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Paramagnetic Properties of Rare Earth Chromium Borates at High Temperatures

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Temperature dependence of the magnetic susceptibility $\chi(T)$ is studied in compounds of $GdCr_3(BO_3)_4$ and $ErCr_3(BO_3)_4$ by the Faradey method in the wide temperature range (293–1200 K). The dependences $\chi^{-1}(T)$ for all crystals show the nonlinear anomalies caused by structural transitions in the crystals. The $\chi^{-1}(T)$ dependences for paramagnetic phase follow the linear Curie–Weiss law. The Curie's temperature and values of magnetic moments corresponding to the chemical formula of the crystals are found.

Key words: exchange interaction, paramagnetic temperature, magnetic susceptibility, magnetic moment, law of Curie–Weiss, the rare earth borates.

Методом Фарадея в інтервалі 293–1200 К виміряно температурну залежність магнетної сприйнятливості $\chi(T)$ рідкоземельних боратів $GdCr_3(BO_3)_4$ та $ErCr_3(BO_3)_4$. У залежностях $\chi^{-1}(T)$ спостерігаються нелінійні аномалії, обумовлені структурними переходами. Встановлено, що залежності $\chi^{-1}(T)$ для парамагнетної фази описуються лінійним закон Кюрі–Вейса. Знайдено температури Кюрі та магнетні моменти, які відповідають хемічній формулі кристалів.

Ключові слова: обмінна взаємодія, парамагнетна температура, магнетна

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сприйнятливість, магнетний момент, закон Кюрі–Вейса, борати рідкоземельних елементів.

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1. INTRODUCTION

Among the rare earth (RE) borates, compounds with 4*f*- and 3*d*-elements are especially attractive, which have unique optical, magnetic, and mechanical properties. These include RE borates $RM_3(BO_3)_4$, where R = RE metal (REM) and M = Fe, Al, Ga, Sc, Cr [1]. Some of the members of this family belong to the class of multiferroics [2]. In works [2–4] it is shown that for RE of ferroborates the magnetoelectric effect reaches 400–500 $\mu C/m^2$ in a magnetic field of 10 kOe. The search for new similar materials is interesting from the point of view of fundamental physics of condensed matter, as well as for practical applications in optoelectronics and spintronics.

These borates are predominantly isostructural to the huntite mineral $CaMg_3(CO_3)_4$ with the space group *R*32 [5].

The crystal structure of huntite consists of three basic units: trigonal prisms CaO_6, octahedra MgO_6, and triangular groups of two types $CO_3(1)$ and $CO_3(2)$. MgO_6-octahedra are connected by common edges, forming chains located along the C_3 axis. CaO_6-prisms connect these chains to each other (Fig. 1).

Recent publications contain data on the magnetic properties of $GdCr_3(BO_3)_4$ [6] obtained at cryogenic temperatures, *i.e.* in its magnetically ordered state. As far as we know, similar studies on the rest of rare earth chromium borates have not been carried out, and at high temperatures [11–14].

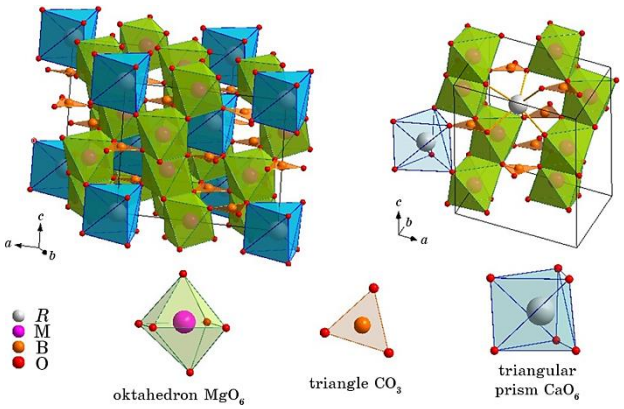

Fig. 1. Crystal structure of $CaMg_3(CO_3)_4$.

The purpose of this work is to determine the crystallization conditions, identify the phases obtained during the crystal synthesis and the magnetic characteristics of $RCr_3(BO_3)_4$ (R—Gd, Er) crystals based on measuring the temperature dependence of the magnetic susceptibility $\chi(T)$ in the temperature range 300–1200 K.

The dependence $\chi(T)$ of the RE of chromium borates is measured by the relative Faraday method (using a standard) with the help of a high-temperature pendulum balance in excess atmospheric pressure of purified helium [7]. The maximum relative error in measuring χ is no more than 3%.

