# MAGNETIC PROPERTIES OF GADOLINIUM OXIDES

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Measurements of the temperature dependence of magnetic properties have been made on gadolinium ferrites with garnet and perovskite structures, and also on gadolinium manganite. It has been established that in the garnet ferrite in the neighborhood of the compensation temperature and of the Curie point there occurs an anomalous increase of the coercive force and an extremely small paraprocess. The temperature dependence of the magnetostriction also exhibits an anomalous behavior. The perovskite gadolinium ferrite has a weak ferromagnetism of the hematite type. The magnitude of this ferromagnetism increases after heating of the specimen above the Curie point in a field. Gadolinium manganite has paramagnetic properties; but in the helium temperature range, magnetic hysteresis phenomena are observed.

RECENTLY there has been great interest in the study of the magnetic properties of oxides (ferrites) of the rare earth elements and of yttrium.[1,2] This interest is due to the fact that many of these compounds have antiferromagnetic or ferromagnetic properties. However, knowledge of the magnetic behavior of such materials is still very scanty. The present article presents the results of an investigation of the temperature dependence of the magnetic properties of several oxides of gadolinium, with both garnet and perovskite structures. In our work the specimens used were of quite large dimensions, as compared with those used in other work.[1,2] This enabled us to get more detailed information about the magnetic properties of the gadolinium oxides. Besides magnetization data, we give below data on the coercive force and the magnetostriction.

The specimens were prepared in accordance with standard ceramic practice from oxides of iron, gadolinium, and yttrium. Carefully ground mixtures of the oxides were given a preliminary anneal at 900° C for six hours in air. Then the materials thus obtained were reground, moulded under high pressure, and finally fired at 1300° C for four hours in air. The specimens were rectangular bars of dimensions 60 × 5 × 5 mm.

The methods used for measurement of the magnetic properties were the ballistic, the magnetometric, and the ponderomotive. The magnetostriction was measured by means of wire feelers with the aid of an electrophotooptical amplifier.

## 1. GADOLINIUM GARNET-FERRITE

The garnet ferrites of the rare-earth elements have the formula $3Me_2O_3 \cdot 5Fe_2O_3$, where Me is one of the rare-earth elements or yttrium. Some of the ions in the garnet lattice may be replaced by other elements. In our experiments we used as such a substituting element yttrium, which has zero atomic magnetic moment. In the garnet ferrite $3Gd_2O_3 \cdot 5Fe_2O_3$, the $Gd^{3+}$ and $Fe^{3+}$ ions have magnetic moments of considerable magnitude; therefore it was of interest to explore the effect of yttrium on the magnetic properties of this ferrite. We prepared a garnet ferrite of composition $3Gd_2O_3 \cdot 4.8Fe_2O_3 \cdot 0.2Y_2O_3$ and made measurements of its saturation magnetization at helium temperatures and of its Curie point; these gave the following values:

$$\sigma_0 = 72.5 \text{ gauss cm}^3/\text{g} = 24\mu_B/\text{mole}, \quad \Theta = 561^\circ \text{ K}.$$

On comparing these values with those obtained by Pauthenet[1] on $3Gd_2O_3 \cdot 5Fe_2O_3$ ($\sigma_0 = 30\ \mu_B$/mole and $\Theta = 570^\circ$K), we see that the introduction of even a small number of Y ions diminishes $\sigma_0$ and $\Theta$ very significantly. This is in qualitative agreement with Néel's[3] ideas on the nature of the magnetic properties of the garnet ferrites; these consist briefly of the following.

The crystal lattice of gadolinium garnet-ferrite is cubic; it contains a large number of $Fe^{3+}$ and $Gd^{3+}$ ions distributed among three types of site: d (tetrahedral sites), a (octahedral sites), and c. To explain the magnetic properties of the gar-

