14th Czech and Slovak Conference on Magnetism, Košice, Slovakia, July 6–9, 2010

Low Temperature Neutron and Synchrotron Diffraction Studies of KEr(MoO$_4$)$_2$ Single Crystal in External Magnetic Field

S. Maťaš[a,b,*], A. Orendáčová[c], K. Prokeš[a], R. Feyerherm[a], E. Dudzik[a] and B. Klemke[a]

[a]Helmholtz-Zentrum Berlin, Hahn Meitner Platz 1, D-14109 Berlin, Germany

[b]Institute of Experimental Physics SAS, Watsonova 47, SK-04001, Slovakia

[c]P.J. Šafárik University, Park Angelinum 1, Košice, SK-04001, Slovakia

We report on low temperature magnetic properties of KEr(MoO$_4$)$_2$ single crystal, which was investigated from 0.28 K to 30 K in magnetic fields up to 6.5 T. Neutron elastic data collected above and below transition temperature $T_{\mathrm{N}} \approx 0.95$ K suggest that an antiferromagnetic ordering establishes at low temperatures. The magnetic model within the $A_x C_z$ mode assuming only magnetic moment at erbium atom positions is suggested. Synchrotron experiment in moderate magnetic fields at temperatures above T_{N} explains the origin of observed signal(s) at $(0K0)$ reflection positions, K odd.

PACS numbers: 75.50.−y, 28.20.Cz, 25.40.Dn

1. Introduction

The alkaline rare-earth molybdates are technologically important materials as they are used as scintillators, laser host materials or chemical reaction inhibitors. Double rare-earth molybdates MRe(MoO$_4$)$_2$ (Re = rare earth, M = alkali metal) crystallize in variety of layered structures. From magnetic point of view some members of this group are close to the ideal 2D Ising system. The KEr(MoO$_4$)$_2$ single crystal orders magnetically at $T_{\mathrm{N}} \approx 0.95$ K and shows very anisotropic properties. Similarly to other members of this molybdate class, the KEr(MoO$_4$)$_2$ system is close to structural instability. However, the system does not undergo a spontaneous Jahn–Teller (JT) phase transition on cooling in zero field, the JT phase transition can be induced by moderate magnetic field.

In this paper we present low temperature data taken on KEr(MoO$_4$)$_2$ single crystal obtained by neutron and synchrotron diffraction technique. The magnetic structure is proposed.

2. Experimental

The non-polarized neutron experiment was performed at E4-diffractometer installed at Helmholtz Zentrum Berlin. The crystal KEr(MoO$_4$)$_2$ has been measured in $(0KL)$ and $(1K1)$ orientations with incident wavelength of 2.45 Å. Magnetization and susceptibility measurements were performed on a commercial magnetometer in a wide temperature range from 2 K to 295 K in fields up to 5 T. Specific heat data were taken by means of adiabatic method in zero field only. In addition, synchrotron X-ray experiment in temperature range from 2 K to 12 K and magnetic fields up to 5 T has been performed at MAGS beam line in a non-resonant mode focused mainly to $(0K0)$ reflection positions.

3. Results and discussion

The single crystal of size $12 \times 12 \times 0.6$ mm^3 has been prepared at the Institute of Low Temperature Physics in Kharkov. KEr(MoO$_4$)$_2$ adopts the *Pbcn* space group, with the following lattice parameters: $a = 5.063$ Å, $b = 18.25$ Å and $c = 7.915$ Å, $\alpha = \beta = \gamma = 90°$ [1, 2]. The structure is built-up from layers of linked molybdenum tetrahedrons and erbium octahedrons separated by a layer of potassium ions. An effective magnetic moment has been estimated by fitting the data to a Curie–Weiss law in the temperature range 20 K to 300 K to values $\mu_{\mathrm{eff}} = 9.8\ \mu_{\mathrm{B}}$, $8.4\ \mu_{\mathrm{B}}$ and $8.7\ \mu_{\mathrm{B}}$ for the a-, b- and c-axes, respectively. These values are to be compared to value $9.58\ \mu_{\mathrm{B}}$ of free-ion Er^{3+} and value $2.83\ \mu_{\mathrm{B}}$ of spin moment Mo^{4+}. The Curie temperatures for principal crystallographic directions $\theta_a = 5.02$ K, $\theta_b = -46.9$ K and $\theta_c = -13.6$ K suggest prevailing antiferromagnetic interaction along the b- and c-direction and ferromagnetic one along the a-direction. The easy magnetic axis has been found to be collinear to the a-axis direction.