2. RESULTS AND ITS DISCUSSION

2.1. Crystal Growth

The borates under study are obtained as a result of spontaneous crystallization from high-temperature solutions-melts. Crystals $GdCr_3(BO_3)_4$ and $ErCr_3(BO_3)_4$ are synthesized by a similar technique from a solution in a melt based on K_2SO_4–$3MoO_3$. At this, their concentration in the initial solution-melt ranged from 17 to 40% wt. Taking into account the tendency of RE chromium borates to form similar paleotypic rhombohedral ($R32$) and monoclinic ($C2/c$) structures, depending on the characteristics and conditions of their crystallization, the belonging to one or another polytype is determined by IR spectroscopy [8, 9].

2.2. Magnetic Properties

The experimental dependences $\chi^{-1}(T)$ of the considered chromium borates are shown in Figs. 2 and 3. It can be seen from the figures that two breaks are observed in these dependences. For $ErCr_3(BO_3)_4$, they are observed at 733 K and 918 K (Fig. 2), and for $GdCr_3(BO_3)_4$—at 588 K and 913 K (Fig. 3).

It should be noted that for these compounds, after the first break, the slope of the dependence $\chi^{-1}(T)$ ($d\chi^{-1}(T)/dT$) decreases, and after the second break, it increases. The dependences $\chi^{-1}(T)$ before and after the breaks are linear, which indicates their subordination to the linear Curie–Weiss law:

$$\chi = \frac{C}{T - \theta_P}, \tag{1}$$

where C is the Curie–Weiss constant, θ_P is the paramagnetic Curie temperature.

It is inexpedient to associate the observed breaks in the dependence

$\chi^{-1}(T)$ of the studied borates with magnetic phase transitions, since their magnetoactive components Gd, Er, and Cr have a magnetically ordered state below room temperature. On the other hand, according to [6], $GdCr_3(BO_3)_4$ exhibits an antiferromagnetic ordered state below 7 K.

The experimental dependences $\chi(T)$ of the studied borates can be described as follows. The crystal structure consists of two magnetic sublattices (subsystems): R (R = Gd, Er) and M (M = Cr). Both magnetic subsystems contribute to the magnetic susceptibility of the considered borates:

$$\chi = \chi^{R} + \chi^{M}. \tag{2}$$

In the case of wide multiplets ($\Delta E >> k_B T$, where ΔE is the energy difference between the ground and the first excited level of 4*f*-electrons), according to the Van Vleck theory of paramagnetism [10], the following expression can be written for the dependence $\chi(T)$ of the subsystems of the studied borates:

$$\chi^{R} = \frac{N_A}{A}\frac{g_J^2 \mu_B^2 J(J+1)}{3k_B T} = \frac{N_A}{A}\frac{\mu_J^2}{3k_B T}, \tag{3}$$

where $\mu_J = g_J(J(J+1))^{1/2}\mu_B$ are the effective numbers of magnetic moments per one free RE ion, J is the quantum number of the total mechanical moment of the ground state of the RE ion, N_A is the Avogadro number, A is the atomic mass of the REM.

In the case of narrow multiplets ($\Delta E << k_B T$) for the dependence $\chi(T)$ of the M subsystem, according to the Van Vleck theory and taking into account the effect of 'freezing' the orbital moments ($L = 0$) of 3*d*-

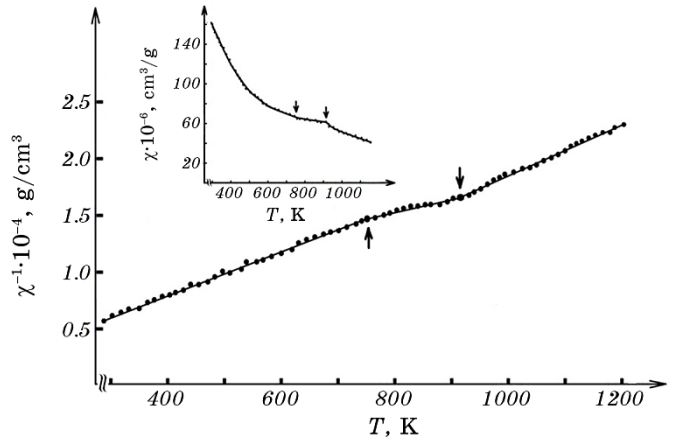

Fig. 2. Dependences $\chi^{-1}(T)$ ($\chi(T)$ in the inset) for $ErCr_3(BO_3)_4$.

electrons, we can write the following expression:

$$\chi^{M} = \frac{N_A}{A}\frac{g_S^2\mu_B^2 S(S+1)}{3k_B T} = \frac{N_A}{A}\frac{\mu_S^2}{3k_B T}, \quad (4)$$

where $\mu_S \approx 2(S(S+1))^{1/2}\mu_B$ are the effective numbers of magnetic moments per one ion Cr^{3+}, S is the quantum number of the total spin mechanical moment of the ground state of the M ion, A is the atomic mass of Cr.

