MAGNETIC PROPERTIES OF TRANSITION METAL BORATES $FeBO_3$, VBO_3, $CrBO_3$*

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The research of magnetic properties of transition metal borates $FeBO_3$, VBO_3, $CrBO_3$ was carried out. New experimental data concerning magnetic structure of $CrBO_3$ is obtained. The exchange and anisotropy field values are determined.

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1. Introduction

The transition metal borates with chemical formula ABO_3 present a family of isostuctural magnetic materials containing $3d$ ions A = Fe, V, Cr, Ti. The basic mechanism responsible for the magnetic ordering is hold to be 90° indirect exchange. ABO_3 crystallizes in a calcite structure, which contains two formula units per unit cell. $FeBO_3$ was first prepared by Bernal *et al.*, in 1963 [1]. Studies of single crystal $FeBO_3$ have shown that it is weak ferromagnetic with $T_N \approx 348$K [2]. Although the literature on $FeBO_3$ is quite extensive, little is known about other representatives of this oxide class. The isotypic transition metal borates $CrBO_3$, VBO_3 and $TiBO_3$ were obtained by Schmid in 1964 [3]. Examination of the compounds VBO_3 and $CrBO_3$ has revealed that VBO_3 is ferromagnetic material with $T_c \approx 32$ K [4]. Chromium borate is antiferromagnetic material ($3d^3$ for Cr^{3+} ion), $T_N \approx 15$ K [4]. Earlier we reported about properties of solid solutions $V_xFe_{1-x}BO_3$ [5,6].

Magnetic properties $FeBO_3$, VBO_3 and $CrBO_3$ are presented in this paper. All crystals were obtained by spontaneous crystallization method [5]. Magnetization measurements were made from 4.2 to 350 K in the field up to 75 kOe.

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2. Results and discussion

It is known that $FeBO_3$ is a canted antiferromagnetic material in which the Fe^{3+} spins are canted slightly from collinear antiparallel alignment. The canting results in a small net moment perpendicular to the threefold c-axis with a cant angle of about 0.92°, giving rise to a net magnetization of 4 emu/g at 4.2 K. The anisotropy and the in-plane anisotropy field is below than 1 Oe, whereas the hard axis anisotropy field is around 3260 Oe. The exchange and Dzialoshinski fields are around 3280 kOe and 101.1 kOe accordingly.

The field dependencies of magnetization of VBO_3 at the different directions of external magnetic field, parallel (curve *1*) and perpendicular (curve *2*) to the crystal surface, at the 4.2 K are represented in Fig. 1. The direction of external magnetic field in the plane is arbitrary as preliminary study showed that in-plane anisotropy is negligibly small. Magnetization behaviour of single crystal VBO_3 is typical for ferromagnet with "easy plane" anisotropy. The

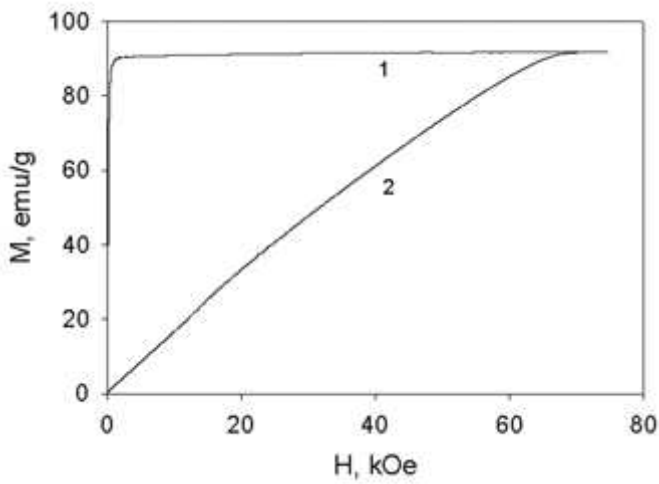

Fig. 1. Magnetization curves at 4.2 K for VBO_3.

threefold c-axis is hard direction and saturation takes place about 65 kOe. The exchange field H_{ex} in VBO_3 is 782 kOe, one order less than one in $FeBO_3$. In Fig. 2 we show the temperature dependence of first constant of single-axis anisotropy of VBO_3 in compare with theoretical curve, given by following expression [7]: $K_1 = K_{10}\,(M(T)/M_s)^3$, where K_{10} is K_1 value at 4.2 K, $M(T)$ is magnetization of VBO_3 in field of 20 kOe, M_s is saturation magnetization. Apparently there is a good agreement. The K_{10} magnitude is 1.2×10^7 erg/cm^3 and anisotropy field H_a is 62.5 kOe. It should be noted that this value is the greatest among iso-structural compounds. The ground

state of V^{3+} ion is F state. It is possible that such large quantity H_a results from spin–orbital coupling which plays an important role in VBO_3. $CrBO_3$ is another representative of family of rhombohedral antiferromagnetic materials.

