

EPR CHARACTERIZATION OF NEW CADMIUM, ZINC AND RARE-EARTH TUNGSTATES AND MOLYBDATES

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Some well known double molybdates and tungstates single crystals, as e.g. $\text{CsDy}(\text{MoO}_4)_2$, $\text{KDy}(\text{WO}_4)_2$, $\text{KLa}_{0.25}\text{Pr}_{0.75}(\text{WO}_4)_2$, $\text{KLa}_{0.25}\text{Pr}_{0.75}(\text{MoO}_4)_2$, as well as new cadmium and rare-earths tungstates or molybdates with the formulas $\text{CdRE}_2\text{W}_2\text{O}_{10}$, $\text{Cd}_{0.25}\text{RE}_{0.50}\text{MoO}_4$, and, rare-earth double molybdate-tungstates $\text{Cd}_{0.25}\text{RE}_{0.50}(\text{MoO}_4)_{0.25}(\text{WO}_4)_{0.75}$ ($\text{RE}=\text{Pr, Nd, Sm-Dy}$) as well as zinc and rare-earth molybdate-tungstates $\text{ZnRE}_2\text{MoWO}_{10}$ ($\text{RE}=\text{Pr, Sm-Dy}$) and $\text{II-Pr}_2\text{W}_2\text{O}_9$ and $\text{II-Pr}_2\text{WO}_6$ were analyzed using EPR method. The obtained compounds crystallize in the scheelite type structure and some of them show solubility in e.g. CdMoO_4 forming solid solutions.

INTRODUCTION

Among different analyzed materials the object of our special attention are rare-earth (*RE*) tungstates and molybdates. These materials have been extensively investigated in past decades as attractive laser hosts or phosphors (Kaminskii, 1996; Pujol, Mateos, Solé, Massons, Gavalda, Solans, Díaz & Aguiló, 2002; Majchrowski, Borowiec, Michalski, Zmija, Dyakonov, Szymczak, Zayarnyuk & Baranski, 2001). Solid-state lasers, based on doped rare-earth molybdates and tungstates, are characterized by high efficiency, very high stability emission, long lifetime and low excitation threshold as well as excellent thermal stability. White light-emitting diodes (WLEDs), called next-generation solid-state lighting, have got much attention in recent years because of their advantages over conventional light sources. High stability, low power consumption, safety and friendliness to the environment are some of the WLEDs advantages (Guzik, Tomaszewicz, Kaczmarek, Cybińska & Fuks, 2010).

The electron paramagnetic resonance (EPR) method in our study plays a peculiar role, as a very sensible method, enabling to obtain information about the local environment and the nature of interaction around magnetic centers.

