MAGNETIC AND MAGNETOELASTIC PROPERTIES OF DYSPROSIUM AND GADOLINIUM

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The temperature dependences of the magnetization, magnetostriction, modulus of elasticity and internal friction of dysprosium and gadolinium have been measured.

Large anomalies, which are strongly affected by a magnetic field, have been detected in the modulus of elasticity and internal friction of dysprosium in the region of the ferromagnetism-antiferromagnetism transition ($\Theta_1 = 85 - 88°$ K). In the same temperature region dysprosium possesses a very large magnetostriction ($\lambda \approx 1000 \times 10^{-6}$) which is of an isotropic nature ($\lambda_{\parallel}$ and $\lambda_{\perp}$ are of opposite sign). It was established that in distinction to the antiferromagnetism-paramagnetism transition ($\Theta_2 = 178°$ K), the transition at 88° K is connected with a change in the nature of the magnetic interaction between the magnetic sublattices in dysprosium.

In gadolinium a maximum magnetization and minimum coercive force and residual magnetization are observed near the temperature 210° K. Magnetostriction vanishes at the same temperature. An anomalous behavior of gadolinium (compared with Ni and Fe) is observed near the Curie point (290.5° K). It is suggested that in the interval 210 — 290.5° K an antiferromagnetic state exists in gadolinium which is, however, destroyed by a weak field.

GREAT interest has arisen recently in studying the magnetic properties of the rare earth metals and alloys. This interest is aroused by the two following reasons:

a) A complicated ferromagnetism-antiferromagnetism-paramagnetism transition is observed in a number of rare-earth metals (Dy, Ho, Er, Tb and Tu). A study of such a complicated magnetic transition is of interest from the point of view both of magnetic theory and of the theory of phase transitions.

b) In the rare earth elements, as distinct from the elements of the iron group, the uncompensated electron spins are in a shell which is screened by the higher lying 5s and 5p electron shells. Because of this, direct exchange interaction between the 4f-electrons of neighboring atoms is evidently made very difficult or completely prevented.

It is assumed that indirect exchange via the free electrons takes place in rare earth metals. In addition, Vonsovskii and Izyumov[1] consider that the 5s and 5p electrons may take an active part in this exchange.

These circumstances must influence the magnetic behavior of rare-earth ferromagnets. In fact, their magnetic behavior is very varied. However, so far we still have very scanty information about the properties of these interesting substances.

It is especially important to study in detail the magnetic and nonmagnetic properties of the rare earth metals in the temperature regions of the ferromagnetic-antiferromagnetic transition (the point Θ_1), antiferromagnetic-paramagnetic transition (Θ_2) and in the intervening temperature range from Θ_1 to Θ_2.

At present we have fairly detailed data on the magnetic properties of Dy, so that it is appropriate to start our consideration with this metal. Trombe[2] and Elliott, Legvold and Spedding[3] have studied the magnetic properties of Dy. These authors established that for dysprosium $\Theta_1 = 85 -$ 90° K and $\Theta_2 = 178°$ K, i.e., Dy is in the ferromagnetic state below 85° K, in the paramagnetic state above 178° K, and in the intermediate region from 85 to 178° K dysprosium shows antiferromagnetic behavior, which is strongly influenced by an external magnetic field. In strong magnetic fields the magnetization curve I(T) has the usual Weiss form. However, in weaker fields a rapid fall in magnetization is found on heating to a certain temperature (in zero field this fall in magnetization takes place at $\Theta_1 = 85°$ K). Further, at $\Theta_2 = 178°$ K a small increase in magnetization is found and a final decrease, as is usual at the Néel point of antiferromagnets.