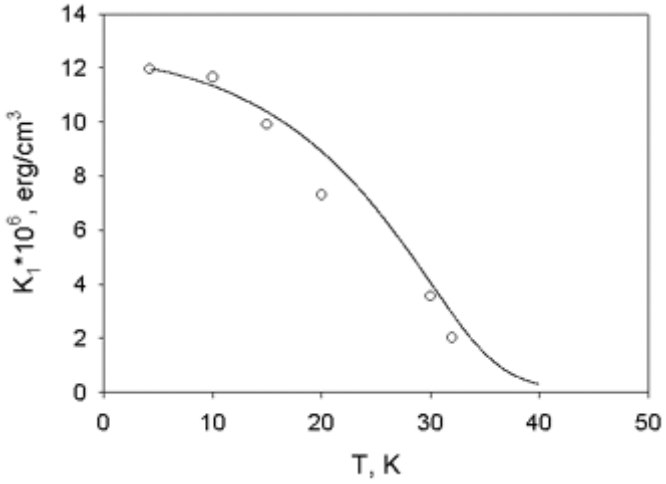

Fig. 2. Experimental and theoretical temperature dependencies of first constant of single-axis anisotropy VBO_3.

In Fig. 3 we give the magnetization curves of the $CrBO_3$ at 7.6 K. The direction *1* corresponds to field applied along two-fold axis in plane, *2* — along perpendicular to plate side, *3* — along three-fold axis. The curve number *3* is linear. Apparently, the magnetization process is due to rotation of sublattice magnetization vectors. The plot indicates that the curves *1* and *2* are accompanied by hysteresis and noise in the range $50\,\text{kOe} < H < 79\,\text{kOe}$ when the magnetic field is applied in plane. It is possible that such instability is caused by competition of exchange, anisotropic interactions and external magnetic field. The difference between the magnetic susceptibility "out of plane" and "in plane" in field less than 50 kOe is 20%. It turned out, that in the range $H > 70\,\text{kOe}$ susceptibility χ is nearly equal for all directions and its value is 2×10^{-3}. Exchange field for $CrBO_3$ is about 383 kOe. So antiferromagnetic exchange interaction Cr–O–Cr is one order less than one in $FeBO_3$. The existence of "spin–flop" transition in hexagonal plane indicate that $CrBO_3$ has considerable "in plane" anisotropy in compare with VBO_3 and $FeBO_3$. The obtained experimental results for $CrBO_3$ are in contradiction with assumption presented in [4] that this compound is a two-sublattice antiferromagnetic with the sublattice moments along c-axis. It follows from our data that vector of antiferromagnetism lies in basic plane.

In the rhombohedral crystals the magnetic moments are usually situated along symmetry axes. It is strange that in $CrBO_3$ these axes are not easy directions. Probably the magnetic structure of this crystal is more complex and detailed study by neutron diffraction and other investigation methods are necessary.

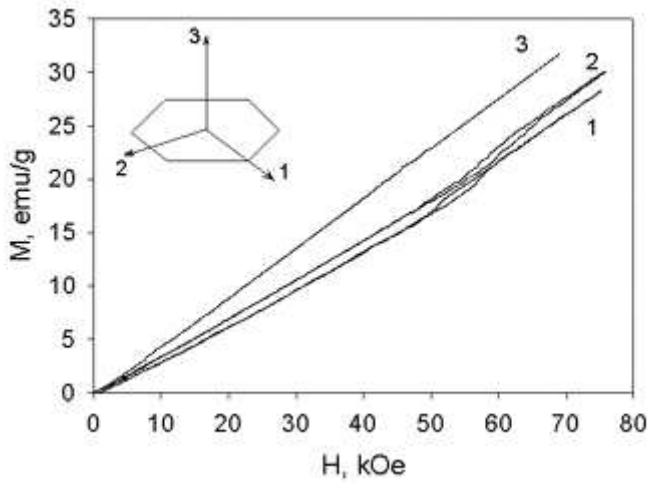

Fig. 3. Magnetization curves at 7.6 K for $CrBO_3$.

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REFERENCES

[1] I. Bernal, C.W. Struck, J.G. White, *Acta Crystallogr.* **16**, 849 (1963).

[2] R.C. LeCraw, R. Wolfe, J.W. Nielsen, *Appl. Phys. Lett.* **14**, 352 (1969).

[3] H. Schmid, *Acta Crystallogr.* **17**, 1080 (1964).

[4] T.A. Bither, Carol G. Frederick, T.E. Gier, J.F. Weiher, H.S. Young, *Solid State Commun.* **8**, 109 (1970).

[5] N.B. Ivanova, V.V. Rudenko, A.D. Balaev, N.V. Kazak, V.V. Markov, C.G. Ovchinnikov, I.S. Edelman, A.S. Fedorov, P.V. Avramov, *Sov. Phys. JETP* **94**, 299 (2002).

[6] V.V. Markov, V.V. Rudenko, I.S. Edelman, N.B. Ivanova, N.V. Kazak, S.G. Ovchinnikov, *Fiz. Met. Metalloved.* **91**, 1 (2001).

[7] S. Chikazumie. *Phisics of Ferromagnetism*, in Russian, Moscow 1987, p. 420.