Ho^{3+} complexes in $KHo(WO_4)_2$ single crystals

S. M. Kaczmarek[a], H. Fuks[a], T. Skibiński[a], G. Leniec[a], J. Hanuza[b], L. Macalik[b], A. Majchrowski[c]

[a] *Faculty of Mechanical Engineering and Mechatronics, Institute of Physics, West Pomeranian University of Technology, Al. Piastów 48, 70-320 Szczecin, Poland*
[b] *Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P. O. Box 1410, 50-950 Wrocław, Poland*
[c] *Institute of Applied Physics, Military University of Technology, 2 Kaliskiego, 00-908 Warszawa, Poland*

Author for correspondence: S. M. Kaczmarek, email: skaczmarek@zut.edu.pl
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Abstract

Well oriented $KHo(WO_4)_2$ single crystal has been investigated by means of very sensitive EPR technique. Low temperature EPR spectra collected at three perpendicular planes of the crystal rotation allowed to find out information about the nature and local symmetry of detected magnetic centers. *g* matrix has been calculated, including its principal values as well as space orientation. As trivalent holmium ions are expected to be EPR silent, observed signal is attributed to different type of complex holmium magnetic systems, arranged with help of some defects like vacancies of W^{6+} ions.

Keywords: Double tungstates; Single crystals; Holmium; EPR; Magnetic complexes

1. Introduction

Nowadays, the tungstates and molybdates of rare-earth elements have been extensively investigated because of their interesting physical properties, e.g. negative thermal expansion, and a wide variety of applications, e.g. phosphors and lasers. Rare-earth double tungstates exhibit structural and magnetic low-dimensionalities, high anisotropy and strong spin-lattice interactions [1-5]. The magnetism of rare-earth double tungstates results from the competition between spin-spin, dipole-dipole and magnetoelastic interactions [3, 4]. The characteristic property of these low symmetry systems is a very low temperature phase transition to antiferromagnetic state. It indicates that the exchange interactions are weak [3].

The holmium double tungstate single crystal is biaxial and pleochroic. The crystal structure of the compound was described in [6-7]. Holmium ions in $KHo(WO_4)_2$ occupy crystallographic site with C_2 symmetry [8]. Under influence of the low symmetry crystal field all the energy levels of the Ho^{3+} ions are singlets. Optical properties of the crystal were described in [5, 8]. It seems to be promising laser host.

Magnetic properties of $KHo(WO_4)_2$ were investigated very rarely in temperature range 5 to 100 K [3, 4]. A strong anisotropy of magnetic properties and anomalous $1/\chi(T)$ behavior along the *x* and *z* axes as well as an unusual hysteresis of the M(H) curve along the *z* axis were found. The anisotropy of magnetic properties observed was found to be due to a low symmetry crystal field acting on rare earth ion. Besides, studies regarding the magnetic susceptibility of heavy rare-earth (Tb – Yb) tungstates from 300 to 900 K were presented in [9]. Magnetic properties of holmium ions were also studied in case of Ho_2WO_6 (4.2 to 350 K) [10] and $(Co,Zn)Ho_4W_3O_{16}$ (4.2 to 280 K) [11] tungstates. For the latter compounds EPR properties were also analyzed.

In this paper we investigate magnetic properties of the $KHo(WO_4)_2$ single crystal using EPR technique in temperature range 3.38 to 300 K.

2. Experimental Details

The monoclinic $KHo(WO_4)_2$ single crystals were grown using the top seeded solution growth method (TSSG) from a $K_2W_2O_4$ flux as described in [1]. The electron paramagnetic resonance spectra were recorded on a conventional X-band Bruker ELEXSYS E 500 CW-spectrometer operating at 9.5 GHz with 100 kHz magnetic field modulation in the temperature range 3.38–300 K. The first derivative of the crystal absorption spectra has been recorded as a function of the applied magnetic field. Temperature and angle dependence of the EPR spectra of the crystal sample was recorded using an Oxford Instruments ESP nitrogen-flow cryostat. EPR measurements have been done with three crystal rotation modes, i.e. with magnetic field operating in ac-, ab- and bc - planes.

