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MAGNETISM AND FERROELECTRICITY

Magnetic Anisotropy of the VBO_3 and $CrBO_3$ Transition-Metal Borates

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Abstract—Temperature and field dependences of the magnetization of VBO_3 and $CrBO_3$ single crystals with the magnetic field applied parallel and perpendicular to the (111) basal plane were measured. VBO_3 was found to have a considerable uniaxial anisotropy with a field $H_a \approx 6.25$ T. $CrBO_3$ was shown to exhibit not only uniaxial but also hexagonal anisotropy. The experimental anisotropy constants were estimated, and their temperature dependences are presented. © *2003 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

Transition metal borates with the chemical formula ABO_3 (A = Fe, V, Cr, Ti) are attracting interest in connection with the rich variety of physical properties exhibited in this isostructural series [1]. Although the Mott–Hubbard strongly correlated dielectric oxides of the 3*d* metals have been investigated intensely due to their nontrivial physical properties, such as the high-temperature superconductivity of cuprates and the colossal magnetoresistance of manganese oxides, a number of the ABO_3 3*d*-metal borates, except $FeBO_3$, remain very poorly studied. As for the VBO_3 and $CrBO_3$ compounds, considered in this study, the literature does contain sufficient information to draw well-grounded conclusions concerning their magnetic structure [2–4], but there are practically no available data on their magnetic anisotropy. Knowledge of the magnitude and character of the anisotropic interactions are essential both to the understanding of the nature of the static and dynamic properties and to searching for possible applications of these materials.

The crystal lattices of the ABO_3 compounds belong to the rhombohedral symmetry group. A number of magnetic structures can exist in these compounds, depending on the actual filling of the *d* shell. For instance, VBO_3 is a collinear ferromagnet with a Curie temperature $T_C \approx 32$ K, $FeBO_3$ is a weak ferromagnet with the Néel temperature $T_N = 348$ K, and $CrBO_3$ is tentatively identified [2] as a collinear two-sublattice antiferromagnet with $T_N = 15$ K and magnetic moments aligned with the (111) threefold symmetry axis. The electron configurations of the magnetic ions V^{3+}, Fe^{3+}, and Cr^{3+} are d^2, d^5, and d^3, respectively. The main mechanism responsible for magnetic order in these compounds is believed to be indirect 90° exchange mediated by the O^{2-} anions.

Of the whole series of the 3*d*-metal borates, experimental studies of the magnetic anisotropy have thus far been performed on $FeBO_3$ only. This compound is known to be an easy-plane weak ferromagnet. A review of experimental data on the magnetic anisotropy of $FeBO_3$ single crystals can be found in [5]. As justly pointed out in [5], there is unfortunately some disagreement between the experimental data on the anisotropy of $FeBO_3$. For instance, the value of the uniaxial-anisotropy field H_a quoted in early studies [6, 7] is approximately 6.25–6.30 T, while in [8] this value is believed to be the sum of the contributions due to both the anisotropy and the Dzyaloshinski fields. In later studies [9, 10], the uniaxial-anisotropy field H_a, as derived from the data on the antiferromagnetic resonance, is reported to be 0.31–0.33 T, whereas the hexagonal anisotropy is considerably weaker and the corresponding field does not exceed 10^{-4} T.

The present communication reports on an experimental study of the temperature and field dependences of magnetization of VBO_3 and $CrBO_3$ single crystals.

2. SAMPLES AND EXPERIMENTAL TECHNIQUES

VBO_3 and $CrBO_3$ single crystals were grown by spontaneous crystallization from melt solutions of the systems M_2O_3–B_2O_3–(70 wt % PbO + 30 wt % PbF_2), where M = V, Cr. The single crystals obtained were thin plates up to 4×4 mm in size and about 0.1 mm thick, with a smooth lustrous surface. Unfortunately, the VBO_3 plates had an irregular shape, thus making in-plane anisotropy measurements impossible; the $CrBO_3$ single crystals were shaped as regular hexagonal plates.