net ferrites, Néel[3] suggested that the lattice of these substances should be considered to be made up of three sublattices, formed respectively by the d, a, and c sites. The $Fe^{3+}$ ions are distributed over the lattices containing d and a sites; there are more of the tetrahedral sites d than of the octahedral a. The $Gd^{3+}$ ions are distributed over the third sublattice c. Between the sublattices d and a there is a strong negative exchange interaction, in consequence of which — and because of the excess of tetrahedral d sites — they acquire a ferromagnetic moment. Furthermore, the $Fe^{3+}$ ions on the d and a sublattices act on the $Gd^{3+}$ ions on the c sublattice, in consequence of which there arises a ferrimagnetic coupling here also, though a weaker one than in the case of d and a. The distribution of magnetizations on all three sublattices can be represented schematically as follows:

$$\underset{Gd^{3+}}{\overset{c}{\longrightarrow}} \quad \underset{Fe^{3+}}{\overset{d}{\longleftarrow}} \quad \underset{Fe^{3+}}{\overset{a}{\longrightarrow}}.$$

The relative length of each arrow represents the magnitude of the magnetization of the corresponding sublattice. From this scheme it is evident that by substitution of nonmagnetic ions for one or another sublattice of $Fe^{3+}$ and $Gd^{3+}$ ions, the resultant magnetic moment of the ferrite can be changed. From consideration of the scheme presented above, it is evident that the $Y^{3+}$ ions must be distributed on a sites; only then can the resultant magnetic moment of the ferrite decrease. This also leads to diminution of the number of $Fe^{3+}$-$O^{2-}$-$Fe^{3+}$ exchange interactions, and hence to a decrease in the magnitude of $\Theta$.

The most interesting peculiarity of the garnet ferrites is this: most of them exhibit a compensation temperature $\Theta_k$; that is, their spontaneous magnetization vanishes not only at the Curie point $\Theta$, but also at a lower temperature $\Theta_k$. At this point there occurs a balancing of the magnetic moments of the sublattices; i.e., here the material becomes antiferromagnetic.

Figure 1 shows the results of measurements of the temperature dependence of the specific magnetization of the garnet ferrite studied, with various magnetic fields applied to the specimen. It is clear that in the neighborhood of −14°C (260°K), there is a compensation point $\Theta_k$. Because of the effect of the magnetic field, however, the compensation is incomplete. In order to determine the exact location of $\Theta_k$, it is necessary to get the curve of spontaneous magnetization, $\sigma_s(T)$. Figure 2 shows such a curve, with coordinates $\sigma_s/\sigma_0$ and $T/\Theta$; the curve was obtained by extrapolating

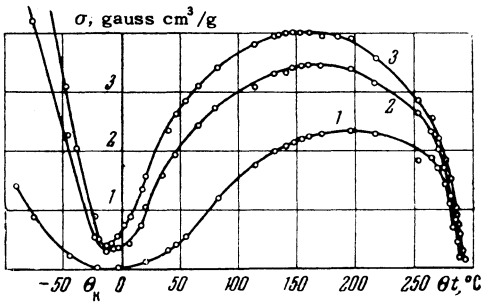


FIG. 1. Dependence of the specific magnetization on temperature at various fields in the garnet ferrite of composition $3Gd_2O_3 \cdot 0.2\ Y_2O_3 \cdot 4.8\ Fe_2O_3$: 1) H = 25.8; 2) H = 129; 3) H = 1550 oe.

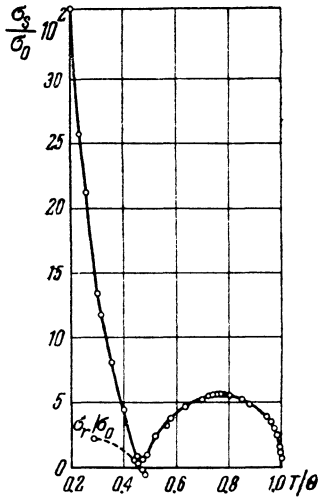


FIG. 2. Temperature dependence of $\sigma_s/\sigma_0$ for the garnet ferrite studied. Dashed curve: temperature dependence of the residual magnetization $\sigma_r/\sigma_0$ in the neighborhood of the compensation point.

the magnetization isotherms $\sigma(H)$ to zero field. The value of $\sigma_0$ was determined from the magnetization isotherm taken at 4.3°K. It is evident that at 258°K the spontaneous magnetization is close to zero. The location of $\Theta_k$ can be determined still more precisely by finding the temperature dependence of the residual magnetization $\sigma_r$. The position of $\Theta_k$ is found from the change of sign of the quantity $\sigma_r/\sigma_0$ (cf. Fig. 2). It should be mentioned that here, as in our earlier work[4] on a lithium chromite-ferrite, we apparently do not have complete compensation of the sublattice magnetizations; this is probably connected with the influence of structural inhomogeneities of the garnet-ferrite specimen under study. The presence of incomplete compensation can also be explained by the development of appreciable magnetization upon application of a field even at the compensation point $\Theta_k$ (cf. Fig. 1).