EXPERIMENTAL

Sample preparation

Single crystals of the double potassium and caesium rare earth molybdates and tungstates were grown by the thermal method developed by Borisov and Klevtsova (1968). They crystallize in the orthorhombic (scheelite like) or monoclinic structure. The $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$ ($\text{RE}=\text{Nd, Sm, Eu, Gd}$, \square - statistically distributed vacancies in cation sublattice) compounds were synthesized by mixing together, at a suitable molar ratio of CdWO_4 and $\text{RE}_2\text{W}_2\text{O}_9$ (Guzik et al., 2010; Tomaszewicz, Kaczmarek & Fuks, 2009). New cadmium and rare-earth metal molybdates with the formula $\text{Cd}_{0.25}\text{RE}_{0.50}\text{MoO}_4$ ($\text{RE} = \text{Pr, Nd, Sm-Dy}$) were synthesized by the solid-state reaction of CdMoO_4 with corresponding $\text{RE}_2(\text{MoO}_4)_3$ (Tomaszewicz, Kaczmarek & Fuks, 2010). The $\text{Cd}_{0.25}\text{RE}_{0.50}\text{MoO}_4$ compounds showed solubility in CdMoO_4 forming the $\text{Cd}_x\text{RE}_{2-2x}(\text{MoO}_4)_{3-2x}$ ($0.50 < x < 1.00$) solid solutions (Tomaszewicz, Kaczmarek, Fuks, Leniec & Skibiński, 2010b). New cadmium and rare-earth metal tungstates $\text{CdRE}_2\text{W}_2\text{O}_{10}$ ($\text{RE}=\text{Y, Nd, Sm, Eu, Gd, Dy, Ho, and Er}$) were obtained by mixing together CdWO_4 and RE_2WO_6 (Tomaszewicz, Kaczmarek & Fuks, 2009). As the starting materials for obtaining cadmium and *RE* metal molybdate-tungstates $\text{Cd}_{0.25}\text{RE}_{0.50}(\text{MoO}_4)_{0.25}(\text{WO}_4)_{0.75}$ ($\text{RE}=\text{Pr, Nd, Sm-Dy}$) cadmium molybdate CdMoO_4 and rare-earth metal tungstates $\text{RE}_2(\text{WO}_4)_3$ were used (Tomaszewicz, Dąbrowska, Kaczmarek & Fuks, 2010a). All the compounds crystallized in the scheelite-type structure. For $\text{ZnRE}_2\text{MoWO}_{10}$ the

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starting materials were ZnWO_4 and Pr_2MoO_6 . Both compounds were synthesized by conventional ceramic methods (Tomaszewicz, Kaczmarek, Moszyński, Skibiński, Dąbrowska & Leniec, 2010c). An equimolar mixture of analytical grade $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ with WO_3 was heated in the air. The compounds crystallize in monoclinic system. The praseodymium(III) tungstates ($\text{Pr}_2\text{W}_2\text{O}_9$ and Pr_2WO_6) have been prepared as polycrystalline powders by thermal treatments of $\text{Pr}_6\text{O}_{11}/\text{WO}_3$ mixtures in the air (Kaczmarek, Tomaszewicz, Moszyński, Jasik & Leniec, 2010). The compounds reveal polymorphic modifications that crystallize in different crystallographic systems. All the above powders were heated after mixing in specific thermal conditions (in atmosphere of static air) (Guzik et al., 2010; Tomaszewicz, Kaczmarek & Fuks, 2009; Tomaszewicz & Kaczmarek, 2010, Tomaszewicz et al., 2010a-c). After each heating period, all mixtures were furnace cooled to room temperature, weighted, ground and examined for their content by XRD method. We investigated the following compounds: $\text{Cd}_{0.25}\text{RE}_{0.50}\square_{0.25}\text{WO}_4$ ($\text{RE}=\text{Gd, Dy, Sm, Eu, Nd}$) (\square -statistical distributed vacancies in the cation sublattice) (Guzik et al., 2010; Tomaszewicz, Kaczmarek & Fuks, 2009), $\text{Cd}_{0.25}\text{RE}_{0.5}\text{MoO}_4$ ($\text{RE}=\text{Pr, Gd, Nd, Sm-Dy}$), $\text{Cd}_x\text{RE}_{2-2x}(\text{MoO}_4)_{3-2x}$ ($\text{RE}=\text{Gd, Dy, Sm, Nd}$) solid solution (Tomaszewicz et al., 2010b), $\text{CdRE}_2\text{W}_2\text{O}_{10}$ ($\text{RE}=\text{Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, AND Lu}$) (Tomaszewicz & Kaczmarek, 2010), $\text{Cd}_{0.25}\text{RE}_{0.5}(\text{MoO}_4)_{0.25}(\text{WO}_4)_{0.75}$ ($\text{RE}=\text{Pr, Nd, Sm-Dy}$), $\text{Cd}_x\text{Gd}_{2-2x}(\text{MoO}_4)_x(\text{WO}_4)_{3-3x}$ solid solution, $\text{Cd}_{0.25}\text{RE}_{0.25}(\text{MoO}_4)_{0.50}(\text{WO}_4)_{0.50}$ ($\text{RE}=\text{Gd, Eu, Nd}$) (Tomaszewicz et al., 2010a-b), $\text{ZnGd}_2\text{MoWO}_{10}$ ($\text{RE}=\text{Pr, Sm-Dy}$) (Tomaszewicz et al., 2010c)

