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LOW-TEMPERATURE SOLID-STATE PHYSICS

Magnetic and Thermal Properties of Single-Crystal $NdFe_3(BO_3)_4$

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Abstract—The neodymium ferroborate $NdFe_3(BO_3)_4$ undergoes an antiferromagnetic transition at $T_N = 30$ K, which manifests itself as a λ-type anomaly in the temperature dependence of the specific heat C and as inflection points in the temperature dependences of the magnetic susceptibility χ measured at various directions of an applied magnetic field with respect to the crystallographic axes of the sample. Magnetic ordering occurs only in the subsystem of Fe^{3+} ions, whereas the subsystem of Nd^{3+} ions remains polarized by the magnetic field of the iron subsystem. A change in the population of the levels of the ground Kramers doublet of neodymium ions manifests itself as Schottky-type anomalies in the $C(T)$ and $\chi(T)$ dependences at low temperatures. At low temperatures, the magnetic properties of single-crystal $NdFe_3(BO_3)_4$ are substantially anisotropic, which is determined by the anisotropic contribution of the rare-earth subsystem to the magnetization. The experimental data obtained are used to propose a model for the magnetic structure of $NdFe_3(BO_3)_4$.

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It has been found that at least two compounds ($GdFe_3(BO_3)_4$, $NdFe_3(BO_3)_4$) of the family of rare-earth ferroborates $RFe_3(BO_3)_4$ (where R is a rare-earth metal ion) have multiferroelectric properties, which imply the coexistence of elastic, magnetic, and electric order parameters [1]. In the latter compound, however, the electric polarization controlled by a magnetic field and the quadratic magnetoelectric effect are much more pronounced [2]. Although rare-earth ferroborates have been studied for a long time, a number of important issues related to the behavior of the systems of transition and rare-earth metals are still unclear.

In this paper, we present the result of an experimentally study of the magnetic and thermal properties of $NdFe_3(BO_3)_4$ single crystals. We measured the magnetic susceptibility $\chi(T)$ and magnetization $M(H)$ in fields as high as 9 T with a Quantum Design SQUID magnetometer and a Quantum Design Physical Properties Measurement System (PPMS) device and measured the specific heat C with Termis and Quantum Design PPMS calorimeters.

The crystal structure of $NdFe_3(BO_3)_4$ (space group D_3^7 ($R32$)) contains spiral chains directed along the trigonal c axis and connected along the edges of the FeO_6 octahedra. Three such chains are connected with each other through NdO_6 prisms and BO_3 triangles, which link the chains into a three-dimensional structure.

The temperature dependences of the magnetic susceptibilities χ_a, χ_b, and χ_c measured along the a, b, and c axes, respectively, are shown in Fig. 1 (here, the b axis is not an axis of crystal symmetry; it is normal to the crystallographic a and c axes). In a high-temperature range, all the curves are virtually coincide and are adequately described by the Curie–Weiss law. A negative value of the Weiss constant ($\Theta \approx -110$ K) indicates an antiferromagnetic character of the main exchange, and the effective magnetic moment ($\mu_{eff} = 11.4\ \mu_B$) is close to the theoretical estimate. At $T_N = 30$ K, the $\chi_{a,b,c}(T)$ and $C(T)$ dependences contain anomalies corresponding to an antiferromagnetic transition in the Fe^{3+} ion subsystem. The anomalies in the $\chi_a(T)$ and $\chi_b(T)$ dependences at $T \approx 6$ K and the Schottky-type anomaly in the $C(T)$ curve at $T \approx 4$ K are not related to ordering in the rare-earth subsystem [3]. They are caused by a change in the population of the levels of the ground Kramers doublet of Nd^{3+} ions split by the magnetic field created by the ordered Fe^{3+} ion subsystem. The contribution of the neodymium subsystem to the specific heat at $T < T_N$ is determined by splitting Δ:

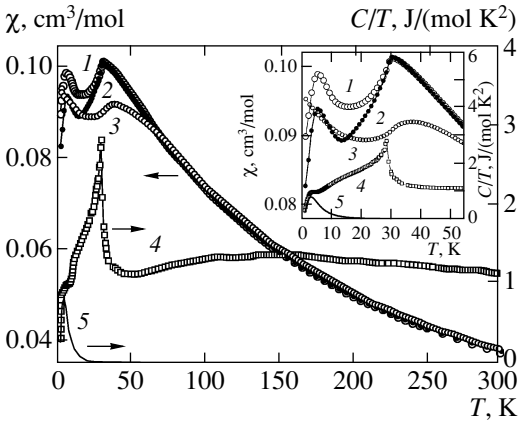

Fig. 1. Temperature dependences of the magnetic susceptibility χ measured along the (*1*) *a*, (*2*) *b*, and (*3*) *c* axes in a field $H = 1$ kOe and (*4*) the specific heat C measured in zero field. (*5*) The contribution $C^{Nd}(T)$ of the neodymium subsystem to the specific heat (Schottky-type anomaly) calculated by Eq. (1) for a splitting $\Delta \approx 12.4$ K = 8.6 cm^{-1} in the ground Kramers doublet of the Nd^{3+} ion. The inset shows these dependences in a smaller temperature range.

