CRITICAL MAGNETIC ISOTHERMS OF SUBSTITUTED IRON GARNETS

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An investigation was made of the critical magnetic isotherms (given by the equation $\sigma_i = a_\Theta H^{1/\delta}$) of tin-substituted iron garnets of Y, Tb, and Gd. It was found that the paraprocess constant a_Θ increased with the increasing degree of substitution of magnetic ions with lead. The rise of the constant was due to the increase in the ferromagnetic moment of a garnet when magnetic ions were replaced in the a and c sublattices, and to the weakening of the a—d exchange interaction of the sublattices. A relatively weak magnetic field, applied in the region of the Curie point to heavily substituted iron garnets, oriented the magnetic moments of Gd^{3+} and Tb^{3+} ions along the field (giving rise to anomalies in the values of the constants a_Θ) because the effective exchange field was greatly weakened by the substitution.

DETAILED studies of the characteristics of magnetic phase transitions in ferromagnets, ferrimagnets, and antiferromagnets are currently of great interest because such studies yield the data necessary for the verification of the conclusions which follow from the statistical theory of phase transitions of the second kind and of critical phenomena.[1,2]

The critical power exponents (α, β, γ, and δ) were recently measured for some substances; these exponents are characteristics of the temperature dependences of the specific heat, spontaneous magnetization, and initial magnetic susceptibility, as well as of the field dependence of the paraprocess (absolute saturation) magnetization near the Curie and Néel points. However, the true values of these power exponents in the direct vicinity of the Curie and Néel points are not yet known. Differences between the values of the critical exponents, obtained by different workers, may be due to a number of reasons. They include imperfection of the samples as well as the absence of a single method for the determination of the magnetic phase transition temperatures. Moreover, the accuracy of the magnetic-neutron-diffraction, etc. measurement methods is still insufficient for the determination of the true temperature dependences of the spontaneous magnetization and susceptibility in narrow temperature intervals near the Curie and Néel points where the strongest magnetic fluctuations are observed (giving rise to insufficient temperature resolution).

The basic deficiency in the determination of the power exponents α and β by the magnetic methods is the measurement of the spontaneous magnetization and the initial magnetic susceptibility in the presence of an external field which strongly affects the magnetic fluctuations and therefore influences the phase transition itself.[3] It is more correct to study the "critical magnetic isotherm" (the paraprocess curve at the Curie point), given by the equation

$$\sigma_i = a_\Theta H^{1/\delta}, \tag{1}$$

where σ_i is the paraprocess magnetization; δ is one of the critical power exponents; a_Θ is a constant representing the intensity of the paraprocess at the Curie point. Studies of the critical magnetic isotherm are attracting investigators concerned with the physics of

phase transitions. Some workers draw an analogy between the critical magnetic isotherm and the critical isotherm of the gas-liquid systems (the pressure dependence of the density[11]). Moreover, the critical power exponent δ is related by simple expressions to the power exponents α, β, and γ.[4]

According to the thermodynamic theory of Landau and the molecular field theory, the value of the critical exponent in Eq. (1) is $\delta = 3$, whereas calculations based on the two-dimensional Ising model give $\delta = 15$, and the approximate three-dimensional Ising model yields $\delta = 5.2$.[2,5] Experimental investigations of nickel yield, depending on the method of analysis of the results, the following values: $\delta = 4.2$,[11] 4.58,[11] and 3.[12]

It seemed desirable to determine the influence of the characteristic features of the magnetic structure of an investigated substance on the parameters of the critical magnetic isotherm. It was expected that the constants a_Θ would be particularly sensitive to the magnetic structure.

The present paper reports an investigation of the critical magnetic isotherms of substituted rare-earth ferrites with the garnet structure. The main attention was concentrated on a study of the constant a_Θ in Eq. (1). The replacement of magnetic with nonmagnetic ions was used to alter the structure and magnetic properties of these substances. These iron garnets had three-sublattice magnetic structures and therefore the paraprocess in the garnets was very complex.[6] All three sublattices (a, d, and c) contributed to the paraprocess magnetization σ_i in the region of the Curie point. Therefore, the replacement of magnetic ions in the sublattices with nonmagnetic ions altered the magnetic moments of these sublattices and their exchange interactions; consequently, the contribution of each sublattice to the paraprocess was affected.