Néel[4] has proposed the following hypothesis to explain the properties of Dy. The hexagonal lat-

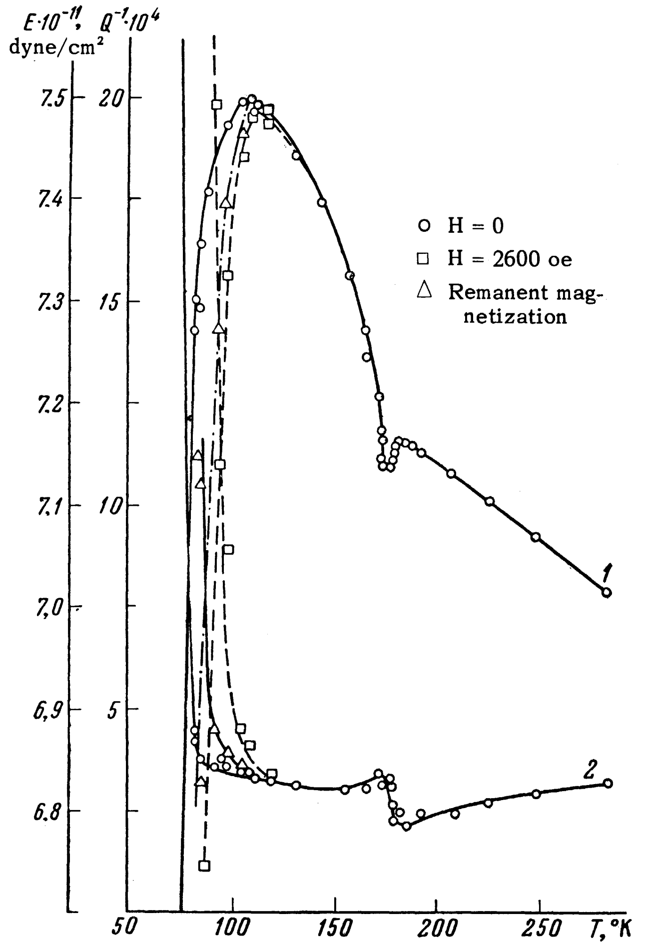

FIG. 1. Temperature dependence of Young's modulus (curve 1) and of internal friction (2) for dysprosium.

tice of Dy is subdivided into two magnetic sublattices. In each of these there is a strong positive exchange interaction i.e., both sublattices are ferromagnetic. However, there is a weak negative interaction between the sublattices on which the influence of magnetic interaction forces can act (magnetocrystalline energy). As a result of this, a parallel or antiparallel configuration of the magnetic moments of the sublattices may be set up. According to Néel, a change in this configuration of the magnetic moments depends on the nature of the temperature variation of the anisotropy constant K_2 at the point Θ_1.

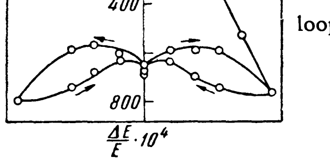

FIG. 2. ΔE-effect hysteresis loop for dysprosium at 85°K.

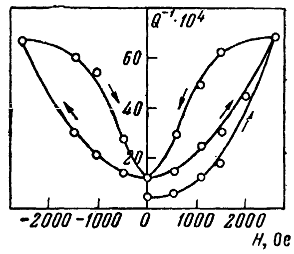

FIG. 3. Internal friction, Q^{-1}, hysteresis loop for dysprosium at 85°K.

On the basis of the suggested hypothesis, Néel has given a qualitative explanation of the magnetization curves between Θ_1 and Θ_2. Enz[5] has recently suggested that in the Dy crystal the spins situated in neighboring basal planes are turned at some angle relative to one another. According to Enz, this arrangement of spins in Dy is explained by the 'competition' between the positive exchange interaction between the spins in neighboring planes and the negative exchange interaction between spins lying in next nearest neighbor planes. The existing experimental material on its magnetic properties is insufficient to verify these suggestions about the structure and the nature of the magnetic transformations in Dy. Additional experimental data are essential for this.

1. THE MAGNETOELASTIC PROPERTIES OF DYSPROSIUM

For a more detailed investigation of the properties of dysprosium we undertook measurements of its magnetoelastic characteristics: the magnetostriction λ, the modulus of elasticity E and the internal friction Q^{-1} (a quantity proportional to the damping decrement of oscillations) near the points Θ_1 and Θ_2 and in the temperature interval between them.

