Influence of the Magnetic Field on the Crystal Structure of Gadolinium

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The results are given of an investigation of the crystal structure of gadolinium at 150–373°K in magnetic fields up to 16 kOe. It is shown that the magnetic deformation of the crystal structure is strongest at the Curie point. The magnetic-field-induced changes in the hcp lattice parameters a and c are of opposite sign at all temperatures. The results are given of the determination of the magnetostriction coefficients of gadolinium. It is pointed out that the anisotropy in the ac plane plays an important part in the magnetic deformation of the crystal lattice of gadolinium.

AN investigation of the influence of the magnetic field on the crystal structure of dysprosium, which belongs to the yttrium subgroup of rare-earth metals, revealed a considerable change in the hcp lattice parameters in the magnetically ordered state,[1] but the presence of a "field" phase transition of the first kind from the antiferromagnetic to the ferromagnetic state made it difficult to study magnetostriction. The only heavy rare-earth metal which exhibits just one type of magnetic order (ferromagnetic) is gadolinium.[2] The purpose of our investigation was to study the influence of the magnetic field on the crystal structure of polycrystalline gadolinium of 99.7% purity at 150–373°K in magnetic fields up to 16 kOe.

The magnetostriction of gadolinium single crystals and polycrystalline samples had been investigated earlier.[3] It was established that a large effect occurred along the principal axis of the hcp lattice ($\lambda_c = \Delta c/c > 0$), whereas the magnetostriction along the a axis was weak and negative. Since the x-ray diffraction method of measuring magnetostriction was basically capable of yielding information on changes in the dimensions and shape of the unit cell, it was possible to determine the true magnetostriction of gadolinium associated with the exchange interaction ("two-ion magnetostriction"[4]) and the "single-ion" anisotropic effects associated with the magnetic interaction of ions.

The experimental method used did not differ basically from that described in [1]. The radiation emitted by a chromium anticathode was used to determine the reflections from the (300), (210), (211), (212), (105), and (203) planes of the hcp lattice in the range of high diffraction angles ($140° < 2\vartheta < 168°$). Since the changes in the interplanar distances were small, the dependences $d_{hkl}(H)$ were approximated by straight lines (Fig. 1). The slopes of these lines were determined by the least-squares method.[5] The hcp lattice parameters were calculated as follows: the (300) line was used to find the parameter a (with an error $\delta a \sim \pm 2 \times 10^{-4}$ Å), the (210) and (105) lines were employed to find the axial ratio c/a [$\delta(c/a) \sim \pm 1 \times 10^{-4}$], and then the parameter c was deduced ($\delta c \sim \pm 3 \times 10^{-4}$ Å).

The isotherms of the field dependences of the parameters a and c of the crystal lattice of gadolinium are plotted in Figs. 2 and 3. It is evident from these figures that the magnetostriction along the principal axis ($\lambda_c = \Delta c/c$) exceeds considerably the magnetostriction at right-angles to the c axis ($\lambda_a = \Delta a/a$) at practically

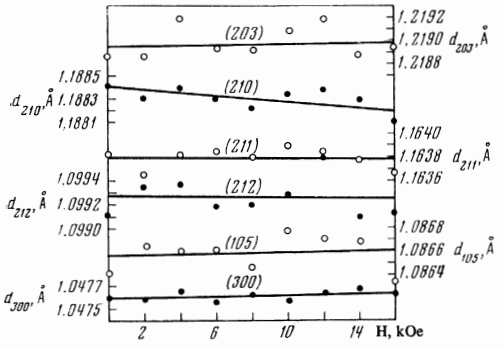

FIG. 1. Field dependences of the interplanar distances at 235°K.

all temperatures (moreover, the values of λ are much greater than the experimental error, whereas the values of λ_a are close to the sensitivity limit of the method employed). The magnetic deformation of the crystal lattice of gadolinium along its principal axis depends strongly on the temperature:

1) the magnetostriction λ_c is strongest and positive at the Curie point (288°K for our sample of gadolinium);

2) at $T > T_c$, the value of λ_c decreases rapidly with increasing temperature and practically disappears at 373°K;

3) at $T < T_c$, the value of λ_c decreases with decreasing temperature, passes through zero at T ~200°K, and becomes negative ($\lambda_c < 0$) at T< 200°K.[1)]