Investigations of mixed rare-earth iron garnets[6,7] yield the following approximate expression for the constant a_Θ of the substituted iron garnets:

$$a_\Theta = k' \frac{\mu_d n_d - \mu_a n_a}{J_{ad}^{1/3}} - k'' \frac{\mu_c(S+1)n_c}{J_{ad-c}^{1/3}} + F\left(\mu_c, \frac{1}{J_{ad-c}}\right). \tag{2}$$
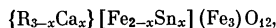
Here, μ_a, μ_d, μ_c are the magnetic moments of ions in the a, d, and c sublattices; n_a, n_d, and n_c are the num-

bers of magnetic ions in the three sublattices; J_{ad} is
the parameter of the exchange interaction between the
a and d sublattices; J_{ad-c} is the parameter of the ex-
change interaction between the total iron sublattice ad
and the rare-earth sublattice c; S is the spin of the
rare-earth ions; k' and k'' are numerical coefficients.
Here, the first term represents the paraprocess con-
stant of the total iron sublattice (i.e., the constant of
yttrium iron garnet), the second term represents the
paraprocess constant of the rare-earth sublattice, and
the third term takes into account the paraprocess of the
antiferromagnetic rare-earth ions.[6] Since the third
term should have little influence on the value of a_Θ, we
shall first consider a_Θ of substituted garnets, taking into
account only the first two terms in Eq. (2).

If the degree of substitution in the a and d sublattices
is not too large, the quantity $J_{ad}^{1/3}$ (or, which is equivalent,
$\Theta_f^{1/3}$, where Θ_f is the Curie temperature) does not vary
greatly from one substituted ferrite to another. There-
fore, in the first approximation, we may assume that
changes in the constant a_Θ are mainly due to changes in
the numerator in Eq. (2). When the degree of substitution
in the a and d sublattices is large, the constant a_Θ is
governed not only by the numerator but also by changes
in the value of $\Theta_f^{1/3}$. The constant a_Θ should increase
when the number of magnetic ions in the sublattice a (or
in the sublattice c) is reduced; this is because the re-
sultant magnetization of the garnet increases and Θ_f de-
creases. When the concentration of nonmagnetic ions
in the d sublattice is increased, the constant a_Θ decrea-
ses at first, passes through a minimum, and then in-
creases due to the magnetization of the a and c sublat-
tices.

We investigated the parameter a_Θ of Eq. (1) of tin-
and calcium-substituted iron garnets of gadolinium,
terbium, and yttrium. We replaced the magnetic ions
in the a and c sublattices, i.e., we investigated the sim-
plest case when the replacement of the magnetic ions
simply increased the constant a_Θ.

We investigated the following compositions of substi-
tuted iron garnets:

$$\{R_{3-x}Ca_x\}[Fe_{2-x}Sn_x](Fe_3)O_{12},$$

where R = Y (system I), Tb (system II), and Gd (system
III); x = 0, 0.3, 0.6, 0.9. As shown in[8], if the concen-
tration was not too high (x ≤ 1.5), Sn^{4+} ions replaced
mainly those iron ions which were in the octahedral (a)
sublattice. Samples were prepared using the standard
ceramic technique. The final firing of the systems II
and III was carried out for six hours at temperatures of
1350°C and 1375°C, respectively, and system I was
fired for ten hours at 1410°C. X-ray diffraction phase
analysis (carried out using a URS-50IM diffractometer
and filtered Co K_α radiation) showed that all samples
consisted of a single phase. The magnetization was de-
termined using a pendulum magnetometer in fields up to
12 kOe. The values of the Curie temperatures, obtained
for systems I and III, were in agreement with those re-
ported in[9]. System II had never been prepared before.
The Curie temperatures were determined using the
method described in[10] (this method is based on the
vanishing of the thermodynamic coefficient α).

Figure 1 shows, on a logarithmic scale, the critical
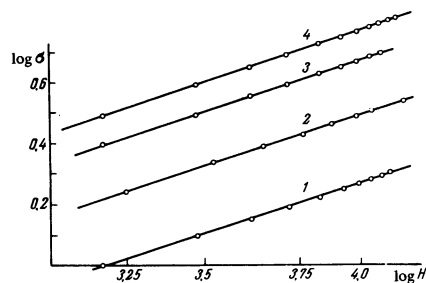magnetic isotherms of substituted gadolinium iron gar-

FIG. 1. Critical magnetic isotherms (dependences of the magnetization
on the field at the Curie point, plotted on a logarithmic scale) of substi-
tuted gadolinium iron garnets $Gd_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$, where x = 0 (1), 0.3
(2), 0.6 (3), and 0.9 (4).

nets. The critical power exponent δ was given by the
tangent of the slope of these isotherms with respect to
the abscissa; the point of intersection with the ordinate
gave the value of the constant a_Θ. All the investigated
substituted garnets had the power exponents δ = 3.0
± 0.1. This result was reasonable because the magnetic
field "suppressed" strongly the magnetic fluctuations
and therefore the Landau and molecular field theories
became applicable at the Curie point itself, which gave
δ = 3.

Figure 2 shows the dependence of the paraprocess
constant a_Θ on the composition of the substituted iron
garnets of systems I, II, and III. Table I gives the values
of a_Θ and of the Curie temperature Θ_f for all the inves-
tigated compositions. As is known, the Curie points of
all iron garnets are governed by the a-d exchange inter-
action of the iron sublattices. In our case, the Curie
points of systems I, II, and III were approximately equal
for the same values of x.

