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# THEORY OF THE ANOMALIES OF PHYSICAL PROPERTIES OF FERRIMAGNETS IN THE VICINITY OF THE MAGNETIC COMPENSATION POINT

K. P. BELOV and S. A. NIKITIN

Moscow State University

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On the basis of the molecular-field method it is shown that at the compensation point of rare-earth ferrite-garnets there should occur anomalies of the magnetocaloric effect, the magnetostriction, and the coercive force, and also of the entropy, the specific heat, and the specific volume (in the presence of an external field). This conclusion is in agreement with experimental data. It is suggested that the compensation point of ferrimagnets in an external magnetic field is a phase transition of the first kind.

THE magnetic compensation point, predicted by Néel[1] and first detected experimentally by Gorter and Schulkes[2] and by Pauthenet,[3] has been attracting the attention of investigators. Study of various phenomena in the vicinity of $T_C$ is of significant interest because of the fact that the magnetic sublattice structure of a ferrimagnet is exhibited most clearly right at this temperature. Near $T_C$, anomalies have been observed in various properties:[4] the coercive force, the magnetostriction, the $\Delta E$-effect, the magnetocaloric effect, the galvanomagnetic and magneto-optical effects, and others.

In this paper we treat, by the molecular-field method, the anomalies of the magnetic, thermal, and magnetoelastic properties near $T_C$. The most suitable model for explanation of the peculiarities of $T_C$ is provided by the rare-earth ferrite-garnets, both as regards the extent to which they have been studied, and as regards the simplicity of the model itself. As was shown in [5], for the purpose of analyzing the properties of ferrite-garnets at temperatures below the Curie point and in fields up to $\sim 10^4$ Oe, it is possible to use an approximation based on the following assumptions: the tetrahedral and octahedral sublattices of iron ions can be combined into a single sublattice, the exchange interaction between the rare-earth ions and the iron ions is in first approximation determined by the spins alone, and the exchange interaction between the rare-earth ions is negligibly small.

Then the Brillouin functions that describe the temperature behavior of the relative magnetization can be written in the form

$$I_1/I_{10} = \mathscr{B}_{s_1}(y_1), \quad I_2/I_{20} = \mathscr{B}_{s_2}(y_2), \tag{1}$$

$$y_1 = \frac{I_{10}}{n\nu_1 kT} H + \frac{2\mu_B s_1}{kT} H_{1\,\mathrm{eff}}, \tag{2}$$

$$y_2 = \frac{I_{20}}{n\nu_2 kT} H + \frac{2\mu_B s_2}{kT} H_{2\,\mathrm{eff}}, \tag{3}$$

$$H_{1\,\mathrm{eff}} = \frac{z_{12}J_{12}s_2}{\mu_B}\frac{I_2}{I_{20}} + \frac{z_1 J_1 s_1}{\mu_B}\frac{I_1}{I_{10}}, \tag{4}$$

$$H_{2\,\mathrm{eff}} = \frac{z_{21}J_{21}s_1}{\mu_B}\frac{I_1}{I_{10}}. \tag{5}$$

Here quantities related to the sublattice of iron ions are labeled with the index 1, and to the sublattice of rare-earth ions with the index 2; the spins of the ions are denoted by $s_i$; $\nu_i$ is the number of atoms in a molecule of the i-th sublattice; $J_{ij}$ is the exchange integral for interaction of an atom of sublattice i with atoms of sublattice j; $z_{ij}$ is the number of nearest neighbors in sublattice j for an atom of sublattice i; k is Boltzmann's constant; $I_i$ is the magnetization of the i-th sublattice; $I_{i0}$ is the same at 0°K; and n is the number of molecules in unit volume.

Ferrite-garnets fulfill well the conditions for occurrence of $T_C$ at low temperatures: the first (iron) sublattice has a small magnetic moment and strong exchange interaction ($H_{1\,\mathrm{eff}} \sim 1.7 \times 10^6$ Oe), whereas the second (rare-earth) sublattice has a large magnetic moment at 0°K and weak exchange interaction ($H_{2\,\mathrm{eff}} \sim 3 \times 10^5$ Oe); that is, $H_{1\,\mathrm{eff}} \gg H_{2\,\mathrm{eff}}$.[5]

According to experimental data,[3,6] the magnetization of the sublattice of iron ions, $I_1$, and consequently—as is seen from formulas (4) and (5)—also $H_{1\,\mathrm{eff}}$ and $H_{2\,\mathrm{eff}}$, change quite slowly with temperature and magnetic field over the whole interval from 0°K to $T_C$. On the contrary, the magnetization of the sublattice of rare-earth ions, $I_2$, has here a rapid field and temperature dependence. As a result, the rare-earth ions are in a "biasing" effective field $H_{2\,\mathrm{eff}}$ that changes slowly with temperature (rapid changes of $I_1$ and $H_{1\,\mathrm{eff}}$ occur upon approach to the Curie point).

