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# Magnetic ordering of Dy<sup>3+</sup> ion in low-dimensional CsDy(WO<sub>4</sub>)<sub>2</sub> double tungstate

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## ABSTRACT

Magnetic ordering of Dy<sup>3+</sup> ion in low-dimensional magnet CsDy(WO<sub>4</sub>)<sub>2</sub>, (CsDyW) has been first studied by means of measurements of the low temperature specific heat over a temperature range of 0.5-23 K. The ordering temperature (T<sub>N</sub>) of the Dy<sup>3+</sup> sublattice was established to be 1.34 K. The experimental data indicate on the antiferromagnetic (AFM) character of Dy<sup>3+</sup> ions interactions. The magnetic behavior above and below T<sub>N</sub> is discussed in the framework of different theoretical models.

**Keywords:** rare-earth tungstate; specific heat; antiferromagnetic ordering; low-dimensional magnet.

## 1. INTRODUCTION

Investigations of the alkaline (M) - rare-earth (Re) double tungstates MRe(WO<sub>4</sub>)<sub>2</sub> are of a special interest because of a possible realization of both magnetic and structural phase transitions in them. The existence of rare-earth ions with closely spaced energy levels in these low-symmetry compounds results in the occurrence of structural phase transitions connected with the manifestation of the cooperative Jahn-Teller effect. Indeed, such structural phase transitions (SPT) have been recorded in a monoclinic KDy(WO<sub>4</sub>)<sub>2</sub> (T<sub>spt</sub> = 6.38 K) and RbDy(WO<sub>4</sub>)<sub>2</sub> (T<sub>spt</sub> = 4.9 and 9.0 K) single crystals. The double tungstates are also considered to be a model system to check the conceptions of the low-dimensional magnetism. These studies are also strongly stimulated by possible applications of these materials as active component in solid state lasers. It is shown [1] that there is possibility of application of rubidium-dysprosium double tungstate as a cooling agent in an adiabatic demagnetization method for obtaining very low temperatures.

The interconnection and mutual influence of spin-spin and Jahn-Teller interactions in low-dimensional compound is expected to lead to interesting peculiarities of magnetic ordering in crystals having Jahn-Teller ion. The magnetic phase transitions (MPT) in related KDy(WO<sub>4</sub>)<sub>2</sub> and RbDy(WO<sub>4</sub>)<sub>2</sub> compounds were observed at T = 0.6 and 0.8 K<sup>1,2</sup> respectively. The presented below measurements of the CsDy(WO<sub>4</sub>)<sub>2</sub> ceramic are a continuation of studies of magnetic ordered state peculiarities in the dysprosium double tungstates.

In this paper the results of specific heat measurements in the CsDy(WO<sub>4</sub>)<sub>2</sub> compound near temperature of the magnetic phase transition are presented. The presence of equivalent Dy<sup>3+</sup> ions in the CsDy(WO<sub>4</sub>)<sub>2</sub> lattice makes this compound to be very convenient for magnetic studies. The measurements were performed as a function of temperature and magnetic field intensity. The obtained results are used for both determination of the magnetic phase transition temperature and elucidation of character of the magnetic ordering.

It should be added that the investigations of magnetic and thermodynamic properties in the cesium - dysprosium double tungstate were not carried out until now.

## 2. SAMPLES AND EXPERIMENTAL

The double cesium-dysprosium tungstate CsDy(WO<sub>4</sub>)<sub>2</sub> has monoclinic symmetry of crystalline lattice at room temperature. The lattice parameters are: a = 8.14 Å, b = 10.45 Å, c = 7.569 Å. The monoclinic angle is equal to 94°33'. The elementary cell contains four structural units. The Dy<sup>3+</sup> ion is surrounded by eight oxygen atoms and has local symmetry C<sub>2</sub><sup>3</sup>. Detailed measurements of the CsDy(WO<sub>4</sub>)<sub>2</sub> structure at low temperatures have not been carried out yet.

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The specific heat measurements have been carried out using a computer controlled quasi-adiabatic calorimeter over a temperature range 0.5-23 K. For these experiments a  $^3\text{He}$  cryostat was used. The sample in the form of powder of  $\text{CsDy}(\text{WO}_4)_2$  formed into a tablet by pressing with small amount of GE 7031 glue was mounted on a sapphire plate with diameter of 20 mm and thickness of 0.3 mm using Apiezon N vacuum grease (strickly, in our experiment we measure heat capacity of mixture with GE 7031 glue because we do not able, on reasonable way, to separate part connected with this small amount of glue). The sapphire plate (sample holder) was parallel to the vertical axis of the experimental setup and to the magnetic field direction. The four-probe method was used in the experiments to measure the resistance of thermometers and heater. The temperature of the sample was determined by two small-sized  $\text{RuO}_2$  thermometers on  $\text{Al}_2\text{O}_3$  ceramic. The small power heat pulses have been used to supply an increase of the temperature between initial and final temperature levels. The temperature difference between these levels near magnetic phase transition was about 1-1.5 mK. The temperature run of every experimental point was measured within 40-60 s.