This temperature dependence of λ_c is in basic agreement with the results of macroscopic measurements.[3] The correlation between the temperature dependence of the magnetostriction, on the one hand, and the thermal expansion coefficient (α) and the magnetization (σ), on the other, can be found from the well-known equation[2]

$$\alpha = \frac{(\partial\lambda/\partial H)_{p,T}(\partial\sigma/\partial T)_{t,H}}{(\partial\sigma/\partial H)_{p,T}}. \qquad (1)$$

The results of magnetic measurements carried out on single crystals[6] show that the temperature dependence of the magnetization of gadolinium is a complex and nonmonotonic curve, but, naturally, the quantity $(\partial\sigma/\partial H)_{p,T}$ is positive. The nature of the temperature

[1)]The opposite tendency is exhibited by the temperature dependence of λ_a: at T>200°K, we have $\lambda_a<0$, whereas at T<200°K, we find that $\lambda_a>0$.

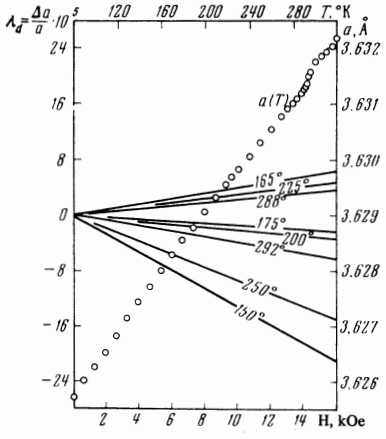

FIG. 2. Isotherms of the field dependences of the parameter a at 150-292°K and the temperature dependence of a.

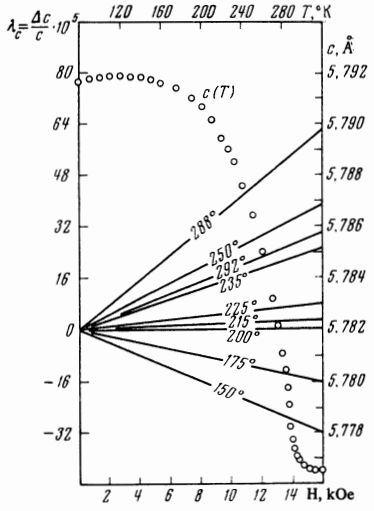

FIG. 3. Isotherms of the field dependences of the parameter c at 150-292°K and the temperature dependence of c.

dependences of the crystal lattice parameters[2] (points in Figs. 2 and 3) shows that in the magnetically ordered state, we have

$$\alpha_\perp = \frac{1}{a}\frac{da}{dT} > 0, \quad \alpha_{II} = \frac{1}{c}\frac{dc}{dT} < 0.$$

Therefore, the values of λ_a and λ_c should have opposite signs, which is in full agreement with the results of our measurements. The change in the signs of λ_a and λ_c at ~200°K is correlated with the change in the sign of the derivative $(\partial\sigma/\partial T)_{p,H}$ which occurs at approximately the same temperature. The systematic difference between the signs and magnitudes of the magnetostriction along different crystallographic axes can be attributed also to the presence of the recently discovered anisotropic shift of the Curie point of gadolinium under the influence of uniaxial pressures applied along the a (σ_{11}) and c (σ_{33}) axes:[8]

$$\frac{dT_c}{d\sigma_{11}} = 0.00 \pm 0.05 \frac{\text{deg}}{\text{kbar}}, \quad \frac{dT_c}{d\sigma_{33}} = -1.55 \pm 0.05 \frac{\text{deg}}{\text{kbar}}$$

If the equation[9]

$$\left(\frac{\partial\omega}{\partial H}\right)_{p,T} = \frac{1}{V}\left(\frac{\partial V}{\partial H}\right)_{p,T} = \frac{T}{T_c}\left(\frac{\partial\sigma}{\partial T}\right)_{p,H}\frac{dT_c}{dp}, \qquad (2)$$

which relates the volume magnetostriction coefficient $[(\partial\omega/\partial H)_{p,T} = V^{-1}(\partial V/\partial H)_{p,T}]$ to the derivative of T_c with respect to the pressure, is rewritten in the "tensor" form[10]