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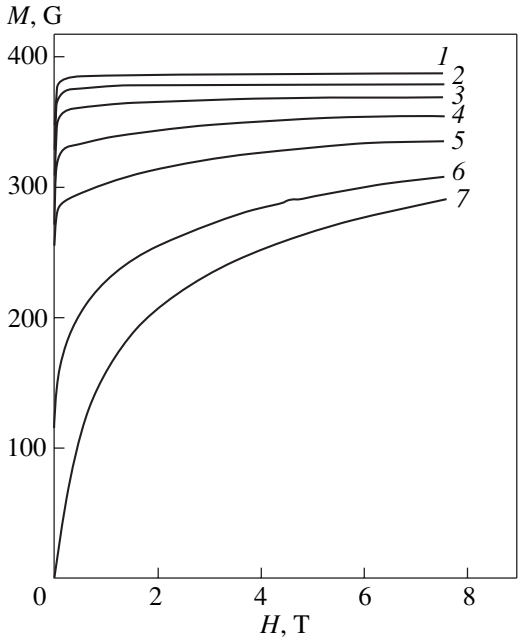

Fig. 1. Magnetic-field dependences of the magnetization of a VBO_3 single crystal measured in a magnetic field parallel to the (111) basal plane at different temperatures *T*: (*1*) 4.2, (*2*) 10, (*3*) 15, (*4*) 20, (*5*) 25, (*6*) 30, and (*7*) 32 K.

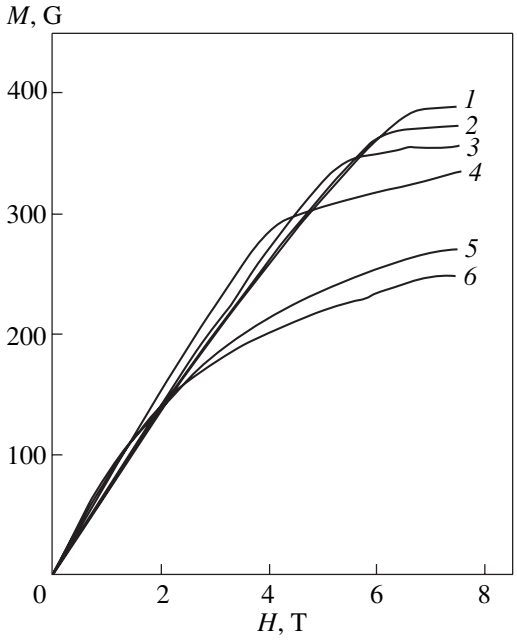

Fig. 2. Magnetic-field dependences of the magnetization of a VBO_3 single crystal measured in a magnetic field perpendicular to the (111) basal plane at different temperatures *T*: (*1*) 4.2, (*2*) 10, (*3*) 15, (*4*) 20, (*5*) 30, and (*6*) 32 K.

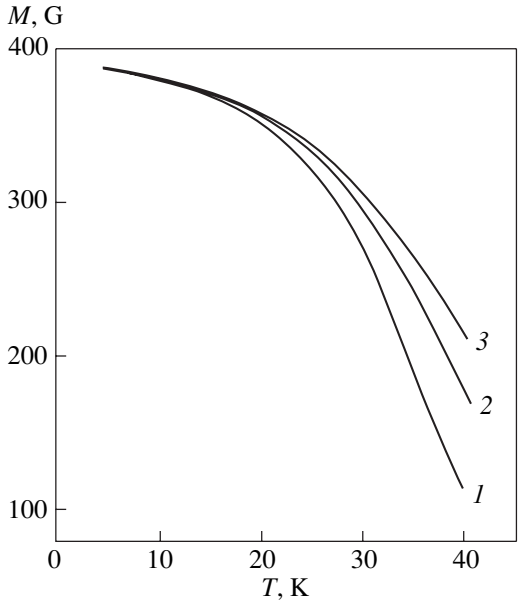

Fig. 3. Temperature dependences of the magnetization of a VBO_3 single crystal measured in a magnetic field parallel to the (111) basal plane for different values of the magnetic-field *H*: (*1*) 2, (*2*) 4, and (*3*) 6 T.

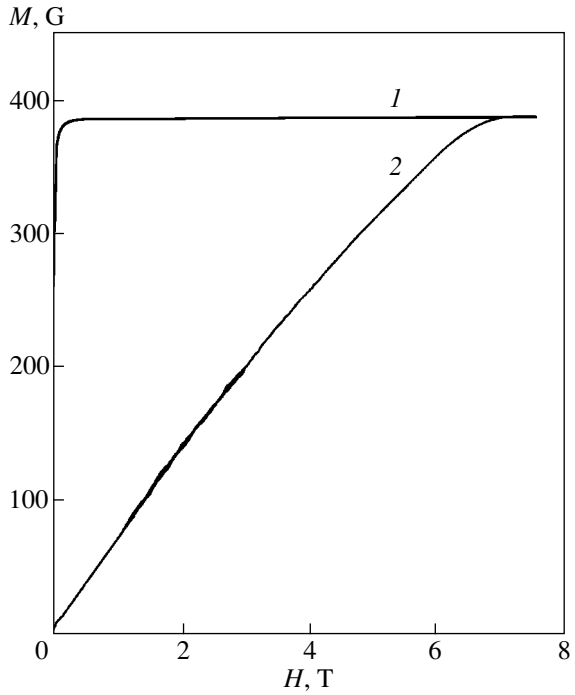

Fig. 4. Magnetization curves of VBO_3 in a magnetic field (*1*) parallel and (*2*) perpendicular to the (111) plane obtained at $T = 4.2$ K.