3. Results and Discussion

Electron paramagnetic resonance (EPR) spectra detected at temperature 8 K along three perpendicular axes of rotation: *a*, *b*, and *c** consist of very wide signal located at magnetic fields above 600 mT. Spectra observed in *ac* and *bc*-planes of magnetic field operation consist of only single Gaussian line (Figure 1a), whereas in *ab*- plane some additional high field components were observed (Figure 1b).

Detailed analysis of EPR spectra allowed us to perform decomposition of the overall signal as a sum of at least two Gaussian lines. Angular dependences of the determined components measured at three perpendicular directions (Figures 2) clearly confirm C_2 symmetry of

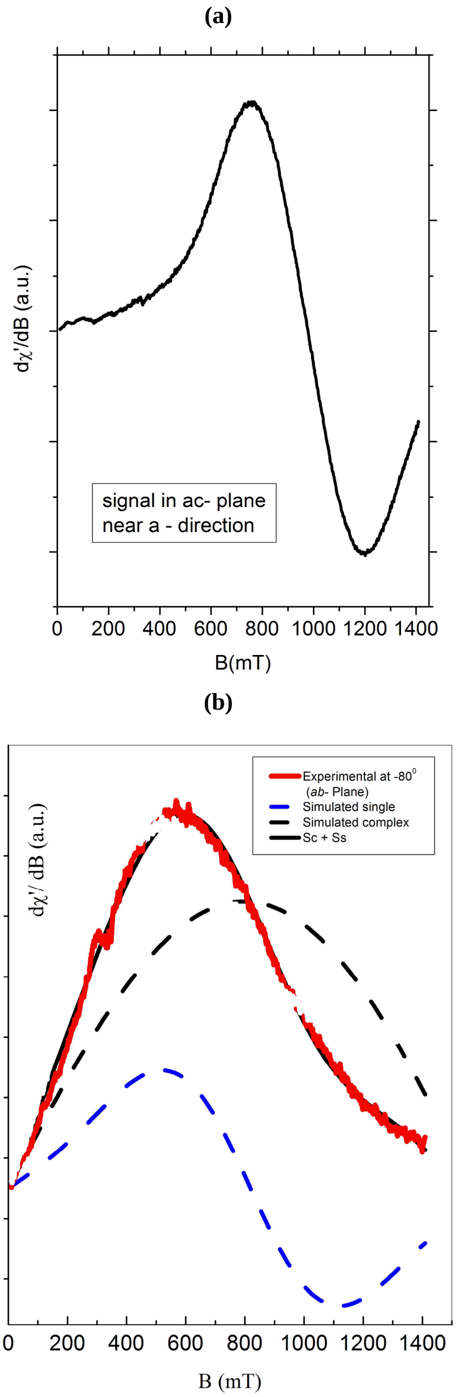

Figure 1. Exemplary EPR spectra of $KHo(WO_4)_2$ single crystal when magnetic field operated in: *ac*- plane (a) and *ab*- plane (b). In the *ab*- plane EPR signal was successfully simulated as a sum of two Gaussian lines.

