CRITICAL MAGNETIC ISOTHERMS OF SUBSTITUTED IRON GARNETS

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An investigation was made of the critical magnetic isotherms (given by the equation \( \sigma_1 = a_0 H^{1/\delta} \)) of tin-substituted iron garnets of \( Y, Tb, \) and \( Gd \). It was found that the paraprocess constant \( a_0 \) 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 \( a_0 \)) 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 critical phenomena.

The critical power exponents \( (\alpha, \beta, \gamma, \) and \( \delta) \) 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 in 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 \( \alpha \) and \( \beta \) 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.\(^{(1)}\) It is more correct to study the "critical magnetic isotherm" (the paraprocess curve at the Curie point), given by the equation

\[
\sigma_1 = a_0 H^{1/\delta}, \tag{1}
\]

where \( \sigma_1 \) is the paraprocess magnetization; \( \delta \) is one of the critical power exponents; \( a_0 \) 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).\(^{(2)}\) Moreover, the critical power exponent \( \delta \) is related by simple expressions to the power exponents \( \alpha, \beta, \) and \( \gamma. \)

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 \( \delta = 5.2, 4.58 \), and \( 3 \).\(^{(3)}\)

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 \( a_0 \) 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 \( a_0 \) 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.\(^{(4)}\) All three sublattices (\( a, d, \) and \( c \)) contributed to the paraprocess magnetization \( \sigma_1 \) 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\(^{(5)}\) yield the following approximate expression for the constant \( a_0 \) of the substituted iron garnets:

\[
a_0 = k' \mu_\alpha n_\alpha - \mu_\alpha n_\alpha - k' \mu_\delta (S + 1) n_\delta + F(\mu_c, r_{ad,c}). \tag{2}
\]

Here, \( \mu_\alpha, \mu_\delta, \mu_c \) are the magnetic moments of ions in the \( a, d, \) and \( c \) sublattices; \( n_\alpha, n_\delta, \) and \( n_c \) are the num-

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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 exchange 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 constant 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. Since the third term should have little influence on the value of $a\Theta$, we shall first consider $a\Theta$ 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 $I^{1/2}$ (or, which is equivalent, $\Theta'$), where $\Theta'$ is the Curie temperature (does not vary greatly from one substituted ferrite to another). Therefore, in the first approximation, we may assume that changes in the constant $a\Theta$ 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 $a\Theta$ is governed not only by the numerator but also by changes in the value of $\Theta'$. The constant $a\Theta$ should increase when the number of magnetic ions in the sublattice a (or in the sublattice c) is reduced; this is because the resultant magnetization of the garnet increases and $\Theta'$ decreases. When the concentration of nonmagnetic ions in the d sublattice is increased, the constant $a\Theta$ decreases at first, passes through a minimum, and then increases due to the magnetization of the a and c sublattices.

We investigated the parameter $a\Theta$ 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 simplest case when the replacement of the magnetic ions simply increased the constant $a\Theta$.

We investigated the following compositions of substituted iron garnets:

$$[R_{1-x}Ca_x][Fe_{2-x}Sn_x](FeO)yCa_0,$$

where $R = Y$ (system I), Tb (system II), and Gd (system III); $x = 0, 0.3, 0.6, 0.9$. As shown in (1), if the concentration was not too high ($x \leq 1.5$), 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-501M diffractometer and filtered Co K$_\alpha$ radiation) showed that all samples consisted of a single phase. The magnetization was determined 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 reported in (2). System II had never been prepared before. The Curie temperatures were determined using the method described in (3) (this method is based on the vanishing of the thermodynamic coefficient $q$).

Figure 1 shows, on a logarithmic scale, the critical magnetic isotherms of substituted gadolinium iron garnets. The critical power exponent $\delta$ 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 $a\Theta$. All the investigated substituted garnets had the power exponents $\delta = 3.0 \pm 0.1$. 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 $\delta = 3$.

Figure 2 shows the dependence of the paraprocess constant $a\Theta$ on the composition of the substituted iron garnets of systems I, II, and III. Table I gives the values of $a\Theta$ and of the Curie temperature $\Theta'$ for all the investigated compositions. As is known, the Curie points of all iron garnets are governed by the a-d exchange interaction 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 $a\Theta$ of substituted iron garnets should, in general, be governed (particular 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 $a\Theta^1$ 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 $a\Theta^1$ with increasing $x$ must be attributed.
for the appearance of the third 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\textsuperscript{3+} is larger than the magnetic moment of Gd\textsuperscript{3+}, the influence of the antiferromagnetic paraprocess is stronger in the substituted terbium garnets than in the gadolinium garnets. This is why the constants $a_0$\textsubscript{Tb} are larger than the constants $a_0$\textsubscript{Gd}.

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

<table>
<thead>
<tr>
<th>System</th>
<th>$\theta_0$ (°K)</th>
<th>$a_{0G}$ (°K)</th>
<th>$a_{0Tb}$ (°K)</th>
<th>$\theta_0$ (°K)</th>
<th>$a_0$ (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.55 23.0 18.7</td>
<td>551 9.4</td>
<td>555 8.6</td>
<td>0.3 20.3 18.1</td>
<td>486 16.0</td>
</tr>
<tr>
<td>II</td>
<td>0.6 407 24.3 18.3</td>
<td>410 23.2</td>
<td>413 21.8</td>
<td>0.9 309 28.9 18.6</td>
<td>314 20.9</td>
</tr>
<tr>
<td>III</td>
<td>21.8 413 23.2</td>
<td>314 20.9</td>
<td>311 27.4</td>
<td></td>
<td></td>
</tr>
</tbody>
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