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Influence of Co moment on magnetic properties of $Co_2Sm_2W_3O_{14}$ tungstate

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Abstract. The $Co_2Sm_2W_3O_{14}$ compound crystallizes in the orthorhombic system, and melts congruently at 1443 K. The magnetic measurements showed that $Co_2Sm_2W_3O_{14}$ is a paramagnet in the temperature range 4.2-225 K showing both the residual magnetic interactions since the paramagnetic Curie-Weiss temperature $\theta \neq 0$ and the uncompensated temperature independent contributions of magnetic susceptibility since $\chi_0 \neq 0$. The Brillouin fit of the Landé factor revealed an increase of the orbital contribution to the total magnetic moment of the compound what seems to be responsible for its hard and spontaneous magnetization at low temperatures.

Introduction

Doped and undoped rare-earth metal tungstates, molybdates and molybdato-tungstates are promising materials to use in the white light emitting diodes (WLEDs) as red phosphors. WLEDs have got many advantages such as low energy consumption, long lifetime, high stability as well as friendliness to an environment, and for these reasons they are called a lighting of the next generation. These host materials with various crystal structures have got excellent luminescence properties and high thermal as well as chemical stability. Their optical properties are mainly determined by charge-transfer transition between O^{2-} and W^{6+}/Mo^{6+} ions within WO_x or MoO_x polyhedra. Furthermore, these phosphors can also effectively transfer energy to Eu^{3+} ions and generate pure red emission of the ions. In recent years, more and more interest has been put in a synthesis of new phosphors with interesting optical properties and containing both *d*- and *f*-electron metal ions [1-5]. The introduction of *d*-electron metal ions can give very interesting magnetic properties, because in the lanthanide elements and their compounds the unpaired 4*f* electrons responsible for the paramagnetism are quite effectively screened from environmental effects by overlying *s* and *p* electrons. Additionally, in the case of samarium and europium narrower multiplet widths comparable to the thermal energy *kT* occur [6]. So, that not all the atoms are in their ground state [7]. Such levels above the ground state may not contribute to the magnetic susceptibility [8]. Similar behaviour has been observed for Sm_2WO_6, revealing low values of the magnetic

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susceptibility of $1.4 \cdot 10^{-5}$ cm^3/g at 5 K and a weak temperature dependence of the magnetic susceptibility without the Curie-Weiss region [9].

The $CoWO_4$-Sm_2WO_6 system is characterized by a formation of two cobalt and samarium tungstates described by the following formulas: $Co_2Sm_2W_3O_{14}$ and $CoSm_4W_3O_{16}$ [10]. Both compounds were obtained by high temperature solid-state reaction using $CoWO_4$ and Sm_2WO_6 mixed at the molar ratio of 2:1 ($Co_2Sm_2W_3O_{14}$) or 1:2 ($CoSm_4W_3O_{16}$) [10]. Both new cobalt and samarium tungstates belonging to two different families of isostructural compounds ($Co_2RE_2W_3O_{14}$ and $CoRE_4W_3O_{16}$, where *RE* = Sm-Gd) crystallize in the orthorhombic system, and they melt incongruently above 1423 K [10].

The main purpose of the present work is an attempt to study and summarize the magnetic properties of the polycrystalline $Co_2Sm_2W_3O_{14}$ compound. To understand an influence of Co moment on its magnetic properties the Brillouin fit of the Landé factor was made.

Experimental

The magnetic susceptibility, χ_σ, was measured in the temperature range 4.2-225 K in the applied external magnetic fields H = 100 Oe using a Faraday type Cahn RG automatic electrobalance. Magnetization isotherms, $\sigma(\mu_0 H)$, were measured at 4.2, 10, 15, 20 and 30 K in applied external magnetic fields up to 15 T using a step magnetometer. Both susceptibility and magnetization were measured in the zero-field-cooled mode (ZFC). The magnetic susceptibility, χ_σ, was expressed as $\chi_\sigma = \chi_0 + C/(T-\theta)$. The optimum values for C, χ_0 and θ were obtained using a method described in detail elsewhere [11]. The Curie-Weiss regions in the temperature interval 20 – 190 K were established. The demagnetization factor has been taken into account during the calibration of the apparatus by the Ni-standard (0.606 μ_B per atom) with cylindrical shape. The measurement error connected with the demagnetisation factor did not exceed 1 %.