A very interesting fact established for our gadolinium garnet is the existence of a maximum on the coercive force vs temperature curve in the neighborhood of $\Theta_k$; there is also an anomalous increase of the coercive force in the Curie point region (cf. Fig. 3). A similar phenomenon had

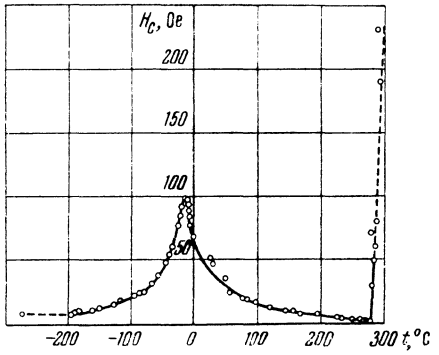


FIG. 3. Dependence of coercive force on temperature in the garnet ferrite $3Gd_2O_3 \cdot 0.2\ Y_2O_3 \cdot 4.8\ Fe_2O_3$.

been observed earlier in our laboratory, for lithium garnet-ferrite, by K. M. Bol'shova and T. A. Elkina. The nature of this increase of $H_C$ is still not altogether clear. It is possible that near the temperatures $\Theta_K$ and $\Theta$, there occurs a peculiar magnetic "heterogeneity." Here the main part of the specimen volume is in a nonmagnetic state, but there are individual small sections in which the material is in a ferromagnetic state. This promotes the development of a "single-domain" structure, and consequently the processes of magnetization reversal will occur with greater difficulty; this will lead to an increase of $H_C$. Formally it is possible to apply here the known relation $H_C \sim K/\sigma_S$, where K is the magnetic anisotropy constant. If K does not decrease with temperature as fast as does $\sigma_S$, $H_C$ must increase because of the decrease of $\sigma_S$.

We now consider a peculiarity of the paraprocess in gadolinium garnet-ferrite. In this material there is observed an anomalous temperature variation of the paraprocess susceptibility. Whereas in ordinary ferromagnetics and ferrimagnetics it increases monotonically with increase of temperature, reaching a maximum near the Curie point,[5] in gadolinium garnet-ferrite its change with temperature has a more complicated character. As is evident from Fig. 4 (experimental data taken from reference 1), starting from 0° K the paraprocess susceptibility at first increases, reaches a maximum, then on further rise of temperature diminishes; again begins to rise on approach to the Curie point; and after passing it, again suddenly drops. The magnitude of the paraprocess susceptibility is not as large in the temperature interval $\Theta - \Theta_K$ as in the region 0° K to $\Theta_K$; this is anomalous. This peculiar temperature variation of the paraprocess susceptibility in gadolinium garnet-ferrite can be explained on the basis of the following considerations. In our previous researches[5] it has been shown that the paraprocess in a ferromagnetic is larger, the larger the size of the magnetic moments of the atoms that take part in the ferromagnetism, and the smaller the exchange interaction between them. In the case of gadolinium garnet-ferrite, the exchange interaction of sublattice c with sublattices d and a is weaker than that of d and a; the magnetic moment of sublattice c is larger than the resultant moment of sublattices d and a. This leads to the consequence that in gadolinium garnet-ferrite at low temperatures, where the magnetization of the ferrite is basically determined by the magnetic moment of sublattice c, a large paraprocess should be observed, as in fact occurs experimentally. This paraprocess, however, should diminish with rise of temperature, since the magnetic moment of sublattice c is compensated by the resultant moment of sublattices d and a. Above the compensation point, the paraprocess operates through the $Fe^{3+}$ ions, between which there is a larger exchange interaction. Here the paraprocess will be weaker, despite the fact that the ferrite is at a higher temperature. In the region of the Curie point we have the usual susceptibility "splash" characteristic of all ferromagnetics and antiferromagnetics.