The magnetic interaction between the R–R, M–M and R–M ions is specified through the parameter θ_P, which is proportional to the energy of these interactions. This is taken into account in formulas (3) and (4) by replacing T by $T - \theta_P$, as a result of which the expression for the empirical Curie–Weiss law (1) for each subsystem, respectively, is obtained.

From the experimental dependences $\chi^{-1}(T)$ of the studied borates according to (1), their main magnetic characteristics θ_P and C are determined, and then, from the value of C, the experimental values of the magnetic moments per formula unit ($GdCr_3(BO_3)_4$ or $ErCr_3(BO_3)_4$) are calculated according to the following expression [obtained from (3) or (4) taking into account (1)]:

$$\mu_{eff} = \frac{1}{\mu_B}\sqrt{\frac{3k_B MC}{N_A}}\mu_B = 2{,}83\sqrt{MC}\mu_B, \quad (5)$$

where M is the molar mass of borate (for example, for $GdCr_3(BO_3)_4$ $M = M_{Gd} + 3M_{Cr} + 4M_B + 12M_O$).

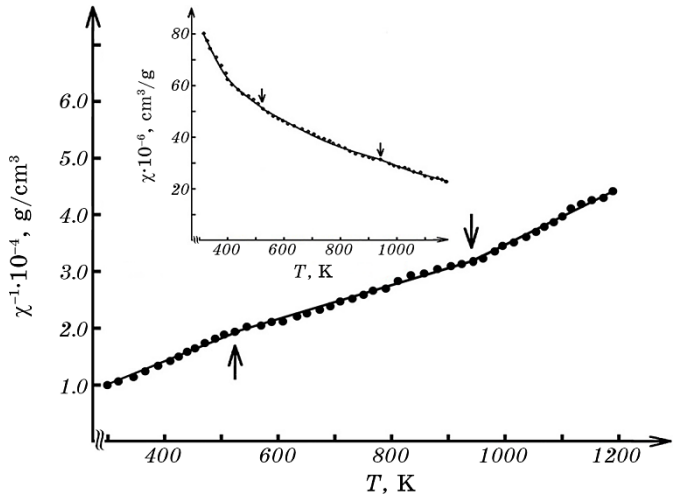

Fig. 3. Dependencies $\chi^{-1}(T)$ ($\chi(T)$ in the inset) for $GdCr_3(BO_3)_4$.

TABLE 1. Main magnetic characteristics of the studied borates.

Sample	Temperature interval, K	θ_P, K	C, 10^{-2}sm^3·K·g^{-1}	μ_{exp}, μ_B	μ_{theor}, μ_B
$ErCr_3(BO_3)_4$	293–733	–36	5.22	15.28	11.7
	733–918	–759	9.80	20.94	
	918–1123	358	3.36	12.26	
$GdCr_3(BO_3)_4$	293–498	–547	2.69	10.87	10.4
	498–913	–703	3.60	12.58	
	913–1173	–257	1.91	9.16	

The theoretical value of the magnetic moments per one chemical formula can be determined by the additivity rule [6]:

$$\mu^2_{theor} = 3\mu^2_M + \mu^2_R = 3g^2_M S_M(S_M + 1) + g^2_R J_R(J_R + 1).$$

The values θ_P, C, μ_{exp} for the compounds under study are presented in Table 1. Analysis of the table shows that the μ_{exp} value for $GdCr_3(BO_3)_4$ ($10.87\mu_B$) satisfactorily corresponds to the results of [6, 15] ($10.6\mu_B$) and the value μ_{theor} ($10.4\mu_B$), for the polymorphic phase state before the first break. For the remaining phase states of this crystal and all phase states of the $ErCr_3(BO_3)_4$ crystal, such a correspondence is not observed.

3. CONCLUSION

Based on the results obtained, the following conclusions can be drawn:
1. For the first time, the dependences of the susceptibility $\chi(T)$ of rare earths of chromium borates $GdCr_3(BO_3)_4$ and $ErCr_3(BO_3)_4$ have been measured in a wide temperature range (300–1200 K). It is found that these dependences are satisfactorily described by the Van Vleck theory of paramagnetism.
2. Based on the dependence $\chi^{-1}(T)$ of the studied borates, the main magnetic characteristics are calculated—the paramagnetic Curie temperature θ_P, the Curie–Weiss constant C and the magnetic moment corresponding to their chemical formula.

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