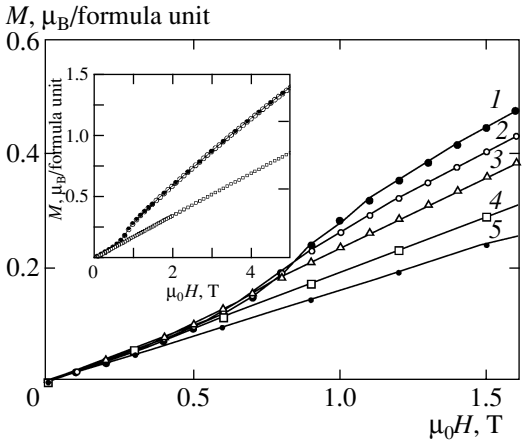

Fig. 2. Field dependences of the magnetization in a field H parallel to the *a* axis at various temperatures: T = (*1*) 2, (*2*) 6, (*3*) 10, (*4*) 28, and (*5*) 70 K. The inset shows the field dependences of the magnetization in a field H parallel to the (○) *a*, (●) *b*, and (□) *c* axes at $T = 2$ K.

$$C^{Nd} = R\left(\frac{\Delta}{T}\right)^2 \frac{e^{\Delta/T}}{\left(e^{\Delta/T}+1\right)^2}, \qquad (1)$$

where R is the gas constant. The $C^{Nd}(T)$ dependence shown in Fig. 1 agrees well with the experimental data at $\Delta \approx 12.4$ K = 8.6 cm^{-1}. This estimated splitting is consistent with spectroscopic data: $\Delta = 8.8$ cm^{-1} at low temperatures [4].

At $T \le T_N$, the difference in the magnetic response of the $NdFe_3(BO_3)_4$ single crystal observed when a magnetic field is directed along the trigonal *c* axis or normal to it is caused by an anisotropic contribution of the rare-earth and iron subsystems to the magnetization. When the magnetic field is oriented along the *c* axis, the magnetization increases linearly with magnetic field (see the inset to Fig. 2). Therefore, we can assume that the magnetic moments of Nd^{3+} ions and the antiferromagnetism vector **L** of the iron subsystem lie in the plane that is normal to the *c* axis of the crystal. For this orientation of the magnetic moments of Fe^{3+} ions with respect to an applied magnetic field, the contribution of the iron subsystem to the total magnetization should be temperature-independent. The weak experimental temperature dependence of the slope of $M(H)$ for a field H applied along the *c* axis indicates that the influence of the rare-earth subsystem is weak. This means that the g_c component of the *g* tensor of the ground Kramers doublet of the Nd^{3+} ion along the trigonal *c* axis is smaller than the g_a component in the *ab* plane. The small value of g_c causes a hyperbolic temperature dependence of the magnetic susceptibility of the rare-earth subsystem and the absence of a Schottky-type anomaly in the $\chi_c(T)$ curve.

The $M_a(H)$ and $M_b(H)$ dependences measured in fields parallel to the *a* and *b* axes, respectively, are virtually the same: they are substantially nonlinear and have different curvatures at $H \le H_{cr}$ and $H \ge H_{cr}$ ($H_{cr} \approx 1$ T). To interpret the observed effect, we note that, in a field of trigonal symmetry, the basal plane of $NdFe_3(BO_3)_4$ has three twofold axes. At low temperatures and weak magnetic fields, the subsystem of Fe^{3+} ions can be considered as an antiferromagnet in which every pair of magnetic sublattices coupled by exchange interaction is characterized by an antiferromagnetism vector **L** that can be equiprobably directed along one of the three equivalent *a* axes in the crystal. Note that all magnetic moments of iron in one *ab* plane are codirected. During magnetization in fields up to 1 T, vectors **L** rotate and become normal to an applied magnetic field; however, the processes of magnetization of the iron subsystem in fields **H** directed along the *a* and *b* axes occur in different ways. When an applied magnetic field is directed along one of the *a* axes, a spin-flop transition occurs in the sublattices where vector **L** is collinear with this *a* axis, and two other **L** vectors rotate smoothly at the same rate toward the direction normal to the applied field. When a field **H** is directed along the *b* axis, one of the **L** vectors is already normal to this field and two others rotate at different rates. Under the action of the effective field acting on Nd^{3+} ions, some of the neodymium sublattices are magnetized and the other sublattices are demagnetized. The magnetization of the iron and rare-earth subsystems specify the $M(H)$ dependence at $H < 1$ T at various temperatures. This model of the magnetic structure in weak fields well describes the position of the Schottky-type anomaly in the $\chi_a(T)$ and $\chi_b(T)$ dependences at $T \approx 6$ K. In terms of

