NEUTRON DIFFRACTION INVESTIGATION OF SINGLE CRYSTAL Gd^{160}

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The isotopic single crystal Gd^{160} was investigated by the neutron diffraction method in the temperature interval from liquid nitrogen to room temperature. It is shown that the gadolinium is a normal ferromagnet at all temperatures below T_C, but the direction of the magnetic moment depends strongly on the temperature. The distribution of the spin density in metallic gadolinium agrees well with that calculated for the Gd^{3+} ion.

THE majority of rare-earth elements have anomalies of various physical properties; these, as shown by the results of neutron-diffraction investigations, are connected with the occurrence of complicated noncollinear structures in these metals[1]. Similar anomalies were observed at temperatures 200–250°K also in gadolinium, and as a result it was suggested[1,2] that a helicoidal magnetic structure is produced in it. Interest in magnetic properties of gadolinium is also due to the fact that its electronic structure differs from that of the majority of rare-earth elements: the Gd^{3+} ion is in the S state (the orbital angular momentum is equal to zero, the g-factor is equal to 2). Therefore it can be assumed that the magnetism of gadolinium is determined only by the spin momentum of the 4f electrons. Such a situation favors an experimental study of the spin density in the crystal, something difficult to do in other rare-earth elements because it is necessary to take into account the influence of the orbital angular momentum.

Direct information concerning both the magnetic structure and the distribution of the spin density can be obtained only from neutron-diffraction data. In the case of gadolinium, neutron-diffraction investigations are made difficult by the exceedingly large absorption of thermal neutrons. Nonetheless, using a large single crystal of natural gadolinium, Will, Nathans, and Alperin[3] succeeded in obtaining a weak reflection from one crystallographic plane, and the satellites, which indicate the occurrence of a noncollinear magnetic structure, were not observed. In their opinion, this indicates that the gadolinium is a normal ferromagnet at all temperatures.

This conclusion does not seem to be fully convincing, owing to the strong influence of the absorption. It can be greatly weakened by using the isotope Gd^{160}, which has a small absorption cross section. We have therefore performed a neutron-diffraction investigation of single-crystal Gd^{160} for the purpose of obtaining more complete and reliable information on the magnetic structure and data on the distribution of the spin density in gadolinium.

EXPERIMENTAL PROCEDURE

Metallic gadolinium was obtained by calcium-thermal reduction of gadolinium oxide with the following isotopic composition: $Gd^{152} + Gd^{154} < 0.1\%$, Gd^{155}–0.2%, Gd^{156}–0.3%, Gd^{157}–0.4%, Gd^{158}–0.9%, and Gd^{160} 98.2%. After distillation in vacuum, the content of the controlled impurities in the metal (wt.%) was: REM impurities–0.3, Fe–0.02, Cu–0.05, Ca–0.001, O_2–0.05. Recrystallization annealing was carried out at 1200° for four hours in a vacuum resistance furnace (5×10^{-6} Torr) with a graphite heater. This yielded tablets consisting of crystals measuring up to several mm. A diamond saw was used to cut such a table a crystal measuring $1.5 \times 2 \times 6$ mm. After etching in an alcohol solution of nitric acid, an x-ray method was used to determine the orientation and perfection of the crystal. One of the faces of the sample was parallel to the basal plane, and the longitudinal axis was parallel to [100]. The block structure of the crystal was ~20′.

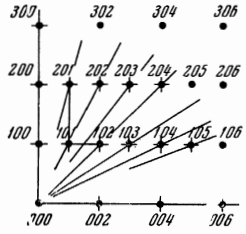

FIG. 1. Projection of the reciprocal lattice of single-crystal Gd^{160} on the (010) plane. The straight-line segments indicate the directions, in reciprocal space, from which the measurements were made.

The neutron-diffraction investigation was performed with a vertical diffractometer[4] with a bent crystal-monochromator of iron silicide[5]. The wavelength of the monochromatic neutrons was ~1.125 Å. For temperature measurements (80–330°K) we used a nitrogen cryostat modified to operate with the vertical diffractometer. The constancy of the temperature (±0.1°) was ensured by a proportional-action temperature regulator NV-220, developed at the Central Engineering Physics Institute in Budapest, Hungary.