Measurements

The EPR measurements were performed with a conventional X-band Bruker EleXsys E500 CW spectrometer operating at 9.5 GHz with 100 kHz magnetic field modulation. Temperature dependence of the EPR spectra was registered in the 3–295 K temperature range using the Oxford flow cryostat to control it. EPR spectra were analyzed using EPR-NMR (Mombourquette, Weil & McGavin, 1999) and SIMPOW (Nilges, SIMPOW) programs.

SELECTED EPR RESULTS AND DISCUSSION

EPR studies of the selected RE^{3+} tungstates, molybdates and molybdato-tungstates were mainly concentrated on magnetically active RE^{3+} ions. These ions play a double role: magnetic probe, revealing information about a local atomic environment and, from the other hand, they are active source of luminescence, deciding on optical properties of these materials.

First of all we have performed EPR and Raman spectroscopy analysis of very well known single

crystals of double tungstates and molybdates ($\text{CsDy}(\text{MoO}_4)_2$, $\text{KDy}(\text{WO}_4)_2$, $\text{KLa}_{0.25}\text{Pr}_{0.75}(\text{WO}_4)_2$, $\text{KLa}_{0.25}\text{Pr}_{0.75}(\text{MoO}_4)_2$, Fuks, Kaczmarek, Leniec, Macalik, Macalik & Hanuza, 2010). From the structure considerations of the studied molybdates and tungstates it follows that in all these materials the RE^{3+} ions appear in the low-symmetry oxygen environment. The shape of the EPR signal suggests that several spin systems can exist in the studied crystals forming a few non-equivalent magnetic centres. The EPR spectra of $\text{CsDy}(\text{MoO}_4)_2$ and $\text{KDy}(\text{WO}_4)_2$ crystals, e.g., consist of a broad and asymmetric line attributed to the Dy^{3+} paramagnetic entities. An additional narrow signal visible at about 330 mT could be due to the Mo^{5+} or W^{5+} ions. Both of those lines emerge as reduced ions from the nominally non-magnetic $6+$ state. Domination of Gaussian shape points to significant dipole–dipole interactions in the Dy^{3+} magnetic system. For the $\text{CsDy}(\text{MoO}_4)_2$ crystal, changes of the integral intensity I_{int} as a function of temperature follow the Curie–Weiss (C–W) law, $I_{int} = C/(T-\theta)$, with negative Curie–Weiss temperature $\theta = -0.64$ K indicating on very weak antiferromagnetic interaction between Dy^{3+} ions. Signal from Mo^{5+} obeys C–W law with negative temperature parameter, $\theta = -1.07$ K, indicating antiferromagnetic interaction between molybdenum paramagnetic entities. C–W law for Dy EPR line is satisfied only in a limited temperature region. The difference ΔI_{int} between the calculated value from the low-temperature C–W law I_{int}^{CW} and observed in experiment I_{int}^{obs} grows as the temperature rises from 10 K and reaches a maximum at about 35 K. It suggests the existence of an excited state located about 35 K over ground one, being non-magnetic state. In case of $\text{KDy}(\text{WO}_4)_2$ crystal magnetic interactions reveal ferromagnetic kind with $\theta = 2.96$ K, whereas signal from W^{5+} obeys C–W law with the negative temperature parameter $\theta = -1.09$ K, indicating antiferromagnetic interaction between tungstate paramagnetic entities. In this case, however, a broad dysprosium line cannot be evaluated properly, due to a strong anisotropy of the line, because some components located in low magnetic fields are additionally observed. Thus, the EPR results for both dysprosium as well as praseodymium: molybdates and tungstates suggested that the transition metal ions are well isolated in these types of structures, showing only weak magnetic interaction.