Results and discussion

The temperature dependences of magnetic susceptibility, $\chi_\sigma(T)$, (Fig. 1) and the magnetization, $\sigma(T)$, recorded at magnetic induction $\mu_0 H$ = 1.0 and 2.0 T (Fig. 2) show paramagnetic behaviour. The value of χ_σ at 5 K is one order of magnitude greater than for Sm_2WO_6 [9]. Fits to a Curie-Weiss law [11] yield: θ = -22 K, $\chi_0 = 1.245 \cdot 10^{-5}$ cm^3/g and $C_\sigma = 3.693 \cdot 10^{-3}$ $K \cdot cm^3/g$. The large and negative value of the Curie-Weiss temperature, θ, may suggest an antiferromagnetic contribution below 4.2 K. The positive value of χ_0 indicates the uncompensated temperature independent contributions of magnetic susceptibility, especially the van Vleck one, typical of compounds, such as Sm_2WO_6 [9], for which the low an extrinsic carrier concentration are observed. The effective magnetic moment μ_{eff} = 5.943 μ_B/f.u. estimated from equation: $\mu_{eff} = 2.83\sqrt{MC_\sigma}$, where the molar mass M = 1194.1 g/mol indicates that the main contribution comes from the Co^{2+} ions (S = 3/2, HS) with $3d^7$ electronic configuration. The Sm^{3+} ions (S = 5/2, HS) with $4f^5$ electronic configuration play a minor role because of the narrower multiplet widths, comparable to kT, which does not contribute to the magnetic moment [8]. The magnetic isotherms depicted in Fig.3 show a spontaneous magnetization which disappears with temperature as well as they have zero coercivity and remanence.

In order to examine the orbital contribution to the magnetic moment, the Brillouin procedure was applied. The experimental virgin magnetization curve, taken from Fig. 3, can be easily fitted by the following expression:

$$\sigma = \sigma_0 B_J(x) \tag{1}$$

where σ_0 is the magnetization at the highest value of $\mu_0 H/T$, $x = g_{fit} J \mu_B H/kT$, g_{fit} is the fitted Landé factor and the Brillouin function B_J is given by [7]:

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$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}\right)x - \frac{1}{2J}\coth\frac{x}{2J} \tag{2}$$

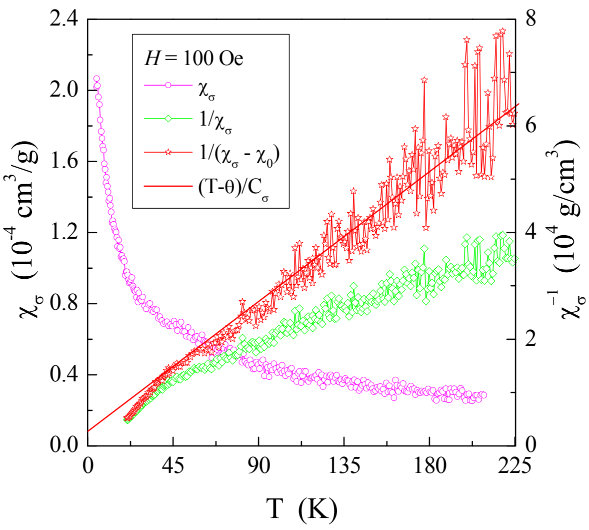

Figure 1. Magnetic susceptibilities χ_σ, $1/\chi_\sigma$ and $1/(\chi_\sigma$-$\chi_0)$ vs. temperature T, recorded at 100 Oe. The solid (red) line indicates the Curie-Weiss region.

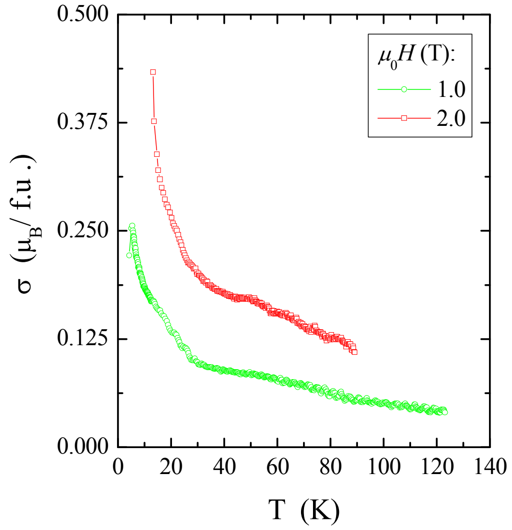

Figure 2. Magnetization σ vs. temperature T recorded at $\mu_0 H$ = 1.0 and 2.0 T.

