10%, of which the systematic error represented 3–5%.

The absolute magnetization of erbium single crystals along the c and b axes was measured in the range 4.2–85 °K using a vibration magnetometer with a superconducting solenoid ($H = 65$ kOe). The error in the magnetization measurements did not exceed 3%.

The critical fields were deduced from the differential susceptibility in the region of a magnetization jump. The error in the determination of these critical fields was 3%.

EXPERIMENTAL RESULTS

Figure 1 shows the experimental dependences of the magnetization along the hexagonal axis on the applied magnetic field, obtained at various temperatures. The c axis was an easy-magnetization direction and the processes of technical magnetization associated with changes in the domain structure were completed in fields 20–40 kOe throughout this temperature range. It is clear from Fig. 1 that at 4.2 °K in fields $H_c = 81.5$–104 kOe (the value 104 kOe was obtained when the field was increasing and 81.5 kOe when the field was decreasing)

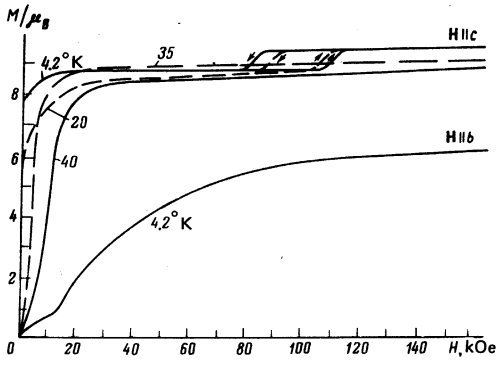

FIG. 1. Dependences of the magnetization on the magnetic field along the easy axis (c axis) and difficult axis (b axis).

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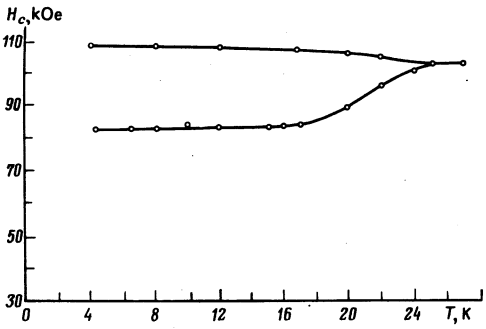

FIG. 2. Temperature dependence of the critical field (the upper curve was obtained by increasing the field and the lower by decreasing it).

the magnetization curve exhibited a jump whose value was 0.81 μ_B. At higher temperatures the magnetization jumps became smoother and their magnitude decreased. These jumps exhibited a hysteresis, which decreased on increase in temperature. Above 27 °K the jumps finally disappeared and no anomalies in the magnetization could be observed within the limits of sensitivity of our apparatus.

We recorded the differential susceptibility curves in the region of the magnetization jumps throughout the investigated temperature range; this improved greatly the accuracy of determination of the critical magnetic fields. Figure 2 shows the temperature dependences of the critical magnetic fields H_c deduced from the differential susceptibility in increasing and decreasing fields. Clearly, H_c is practically independent of temperature right up to $T = 18$ °K, whereas in the $20 < T < 24$ °K range there is a change in H_c accompanied by a reduction in the hysteresis.

Figure 3 shows the dependence of the derivative of the magnetization with respect to the field (at $H = H_c$) on the reciprocal temperature, plotted on the basis of the differential susceptibility recorded in decreasing fields. The dependence was clearly linear right up to $T = 18$ °K.[1)]

The nature of the dependence of the magnetization on the magnetic field applied in the basal plane was determined by measurements of the magnetization along the b axis of erbium single crystals. Figure 1 shows the magnetization curve recorded in $\mathbf{H} \| \mathbf{b}$. We can see that the b axis is a direction of difficult magnetization and a field of 16 kOe destroyed the helical magnetic