EXPERIMENTAL RESULTS

It can be regarded as reliably established that gadolinium is a normal ferromagnet at low temperatures ($T < 200°K$). This means that no diffraction maxima should be observed on the neutron diffraction patterns, except those due to the chemical unit cell. If a noncollinear magnetic structure arises in the temperature interval 200–250°K, the neutron diffraction patterns should reveal next to main reflections also additional magnetic maxima (satellites). To observe them, we obtained at $T > 210°K$ neutron diffraction patterns corresponding to different directions in the reciprocal lattice, as shown in Fig. 1.

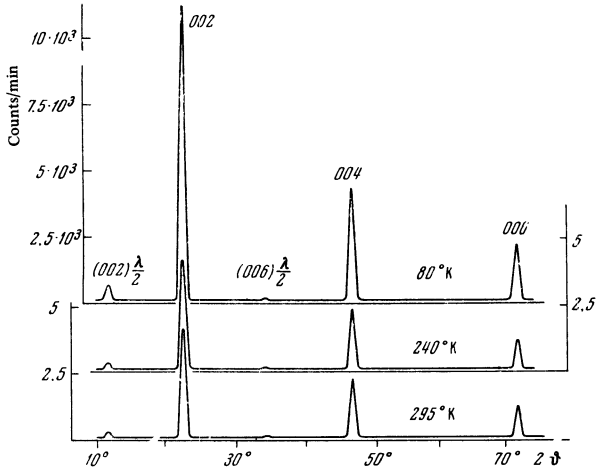

FIG. 2. Neutron diffraction patterns of Gd^{160}, corresponding to the direction [100] in the reciprocal lattice, at 80, 240, and 295° K.

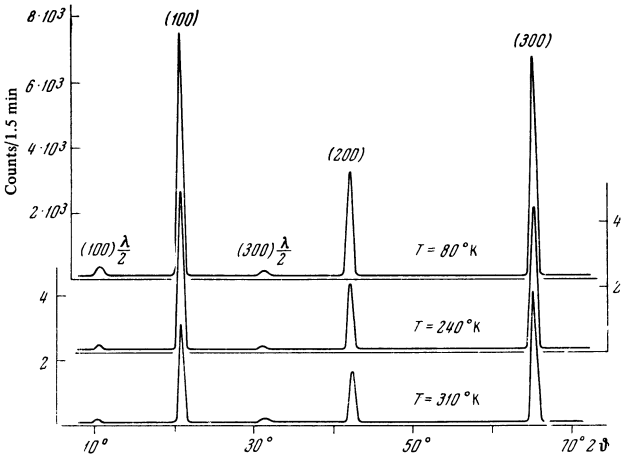

FIG. 3. Neutron diffraction patterns of Gd^{160}, corresponding to the direction [001] in the reciprocal lattice, at 80, 240, and 310°K.

The much smaller absorption of thermal neutrons by the isotopic sample, compared with the natural gadolinium (18000 and 500 b, respectively) made it possible to obtain, unlike in[3], a large number of diffraction maxima of appreciable intensity. Together with reflections of the fundamental wave length $\lambda = 1.125$ Å, reflections of second order, corresponding to $\lambda/2$, were observed both above and below the Curie point, and their intensities amounted to ~1% of the main maxima.

By way of an example, Figs. 2 and 3 show neutron diffraction patterns corresponding to the directions [100] and [001] in the reciprocal lattice. These, as well as all the remaining neutron diffraction patterns, show no satellites in the entire investigated temperature interval. If a helicoidal structure were to arise, satellites with intensity ~0.02% of the intensity of the main diffraction maxima could have been reliably recorded (with allowance for the experimental effect background ratio). The advantage of using the isotopic sample, to establish the presence or absence of satellites can be clearly seen from the fact that the intensity of the diffraction maxima of second order ($\lambda/2$) on our neutron diffraction patterns is equal to the intensity of the main reflection observed in[3].

In addition, no broadening of the diffraction maxima was observed at all temperatures. Starting from the experimental angular resolution we can estimate the lower limit of the pitch of the helicoid as being ~30--50 lattice periods. The results show that even if a helicoidal magnetic structure were to be realized in the gadolinium, it would be characterized by a large, almost macroscopic pitch of the helix. It can therefore be assumed that at all temperatures the gadolinium is a normal ferromagnet.