Here we consider the case when the magnetic field and the magnetizations of the sublattices are collinear with one another; this is realized in fields less than $\sqrt{H_A H_{2\,\mathrm{eff}}}$, where $H_A$ is the magnetic anisotropy field (this condition is satisfied in fields up to 10 to 15 kOe). With increase of the field H, angular configurations of the magnetizations appear.[7-9]

The net magnetization of the ferrite-garnet is $I = I_1 + I$ ; for $T < T_C$ we have $I_2 > I_1$, and for $T > T_C$, $I_2 < I_1$. If a magnetic field is applied, the resulting magnetization is oriented along the field; therefore for $T < T_C$ the vector $\mathbf{I}_2$ is directed along the field ($\mathbf{I}_1$ opposite to the field), while for $T > T_C$ it is directed opposite to the field ($\mathbf{I}_1$ along the field). Thus in a magnetic field, the orientations of the sublattices reverse in the vicinity of $T_C$.

Furthermore, in a magnetic field the following fundamental situation occurs: the absolute values of the sublattice magnetizations also undergo changes on passage through $T_C$ (because of the effect of the paraprocess). In fact, it follows from equations (1)–(5) that the magnetization of the rare-earth sublattice near $T_C$ is

$$I_2' = I_{20}\mathcal{B}_{s_2}\left(\frac{I_{20}}{n\nu_2 kT}H + \frac{2\mu_B s_2}{kT}H_{2\,\mathrm{eff}}\right) \tag{6}$$

for $T < T_C$ and

$$I_2'' = I_{20}\mathcal{B}_{s_2}\left(\frac{I_{20}}{n\nu_2 kT}H - \frac{2\mu_B s_2}{kT}H_{2\,\mathrm{eff}}\right) \tag{7}$$

for $T > T_C$, since the external magnetic field is added to the effective exchange field $H_{2\mathrm{eff}}$ for $T < T_C$ and subtracted from it for $T > T_C$. From this it is seen that $|I_2''| < |I_2'|$.

The magnetization of the sublattice of iron ions, $I_1$, undergoes a similar change, except that $|I_1'| < |I_1''|$. Since the paraprocess in this sublattice is very small near $T_C$, this change is considerably smaller than that of the rare-earth lattice and may be neglected.

On passage through the compensation point with $H \neq 0$, the orientations of the sublattice magnetizations and the degree of long-range order in each sublattice change; therefore in a field, there should be observed at the compensation point anomalies of the thermal, magnetoelastic, and other physical properties of a ferrimagnet. We shall examine these anomalies with application to a rare-earth ferrite-garnet.

In calculating the magnetocaloric effect $\delta T$ and the anomaly of the specific heat $\Delta C$ near $T_C$, we use the well-known thermodynamic formulas

$$\delta T = \frac{T(\partial \mathrm{I}/\partial T)_{H,V}}{C_{H,V}}d\mathrm{H}, \tag{8}$$

$$\Delta C = C_{V,H} - C_{V,I} = -T\left(\frac{\partial \mathrm{I}}{\partial T}\right)_{V,H}\left(\frac{\partial \mathrm{H}}{\partial T}\right)_{V,I}. \tag{9}$$

Here $C_I$ is the specific heat in the absence of the spontaneous magnetization, whereas $C_H$ includes the additional part of the specific heat caused by the magnetization.