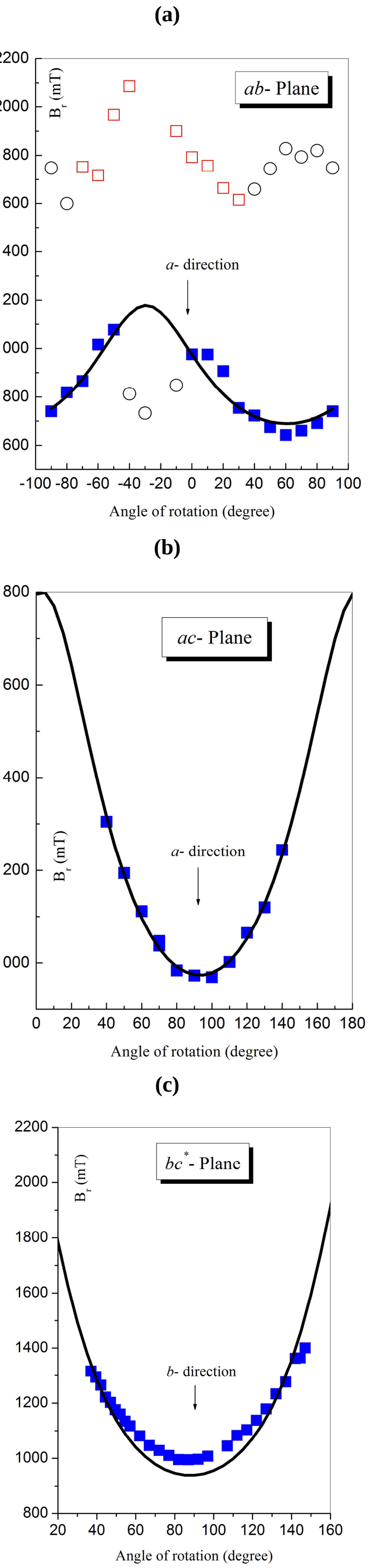

Figure 2. Angular dependences of the resonance position, when crystal was rotated around *c**, *b* and *a* experimental axes, i.e. magnetic field operated in *ab*- and *ac*- and *bc*- planes, respectively. Solid points represent positions of main signal, whereas open points represent estimated position of another complex signals.

responsible magnetic centres, as could be expected for holmium ions in this type of crystal structure.

Ho^{3+} ion is a non-Kramer's ion, and due to specific splitting of its energy levels in double tungstates, is expected to be EPR silent, with ground state S=0. Only high frequency investigations are expected to reveal an EPR signal of Ho^{3+} involving formation of mixed hyperfine and Stark sublevels [12]. On the other hand, there are some reports about EPR resonance signal of Ho^{3+} ions, if holmium ions are arranged into bigger magnetic system, via bridges created by specific vacancy states [13]. So we believe that X- band EPR signal

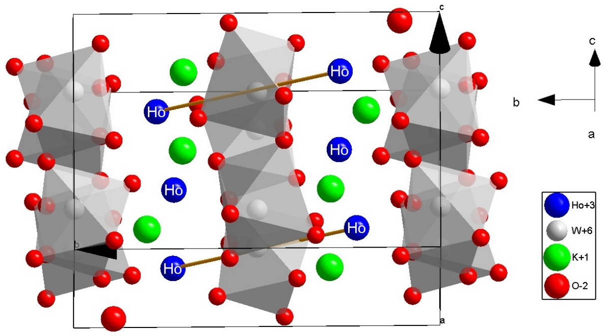

Figure 3. The view of $KHo(WO_4)_2$ structure in *bc*- plane. Ho positions are signed, W positions are inside octahedra.

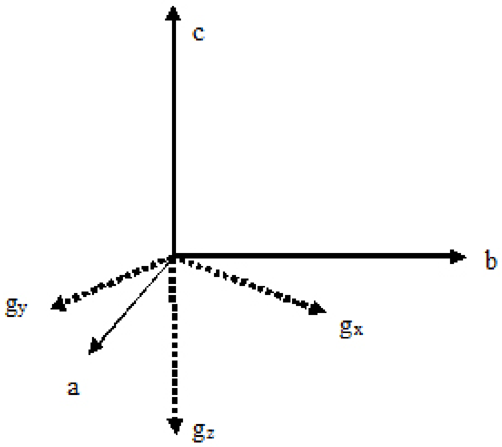

Figure 4. Spatial orientation between *g* matrix principal axes and *abc*- experimental axes.

Table 1. Principal values of *g* matrix calculated by using EPR–NMR program for $KHo(WO_4)_2$ single crystal. Θ and ϕ are polar and azimuthal angles of principal axes with respect to experimental *abc* system.

g_x	g_y	g_z
0.8443	0.5775	0.2774
Polar and azimuthal angles of principal axes with respect to *abc* experimental system		
$\Theta = 92$	$\Theta = 91$	$\Theta = 178$
$\phi = 47$	$\phi = 317$	$\phi = 211$

observed by us in $KHo(WO_4)_2$ single crystal indeed originates from Ho^{3+} ions, being a part of complex magnetic systems containing also different vacancy states.