Inasmuch as the width of the diffraction maxima does not change with changing temperature, measurements of the temperature dependences of the intensities of the diffraction maxima were made by using their peak values. The results of these measurements (Fig. 4) indicate that the angle between the direction of the magnetic moment and the C axis changes significantly with temperature. This effect, however, is strongly masked by the presence of a domain structure. To take into account its influence, it was assumed that the crystal consists of domains, in which the directions of the magnetic moment are different, but form the same angle with the C axis, corresponding to the formation of a cone of easy-magnetization axis. Such a model leads to the following formula for the factor q^2, which takes into account the mutual orientation of the magnetic moment and the scattering vector for the given crystallographic plane:

$$q^2 = 1 - {}^1/_2 \cos^2\alpha_0 \sin^2\alpha - \sin^2\alpha_0 \cos^2\alpha, \quad (1)$$

where α is the angle between this plane and the basal plane, and α_0 is the angle between the direction of the magnetic moment and the basal plane. In particular, for the (002) plane, formula (1) assumes the simpler form $q^2 = \cos^2\alpha_0$. The intensities I_{nuc} and I_m of the nuclear and magnetic scattering are determined, as is well known, by the formulas

$$I_{nuc} = RV \frac{N_c^2 F_{nuc}^2 e^{-2W}}{\sin 2\vartheta} A_{hkl}, \quad (2)$$

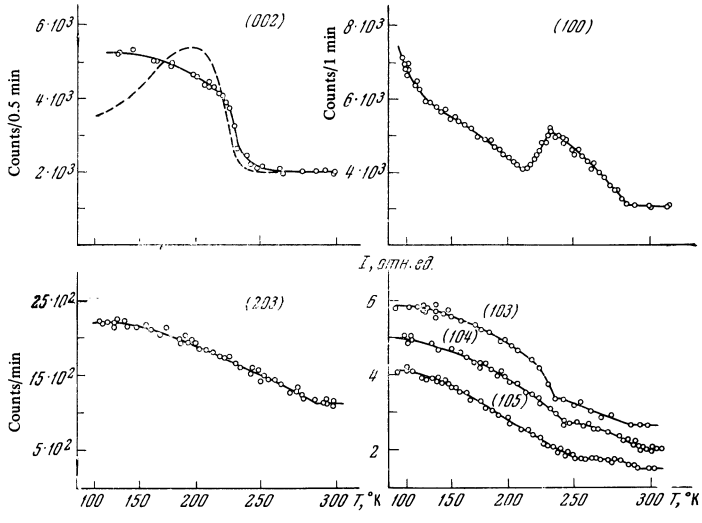

FIG. 4. Temperature dependence of the peak values of the diffraction maxima for Gd^{160}. Dashed curve – data of [3].

$$I_m = RV \frac{N_c^2 F_m^2 q^2 B_S^2 e^{-2W}}{\sin 2\theta} A_{hkl}, \quad (3)$$

where F_{nuc} and F_m are the nuclear and magnetic structure factors, e^{-2W} is the Debye-Waller factor, and A_{hkl} is the absorption factor.

To calculate the factor q^2 and to determine the angle α_0 from it at a given temperature, account was taken of the change of the spontaneous moment with temperature (the Brillouin function B_S for the spin ($7/2$), and also the Debye-Waller factor (Θ_{Gd} = 173°K as given in[6]). As the result, we obtained the temperature dependence of the angle α_0 as shown in Fig. 5. Consequently, in the interval 250–290°K the gadolinium crystal has one easy-magnetization axis (C axis). At 210–250°K, the easy-magnetization axis is deflected from C axis in such a way that the angle between the basal plane and the easy-magnetization axis changes from 90 to 38°. At temperatures 80–210°K, a small change of this angle takes place. These results agree qualitatively both with the results of the magnetic measurements[1] and with the data of[3].

The difference between the magnetic data and our data is due apparently to the influence of the field in which the magnetic measurements were made. The causes of a certain discrepancy with the results of[3] are not clear. We can only assume that they are connected with differences in the purity of the samples and in the character of the domain structure.