The paraprocess model just described is confirmed by our measurements of the magnetostriction of gadolinium garnet-ferrite. Figure 5 gives isotherms of the magnetostriction, measured in the temperature interval −169 to +10° C. It can be seen that at low fields the magnetostriction is negative, at higher fields there develops a positive component of magnetostriction because of the paraprocess. In our ferrite it is especially large at

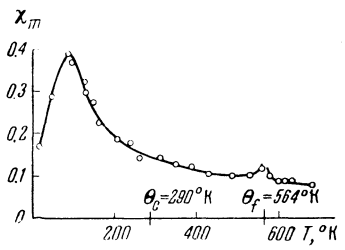


FIG. 4. Dependence of the paraprocess susceptibility on temperature in the garnet ferrite $3Gd_2O_3 \cdot 5Fe_2O_3$.

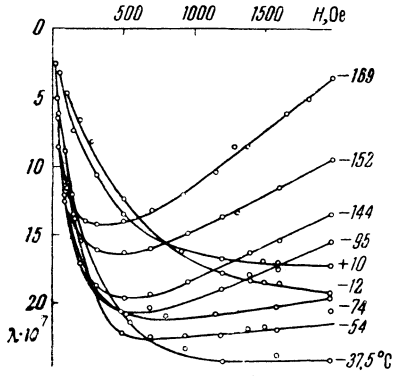


FIG. 5. Dependence of magnetostriction on temperature in the garnet ferrite $3Gd_2O_3 \cdot 0.2\ Y_2O_3 \cdot 4.8\ Fe_2O_3$ (the figures on the curves show the temperature in degrees C).

low temperatures (at −169° C). On approach to the compensation point the paraprocess magnetostriction decreases, since here the paraprocess diminishes in accordance with Fig. 4.

In the neighborhood of the compensation point itself, it was not possible to observe the paraprocess, because here the magnetic fields used were insufficient for attainment of technical saturation of the specimen.

Finally, we present the results of a study of the paraprocess magnetization in gadolinium garnet-ferrite in the immediate vicinity of the Curie point. We have analyzed the magnetization curves in the Curie point region according to the thermodynamic formula $H/\sigma = \alpha + \beta\sigma^2$, where $\alpha$ and $\beta$ are thermodynamic coefficients.[5] The values of $\alpha$ and $\beta$ provide a method of determining the temperature behavior of $\sigma_S$ (from the relation $\sigma_S^2 = -\alpha/\beta$). Figure 6 shows the dependence of

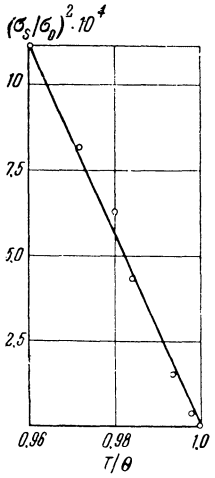


FIG. 6. Dependence of $(\sigma_S/\sigma_0)^2$ on $(T/\Theta)$ in garnet ferrite near the Curie point.

$(\sigma_S/\sigma_0)^2$ on $T/\Theta$. It is clear that the equation

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

is satisfied. However, in contrast to other ferrites and ferromagnetics, the calculated value of $\xi$ here is extremely small (cf. table). The table also shows, for comparison, the values for several ferrimagnetics and ferromagnetics.

| Material | $\xi$ | $b_\Theta$ | $\sigma_0$ | $\Theta$, °K |
|---|---|---|---|---|
| $3Gd_2O_3 \cdot 0{,}2Y_2O_3 \cdot 4{,}8Fe_2O_3$ | 0,04 | 0,046 | 72,5 | 561 |
| Ni | 6,95 | 0,8 | 55,2 | 624 |
| 20% Cu; 80% Ni | 3,44 | 0,5 | 35,9 | 428 |
| 35,5% MnO; 15% ZnO; 49,5% $Fe_2O_3$ | 0,1—0,7 | 0,805 | 152,0 | 467,5 |