We have mentioned that the rise of the constant a_Θ of
substituted iron garnets should, in general, be governed
(particularly in the case of large degrees of substitution)
by the rise of the resultant magnetization and by the
weakening of the exchange interactions. It follows from
Table I that the quantity $a_\Theta \Theta_f^{1/3}/n$ is approximately the
same for all the substituted yttrium iron garnets. (Here,
n is the difference between the numbers of magnetic ions
in the a and d sublattices). Thus, the nonlinear rise of
the constant $a_{\Theta\,Y}$ with increasing x must be attributed
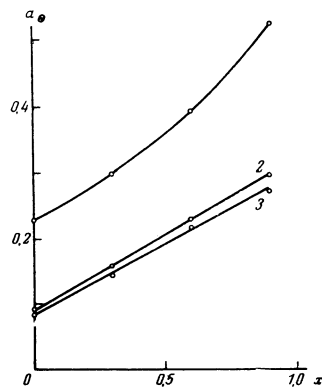

FIG. 2. Dependence of the paraprocess constant a_Θ on the composi-
tion of substituted iron garnets: 1) $Y_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$; 2) $Tb_{3-x}Ca_x$
$Fe_{5-x}Sn_xO_{12}$; 3) $Gd_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$.

Table I. Parameters of critical magnetic isotherms of substituted iron garnets

x	System I			System II		System III	
	θ_f,°K ($\pm2°$)	$a_\Theta Y \cdot 10^2$ (±0.5)	$a_\Theta \dfrac{\theta^{1/3}}{n}$	θ_f,°K ($\pm2°$)	$a_\Theta Tb \cdot 10^2$ (±0.5)	θ_f,°K ($\pm2°$)	$a_\Theta Gd \cdot 10^1$ (±0.5)
0	551	23.0	18.7	551	9.4	555	8.6
0.3	481	30.1	18.1	486	15.9	494	14.6
0.6	407	39.4	18.3	410	23.2	413	21.8
0.9	302	52.9	18.0	314	30.0	311	27.4

to the influence that the weakening of the a—d exchange interaction has on the paraprocess.

The paraprocess constant of the rare-earth gadolinium and terbium garnets also becomes larger when the degree of substitution increases (Fig. 2) but at all values of x this constant is smaller than $a_\Theta Y$. This is due to the fact that an increase in the sublattice magnetization due to the paraprocess occurs in the iron and rare-earth sublattices but the increments in the sublattice magnetizations are directed oppositely (because of the negative exchange interaction).

The nonlinear rise of the paraprocess constant due to weakening of the exchange interaction occurs in the iron and rare-earth sublattices. Consequently, the nonlinear increments in the constant are mutually compensated. This results in a linear dependence $a_\Theta(x)$ for the rare-earth garnets considered as a whole.

If only the first two terms in Eq. (2) are used, we may expect the value of a_Θ of the terbium garnet to be smaller than the corresponding constant of the gadolinium garnet because the product $\mu_c(S+1)$ is larger for terbium ions than for gadolinium ions. However, our measurements gave the opposite results: $a_\Theta Tb$ was larger than $a_\Theta Gd$ and the difference between the values of $a_\Theta Tb$ and $a_\Theta Gd$ increased with the increasing degree of substitution (Fig. 2).

Such anomalous behavior of the constant a_Θ can be explained by including the third term in Eq. (2). Near the Curie point, the exchange field exerted by the iron sublattices on the rare-earth ions becomes much weaker because of a reduction in the spontaneous magnetization. The substitution of nonmagnetic ions also weakens the exchange interactions between the iron and rare-earth sublattices, i.e., it reduces the effective exchange field. Under these conditions, even a relatively weak external field orients the rare-earth ion moments along the field, i.e., the antiferromagnetic paraprocess appears in the rare-earth sublattice and this process is responsible for the appearance of the third term in Eq. (2). The additional magnetization due to this paraprocess is directed in the same way as the magnetization of the paraprocess of the iron sublattice [represented by the first term in Eq. (2)] and consequently, it must be sub-

tracted from the paraprocess magnetization of the rare-earth sublattice [represented by the second term in Eq. (2)]. The stronger the external field, the heavier is the substitution with nonmagnetic ions, and the greater the value of the magnetic moment of the rare-earth ion, the stronger is the antiferromagnetic process. Since the magnetic moment of Tb^{3+} is larger than the magnetic moment of Gd^{3+}, the influence of the antiferromagnetic paraprocess is stronger in the substituted terbium garnets than in the gadolinium garnets. This is why the constants $a_\Theta Tb$ are larger than the constants $a_\Theta Gd$.

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