From the ratio of the intensities of the magnetic and nuclear scatterings of different diffraction peaks we determine the form factor, using the formula

$$f(k) = \frac{b}{e^2\gamma S/mc^2} \left[\frac{I^{(1)}_{exp} \exp\{2W^{(1)} - 2W^{(2)}\} - I^{(2)}_{exp}}{I^{(1)}_{exp} q^2 B_S^2} \right]^{1/2}, \quad (4)$$

where $I^{(1)}_{exp}$ and $I^{(2)}_{exp}$ are the integral intensities of the diffraction maxima for T_1 = 80°K and T_2 = 300°K, respectively; $e^{-W^{(1)}}$ and $e^{-W^{(2)}}$ are the Debye-Waller factors at the indicated temperatures; b is the nuclear-scattering amplitude and 2S = 7.12 μ_B[2]. We have neglected here the corrections for the primary and secondary "magnetic" extinctions. This is justified in view of the small thickness of the sample (2 mm), the noticeable absorption (μ = 9 cm^{-1}), and the fact that the experimental ratios F_{nuc}/F_m lie in the range 0.6–1.7 for all the observed diffraction maxima. According to Hamilton[7] (see also[8]), such values of F_{nuc}/F_M correspond to extinction coefficients that differ by not more than several percent, under the condition that the extinction coefficient for the purely nuclear reflections is close to unity. The latter was estimated from a comparison of the calculated values of the intensities of the peaks 100, 200, 300, and 002, 004, 006 with the experimental values measured above T_C. We used here the absorption factor for a cylindrical sample[9] at 2r = 0.19 cm, μr = 0.87. The following values were obtained:

hkl:	002	004	006	100	200	300
I_{exp}:	149	79,5	49,5	150	87	226
I_{theor}:	149	77	50	176	87	220

We see that the calculated and measured values are in satisfactory agreement, thus indicating that there is no noticeable extinction for nuclear reflections and justifying the neglect of the extinction corrections in the determination of f(k).

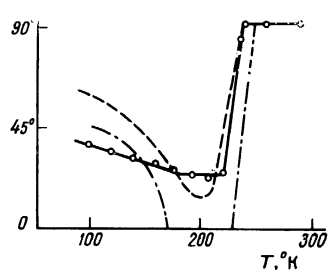

FIG. 5

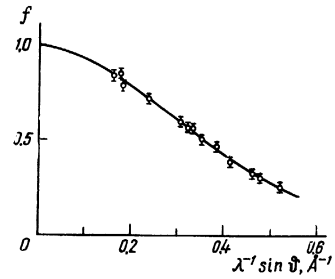

FIG. 6

FIG. 5. Temperature dependence of the angle α_0 between the direction of the magnetic moment and the basal plane: dashed-dot–from magnetic measurement data [2], dashed–from data of [3], solid–our data.

FIG. 6. Experimental values of the form factor for Gd^{160}. The solid curve corresponds to the spherical part of the form factor of the 4f electrons of the Gd^{3+} ions [10].

The Debye temperature Θ = 173°K was assumed the same for all the reflections, since no noticeable anisotropy of the Debye-Waller factor was found in the experiments.

The values of f(k) calculated from the experimental data using formula (4) are shown in Fig. 6. A comparison of these values with the theoretical curve calculated by Blume, Freeman, and Watson for Gd^{3+} [10] shows satisfactory agreement. This means that the distribution of the spin density in metallic gadolinium differs little from the distribution of the density in the Gd^{3+} ion and that consequently, in this respect, the conduction electrons have a weak influence on the 4f shell which lies close to the nucleus.

In the future we hope to obtain information concerning more subtle details of the distribution of the spin density, extending the measurements into the region of higher values of the wave vector. The experimental data yielded the values p/b, where p = ($e^2\gamma/mc^2$). Sf(k) is the magnetic analog of the nuclear-scattering amplitude b. Using the value of the magnetic moment of Gd, namely μ = 7.12 μ_B (magnetic measurement data), the values of b were calculated for Gd^{160}. It turned out to be 0.93 ± 0.02 × 10^{-12} cm, in good agreement with the results of Child and Moon[11]. Absolute measurements with a nickel standard yielded close values, but with a much larger error.

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