Vacancy states in double tungstates are generated by tungsten ions. Some quantity of reduced W^{5+} ions could exist in basic compound, and after synthesis they are forced to be oxidised to W^{6+} state, but charge equilibrium in the structure leads to generation of vacancy states near W positions. At such dense holmium system, specific relation between planar and inter planar W and Ho position leads to creation of complex magnetic arrangements. Figure 3 shows the view of $KHo(WO_4)_2$ structure in *bc*- plane. As one can see the distance between Ho^{3+} ions along *b*- axis is much higher than along *c*-axis. But if there are some vacancy states on W positions (light octahedra), Ho^{3+} ions are connected via vacancy bridge also along *b*- direction. Higher distance between holmium ions along *b*- direction seems to agree with lowest resonance position observed for this direction in *bc*- plane (Figure 2c).

The main signal, exposed as solid points in Figure 2 has been simulated using EPR-NMR program [14], with employing simplest model for spin Hamiltonian S= 1/2. The result of simulation (solid line) is good enough. Higher resolution is rather not expected in this case, as mentioned lines are visible just at specific angles, at extremely high magnetic fields, additionally being overlapped by other lines in *ab*-plane. Results of calculations of *g* matrix parameters and its spatial orientation with respect to experimental axes are gathered in Figure 4 and Table 1.

As one can see, obtained *g* spectroscopic values are very low, much far from free electron value g_e=2. Strong deviation from *g*=2 seems to be characteristic feature of holmium ions. Values of g parameters reported in [13] were much higher than 2. Also other reports concerning to EPR signal of instable Ho^{2+} ions [15, 16] demonstrate exceeding of *g*=2. Observed in Table 1 relation: $g_x \neq g_y \neq g_z$ indicates the rhombic distortion in the position of responsible magnetic ions.

EPR lines ascribed to the main magnetic centres have been analysed as a function of temperature (Figure 5a, b, 6 and 7a, b) for *ac*- anb *bc*- orientations. In case of *ac*- crystal orientation (Figure 5a), integral intensity of the EPR lines as a function of temperature increases at first from 3.38 K up to 5 k and next decreases fulfilling Curie-Weiss relation: $\chi = c/(T-\theta)$ with negative characteristic parameter θ = -2.05 K, what indicates the antiferromagnetic interactions between the magnetic centres. Above 20 K it still decreases but now it obeys Curie-Weiss relation with θ = 23.96 K what indicates the ferromagnetic like interactions. The maximum observed for low temperatures at about 5 K may indicate the presence of complex magnetic centres (pairs, clusters) or magnetic phase transition. We have observed much clear shape of the maximum for a sample with an arbitrary orientation (Figure 5c). Such phase transition at 5.5 K have been registered by Borowiec et. al. [3, 4]. In the shape of magnetic susceptibility, at T=20 K, they observed the lines change the angle of inclination in *a* and *c** directions. In case of *ac*- plane we have observed very close behavior of the integral intensity (Figure 5a) being representative to EPR magnetic susceptibility, χ_{EPR}. Besides usual Curie-Weiss fitting we performed fitting of the χ_{EPR} to modified Curie-Weiss law with additional constant term of background susceptibility (dashed line in Figure 5a), similar to Borowiec et al. [3]. From the fitting it results that in case of *ac*- plane antiferromagnetic interactions dominate with Curie-Weiss temperature θ = -7.85 K.

We have also measured and calculated temperature dependences of the EPR signal in *bc*-plane (Figure 5b). The dependences do not differ qualitatively from the ones above mentioned for *ac*-plane. From the fitting by modified Curie-Weiss law it results that Curie-Weiss temperature θ = -11.60 K. Both figures (Figure 5a, b) confirm complex nature of magnetic interactions and conclusion on anisotropy of magnetic properties of the crystal [3, 4].