Figure 7 shows the dependence of the paraprocess magnetization $\sigma$ on $H^{1/3}$ right at the Curie point. Here the relation $\sigma = b_\Theta H^{1/3}$, derived from thermodynamic theory:[5] is fulfilled; $b_\Theta$ describes the inclination of the magnetization curve at the

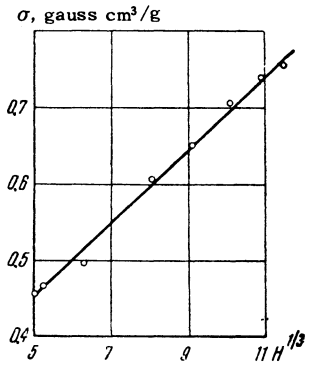


FIG. 7. Dependence of magnetization on $H^{1/3}$ near the Curie point.

Curie point. According to qualitative considerations, the value of $b_\Theta$ should be larger, the larger the value of $\sigma_0$ in the material under study ($b_\Theta \sim \sigma_0/\sqrt[3]{\Theta}$). However, as is evident from the table, for the garnet ferrite the value of $b_\Theta$ is extremely small and not consistent with the high value of $\sigma_0$ for this ferrite. The reason for this lies in the fact that the paraprocess at the Curie point is basically determined by sublattices a and d, whose resultant magnetization is small.

## 2. GADOLINIUM PEROVSKITE-FERRITE

According to earlier investigations,[1,2] the compound $Gd_2O_3 \cdot Fe_2O_3$ (or $GdFeO_3$) is antiferromagnetic with a weak parasitic ferromagnetism. Its magnetic behavior is in many respects similar to that of hematite ($\alpha Fe_2O_3$), and also to that of $CoCO_3$ and $MnCO_3$, which have recently been studied in detail by Borovik-Romanov and coworkers.[6] The similarity consists in the fact that these materials obey the law $\sigma = \sigma_S + \chi H$, where $\sigma_S$ is a spontaneous magnetization of small magnitude, and where $\chi$ is a field-independent susceptibility. Figure 8 gives a series of curves $\sigma(H)$ taken on $Gd_2O_3 \cdot Fe_2O_3$. It is evident that over a wide field interval the isotherms $\sigma(H)$ are straight lines, which cut off on the axis of ordinates a segment equal to $\sigma_S$. There is nevertheless a difference in the behavior of $Gd_2O_3 \cdot Fe_2O_3$ as compared with the substances mentioned above. The difference is that in the material studied by us, $\sigma_S$ is unstable. Heating of the specimen to the Curie point in the presence of a field causes an increase of $\sigma_S$.

Figure 9 gives a series of magnetization isotherms taken after heating of the specimen above the Curie point. It is evident that larger values of $\sigma_S$ are now cut off on the axis of ordinates.

Figure 10 shows the temperature dependence of $\sigma_S$ at the time of the first and of the second heating of the specimen. It is evident that below 100° the value of $\sigma_S$ decreases. On the

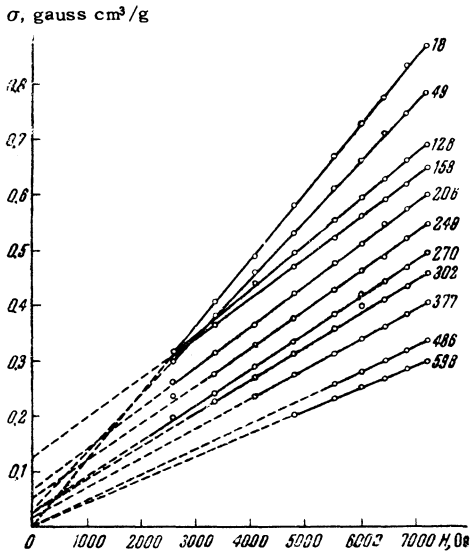


FIG. 8. Dependence of magnetization on field at various temperatures for gadolinium perovskite-ferrite, $Gd_2O_3 \cdot Fe_2O_3$ (the figures on the curves indicate the temperature in degrees C).