In order to calculate $\Delta T$ and $\Delta C$, it is necessary to find $(\partial I/\partial T)_{H,V}$ and $(\partial H/\partial T)_{V,I}$. In rare-earth ferrite-garnets near $T_C$, according to the experimental data,[5,6] the relations

$$\left|\frac{\partial I_2}{\partial T}\right| \gg \left|\frac{\partial I_1}{\partial T}\right|, \quad \left|\frac{\partial I_2}{\partial H}\right| \gg \left|\frac{\partial I_1}{\partial H}\right|. \tag{10}$$

are satisfied. From (1)–(3) we get

$$\left(\frac{\partial \mathrm{I}}{\partial T}\right)_{H,V} = -\frac{I_{20}}{kT^2}\frac{\partial \mathcal{B}_{s2}}{\partial \nu_2}\left(\frac{I_{20}}{n\nu_2}\mathrm{H} + 2\mu_B s_2 \mathrm{H}_{2\,\mathrm{eff}}\right). \tag{11}$$

We find the value of $(\partial H/\partial T)_{V,I}$ from the condition that the total differential of the magnetization vanish, $dI(H, T) = 0$, and from the relations (10):

$$\left(\frac{\partial \mathrm{H}}{\partial T}\right)_{V,I} = \frac{1}{T}\left(\mathrm{H} + \frac{2n\nu_2\mu_B s_2}{I_{20}}\mathrm{H}_{2\,\mathrm{eff}}\right). \tag{12}$$

On substituting (11) in (8) and integrating with respect to the field, we get for the magnetocaloric effect

$$\Delta T = \frac{I_{20}}{C_{H,V}\,kT}\frac{\partial \mathcal{B}_{s_2}}{\partial y_2}\mathrm{H}\left(\frac{I_{20}}{2n\nu_2}\mathrm{H} + 2\mu_B s_2 \mathrm{H}_{2\,\mathrm{eff}}\right). \tag{13}$$

Since the vectors H and $H_{2\mathrm{eff}}$ are parallel for $T < T_C$

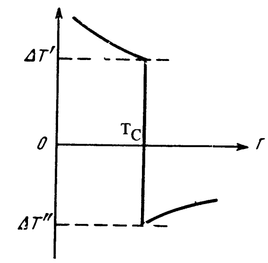


FIG. 1

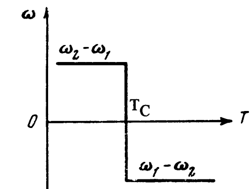


FIG. 2

FIG. 1. Temperature dependence of the magnetocaloric effect near $T_C$.

FIG. 2. Temperature dependence of paraprocess magnetostriction near $T_C$.

and antiparallel for $T > T_C$, and since $H \ll H_{2\mathrm{eff}}$, it follows from (13) that for $T < T_C$, $\Delta T' > 0$, whereas for $T > T_C$, $\Delta T'' < 0$; that is, at the compensation point we have a change of sign and a discontinuity of the magnetocaloric effect. In general $|\Delta T'| > |\Delta T''|$; but in a weak field, $H \ll H_{2\mathrm{eff}}$, these quantities are practically equal. Figure 1 gives a sketch of the behavior of the magnetocaloric effect near $T_C$ according to (13). We note that on going from gadolinium ferrite-garnet to a ferrite-garnet with a lower compensation point, the discontinuity $2\Delta T$ of the magnetocaloric effect, as follows from (13), increases in inverse proportion to the size of the compensation-point temperature. These deductions of the theory have recently been confirmed by measurements of the magnetocaloric effect of rare-earth ferrite-garnets.[10]

On substituting (11) and (12) in (9), we find that the value of the magnetic part of the specific heat is

$$\Delta C = \frac{I_{20}^2}{n\nu_2 kT^2}\frac{\partial \mathcal{B}_{s_2}}{\partial y_2}\left[\left(\frac{2n\nu_2\mu_B s_2}{I_{20}}\mathrm{H}_{2\,\mathrm{eff}}\right)^2 + \frac{4n\nu_2\mu_B s_2}{I_{20}}\mathrm{H}_{2\,\mathrm{eff}}\;\mathrm{H}\right]. \tag{14}$$

Near $T_C$, we may consider $y_2 \ll 1$ to a sufficient degree of accuracy; then we have

$$\mathcal{B}_{s_2}(y_2) \approx \frac{s_2+1}{3s_2}y_2. \tag{15}$$

In view of the fact that $H_{2\mathrm{eff}}H > 0$ for $T < T_C$ and $H_{2\mathrm{eff}}H < 0$ for $T > T_C$, we get for the value of the discontinuity of the specific heat at the compensation point

$$\Delta C' - \Delta C'' = \frac{8}{3}\frac{I_{20}}{kT}(s_2+1)\mu_B H_{2\,\mathrm{eff}}\,H. \tag{16}$$

