Magnetic Properties of the $RbNd(WO_4)_2$ Single Crystal

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The magnetic investigations as a function of the temperature and magnetic field for the rubidium neodymium double tungstate $RbNd(WO_4)_2$ single crystal have been performed. The magnetization was measured in the temperature range from 4.2 to 100 K and for the magnetic field up to 1.5 T. The crystal field and exchange parameters were found.

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1. Introduction

The rubidium neodymium tungstate $RbNd(WO_4)_2$ (RbNdW) is the representative of the family of alkaline (A) and rare earth (Re) double tungstates $ARe(WO_4)_2$ (AReW). RbNdW belongs to the monoclinic system with space group C2/c, which is isostructural with α -KY(WO₄)₂ [1–3]. This crystal is usually grown by high temperature solution method in order to obtain the low temperature monoclinic phase. At present, the AReW tungstates having the low-symmetric (e.g., monoclinic) crystalline structure and the atom arrangements in forms of chains or layers are intensively studied. Structural, optical, and magnetic investigations of the KDyW, KHoW, KErW, KGdW, KYbW, KTmW and RbDyW compounds were performed earlier [1, 4–8]. Many of them show complicated structural phase transitions (SPT), caused by the cooperative Jahn-Teller effect (CJTE), and magnetic phase transitions. Unlike the high symmetry crystals, they are characterized by strong magnetic anisotropy, low local symmetry and low-dimensional magnetic structure, and they exhibit strong spin-lattice coupling [1, 8–10]. The rubidium neodymium double tungstate was also studied, especially its structural and spectroscopic properties [1–3].

In this paper, we show the new results of magnetization measurements for the rubidium neodymium double tungstate $RbNd(WO_4)_2$ (RbNdW) single crystal.

2. Magnetic properties of $RbNd(WO_4)_2$

The temperature, magnetic field and angular magnetization dependences of the RbNd(WO₄)₂ single crystal were investigated using the vibrating sample magnetometer (PAR Model 450) in a temperature range from 4.2 to 100 K for magnetic field up to 1.5 T. The field was applied both in the *ac* plane and along the *b*-axis. The electron configuration of Nd^{3+} is $4f^3$. In the crystal field of the monoclinic symmetry the ground multiplet ${}^{4}I_{9/2}$ splits into five Kramers doublets.

An angular dependence of the magnetization has allowed to determine the magnetic x and z-axes, which correspond to the directions of minimal and maximal values of magnetization in the ac crystallographic plane, respectively (Fig. 1). The angle between c- and z-axes in clockwise direction is equal to 86° and the angle between a- and x-axes is equal to 46° . The third main magnetic y-axis is parallel to the second-order axis C_2 and coincides with the crystallographic b-axis perpendicular to the ac plane.



Fig. 1. The angular dependence of magnetization for $RbNd(WO_4)_2$ single crystal in the *ac* crystallographic plane. The *a* and *c* are the crystallographic axes, *x* and *z* are the magnetic axes.

The magnetic field dependences of magnetization M_i along all magnetic x-, y- and z-axes do not display the magnetization saturation in temperature interval from 4.2 to 100 K and in magnetic field up to 1.45 T (Fig. 2), that is characteristic for paramagnet.

For a weak magnetic field H we may use linear relation for susceptibility $\chi_i(T) = M_i/H$. The experimental temperature dependences $\chi_i(T)$ were analyzed using the Curie–Weiss law

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Fig. 2. The magnetic field dependences of the susceptibility along three magnetic axes at T = 6 K. \Box along x-axis, \bigcirc along y-axis, \triangle along z-axis.

$$\chi_i = \chi_{0i} + \frac{C_i}{T - \theta_i}.\tag{1}$$

General fitting was used for finding the parameters: χ_{0i} (temperature independent part of the susceptibility), the Curie constant $C_i = N_{\rm A}(\mu_{\rm B}g_i)^2 J(J+1)/3k_{\rm B}$ and θ_i (paramagnetic temperature) (see Table I).

TABLE I

The fitting parameters for the Curie–Weiss law.