The temperature and magnetic field dependences of magnetization were performed using a vibrating-sample magnetometer with a superconducting solenoid within the temperature range 4.2–350 K and in magnetic fields of up to 7.5 T [11].

3. EXPERIMENTAL RESULTS

The magnetic-field dependences of the magnetization $M(H)$ measured at various temperatures on VBO_3 single crystals in fields parallel and perpendicular to the

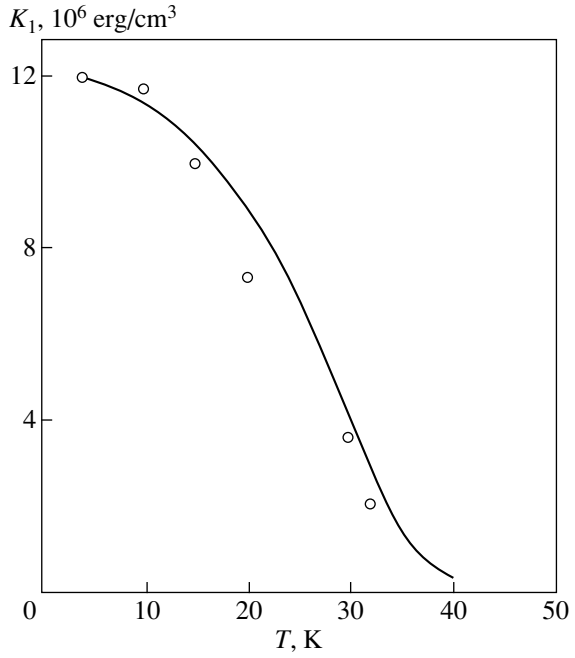

Fig. 5. Experimental (circles) and calculated (solid line) temperature dependences of the uniaxial-anisotropy constant of VBO_3.

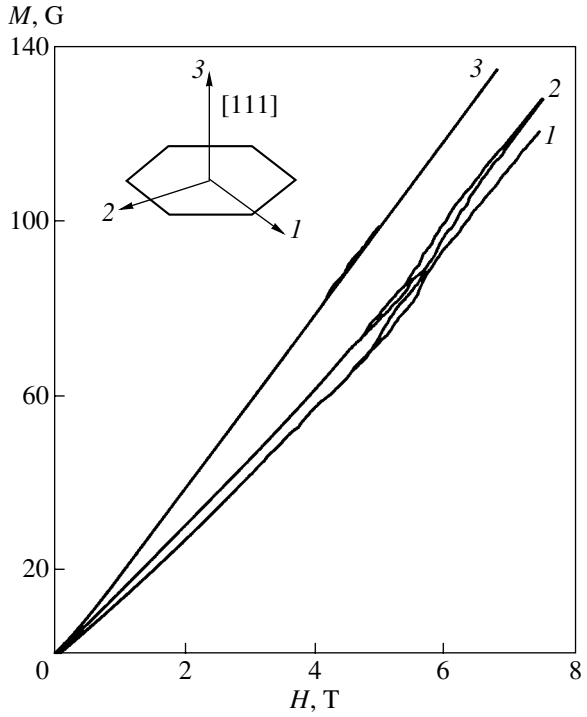

Fig. 6. Magnetization curves of a $CrBO_3$ single crystal obtained at T = 7.6 K.

(111) basal plane, which coincided with the plane of the plate, are displayed in Figs. 1 and 2, respectively, with due account of the demagnetization factor. The field orientation in the plane was chosen arbitrarily, because preliminary measurements showed the in-plane anisotropy to be negligible compared with the uniaxial one. Figure 3 displays temperature dependences of the magnetization $M(T)$ measured in various fields parallel to the plane of the crystal plate. As seen from Figs. 1–4, the behavior of the VBO_3 magnetization is characteristic of easy-plane ferromagnets [12]. The first uniaxial-anisotropy constant K_1, as calculated using the area method, was found to be approximately 1.2×10^7 erg/cm^3 (T = 4.2 K), which corresponds to a magnetic-anisotropy field H_a = 6.25 T. This is the largest value among the anisotropy fields of known rhombohedral antiferromagnets [13].