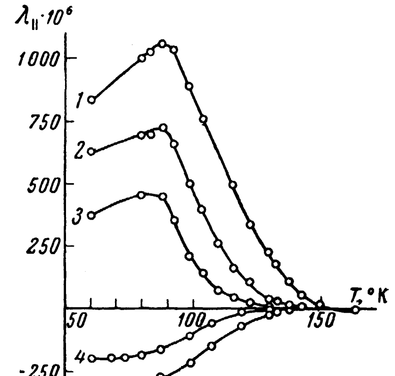

FIG. 4. Temperature dependence of the magnetostriction of dysprosium in constant magnetic field: curve 1 – longitudinal magnetostriction $\lambda_{\|}$ in a field H = 15,000 oe; 2 – $\lambda_{\|}$ in a field H = 9,500 oe; 3 – $\lambda_{\|}$ in a field H = 6,500 oe; 4 – transverse magnetostriction $\lambda_{\perp}$ in a field H = 15,000 oe; 5 – $\lambda_{\perp}$ in a field H = 9,500 oe.

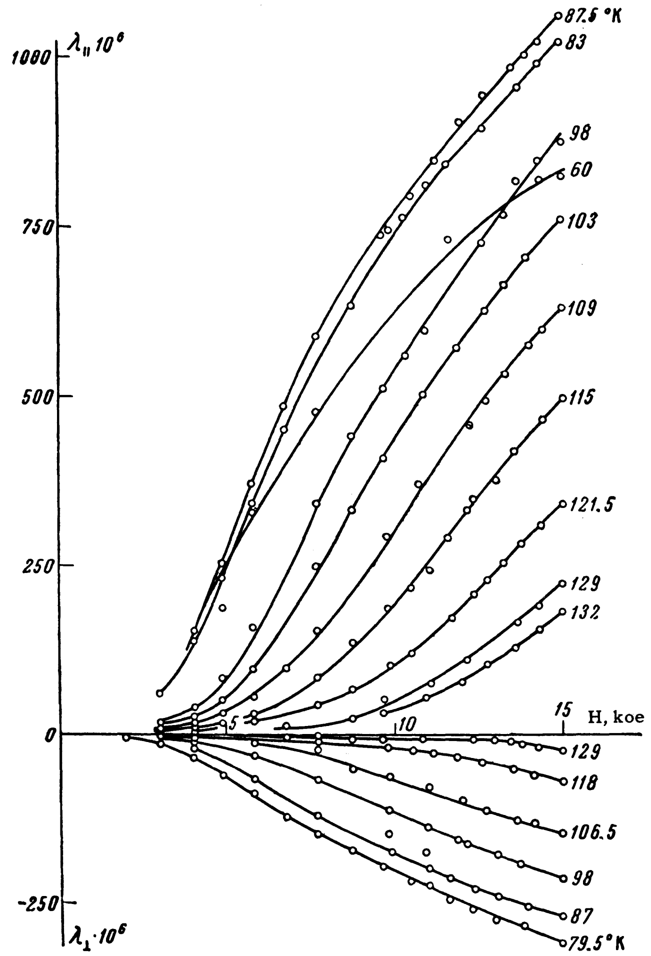

FIG. 5. Isotherms of longitudinal, $\lambda_{\parallel}$, and transverse, $\lambda_{\perp}$, magnetostriction for dysprosium.

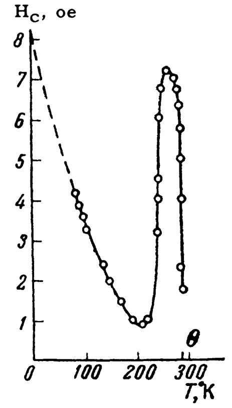

FIG. 7. Temperature dependence of the coercive force of gadolinium.