$$\left(\frac{\partial\lambda_a}{\partial H}\right)_{p,T} = \frac{1}{a}\left(\frac{\partial a}{\partial H}\right)_{p,T} = \frac{T}{T_c}\left(\frac{\partial\sigma}{\partial T}\right)_{p,H}\frac{dT_c}{d\sigma_{11}},$$
$$\left(\frac{\partial\lambda_c}{\partial H}\right)_{p,T} = \frac{1}{c}\left(\frac{\partial c}{\partial H}\right)_{p,T} = \frac{T}{T_c}\left(\frac{\partial\sigma}{\partial T}\right)_{p,H}\frac{dT_c}{d\sigma_{33}}, \qquad (3)$$

it becomes evident that the anisotropy of the magnetostriction of gadolinium is strongly correlated with the anisotropy of the quantity $dT_c/d\sigma_{ij}$.

In discussing the temperature dependence of the magnetic deformation of the crystal lattice of gadolinium it is useful to consider the isotropic structural and magnetic characteristics such as the atomic volume and the magnetization of polycrystalline samples.[11] The point is that the $\sigma(T)$ dependences along different axes of a gadolinium single crystal are determined, to a great extent, by the orientation of magnetic moments which tend to align themselves parallel to the magnetic field vector. The rotation processes in a polycrystalline sample consisting of grains of different orientation are "averaged out" directionally and, therefore, the results obtained for polycrystals provide more objective information on the true nature of the temperature dependence of the magnetization. Moreover, it is known that the temperature dependences of the magnetization and of the anomalous component of the atomic volume (i.e., the volume of a magnetic substance obtained after subtracting the quantity found by extrapolation from the paramagnetic region) are strongly correlated[12] and, in virtue of Eq. (2), the sign of the volume magnetostriction coefficient $V^{-1}(\partial V/\partial H)_{p,T}$ should be opposite to the sign of the volume thermal expansion coefficient. $\alpha_V = V^{-1}(\partial V/\partial T)$ because $dT_c/dp < 0$.[3][8]

A comparison of the V(H) isotherms and of the volume expansion curve V(T), which is made in Fig. 4, demonstrates that the temperature dependence of the volume magnetostriction is directly related to the extremal nature of the temperature dependence of the atomic volume.

So far we have considered the magnetic deformation of the crystal lattice of gadolinium on the assumption that this deformation is isotropic, i.e., that the symmetry of the deformation effect is the same as the symmetry of the hcp lattice. Under these conditions, the magnetostriction can be described simply by two coefficients (λ_a and λ_c). However, experimental studies have revealed structural effects which are clear evidence of the anisotropy of the magnetostriction of gadolinium. Thus, when $H \neq 0$, we have

$$D = \begin{vmatrix} h_1^2 + h_1k_1 + k_1^2, & l_1^2, & d_{h_1k_1l_1}^{-2} \\ h_2^2 + h_2k_2 + k_2^2, & l_2^2, & d_{h_2k_2l_2}^{-2} \\ h_3^2 + h_3k_3 + k_3^2, & l_3^2, & d_{h_3k_3l_3}^{-2} \end{vmatrix} \neq 0 \qquad (4)$$

[2]The results of these measurements do not differ greatly from the results reported in[7] and they will not be discussed in detail.

[3]The change in the sign of $\partial\lambda_a/\partial H$ and $\partial\lambda_c/\partial H$ at ~ 200°K can be explained in a similar manner because the magnetizations along the a and c axes have maxima at approximately the same temperature.[6]

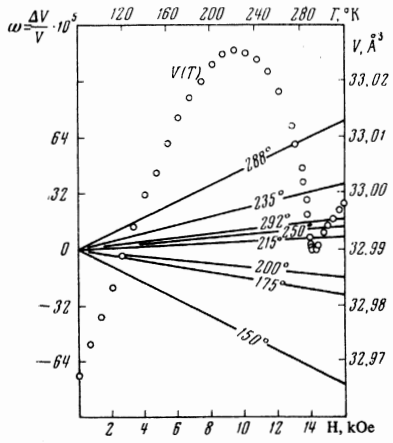

FIG. 4. Isotherms of the field dependences of the atomic volume at 150-292°K and the temperature dependence of the atomic volume.