Figure 5 compares the experimental temperature dependence of the uniaxial-anisotropy constant for VBO_3 (symbols) with a theoretical curve calculated from the relation [14]

$$K_1(T) = K_{10}\left(\frac{M(T)}{M_S}\right)^3,$$

where K_{10} is the value of K_1 at T = 4.2 K, $M(T)$ is the VBO_3 magnetization in a field of 2 T, and M_S is the saturation magnetization. The experimental dependence is seen to be in good agreement with the calculated curve.

Using the paramagnetic Curie temperature Θ = 34 K determined in [2] and the magnetic moment $M = 1.8\mu_B$ measured by us earlier [1], we estimated the exchange field in VBO_3 as $H_E \approx 78.2$ T; this figure is lower by an order of magnitude than that for $FeBO_3$.

The magnetization curves for $CrBO_3$ are displayed in Fig. 6 for three magnetic field directions. Curves *1* and *2* correspond to two directions in the basal plane; namely, direction *1* points to the corner of the hexagonal plate, and direction *2* is perpendicular to a side of the plate. Curve *3* corresponds to the magnetic field aligned with the [111] axis. The magnetic field orientations are shown in the inset to Fig. 6. Figure 7 plots temperature dependences of the magnetization in a field of 0.5 T oriented in directions *1* and *3*.

As seen from Fig. 6, the $M(H)$ curve for $CrBO_3$ measured in the [111] direction is a straight line without any features, which apparently corresponds to the sublattice magnetization vectors canting toward the magnetic field direction. At the same time, the magnetization curves measured in an in-plane field exhibit a break in the interval 5–6 T; this break is accompanied by hysteresis and noise, which indicate instability of the magnetic state occurring in this field interval. According to [12], this instability may reflect that the exchange and anisotropic interactions compete with the effect of the external magnetic field. Thus, application of an in-plane magnetic field apparently initiates a spin-reorientation transition. This conjecture is buttressed by the hysteresis observed in the temperature dependences of magnetization (Fig. 8). A similar spin-reorientation phase transition was also observed to occur in the Cr_2O_3

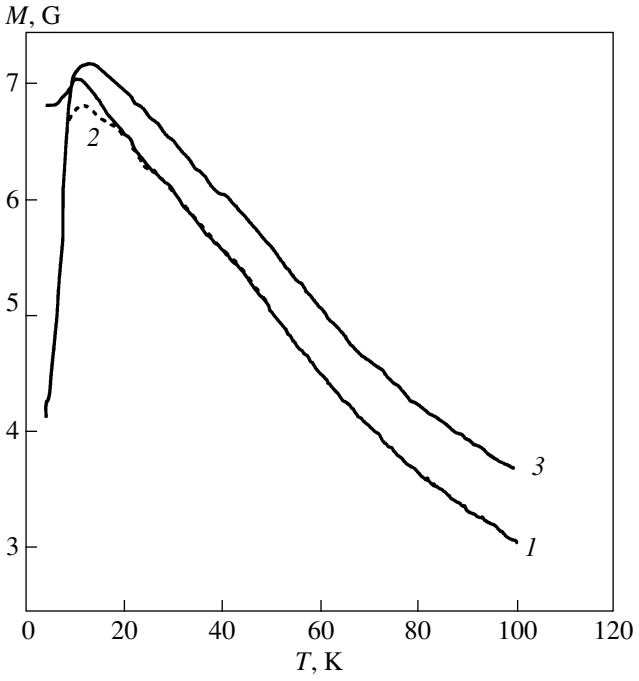

Fig. 7. Temperature dependences of the magnetization of a $CrBO_3$ single crystal measured in a magnetic field of 0.5 T.

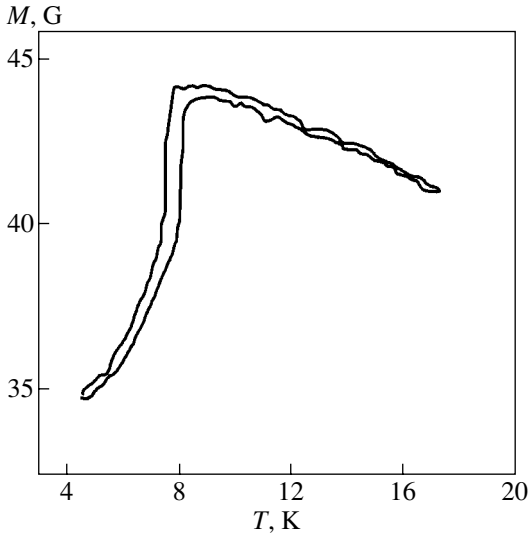

Fig. 8. Temperature dependence of the magnetization of $CrBO_3$ measured in a magnetic field of 7.5 T in direction *1*.