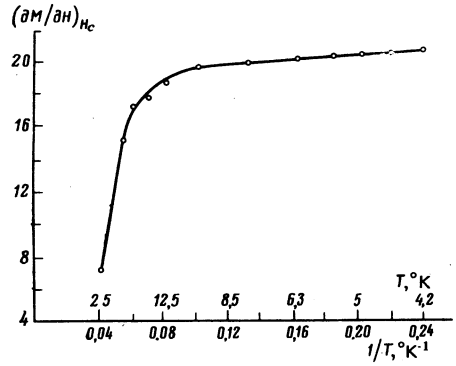

FIG. 3. Dependence of the derivative of the magnetization with respect to the field on the reciprocal temperature.

structure at $T = 4.2$ °K. A further increase of the field caused the magnetization to rise slowly and in $H = 190$ kOe it reached the value of $M = 6.20\ \mu_B$ per atom.[2)]

Our values of the magnetization along the hexagonal axis in the range $H < H_c$ were in good agreement with the data reported in Ref. 7 but exceeded slightly the values of the weak-field magnetization reported in Ref. 8.

DISCUSSION OF RESULTS

It is natural to assume that the magnetization jumps observed in strong fields along the hexagonal axis are due to destruction of the conical structure and appearance (in a magnetic field) of a collinear magnetic structure with the magnetization parallel to the hexagonal axis.[3)] It follows from the experimental results that the transition to the collinear phase is a sudden first-order phase transition. We shall attempt to explain phenomenologically the magnetization jumps and we shall allow for the Zeeman energy, magnetic anisotropy energy, and energy of the exchange interaction responsible for the helical structure of the projections of the magnetic moments on the basal plane of an erbium crystal.

Using three anisotropy constants and two exchange interactions, we can represent the energy of erbium in a field parallel to the hexagonal axis by

$$E(\theta) = (g-1)^2 J^2 [I(Q) - I(0)] \cos^2\theta + H_a - HM\cos\theta, \qquad (1)$$

where g is the Landé factor; J is the total mechanical momentum; θ is the cone half-angle; $I(Q)$ and $I(0)$ are the exchange constants; H is the applied magnetic field; M is the total magnetic moment; H_a is the anisotropy energy given by

$$H_a = K_2^0 P_2^0(\cos\theta) + K_4^0 P_4^0(\cos\theta) + K_6^0 P_6^0(\cos\theta);$$

here, K_2^0, K_4^0, and K_6^0 are the anisotropy constants; $P_2^0(\theta)$, $P_4^0(\theta)$, and $P_6^0(\theta)$ are the reduced Legendre polynomials. Minimization of Eq. (1) can be used to find the equilibrium value of the orientation of the erbium magnetization relative to the field.

However, our calculations indicate that if we use the anisotropy and exchange parameters of erbium given in Refs. 5 and 11, we find that the rotation of magnetic moments in the field is continuous and the transition to the collinear phase is of the second order. Variation of the parameters makes it possible to construct an S-type curve for $\cos\theta(H)$, which is characteristic of first-order phase transitions and describes a magnetization jump, but in this case the state of erbium in zero field does not agree with the experimental data ($\theta = 24$–$29°$ in $H = 0$).

An analysis of equations derived from Eq. (1) thus shows that the presence of magnetization jumps along the hexagonal axis cannot be explained by simple technical magnetization processes.

We can try to explain the observed anomalies bearing in mind that effects associated with a change in the spectrum due to level crossing may occur in strong fields. Such anomalies have been found, for example, in iron garnets containing holmium as an impurity.[12]

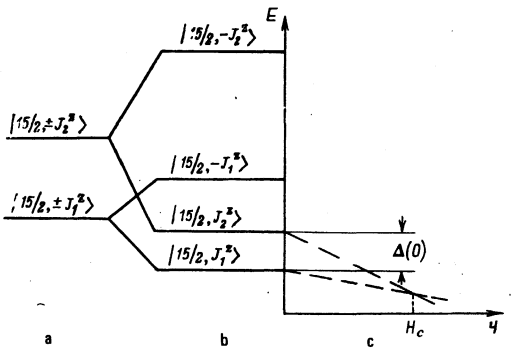

FIG. 4. Schematic representation of the positions of lower levels: a) in the paramagnetic range; b) in the ferromagnetic range with splitting of the "initial" levels due to exchange field; c) shift of the levels in a magnetic field.