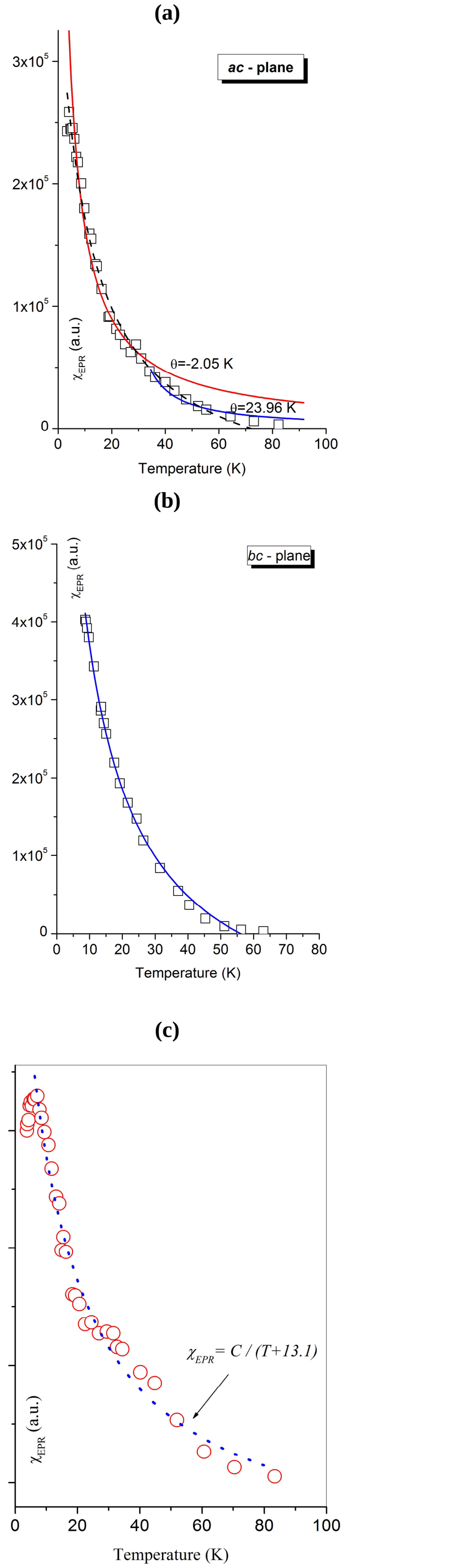

Figure 5. Integral intensity of the experimental EPR lines as a function of temperature (circles) and simulated lines (solid and dashed lines) fitted according to: Curie-Weiss relation $\chi_{EPR}= C / (T-\theta)$ for two sectors (solid lines) and modified Curie-Weiss relation $\chi_{EPR}= C_1+C / (T-\theta)$ (dashed line) in *ac-* plane (a), *bc-* plane (b) and in an arbitrary orientation (c).

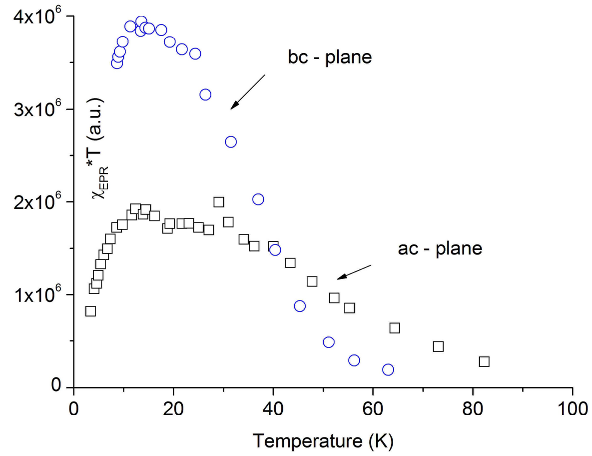

Figure 6. The product of EPR lines integral intensity and temperature as a function of temperature for *ac-* and *bc-* planes. Changes of the inclination of the function at ~15 K indicate the domination of antiferromagnetic and ferromagnetic interactions below and above this temperature, respectively.