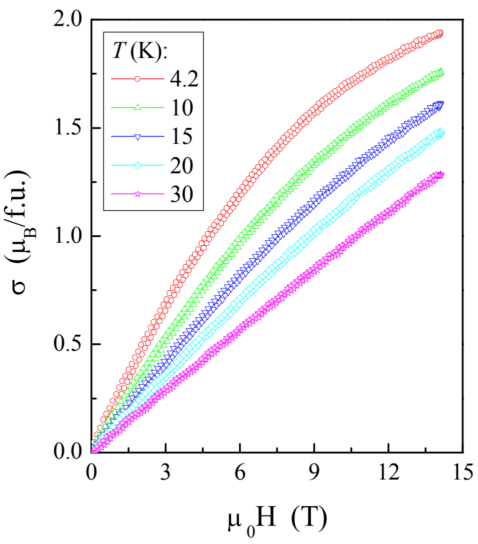

Figure 3. Magnetization σ vs. magnetic field $\mu_0 H$ at 4.2, 10, 15, 20 and 30 K.

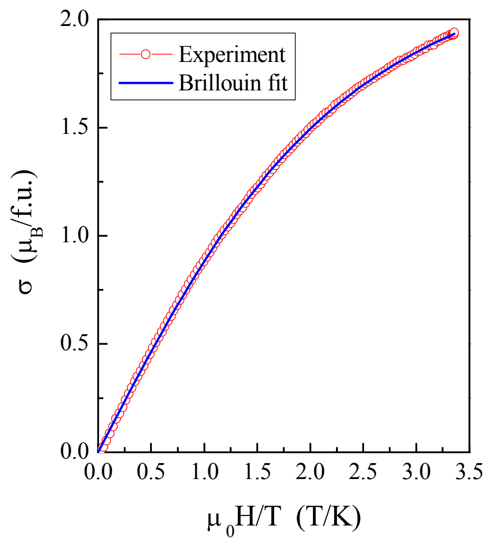

Figure 4. σ vs. $\mu_0 H/T$ at 4.2 K for angular momentum J = 7 and σ_0 = 2.53 μ_B/f.u.

For the tungstate under study we have two angular momenta $J_1(Co^{2+})$ and $J_2(Sm^{3+})$. In this case the addition rule for angular momenta was used: the magnitude of the sum of two angular-momentum vectors can vary from the sum of their magnitudes $\boldsymbol{J}_1 + \boldsymbol{J}_2$ (parallel case) to the difference of their magnitudes $|\boldsymbol{J}_1 - \boldsymbol{J}_2|$ (antiparallel case) by integer steps [12]. Thus, we have 2 ≤

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$J \leq 7$ for $Co_2Sm_2W_3O_{14}$. The Brillouin procedure gave the best fitting when the agreement index R^2 reached maximum (0.99991) for $J = 7$ and $\sigma_0 = 2.53$ μ_B/f.u. The Brillouin function together with experimental data of magnetic moments is shown in Fig. 4. The agreement is satisfactory and these data are seen to fall on the universal Brillouin curve, indicating paramagnetic response [13]. The value of $g_{fit} = 0.208$ is lower in comparison with theoretical one for the free Sm ion with $g = 2/7$ [7]. So, the results mentioned above give an evident justification for stronger spin-orbit coupling, which influences essentially on the magnetic properties of the tungstate under study.

Summary

We have measured the static susceptibility as well as the magnetization isotherms in the ZFC mode of powdered $Co_2Sm_2W_3O_{14}$. The results showed a paramagnetic behaviour depending on strength of the spin-orbit coupling driven from the Brillouin fit of the Landé factor. The Co^{2+} ions strongly influence on the magnetic properties and spin arrangement at low temperatures.

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