Figure 1 shows the results of measurements of the temperature dependence of the modulus E and of Q^{-1} in a polycrystalline specimen of Dy, made by a radio-frequency method (at 128 kc/sec).[6] Similar dependences are obtained for the shear modulus and internal friction for torsional oscillations. The curves of Fig. 1 confirm the existence of two points Θ_1 and Θ_2 for Dy. In our case these are $\Theta_2 = 175°$ K and $\Theta_1 = 88°$ K.

It can be seen from Fig. 1 that the nature of the anomalies in E and Q^{-1} in Dy at Θ_2 are the same as in the antiferromagnetic compound Cr_2O_3,[7,9] i.e., Θ_2 is a Néel point. The anomalies in E and Q^{-1} at the point Θ_1 are of quite a different nature. From Fig. 1 it is seen that the anomalies in E and Q^{-1} at Θ_1 are very great, much larger than at Θ_2. In addition, as distinct from the point Θ_2, a magnetic field has a strong influence on the modulus E (ΔE effect) and on the magnitude of Q^{-1}.

Further, irreversible changes in the magnitudes of E and Q^{-1} are observed on applying and removing the magnetic field. Figure 2 shows the hysteresis loop of the ΔE effect, measured for dysprosium in the region of Θ_1. An analogous loop is also found for the internal friction (Fig. 3). All this points to Θ_1 not being a second-order phase transition; rather it recalls a first-order magnetic transition. This transition is not related to any structural transformation, since x-ray studies[8] established the absence of changes in the crystallographic symmetry and lattice parameters of Dy in this temperature interval.

The results of measurements of magnetostriction are shown in Fig. 4. We must consider the

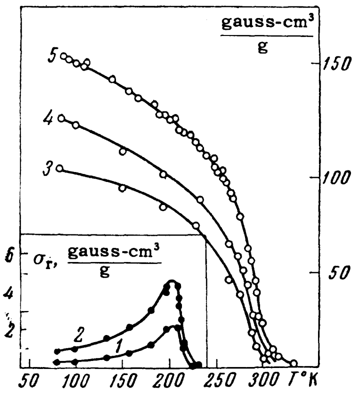

FIG. 6. Temperature dependence of the magnetization of gadolinium in different fields: curve 1 – H = 0.32 oe, 2 – H = 0.64 oe, 3 – H = 400 oe, 4 – H = 1,000 oe, 5 – H = 2,000 oe.

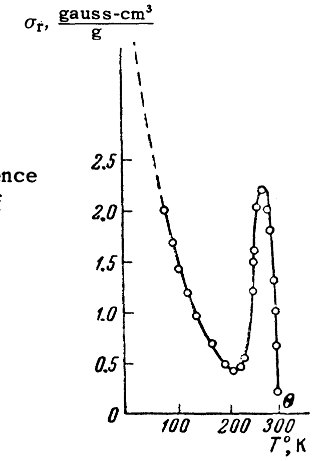

FIG. 8. Temperature dependence of the remanent magnetization of gadolinium.

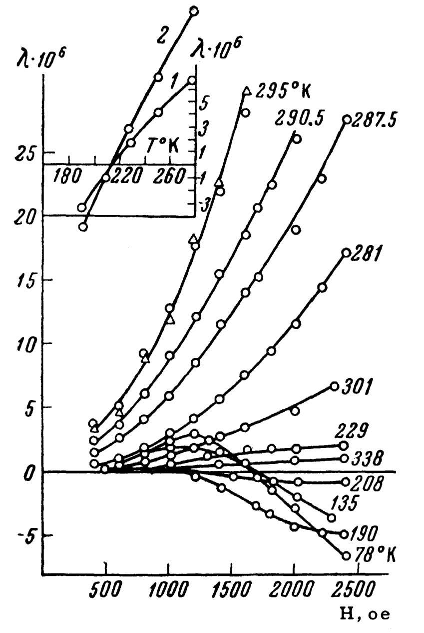

FIG. 9. Isotherms of the longitudinal magnetostriction, $\lambda_{\parallel}$, for gadolinium. Inset – temperature dependence of $\lambda_{\parallel}$ in fields: curve 1 – H = 1,700 oe, 2 – H = 2,500 oe.