We shall consider the energy level scheme of an erbium ion in the ground state $^4I_{15/2}$ ($L=6, S=3/2, J=15/2$). The term with $J=15/2$ lies about 10^4 °K below the nearest excited term with a different value of J and this is due to the strong spin–orbit interaction. The crystal field splits the lower level into sublevels by amounts of the order of 10 °K (Refs. 13 and 14). In the paramagnetic phase each of these sublevels is a mixture of states with different values of the projections of the magnetic moment J^z onto the c axis and the lowest of them is the level with $J^z<15/2$ (Ref. 14), so that in the paramagnetic range the ground state of erbium is inverted. In the ferromagnetic range there is a further splitting and the lowest in this mixture is a level with a positive J^z. Levels with the opposite orientation ($-J^z$) lie higher by an amount equal to the exchange field IJ $\sim 10^2$–10^3 °K (here, I is the exchange integral). If the lowest level is the one with $J_1^z=15/2$, the magnetic moment is directed parallel to the hexagonal c axis but, as pointed out above, it follows from the magnetization measurements (Fig. 1) and from the neutron diffraction and NMR data[1,5] that the magnetic moment is directed at an angle to the c axis. Thus, $J_1^z<15/2$ and the ground state of erbium in the ferromagnetic range is again inverted, i.e., $J_2^z>J_1^z$. It must be stressed that this is associated with the crystal field, which determines the direction of the magnetization vector J (magnetocrystalline anisotropy). The energy level scheme under discussion is shown in Fig. 4.

The magnetic moment of an ion can be represented by

$$M^z=g_J\mu_B\sum_i n_iJ_i^z. \qquad (2)$$

Here, n_i is the probability of occupation of the ith level and g_J is the Landé factor. The occupation probability n_i is given by

$$n_i=\exp(-E_i/kT)\Big/\sum_i\exp(-E_i/kT).$$

At low temperatures, when $kT\ll\Delta=E(J_2^z)-E(J_1^z)$ (Δ is the difference between the energies of the ground and first excited levels), it is sufficient for our purpose to consider only the ground and nearest excited levels. We then find

$$n_2=n_1\exp(-\Delta/kT),\quad n_1+n_2=1.$$

Hence, it follows that

$$n_1=\frac{1}{1+\exp(-\Delta/kT)},\quad n_2=\frac{\exp(-\Delta/kT)}{1+\exp(-\Delta/kT)}.$$

In a field H parallel to the z axis, we have

$$E_i(H)=E_i(0)-J_i^zg_J\mu_BH,$$

and, therefore, $\Delta(H)=\Delta(0)-g_J\mu_BH(J_2^z-J_1^z)$ and the following expression is obtained for the magnetization of Eq. (2):

$$M^z=g_J\mu_B\left(\frac{J_1^z}{1+\exp[-\Delta(H)/kT]}+\frac{J_2^z}{1+\exp[\Delta(H)/kT]}\right). \qquad (3)$$

An increase in the magnetic field H causes the levels to come together because $J_1^z<J_2^z$ and the levels cross in a field $H=H_c=\Delta(0)/\{g_J\mu_B(J_2^z-J_1^z)\}$; according to Eq. (3), the value of $M^z(H)$ then has a jump in the limit $T\to0$. At finite temperatures the jump disappears.

Differentiating Eq. (3) with respect to H at the point $H=H_c$, we obtain the following expression for the temperature dependence of the susceptibility:

$$\chi(T)=\frac{\partial M^z}{\partial H}\Big|_{H=H_c}=\frac{g_J^2\mu_B^2}{4kT}(J_2^z-J_1^z). \qquad (4)$$

The experimental temperature dependence of $\partial M^z/\partial H$, shown in Fig. 3 is in good agreement with Eq. (4) below 12 °K. In the range $T<\Delta\sim10$ °K we can use the slope of $\chi(T)$ and Eq. (4) to estimate $\delta J^z=J_2^z\approx0.54$, because the magnetization jump $\Delta M^z=g_J\mu_B\delta J^z=0.64\mu_B$ per atom is in reasonable agreement with the experimental value of 0.81 μ_B per atom. In all the above estimates the g factor is assumed to be 1.17, as for a free ion.