isostructural compound in the same critical-field interval [15]. The ratio of the magnetic susceptibilities corresponding to the directions parallel and perpendicular to the basal plane is approximately 1.24 in the low-field region. In the high-field region, curves *1–3* in Fig. 6 have similar slopes, which possibly corresponds to a magnetic susceptibility $\chi_\perp \approx 2 \times 10^{-3}$ in a magnetic field perpendicular to the antiferromagnetism vector.

Our set of experimental data does not permit us to fit the magnetic properties of $CrBO_3$, as was done in [2], to a simple model of a collinear two-sublattice antiferromagnet with magnetic moments aligned with the [111] axis. It appears more likely that the antiferromagnetism vector of $CrBO_3$ makes a small angle with the basal plane, because when the crystal is magnetized perpendicular to (111), the $M(H)$ relation has a simple shape characteristic of the sublattice magnetic moments being canted toward the magnetic field. At the same time, the existence of hysteresis and of a region of magnetic-state instability with magnetization produced along mutually perpendicular crystallographic directions *1* and *2* in the basal plane apparently implies that neither of these two directions is the easiest magnetization axis. Otherwise, one of the two magnetization curves would be a straight line, whereas the other would exhibit a more or less pronounced jump or break corresponding to a spin flop. Thus, the magnetic structure of $CrBO_3$ is apparently more complex than was assumed in [2] and magnetization experiments alone cannot determine this structure reliably. Our experimental data should be correlated with studies of neutron scattering, AFMR, measurements of magnetostriction or ultrasound propagation through the sample, etc.

By extrapolating the $M(H)$ dependence to high fields using the $\chi_\perp$ value found above, we estimated the exchange field E in $CrBO_3$ to be 38.2 T. The totality of our results is presented in the table together with known data for $FeBO_3$.

4. DISCUSSION OF RESULTS

As is evident from the experimental data presented above, the anisotropic properties of the $FeBO_3$, VBO_3, and $CrBO_3$ borates exhibit both common features and substantial differences. A common feature is that the dominant component of the magnetic moment in all three compounds apparently lies in the (111) plane. The anisotropies of these compounds are naturally different

Magnetic properties of $FeBO_3$, VBO_3, and $CrBO_3$

Compound	$T_{C,N}$, K	μ_S, μ_B	H_a, T	K_1, erg/cm^3	H_E, T
$FeBO_3$	348	5.9	0.3 [10]		580 [5]
VBO_3	32 [2]	1.81	6.25	12×10^6	78.2
$CrBO_3$	15 [2]	3.73 [2]			38.2

in magnitude due to the types of magnetic ordering in these compounds being completely different.

The problem of the nature of magnetic anisotropy cannot be considered solved at present even for the well-known compound $FeBO_3$. Although the *S* state with zero orbital magnetic moment is the ground state of the Fe^{3+} ion, it is believed [16] that, in addition to the magnetic dipole interaction, the single-ion mechanism contributes noticeably to the anisotropy and that the orbital magnetic moment is induced by the field created by the trigonally distorted rhombohedral crystal lattice. The same distortions can bring about partial unfreezing of the Cr^{3+} orbital angular momentum.

The *F* state is the ground state of the V^{3+} ion. Although the magnetic moment of V^{3+} ($1.63\mu_B$) is believed to be the sum of the spin and orbital moments, its experimental value ($1.81\mu_B$), derived by us from measurements of the static magnetization [1], suggests that part of the orbital angular momentum is quenched by the crystal field. One cannot exclude the possibility that the high uniaxial anisotropy in VBO_3 originates from a stronger spin–orbit coupling.

As for the third known source of magnetic anisotropy (anisotropic exchange), this mechanism, together with the spin–orbit coupling, may play a substantial role in generating anisotropy in cases where the orbital angular momentum is not quenched. Furthermore, although its contribution to the anisotropy of rhombohedral antiferromagnets is believed to be small [13], it is possibly that this contribution accounts for the small discrepancy between the critical temperatures observed when magnetizing $CrBO_3$ in different directions (Fig. 8). At any rate, in order to estimate the effect of various microscopic sources of magnetic anisotropy, one has to carry out theoretical calculations, which could be subsequently compared with data obtained from a series of different experiments.

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