Dependences presented in Figures 5 a-c represent average interactions between magnetic centres in a wide range of temperatures. In Figure 6 we have shown the product of integral intensity and temperature, being proportional to a square root of the magnetic moment of interacting ions. As can be seen, below 20 K, interactions between magnetic centres are strongly antiferromagnetic in type, while above this temperature they have got rather ferromagnetic character.

Figures 7a, b show g and ΔB parameters of the main EPR line calculated at *ac-* and *bc*-planes of the $KHo(WO_4)_2$ single crystal. As could be seen the position of EPR resonance line and the linewidth significantly change with a temperature. Both dependences reflect strong spin-spin and spin- lattice interactions between the holmium ions.

As could be seen from the roadmap presented in Figure 2a, for magnetic fields above 1600 mT, additional wide lines emerge. Unfortunately, positions of these lines are located above experimentally reachable magnetic fields, so full description of these signals is ambiguous. Roughly estimation allows suggest that high field signal cannot be described as a single line. This inhomogeneous signal probably reflects an existence of complex holmium magnetic sites with effective spin S> ½. Some confirmations to this explanation may be specific maximum in *I(T)* dependency presented in Figure 5a and weak resonance signal observed at about 350 mT (Figure 1).

4. Conclusions

EPR signal registered for $KHo(WO_4)_2$ single crystal consisted of wide and asymmetric signal located at magnetic fields above 600 mT. It clearly confirmed C_2 symmetry of responsible holmium magnetic centres. The observed X- band EPR signal could originate from complex arrangement of Ho^{3+} ions with effective spin S=1/2. Magnetic complexes are generated by vacancies near W^{6+} position.

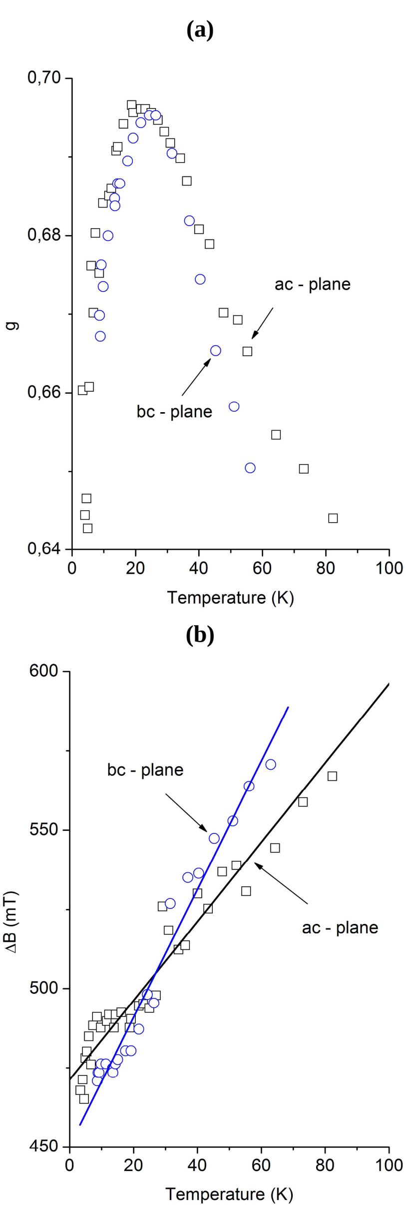

Figure 7. Effective spectroscopic parameters: g (a) and linewidth ΔB (b) of the main EPR signal observed in *ac*- and *bc*- planes.

Fitting of angle dependencies of EPR resonance signal detected in three planes, allowed calculating the *g* matrix parameters and its spatial orientation with respect to experimental axes. It indicates the rhombic distortion of holmium centres. Responsible magnetic centres show significant antiferromagnetic interactions with characteristic parameter θ being dependent on crystal orientation confirming magnetic anisotropy of the $KHo(WO_4)_2$ single crystal.

Additional wide lines were observed over 1600 mT. This high field signal reflects the existence of complex holmium magnetic centres, forming magnetic systems with S>1/2.

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