### 3. RESULTS

#### 3.1. Zero field heat capacity

The zero-field specific heat as a function of temperature for  $\text{CsDy}(\text{WO}_4)_2$  is displayed in Fig. 1. As it is seen, the specific heat has the peak at  $T = 1.34$  K. A nonsymmetrical shape of the  $C(T)$  anomaly near  $T_C$  is obviously due to that the specific heat temperature dependence has a different character below and above  $T_N$ . The  $C(T)$  dependence is similar to the low temperature behavior of specific heat in both potassium-dysprosium  $\text{KDy}(\text{WO}_4)_2$  and rubidium-dysprosium  $\text{RbDy}(\text{WO}_4)_2$  tungstates. This dependence has clearly defined  $\lambda$ -type shape and its value at  $T_N$  is considerably reduced in comparison with  $\text{KDy}(\text{WO}_4)_2$  and  $\text{RbDy}(\text{WO}_4)_2$  compounds. In above compounds the peak of  $C(T)$  dependence has been explained as being due to the antiferromagnetic ordering of the  $\text{Dy}^{3+}$  sublattice. By analogy and on the base of the below presented results we assume that in  $\text{CsDy}(\text{WO}_4)_2$  the  $C(T)$  anomaly is also connected with AFM phase transition.

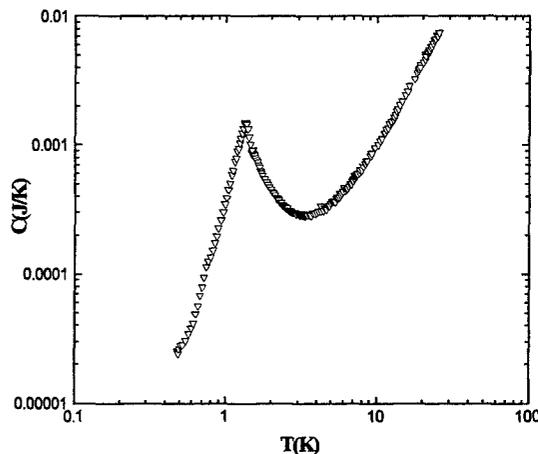


Fig. 1. Temperature dependence of the  $\text{CsDy}(\text{WO}_4)_2$  specific heat near magnetic phase transition.

One can say with reasonable confidence that the  $C(T)$  dependence characterizes the magnetic contribution to the total specific heat because the contributions to  $C(T)$  from both lattice and crystal field splitting are negligible in the considered temperature range. The estimation of the contribution of the crystal field splitting to the total specific heat of  $\text{CsDy}(\text{WO}_4)_2$  at low temperatures has shown that it is less than 1%. The Debye temperature in these compounds is high and the contribution of phonons is very small. The  $\text{CsDy}(\text{WO}_4)_2$  is an insulator and the conduction electrons do not contribute to the specific heat. In the temperature region 1.5-2.5 K, the experimental data are well described by the quadratic dependence, namely,  $C_m / R = 0.365 / T^2$  which characterizes the magnetic contribution to the specific heat. Therefore, the  $C(T)$  dependence at  $H = 0$ , shown in Fig. 1, mainly characterizes the magnetic specific heat.

We have analyzed the data of  $C(T)$  dependence above and below  $T_N$  and have estimated the  $\text{Dy}^{3+}$  ions exchange parameters ( $J/k$ ) using the theoretical models for both simple cubic (3D Ising) and quadratic (2D Ising) lattices as well as the analysis of the magnetic specific heat behavior at  $T > T_N$ . In the case of the Ising model, the value of  $T_N$  was taken from experiment and the effective spin  $S = 1/2$  was used.

The measurements of the  $C(T)$  dependence and the high temperature analysis have been carried out in a temperature range up to 3.5 K only. This is due to the influence of the tail of the Jahn-Teller transition on the  $C(T)$  data at higher temperatures (the temperature behavior of the magnetic susceptibility at  $T > 5$  K indicates the approach to a structural phase transition which was observed at 29 K).