We consider further the behavior of the magnetoelastic properties near $T_C$. The paraprocess magnetostriction $\omega$ can be found from formulas (6) and (7) and the well-known thermodynamic relation

$$\omega = \frac{1}{V}\left(\frac{\partial V}{\partial \mathrm{H}}\right)_{P,T} = -\left(\frac{\partial \mathrm{I}}{\partial P}\right)_{H,T}.$$

The paraprocess magnetostriction $\omega$ will in general be composed of the paraprocess magnetostrictions $\omega_2$ of the sublattice of rare-earth ions and $\omega_1$ of the sublattice of iron ions: $\omega = \omega_2 - \omega_1$ for $T < T_C$ and $\omega = \omega_1 - \omega_2$ for $T > T_C$.

On neglecting, because of their smallness, terms that take account of the change of density of the specimen and change of the magnetic moments of the atoms under the influence of pressure, an expression for $\omega$

can be obtained, which takes account of the change of magnetization resulting from change of the effective fields under the influence of pressure:

$$\omega_1 = -\left(\frac{\partial I_1}{\partial P}\right)_{H,T} = -I_{10}\frac{2\mu_B s_1}{kT}\frac{\partial \mathcal{B}_{s_1}}{\partial y_1}\left(\frac{\partial H_{1\,\mathrm{eff}}}{\partial P}\right)_{H,T} \quad (17)$$

$$\omega_2 = -\left(\frac{\partial I_2}{\partial P}\right)_{H,T} = -I_{20}\frac{2\mu_B s_2}{kT}\frac{\partial \mathcal{B}_{s_2}}{\partial y_2}\left(\frac{\partial H_{2\,\mathrm{eff}}}{\partial P}\right)_{H,T}. \quad (18)$$

Figure 2 gives schematically the behavior of the paraprocess magnetostriction near $T_C$. The most favorable conditions for observation of the effect of change of sign of the paraprocess magnetostriction occur in gadolinium ferrite-garnet. In other ferrite-garnets, in which the rare-earth ion has an orbital moment, this phenomenon will be masked by the presence of a large anisotropic magnetostriction peculiar to these ferrites. It is to be expected that $\omega_2 \gg \omega_1$, since the paraprocess in the sublattice of iron ions is very small, that is $\omega_2 \approx \omega$.

The part of the thermal expansion that is caused by long-range magnetic order in the sublattices is determined from the thermodynamic relation

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_H - \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_I = -\frac{1}{V}\left(\frac{\partial V}{\partial \mathrm{H}}\right)_T\left(\frac{\partial \mathrm{H}}{\partial T}\right)_{V,I}. \quad (19)$$

On using formulas (17)—(19), we find the coefficient of thermal expansion for $T < T_C$:

$$\alpha' = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_H = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_I + I_{20}\frac{\partial \mathcal{B}_{s_2}}{\partial y_2}\frac{2\mu_B s_2}{kT^2}\left(\frac{\partial H_{2\,\mathrm{eff}}}{\partial P}\right)_{H,T}\cdot\left[H + \frac{2n\nu_2\mu_B s_2}{I_{20}}H_{2\,\mathrm{eff}}\right] \quad (20)$$

and for $T > T_C$:

$$\alpha'' = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_H = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_I - I_{20}\frac{\partial \mathcal{B}_{s_2}}{\partial y_2}\frac{2\mu_B s_2}{kT^2}\left(\frac{\partial H_{2\,\mathrm{eff}}}{\partial P}\right)_{H,T}\cdot\left[H - \frac{2n\nu_2\mu_B s_2}{I_{20}}H_{2\,\mathrm{eff}}\right]. \quad (21)$$

The discontinuity of the coefficient of thermal expansion at the compensation point (in the presence of the field) is

$$\alpha' - \alpha'' = \frac{4\mu_B s_2 I_{20}}{kT^2}\frac{\partial \mathcal{B}_{s_2}}{\partial y_2}\frac{\partial H_{2\,\mathrm{eff}}}{\partial P}H. \quad (22)$$

The entropy of a magnet composed of several magnetic sublattices is not changed if the directions of all the spins of a given sublattice are reversed.[11] Therefore transformations in which the directions of the sublattice magnetizations are merely reversed without change of their magnitudes occur without change of entropy. Consequently, at the compensation point, in the absence of a magnetic field (or in a very weak magnetic field, when there is practically no change of the spontaneous magnetizations of the sublattices), there is also no change of entropy; furthermore, here there is also no change of the exchange-interaction energy, since the antiparallelism of the sublattices is maintained. For this last reason, taking account of the dependence of the exchange integrals on the lattice parameter does not change the character of the transition at $T_C$.