the model of a conventional two-sublattice antiferromagnet, this anomaly should be observed at a higher temperature.

The behavior of the magnetization of the $NdFe_3(BO_3)_4$ single crystal in a magnetic field applied in the *ab* plane at $H \geq 1$ T is explained by the fact that the antiferromagnetism vector **L** of the iron subsystem is uniform throughout the sample and normal to the field direction. As the magnetic field increases, the iron sublattices become canted toward the field direction, which results in a linear contribution to the field dependence of the magnetization from the iron subsystem:

$$M^{\mathrm{Fe}} = \chi_{\perp} H,$$

where $\chi_{\perp}$ is the transverse magnetic susceptibility. The rare-earth subsystem can be represented in the form of two sublattices each of which has a magnetic-moment component along an applied field. The contribution of the rare-earth subsystem to the magnetization is caused by the splitting of the ground Kramers doublet of the Nd^{3+} ion by the effective field H_{eff} created by the iron subsystem–induced field H_{ex} and the applied field H:

$$M^{\mathrm{Nd}} = \frac{g_a \mu_{\mathrm{B}}}{2} \tanh \frac{g_a \mu_{\mathrm{B}} H_{\mathrm{eff}}}{2kT} \cos\beta, \qquad (2)$$

$$H_{\mathrm{eff}} = \sqrt{H_{\mathrm{ex}}^2 + H^2 + 2H_{\mathrm{ex}} H \cos\alpha}, \qquad (3)$$

where α is the angle the spin of the Fe^{3+} ion makes with the applied-field direction and β is the angle between the magnetic moment of the Nd^{3+} ion and the magnetic field,

$$\cos\beta = \frac{H_{\mathrm{eff}}^2 + H^2 - H_{\mathrm{ex}}^2}{2HH_{\mathrm{eff}}}.$$

The magnetic field H_{ex}, which results in the splitting Δ of the ground Kramers doublet of Nd^{3+} ions (in the absence of an applied magnetic field H), is connected with this splitting by the relation

$$g_a H_{\mathrm{ex}} \mu_{\mathrm{B}} = k\Delta,$$

where k is the Boltzmann constant. At $H > 1$ T, the experimental $M(H)$ curves are well described by the sum of the contributions from the iron (M^{Fe}) and neodymium (M^{Nd}) subsystems at $g_a = 2.3$ and $H_{\mathrm{ex}} = 8$ T for Nd^{3+} ions and at $\chi_{\perp}^{a} = 0.16\mu_{\mathrm{B}}$/T for Fe^{3+} ions. The difference in the values estimated from the $M_c(H)$ and $M_a(H)$ dependences ($\chi_{\perp}^{c} = 0.17\ \mu_{\mathrm{B}}$/T and $\chi_{\perp}^{a} = 0.16\ \mu_{\mathrm{B}}$/T, respectively) is caused by the small contribution of the rare-earth subsystem to the magnetization in the case when a field is applied along the *c* axis.

The experimental data on the magnetic and thermal properties of the neodymium ferroborate $NdFe_3(BO_3)_4$ suggest that magnetic ordering in this compound at $T_{\mathrm{N}} = 30$ K occurs only in the subsystem of Fe^{3+} ions, whereas the subsystem of Nd^{3+} ions remains polarized by the magnetic field of the iron subsystem. A change in the population of the levels of the ground Kramers doublet of neodymium ions manifests itself as Schottky-type anomalies in the $C(T)$ and $\chi(T)$ dependences at low temperatures. At low temperatures, the magnetic properties of single-crystal $NdFe_3(BO_3)_4$ are substantially anisotropic, which is determined by the anisotropic contributions of the rare-earth and iron subsystems to the magnetization. Based on the experimental data obtained, we proposed a model for the magnetic structure of $NdFe_3(BO_3)_4$.

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