Using the high temperature expansion for a specific heat within the frame of the 3D Ising model we used the relationship between critical temperature and exchange interaction parameter of the form  $2T_N/zJ = -0.752$  where  $z = 6$  is the

coordination number of the simple cubic lattice. The  $T_N$  and paramagnetic temperature  $\theta$  are related by the expression:  $T_N = 0.752\theta$  where  $\theta = 2/3S(S+1)zJ$ . The value of  $J$  is obtained to be equal to  $-0.336$  K.

We have compared the experimental  $C(T)$  dependence with the theoretical one for 2D antiferromagnet, too. The value of the exchange interaction parameter determined from equation of  $J/k = T_N (\ln\sqrt{2} - 1)$  is equal to  $-1.18$  K. Note that in this case we used the relationship between critical temperature and exchange interaction parameter of the form  $2T_N/zJ = -0.567$  where  $z = 4$ .

The behavior of specific heat correlates reasonably with theoretical  $C(T)$  dependence for 2D Ising model below  $T_N$ , whereas at  $T > T_N$  it can be well described by neither 2D or 3D Ising. The behavior of  $C(T)$  at  $T > 1.5 T_N$  correlates with theoretical  $C(T)$  dependence for 2D Ising model better than for 3D one.

The high temperature  $C(T)$  dependence is fitted also by  $1/T^2$  law, namely,  $4C_M T^2 / R = zJ^2 / k^2$  ( $z=4$ ). The exchange parameter determined by such procedure is equal to  $J/k = -1.298$  K. Note that the experimental  $J/k$  is in reasonable agreement with  $J/k$  one obtained for 2D Ising model only.

The  $J/k$  parameters are effective and consist of two contributions which result from the exchange and dipole-dipole interactions. Taking into account the low temperature of magnetic phase transition, it can be assumed that the exchange interaction is weak and the contribution of dipole-dipole interactions to spin-spin interactions may be essential. Unfortunately, the absence of data on the low temperature structure of  $\text{CsDy}(\text{WO}_4)_2$  does not allow to calculate exactly the dipole-dipole contribution of the Dy - Dy interactions.

An important parameter determining the character of magnetic phase transition is the critical index. It can be determined from the behavior of the specific heat in the critical region. The slope of the specific heat versus reduced temperature curve in a log-log plot close to  $T_N$  directly determines the critical index. As it is well known, the critical behavior of the specific heat in the limit  $T \rightarrow T_N$  above and below  $T_N$  is characterized by the critical exponents in the following equations :

$$\begin{aligned} C/R &\propto A (1 - T/T_N)^{-\alpha} \text{ for } (T < T_N); \\ C/R &\propto A (1 - T_N/T)^{\alpha} \text{ for } (T > T_N). \end{aligned}$$

The values  $\alpha$  and  $\alpha'$  are known for the 3D Ising model ( $\alpha = \alpha' = 1/8$ ), while for 2D Ising model the critical exponents are close to zero. The analysis have shown that the critical exponents for  $\text{CsDy}(\text{WO}_4)_2$  are close to zero that corresponds to the theoretical value expected for the 2D Ising system.

It is interesting to estimate how much entropy is released at and above the magnetic transition ( $T = 0.5 - 3.5$  K). At  $T > 4$  K calculations present definite difficulties because it is necessary to take into account both the lattice specific heat and the contribution connected with a structural transition. The temperature dependence of the magnetic entropy of  $\text{CsDy}(\text{WO}_4)_2$  near  $T_N$  has been obtained by integrating the specific heat

$$\Delta S_{\text{mag}}(T) = \int_0^T (C(T)/T) dT.$$

Above  $T_N$  the entropy should approach the value  $R \ln 2$  in accordance with the molar entropy of the electronic doublet of the ground state of the  $\text{Dy}^{3+}$  ion. In our case, the entropy is only 40% of  $R \ln 2$  at  $T_N$  and 70% of  $R \ln 2$  at 4 K. Note that for  $T > 4$  K the contributions from the lattice and structural phase transition ( $T_{\text{sp}} = 29$  K) appear in  $C(T)$  dependence (Fig. 1) and correspondingly in  $S(T)$  value which can only decrease  $\Delta S_{\text{mag}}$ .