	χ_{0i}	C_i	~	θ_i
	[emu/mol]	$[\mathrm{emu}\mathrm{K/mol}]$	g_i	[K]
$H \ x \ H = 0.125 \ \mathrm{T}$	2.7×10^{-3}	1.161	3.52	-105.13
$H \parallel y H = 0.1 \text{ T}$	1.06×10^{-3}	5.55	7.69	-101.1
$H\ z\ H=0.1\ {\rm T}$	3.03×10^{-3}	1.13	3.59	-0.654

The results of fitting are also presented in Fig. 3. The paramagnetic temperature has a large value along the x- and y-directions.



Fig. 3. The temperature dependences of the inverse susceptibility along three magnetic axes: points (experiment, $\Box, \bigcirc, \bigtriangleup)$ and line (theory, the fitting for the Curie–Weiss law). \Box along *x*-axis, \bigcirc along *y*-axis, \bigtriangleup along *z*-axis.

The obtained values of the paramagnetic Curie temperature were used to find the crystal field parameters. For the C_2 symmetry of Nd³⁺ site $\hat{H}_{\rm cr}$ involves 15 nonzero crystal field parameters because for the axis parallel to the C_2 axis the crystal field parameters with the odd q are equal to zero. Following to Ref. [11] we shall restrict consideration only to second order crystal field parameters.

Our system has the symmetry axis of the second order that excludes in crystal field Hamiltonian the Stevens operators with odd powers. According to that the Hamiltonian has the following form with the first nonvanishing terms:

$$\hat{H}_{\rm cr} = B_2^0 \left(3J_z^2 - J(J+1) \right) + B_2^2 \left(J_x^2 - J_y^2 \right). \tag{2}$$

We attempted to estimate crystal field parameters B_2^0 and B_2^2 . At high temperatures, the relations between the crystal field parameters and crystal field contribution in paramagnetic temperatures $\theta_i^{\rm cr}$ in the *i* direction have a form

$$\theta_x^{\rm cr} = \frac{1}{2} \xi \left(B_2^0 - B_2^2 \right),
\theta_y^{\rm cr} = \frac{1}{2} \xi \left(B_2^0 + B_2^2 \right),
\theta_z^{\rm cr} = -\xi B_2^0,$$
(3)

where $\xi = \frac{1}{5} (2J - 1) (2J + 3)$ [11]. For J = 9/2, we have $\xi = 96/5$. In our case, the *x*-, *y*- and *z*-axes coincide with the *c*-, *a*-, and *b*-axes, respectively. Then the paramagnetic temperature θ_i can be expressed as [11]:

$$\theta_i = \theta_i^{\rm cr} + \theta_i^{\rm exch},\tag{4}$$

where the exchange contribution in paramagnetic temperature is equal to

$$\theta^{\text{exch}} = \frac{2}{3}J(J+1)J(0) = \frac{33}{2}J(0).$$

The $J(0) = zJ_{\text{ex}}$, where z — number of the nearest neighbours of the rare-earth ion. J_{ex} is the parameter of the pair exchange interaction.

Since the contribution of the crystal field in sum of the paramagnetic temperatures along the 3rd direction is equal to zero, only the 3rd contribution from exchange remain. From relation $\theta_x + \theta_y + \theta_z = \frac{99}{2}J(0)$ we obtain J(0) = -4.18 K, and the crystal field contribution in paramagnetic temperatures is equal to

 $\theta_x^{\rm cr} = 68.3 \text{ K}, \quad \theta_y^{\rm cr} = -36.16 \text{ K} \text{ and } \theta_z^{\rm cr} = -32.16 \text{ K}.$

Then we obtain the following parameters of the crystal field Hamiltonian $B_2^0 = 1.68$ K, $B_2^2 = -5.44$ K. It gives five Kramers doublets with energies of 0, 85.4, 149.4, 191.9 and 213.9 K.

In summary, we have found that the magnetization shows a strong anisotropy in temperature range studied. In the temperature range up to 100 K, the experimental curves of susceptibility follow the Curie–Weiss law. By fitting the calculated susceptibility to the experimental data, the crystal field and exchange parameters and g-factors along main crystal directions were calculated.

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