As has already been mentioned earlier (see (6) and (7)), on passage through $T_C$ in a magnetic field there occurs a discontinuous change of the degree of long-range magnetic order in the sublattices; therefore in a magnetic field there should also occur at $T_C$ a discontinuous change of entropy. This suggests that in a magnetic field, the compensation point, at least from the formal side, should possess the properties of a phase transition of the first kind. In the absence of a field, the compensation point is an isolated point on the H-T plane. We shall show that the entropy S, which is a first derivative of the thermodynamic potential $\Phi$ ($S = -(\partial\Phi/\partial T)_P$), experiences a discontinuity at $T_C$ (in the presence of a field).

In fact, by starting from the known thermodynamic relation

$$(\partial S/\partial \mathrm{H})_{T,V} = (\partial \mathrm{I}/\partial T)_{V,H}$$

and formulas (6) and (7), it is possible by integration with respect to the field to calculate the discontinuity of entropy, and consequently also the heat discontinuity of the transition, $\Delta Q = T\Delta S$, at the compensation point:

$$\Delta S = S' - S'' = -\frac{8n\nu_2\mu_B s_2 H_{2\,\mathrm{eff}}}{I_{20}}\frac{\partial \mathcal{B}_{s_2}}{\partial y_2}H. \quad (23)$$

The phase transformation of the first kind is accompanied by a discontinuity of the specific volume. On integrating (20) and (21) with respect to temperature, we determine the discontinuity of specific volume at $T = T_C$:

$$\left(\frac{\Delta V}{V}\right)' - \left(\frac{\Delta V}{V}\right)'' = -\frac{8I_{20}\mu_B s_2}{kT^3}\frac{\partial \mathcal{B}_{s_2}}{\partial y_2}\frac{\partial H_{2\,\mathrm{eff}}}{\partial P}H. \quad (24)$$

Thus at the compensation point in the presence of a field, the entropy and the specific volume experience a break that is characteristic of phase transitions of the first kind.

Finally, we note that the chief reason for the occurrence of anomalies of the coercive force $H_c$ at the compensation point of ferrite-garnets[12] is the paraprocess. The value of $H_c$ is easily found from (1)—(3) and the expansion (15) as the field at which the resultant magnetization becomes zero:

$$I_2 - I_1 = I_{20}\frac{s_2+1}{3s_2}\left(-\frac{I_{20}}{n\nu_2 kT}H_c + \frac{2\mu_B s_2}{kT}H_{2\,\mathrm{eff}}\right) - I_1 = 0.$$

From this we get

$$H_c = \left(\frac{T_K}{T} - 1\right)\frac{1}{\chi_2}I_1. \quad (25)$$

This formula agrees with the results of papers [13,14] at temperatures close to $T_C$. The coercive force vanishes at the compensation point; physically, this is due to the absence of spontaneous magnetization at $T_C$. On departure from $T_C$, the coercive force $H_c$ increases. This is explained by the fact that $H_c$ in this case is the magnetic field that is necessary in order to induce (paraprocess) a magnetization of the rare-earth sublattice equal, but of opposite sign, to the spontaneous magnetization $I_s$ of the ferrimagnet. The value of $I_s$ increases with departure from $T_C$, therefore $H_c$ also increases.

In such ferrimagnets as lithium ferrite-chromite, the paraprocess in the sublattices is small, and full compensation at $T_C$ is absent; therefore $H_c$ does not vanish at the compensation point, and there is observed only an increase of $H_c$ with approach to $T_C$.[15,16] Here the coercive force is determined by a process of irreversible rotation of the spontaneous magnetization of single-domain particles; according to this mechanism, $H_c \sim K/I_s$. Decrease of $I_s$ for $T > T_C$ leads to increase of $H_c$.

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