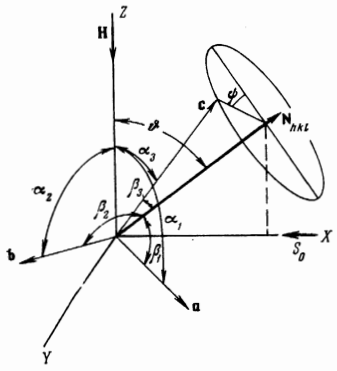

FIG. 5. Configuration used in diffraction experiments in magnetic fields: **H** is the magnetic field vector; $\mathbf{S}_0$ is the direction of the incident x-ray beam; $\mathbf{N}_{hkl}$ is the normal to the reflection plane; X, Y, and Z are the axes in the laboratory system of coordinates.

and the magnitude of this determinant increases with increasing magnetic field intensity. Measurements of the field dependences of the interplanar distances $(\Delta d/d)_{hkl}(H) = \lambda_{hkl}(H)$ can be used, at least in principle, to determine all the magnetostriction coefficients of a crystal. For a given direction of the measurements (e.g., the normal to the reflection plane $\mathbf{N}_{hkl}$ in Fig. 5) and of the magnetization (which coincides with the direction of the vector **H**) the magnetic deformation is of the form[4]

$$\begin{aligned}\lambda = {}& \lambda_1^{\alpha,0}(\cos^2\beta_1 + \cos^2\beta_2) + \lambda_2^{\alpha,0}\cos^2\beta_3 \\ & + \lambda_1^{\alpha,2}(\cos^2\beta_1 + \cos^2\beta_2)(\cos^2\alpha_3 - 1/3) + \lambda_2^{\alpha,2}\cos^2\beta_3(\cos^2\alpha_3 - 1/3) \\ & + \lambda^{\gamma,2}[1/2(\cos^2\beta_1 - \cos^2\beta_2)(\cos^2\alpha_1 - \cos^2\alpha_2) \\ & + 2\cos\beta_1\cos\beta_2\cos\alpha_1\cos\alpha_2] + 2\lambda^{\varepsilon,2}(\cos\beta_1\cos\alpha_1 \\ & + \cos\beta_2\cos\alpha_2)\cos\beta_3\cos\alpha_3. \end{aligned} \quad (5)$$

The coefficients $\lambda_1^{\alpha,0}$ and $\lambda_2^{\alpha,0}$ represent the deformation of the crystal lattice along the a and c axes in the absence of the magnetic field;[4] $\lambda_1^{\alpha,2}$ describes the deformation of the lattice in the basal plane and $\lambda_2^{\alpha,2}$ the deformation along the principal axis; $\lambda^{\gamma,2}$ represents the distortion of the symmetry in the basal plane and $\lambda^{\epsilon,2}$ the distortion in the plane perpendicular to the basal plane. The angles β_i between the normal $\mathbf{N}_{hkl}$ and the crystallographic axes can be calculated most conveniently in the orthohexagonal (orthorhombic) system of coordinates:

$$\cos^2\beta_i = \frac{h_i^2/a_i^2}{\Sigma h_i^2/a_i^2}, \quad (6)$$

where h_i are the indices and a_i the parameters in the orthorhombic system. It follows from Fig. 5 that the angles α_i between the field directions and the crystallographic axes of a crystal in a reflection configuration can be found from relationships of the type

$$\cos(\widehat{\mathbf{aH}}) = \cos\alpha_i = \cos\beta_i\cos\vartheta + \sin\beta_i\sin\vartheta\cos\psi, \quad (7)$$

where ϑ is the diffraction angle and ψ is the azimuthal angle, measured from an arbitrary direction in the diffraction plane. Since the diffraction pattern is formed by grains with different values of the coordinate ψ, it is necessary to carry out the relevant averaging,[1] which gives

$$\cos^2\alpha_i = \cos^2\beta_i\cos^2\vartheta + 1/2\sin^2\beta_i\sin^2\vartheta. \quad (8)$$