The observed behavior of  $\Delta S_{\text{mag}}$  is due to the characteristic features of the magnetic ordering of  $\text{CsDy}(\text{WO}_4)_2$ . At structural phase transition, in the sample two or more crystallographic sublattices can appear. At AFM ordering, below the Neel temperature additional separation into two or more magnetic sublattices occurs in each crystallographic sublattices. In the  $\text{CsDy}(\text{WO}_4)_2$  compound, the AFM interactions are dominant and the crystal separates into four magnetic sublattices at  $T < T_N$ . In the case when the sample can separate into a large number of sublattices, actually into clusters, the value of  $\Delta S_{\text{mag}}$  is not expected to reach  $R \ln 2$ .

### 3.2. Magnetic field heat capacity

We have also studied the magnetic field effect on the specific heat in  $\text{CsDy}(\text{WO}_4)_2$  compound. As can be seen in Fig. 2, the  $C(T)$  dependence in magnetic field show that the interactions of  $\text{Dy}^{3+}$  ions have an antiferromagnetic character because the peak of the specific heat shifts to lower temperatures and the magnitude of the maximum of specific heat decreases with increasing magnetic field. The magnetic phase  $H-T_N$  diagram constructed using the  $T_N$  values corresponding to the specific heat maximum (Fig. 2) characterizes the metamagnetic transition from antiferromagnetic (AFM) to the paramagnetic (PM) phase. The experimental phase boundary of AFM to PM state was compared to the theoretical  $T_N(H)$  dependence for the Ising antiferromagnet. The latter was calculated by the high temperature expansion method describing

the shift of the anomaly of the magnetic susceptibility in a magnetic field by the following equation :

$$T_N(H) = T_N(0) \{1 - (H / H_{cr})^2\}^\zeta,$$

where  $H_{cr}$  is the transition field at  $T = 0$  K,  $\zeta = 0.87$  and  $0.35$  for square and simple cubic lattices, respectively. For the  $\text{CsDy}(\text{WO}_4)_2$  compound, the experimental  $T_N(H)$  dependence agrees better with the above expression for  $\zeta = 0.87$ . This also suggests that the magnetic ordering of  $\text{Dy}^{3+}$  sublattice has the two-dimensional character.

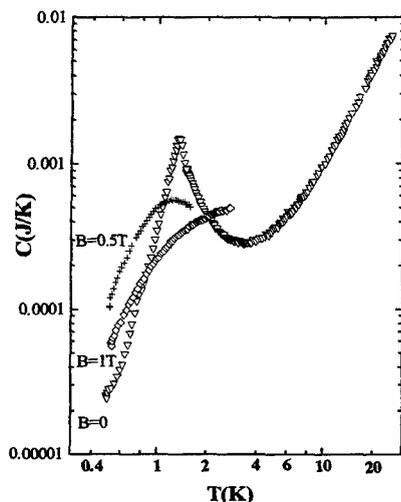


Fig. 2. Temperature dependence of the  $\text{CsDy}(\text{WO}_4)_2$  specific heat near magnetic phase transition for various magnetic field strengths .

dependence of the specific heat is indicative of the antiferromagnetic character of Dy ions interactions. The experimental phase boundary between the antiferromagnetic and paramagnetic phases is in a reasonable agreement with the theoretical  $T_N(H)$  dependence for 2D Ising antiferromagnet. The experimental value of the effective exchange parameter was obtained to be equal to  $J/k = -1.298$  K. Both the sign of  $J/k$  and the character of the temperature dependence of the specific heat in a magnetic field indicate the antiferromagnetic character of the  $\text{Dy}^{3+}$  ions interactions. The  $J/k$  parameter was estimated by various methods. The experimental  $J/k$  value was shown to correlate with theoretical value for 2D Ising model better than for 3D one.

#### ACKNOWLEDGMENTS

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#### 5. CONCLUSIONS

The magnetic ordering of Dy ions in the  $\text{CsDy}(\text{WO}_4)_2$  has been studied for the first time at very low temperatures  $0.5 < T < 23$  K. The Neel temperature was determined to be equal to 1.34 K. The peculiarities of magnetic ordering of  $\text{Dy}^{3+}$  ions was discussed. Data of the above analysis give no single-valued answer as to what model well describes the specific behavior near  $T_N$ . The temperature dependence of the specific heat at  $T > T_N$  can not be well described by 2D and 3D Ising models. The  $C(T)$  dependence below  $T_N$  is in reasonable agreement with 2D Ising model. The behavior of the specific heat at  $T > 1.5T_N$  correlates with theoretical  $C(T)$  dependence for 2D Ising model better than for 3D one. The comparison of the calculation with the experiment data shows that a part of the expected  $R \ln 2$  entropy is missing. The magnetic field