Our neutron elastic data taken at a low temperature did not confirm any magnetic signal at reflection positions described by the wave vector $\tau_{af} = (1/2, 1/2, 0)$ as suggested by Anders et al. [1, 2]. Additional signal, however, has been identified at several forbidden nuclear

---

[*] corresponding author; e-mail: `slavomir.matas@helmholtz-berlin.de`

reflection positions of the $(0K0)$ and $(00L)$ type where K, L is odd and on top of allowed nuclear reflections. The magnetic contribution has been determined by subtracting the reference signal taken at $T = 2$ K ($T > T_{\mathrm{N}}$) from the low temperature signal taken at $T = 0.28$ K. Typical omega scan across a reciprocal node was first integrated, corrected for a Lorenz factor and then refined according our magnetic model(s) with help of Fullprof program [3].

Figure 1 shows heat capacity data in the temperature range from 0.35 K to 1.1 K and integrated intensity across the (001) reflection as a function of temperature. By fitting the experimental temperature dependence to an empirical formula $I_{\mathrm{S}} = I_0(1-T/T_{\mathrm{N}})^{2\beta}$ in the region close to the magnetic phase transition the critical coefficient has been determined to have a value of $\beta = 0.107 \pm 0.017$ K. The value of the critical parameter is consistent with a critical exponent worked out by Monte Carlo simulation for 2D Ising lattice, $\beta_{2\mathrm{D}} = 0.125$ [4]. Similar behavior has been also found for reflections of type $(1K1)$, $K =$ odd.

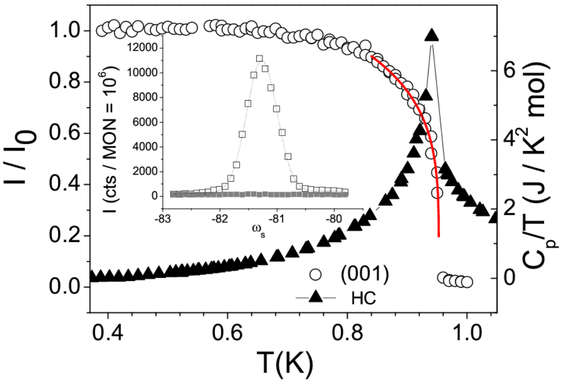

Fig. 1. The heat capacity data and normalized intensity at the reflection (001), the inset shows omega scan across (001) reflection at temperature 0.28 K (□) and 1 K (■).

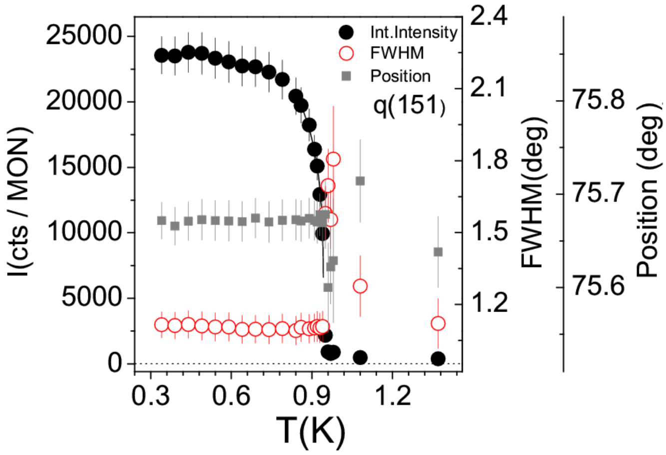

Fig. 2. The integrated intensity, FWHM and position of (151) reflection.