CONCLUSIONS

It follows from our experimental results that the low-temperature transition to a collinear magnetic structure, which occurs in erbium in a field parallel to the hexagonal axis, is a first-order phase transition. It can be explained by a change in the ground state of erbium in the applied field associated with inversion of the ground and excited states.

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[1)]The dependence of the susceptibility on the reciprocal temperature is similar in a rising field.

[2)]Our measurements of the magnetization along the b axis of Er single crystals right up to 250 kOe at $T=4.2$ °K showed no magnetization jump and in the range of fields $H>16$ kOe the magnetization was characterized by a smooth rotation of the magnetization vector from the c axis to the basal plane.

[3)]In fields $H>H_c$ the magnetization became higher than the value calculated theoretically from $M=g_JJ$ on the assumption of a complete parallel orientation of the spins of the 4f electrons of a trivalent erbium ion, and was also greater than the experimental value of the total magnetization deduced from the neutron-diffraction data.[10] Clearly, this discrepancy was due to the additional contribution made to the magnetization of erbium by the polarization of conduction electrons (see, for example, Ref. 10).

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A model of a liquid crystal

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A model of a liquid crystal composed of ordered "liquid columns" is considered. The character of the phase transition from the solid crystal to this mesophase (H_1) and of the further transitions to the nematic liquid crystal and the isotropic liquid is considered. A simple molecular model with a crystal—H_1—isotropic-liquid phase diagram is proposed.

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1. Very recently, Chandrasekhar *et al.*[1] have studied the phase diagrams of hexaphenyl n-alkonates. A characteristic feature of these compounds is the disk-like shape of the molecules. The thermodynamic, optical, and x-ray studies of the mesophase carried out in Ref. 1 permit us to propose the following structure for it; two-dimensional hexagonal ordering of the centers of mass of the molecules, but absence of translational order in the direction perpendicular to these layers. Schematically, such a structure can be represented in the form of "liquid" columns of disk-shaped molecules, packed in a hexagonal lattice (the ratio of the diameter of the "disk" to its thickness is ~6–7). Since, in the sense of its elastic properties, such a mesophase is similar to the anisotropic "solid" mesophase of the H type (but, possibly, does not coincide with it), henceforth we shall designate this phase as H_1.

It should be noted that the above interpretation of the x-ray patterns and optical textures[1] is not, of course, unique. Therefore, it is necessary to study other properties of this mesophase. The present paper is devoted to an analysis of the possible features of the H_1 phase. The characteristics of the H_1 mesophase in the vicinity of the transitions to the solid-crystalline, ordinary nematic, and isotropic phases are considered in the framework of the Landau theory. It is especially necessary to mention the transition to the crystalline phase. According to the Landau theory (see below), the crystallization of the H_1 phase is a rare example in which the phase transition of complete solidification can be a second-order transition.

In the three alkonates studied in Ref. 1 the nematic phase was absent; in principle, however, the situation with a nematic phase should also be investigated. In the Appendix we consider a simple molecular model with a crystal—H_1—isotropic-liquid phase diagram. It should also be emphasized that the heats of the crystal—H_1-phase and H_1-phase—isotropic-liquid transitions (~10 kcal/mole) are greater by at least an order of magnitude than the characteristic heats of transitions from a nematic liquid crystal to an isotropic liquid. Therefore, in its narrow range of existence (of the order of a few degrees), the nematic phase might not be distinguished by the calorimetric method of Ref. 1.

In Sec. 2 of the paper we study the phase transition from the solid-crystalline phase to the intermediate, H_1 phase. We use de Gennes' model[2] of the nematic–smectic-A liquid-crystal phase transition. The condition that the two-dimensional lattice be rigid requires that the Frank constant K_{11} become infinite. This condition ($K_{11}\to\infty$, and not $K_{11}\to 0$ as in the de Gennes model) removes the divergences (characteristic for the smectic phases) of the fluctuations of the order parameter (in agreement with the well known Landau-Peierls theorem[3]).

In Sec. 3 we consider certain properties of the H_1 phase—in particular, the spectrum of the low-frequency

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