As a continuation of these investigations we have analyzed EPR properties of some new molybdates, tungstates and molybdato-tungstates of RE ions in the form of polycrystalline powders. Gd^{3+} ion giving an intense EPR line visible even at room temperature seems to be a natural object of interest. The ion has almost the same size as Eu^{3+} (0.938 Å versus 0.947 Å) and therefore it should behave in the same manner as Eu^{3+} entering the host. The following samples: $\text{Cd}_{0.25}\text{Gd}_{0.5}(\text{MoO}_4)_{0.25}(\text{WO}_4)_{0.75}$, $\text{Cd}_{0.25}\text{Gd}_{0.50}\square_{0.25}\text{WO}_4:\text{Eu}^{3+}$, $\text{Cd}_{0.25}\text{Gd}_{0.5}\text{MoO}_4$ and $\text{Cd}_x\text{Gd}_{2-2x}(\text{MoO}_4)_{3-2x}$ solid solution have been studied by using EPR

technique in 80 - 300 K range (Guzik et al. 2010, Tomaszewicz et al. 2010a, b). For all samples we have detected a wide resonance line, being an envelope of unresolved anisotropic fine structure of the Gd^{3+} ions in powder. The shape of this line is close to the Gaussian type shape, which is a result of specific overlapping of the powder EPR spectrum, additionally indicating on possible dipole-dipole interactions between gadolinium ions.

At lower gadolinium concentration, the EPR signal has rather asymmetric shape, while with increasing the Gd^{3+} content the line becomes more symmetric. For diluted compounds, with $2-2x \leq 0.2$, by employing proper crystal structure parameters (B_q^k) to a spin Hamiltonian it was possible to obtain information about a local symmetry of the RE^{3+} position. The best simulation of the EPR signal was performed for a temperature of about 120 K by using the EPR-NMR program (Mombourquette, Weil & McGavin, 1999) and the following spin-Hamiltonian:

$$H_s = \mu_B B g S + D \left[S_z^2 - \frac{1}{3} S(S+1) \right] + E(S_x^2 - S_y^2) + B_4^0 O_4^0 \quad (1)$$

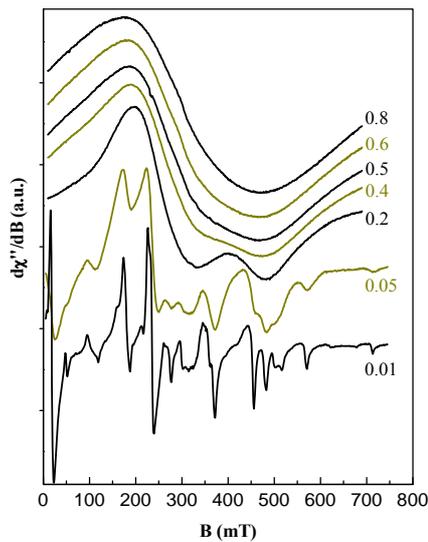


Fig. 1. EPR signals of $Cd_xGd_{2-2x}(MoO_4)_{3-2x}$ samples measured at 120 K with different Gd^{3+} concentration ($2-2x$), from 0.01 to 0.8.

It is obvious that the internal magnetic field, relaxation processes and local crystal field depend in some extent on the gadolinium content. The calculated value of B_4^0 parameter suggests that Gd^{3+} ions can have local octahedral surrounding in the compounds with no rhombic distortion ($E \sim 0$) (Tomaszewicz et al., 2010a).

Table 1. Temperature parameter θ of Curie-Weiss relation for different concentrations of Gd^{3+} ions in $Cd_xGd_{2-2x}(MoO_4)_x(WO_4)_{3-3x}$

$2-2x$	0.01	0.05	0.2	0.4	0.6	0.8
θ	2.7	2.3	7.9	9.4	32.7	33.6

In case of $Cd_xGd_{2-2x}(MoO_4)_x(WO_4)_{3-3x}$ compound, as could be expected, samples with small gadolinium content revealed resonance lines attributed to the isolated Gd^{3+} ions (Fig. 2).