If we consider the magnetic-field-induced relative changes in the interplanar distances $\Delta d/d$ for several (hk$l$) crystallographic planes, we obtain a system of equations analogous to Eq. (5) and linear with respect to $\lambda_1^{\alpha,2}$, $\lambda_2^{\alpha,2}$, $\lambda^{\gamma,2}$, and $\lambda^{\epsilon,2}$. A solution of such a system of equations for the (201), (300), (105), and (211) hexagonal planes is

$$\begin{aligned}\lambda_1^{\alpha,2} &= 4.5\left(\frac{\Delta d}{d}\right)_{210} + 2.6\left(\frac{\Delta d}{d}\right)_{300}, \\ \lambda_2^{\alpha,2} &= -20.4\left(\frac{\Delta d}{d}\right)_{210} + 1.8\left(\frac{\Delta d}{d}\right)_{300} \\ &\quad - 4.5\left(\frac{\Delta d}{d}\right)_{105} + 17.7\left(\frac{\Delta d}{d}\right)_{211}, \\ \lambda^{\gamma,2} &= -4.5\left(\frac{\Delta d}{d}\right)_{210} + 3.6\left(\frac{\Delta d}{d}\right)_{300}, \\ \lambda^{\varepsilon,2} &= -18.6\left(\frac{\Delta d}{d}\right)_{210} + 1.3\left(\frac{\Delta d}{d}\right)_{300} \\ &\quad + 0.4\left(\frac{\Delta d}{d}\right)_{105} + 17.5\left(\frac{\Delta d}{d}\right)_{211}. \end{aligned} \quad (9)$$

By way of illustration Fig. 6 shows the field dependences of the coefficients $\lambda_1^{\alpha,2}$, $\lambda_2^{\alpha,2}$, $\lambda^{\gamma,2}$, and $\lambda^{\epsilon,2}$ at 235° K [the initial dependences d(H) are plotted in Fig. 1]. The dashed lines represent the limits of the shortest confidence interval.[5] It is worth noting that the magnetostriction in the basal plane $\lambda_1^{\alpha,2}$ as well as the orthorhombic distortions $\lambda^{\gamma,2}$ are small compared with the magnetostriction along the principal axis $\lambda_2^{\alpha,2}$ and with the monoclinic distortions[5] $\lambda^{\epsilon,2}$. However, it should be stressed that because of the low precision of the x-ray diffraction determinations of the magnetostriction constants, the results obtained are of semiquantitative nature.

[4] They can be found by extrapolation of the dependences a(T) and c(T) from the paramagnetic region.

[5] Incidentally, macroscopic measurements[3] failed to reveal a significant contribution of the monoclinic distortions to the magnetostriction of gadolinium.

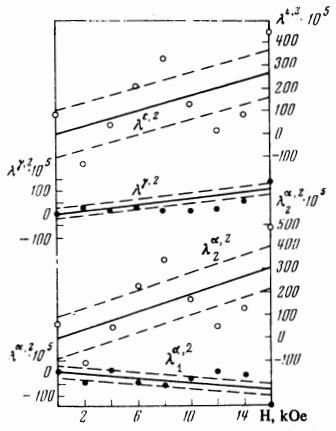

FIG. 6. Field dependences of the magnetostriction coefficients at 235°K. The dashed lines represent the shortest confidence intervals.

CONCLUSIONS

The reported results of an investigation of the effects of magnetic fields up to 16 kOe on the structure of gadolinium at 150–373° K demonstrate that the nature of the changes in the crystal lattice parameters caused by the application of the magnetic field responsible for the volume magnetostriction are strongly correlated with the nature of the temperature, field, and pressure dependences of other thermodynamic quantities. The "mismatch" of the dependences $d_{hkl}(H)$ is direct evidence of the presence of oriented distortions in the hcp lattice and it can be used to establish easily the nature of these distortions: as expected, the crystal lattice of gadolinium is distorted in the ac plane in which the magnetic anisotropy is strongest.

The relatively low precision of the x-ray diffraction measurements does not make it possible to carry out a detailed study of the field (and, consequently, the temperature) dependences of the magnetostriction coefficients of gadolinium. If we approximate the $d_{hkl}(H)$ dependences by straight lines, we relate the magnetostriction solely to changes in the exchange energy. However, in the range of temperatures and magnetic fields in which our experiments were carried out the magnetic structure of gadolinium can change by a "field" phase transition of the second kind.[13] A considerable increase in the precision of x-ray diffraction measurements in magnetic fields should make it possible to refine the information about the nature of the influence of the magnetic field on the crystal structure of gadolinium.

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