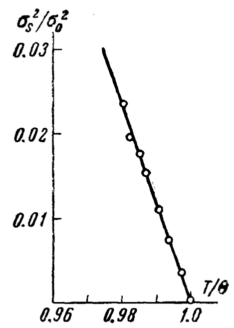

FIG. 10. Relative spontaneous magnetization of gadolinium near the Curie temperature.

following facts in this respect: a) the magnetostriction in the neighborhood of Θ_2 reaches a record high value (greater than 1000×10^{-6}) and is still not saturated in a field of 15,000 oe. The magnetostriction decreases on departing from Θ_2 into both the ferromagnetic and antiferromagnetic regions; b) the magnetostriction at Θ_1 is anisotropic; $\lambda_{\parallel}$ and $\lambda_{\perp}$ have different signs and are different in magnitude; c) from the form of the magnetostriction isotherms taken in the temperature interval from Θ_1 to Θ_2 (Fig. 5), it follows that at every given temperature there exists some critical field H_c at which λ starts to increase rapidly. The value of H_c increases as Θ_2 is approached; d) there are no signs of the existence of volume magnetostriction near Θ_1, which usually accompanies the ferromagnetic Curie point.

It thus follows from the data presented on magnetostriction (and also from the data on E and Q^{-1}) that Θ_1 is not a ferromagnetic Curie point in the usual meaning of that phrase. The spontaneous magnetization of dysprosium is not destroyed there. Since the magnetostriction is anisotropic at Θ_1, it follows that magnetic interaction forces play an important part and in this way confirm Néel's hypothesis. However, the question of the role of the temperature variation of the anisotropy constant K_1 at Θ_1 remains uncertain (the measurement of the temperature dependence of K_1 has not yet been carried out for dysprosium).

On the other hand, our data show that the maximum value of magnetostriction occurs at Θ_1. The question arises as to whether a change in the temperature variation of the magnetostriction constant does not play an important part in this transition. This question can be resolved after measuring the temperature dependence of the constant K_1 in Dy.

2. MAGNETIC AND MAGNETOELASTIC PROPERTIES OF GADOLINIUM

Although the ferromagnetism of gadolinium was found earlier than that of the other rare earth elements, less attention has been paid to its properties, evidently because a transition point Θ_1 was not found for it. Gadolinium is considered a "normal" ferromagnet. In fact, in fields from hundreds of oersteds upwards, the temperature dependence of magnetization shows the usual "Weiss" curve (Fig. 6).

However, we found anomalies in the temperature variation of magnetization in weak fields (measured on a toroid, Fig. 6) also a coercive

	σ_0, $\frac{\text{gauss-cm}^3}{\text{g}}$	μ_D	Θ°, K	ξ	$\sigma_0/\Theta^{1/3}$	$\Theta^{-1/3}$	ΔT at 5000 oe	ΔC_p $\frac{\text{cal}}{\text{g-deg}}$	$\Theta_p - \Theta_f$
Gd	235.5	7.12	290,5	1.17	33,0	0,15	1.0	0.045	11.5
Ni	56.8	0.6	631	6,75	6.6	0.12	0,45	0,032	14.0
Fe	221,8	2.22	1036	6,8	22,1	0.10	1.4	0.16	22,0
Alloy { 36% Ni, 64% Fe	184.4		565	1.44	22.0	0.12		0.0042	37,0
$3Gd_2O_3 \cdot 5Fe_2O_3$	84	29	570	0,06					
Ferrite { 35% MnO, 15% ZnO, 49.5% Fe_2O_3	152		467	0,1—0,7					

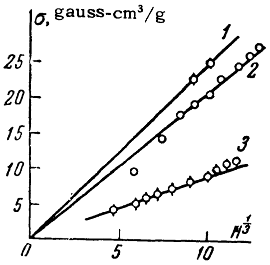

FIG. 11. The dependence of magnetization on $H^{1/3}$ at the Curie temperature: curve 1 – Fe, 2 – Gd, 3 – Ni.