Figure 2 displays the integrated intensity, vanishing at the transition temperature of 0.95 K, the full width at half maxima and the reflection position of (151) reciprocal node as a function of temperature. Signals at $(1K1)$, $K =$ odd and $(00L)$, $L = 1$, 3 reflection positions vanish with increasing temperature at T_{N}, but for $(0K0)$, $K =$ odd does not. At $T = 2$ K, the integrated intensity of the forbidden nuclear reflection (030) shows a peculiar dependence as a function of applied magnetic field [5]. However, on the basis of neutron diffraction only it is not possible to conclude whether the extra signal seen at intermediate fields is of nuclear or magnetic origin. Our results taken at the MAGS synchrotron beamline show a presence of considerable structural contribution to this reflection position even up to room temperature.

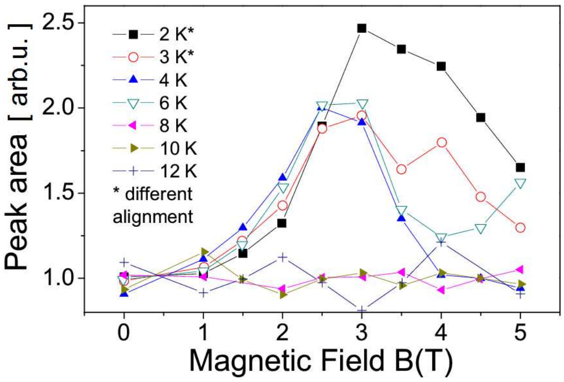

Fig. 3. The field dependence of integrated intensity at the (030) forbidden nuclear reflection at temperatures of 2, 3, 4, 6, 8, 10 and 12 K for $B \parallel c$ taken at MAGS beamline HZB Berlin.

The field dependence of (030) reflection taken at different temperatures 2, 3, 4, 6, 8, 10 and 12 K for $B \parallel c$ is presented in Fig. 3. From comparison of intensity ratios of synchrotron and neutron measurements we can conclude that the high temperature signal (≈ 2 K) in applied fields contains both magnetic and structural contributions and the majority of signal seen in intermediate fields at low temperatures is of magnetic origin. Our magnetic model assuming the $\mathrm{A}_x\mathrm{C}_z = (+--+)_x\ (++--)_z$ components of magnetic moment of total size 8.75 μ_{B} at the erbium atom positions: $\mathrm{Er}_1(0, y, 0.25)$, $\mathrm{Er}_2(0, 1-y, 0.75)$, $\mathrm{Er}_3(0.5, 0.5-y, 0.75)$, $\mathrm{Er}_4(0.5, 1+y, 0.25)$, $y = 0.008$ can explain well the appearance of magnetic signal at forbidden reflection positions, however, only qualitative agreement was reached. The appearance of nonzero signal at (030) reflection position for a wide temperature range is surprising and suggests that the literature crystal structure is not correct.

4. Conclusions

The neutron data taken at the low temperature shows an additional signal at several forbidden nuclear reflection positions of the $(0K0)$ and $(00L)$ type where K, L is odd and on top of allowed nuclear reflections. No signal has been detected at positions described by a wave vector $\tau_{af} = (1/2, 1/2, 0)$ as suggested by Anders et al. [1, 2]. The easy magnetic axis has been found to be collinear to the *a*-axis direction. Magnetic structure is qualitatively described within a magnetic model assuming magnetic moment at the erbium atoms only and having two components $\mathrm{A}_x\mathrm{C}_z$. The (030) reflection has been confirmed by synchrotron experiment to have also structural component, the signal persists up to a room temperature. This fact implies that the literature crystal structure is not correct and has lower symmetry, most probably one of *Pbcn* subgroup.

Acknowledgments

We would like to thank A.G. Anders for providing the crystal for neutron and synchrotron measurements.

References

[1] A.G. Anders, S.V. Volotskii, O.E. Zubkov, *Low Temp. Phys.* **20**, 105 (1994).

[2] A.G. Anders, S. Volockii, O.E. Zubkov, *Low Temp. Phys.* **20**, 137 (1994).

[3] T. Roisnel, J. Rodriguez-Carvajal, *Mater. Sci. Forum* **378**, 118 (2001).

[4] J. García, J.A. Gonzalo, *Physica A Stat. Mech. Appl.* **326**, 464 (2003).

[5] S. Maťaš, A. Orendáčová, K. Prokeš, B. Klemke, *J. Phys. Conf. Series.*