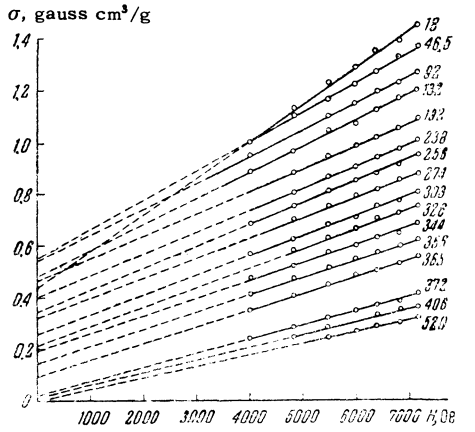


FIG. 9. Same as Fig. 8 after heating above the Curie point in a magnetic field.

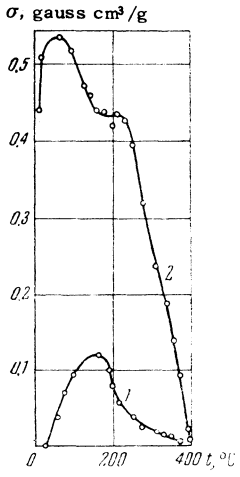


FIG. 10. Temperature dependence of the spontaneous magnetization of $Gd_2O_3 \cdot Fe_2O_3$ in a magnetic field: 1) after first heating; 2) after second.

other hand, our measurements at helium temperatures have shown that at those temperatures $\sigma_S$ reaches a large value. It must be concluded that the character of the $\sigma_S(T)$ curves in the substance under investigation is very complicated. This is consistent with the results of references 1 and 2.

## 3. GADOLINIUM PEROVSKITE-MANGANITE

X-ray analysis has shown that the compound $Gd_2O_3 \cdot Mn_2O_3$ has the perovskite structure. Its magnetization curves are of purely paramagnetic character (cf. Fig. 11); however, the values of the

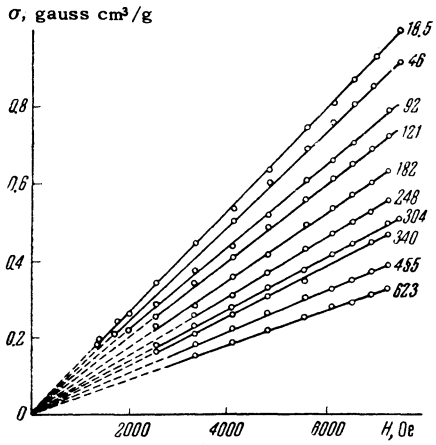


FIG. 11. Dependence of magnetization on field at various temperatures for $Gd_2O_3 \cdot Mn_2O_3$ (the figures on the curves show the temperature in degrees C).

susceptibility are two orders of magnitude larger than in ordinary paramagnetics ($\chi \sim 10^{-4}$). The values of the constants C and $\Theta$ also differ from the values for classical paramagnetics. In measurements in the helium temperature range, the function retains its straight-line form. Here, in contrast to the behavior at room temperature, the susceptibility becomes very large; and on decrease of the field, hysteresis occurs. From Fig. 12 it is

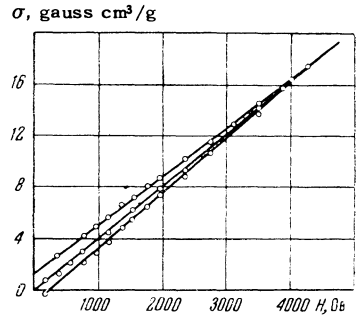


FIG. 12. Magnetic hysteresis in $Gd_2O_3 \cdot Mn_2O_3$ at 4.3°K.

clear that, though the residual magnetization is small, the coercive force reaches 250 oe. From this it was concluded that in this substance, as in $Gd_2O_3 \cdot Fe_2O_3$, parasitic ferromagnetism can be produced by extreme cooling.

We also made an attempt to synthesize the com-

pound $3Gd_2O_3 \cdot 5Mn_2O_3$. It was conjectured that this compound would have the garnet structure. Since instead of $Fe^{3+}$ ions there will be $Mn^{3+}$ ions, it was expected that this compound would be strongly magnetic. The measurements, however, showed that the substance obtained had magnetic properties identical with those of $Fe_2O_3 \cdot Mn_2O_3$. X-ray studies showed that the synthesized material had the perovskite structure; no garnet structure is formed.

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