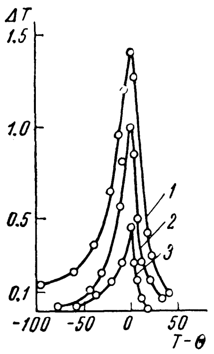

FIG. 12. Magnetocaloric effect near the Curie temperature: curve 1 – Fe, 2 – G, 3 – Ni.

force H_c (Fig. 7) and remanent magnetization σ_r (Fig. 8). The minimum values of H_c and σ_r and the maximum magnetization in weak fields occur at a temperature of 210°K. Above this temperature the magnetization falls rapidly, and the values of H_c and σ_r increase sharply up to the Curie point (Θ = 290.5°K). We should remark that the existence of these anomalies is not connected with the presence of impurities in the Gd specimens and with their thermal treatment. Our experiments were carried out on Gd specimens of 99.5 and 99.8% purity with different thermal treatment, and the anomalies were invariably found at 210°K.

There is also a magnetostriction minimum at 210°K which here changes sign (see Fig. 9).

In considering all these experimental facts one could limit oneself to the statement that a temperature is found in Gd (similar to the 217° point for Ni and 294°C for Co) at which there are temperature anomalies in the permeability μ and in H_c, and that these anomalies are apparently brought about by an anomalous temperature variation of the magneto-crystalline anisotropy constant K_1 (the temperature variation of K_1 in Gd has not yet been measured). We should note straight away that in Gd, as distinct from Ni and Co, there are two singularities in the behavior of the magnetic properties in the region of the Curie point Θ.

First, the magnetic transformation for Gd near the point Θ has an exceptionally "spread-out" nature. The slope of the decrease of spontaneous magnetization with temperature is very small. This slope can be measured[10] by the value of the coefficient ξ in the formula

$$(\sigma_s/\sigma_0)^2 = \xi(1 - T/\Theta).$$

While ξ = 6 – 7 for Ni and Fe, it is 1.17 in Gd (see Fig. 10 and the table). Such a small value of ξ usually occurs in ferrites[10] and in some alloys.

Second, one would expect that the paraprocess at Θ should be very large in Gd, since the magnetization is especially high and the Curie temperature low. One can estimate the magnitude of the paraprocess from the slope of the true magnetization curve σ_i right at the Curie point: $\sigma_i = aH^{1/3}$. From theory[10] it follows that the value of $a \sim \sigma_0/\Theta^{1/3}$, i.e., the greater σ_0 and the smaller Θ, the greater is the slope of the straight line $\sigma_i(H^{1/3})$ at the point Θ.

Table I shows the calculated values of $\sigma_0/\Theta^{1/3}$ for Gd, Fe and Ni. It can be seen that this ratio is considerably larger for Gd than for Ni and Fe. However, experiment gives other values for a. It can be seen from Fig. 11 that the value of a for Gd is less than for Fe and slightly larger than for Ni. In Gd we thus have a sort of "depressed" paraprocess.

This is confirmed by the results of measuring the magnetocaloric effect, ΔT, near the Curie point, shown in Fig. 12 for a field H = 5000 oe for Gd (our data), for Ni (data of Weiss and Forrer[11]) and for Fe (data of Potter[12]). For Gd the magnetocaloric effect at Θ is smaller than for Fe and slightly greater than in Ni (see Table I).

We are at present not clear about the nature of the magnetic anomalies of Gd at 210°K and of the unusual behavior of its magnetic properties in the temperature interval from 210° to Θ.

It is possible that it is to be explained by Gd, like Dy, being in the antiferromagnetic state between 210 and 290.5°K which is destroyed by a weak field.

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