These ions are affected by local crystal field giving a complex resonance signal with fine structure. As concentration of Gd^{3+} ions increases, the EPR lines became wider due to more intense relaxation processes. With the increase of Gd^{3+} ions content, the exchange interaction between Gd^{3+} ions became more significant, which is observed in changes of θ parameter calculated according to the Curie-Weiss relation: $I = C/(T - \theta)$ (see Tab. 1).

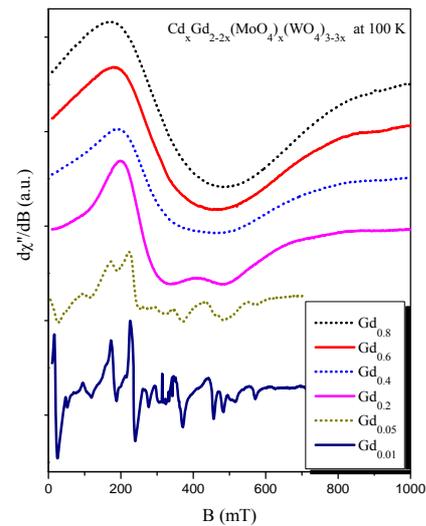


Fig. 2. The EPR spectra of $Cd_xGd_{2-2x}(MoO_4)_x(WO_4)_{3-3x}$ solid solutions with different x content at the temperature of 100 K.

The shape of the EPR spectra of the $Cd_{0.25}Gd_{0.5} \square_{0.25}WO_4:Eu^{3+}$, \square – vacancy, solid solution suggested a local low symmetry environment of Gd^{3+} sites in the investigated samples (Guzik et al. 2010). Only samples with enough large concentration of Gd^{3+} ions revealed strong antiferromagnetic interactions with the Curie-Weiss temperature parameter, e.g., $\theta = -25.6$ K (10 mol.% Eu^{3+}). A change in the magnetic interaction type with a change in the nominal Eu^{3+} concentration, observed here, indicated on possible limits of the concentration quenching phenomenon observed in the same range of the Eu^{3+} concentration in the optical spectra. This compound seems to be an efficient red phosphor for white light diode purposes.

In the $\text{Cd}_{0.995}\text{Gd}_{0.01}(\text{MoO}_4)_{0.995}(\text{WO}_4)_{0.015}$ sample, where content of gadolinium is smaller, a share of CdMoO_4 in solid solution is significant. As a result, the hyperfine structure of six narrow lines of pentavalent ^{95}Mo (abundance 15.9%) and ^{97}Mo (abundance 9.6 %) isotopes ($S=1/2, I=5/2$) is visible in EPR experiment (Fig. 3). It may be attributed also to Mn^{2+} uncontrolled ions, because hyperfine parameter $A_{iso}=9.6$ mT (usually ~ 8.6 mT for Mn^{2+} in glasses), moreover, there is missing a central line, characteristic for Mo^{5+} ions (Garces, Chirila, Murphy, Foise, Thomas, Wicks, Grencewicz, Halliburton & Giles, 2003; Podgórska, Kaczmarek, Drozdowski, Wabia, Kwaśny, Warchoń & Rizak, 2004). Nevertheless, from XPS measurements we know that manganese ions are absent in the compounds but Mo^{5+} ions are clearly observed (Kaczmarek et al., 2010). To explain the origin of the hyperfine structure we assumed that there are Mo^{5+} pairs in the compounds. In the presence of the pairs the main line can be split forming the observed spectrum. Supposing the simplest complex model, i.e. the existence of magnetic pairs Mo-Mo with $S=1$ we have performed EPR-NMR simulation employing the spin Hamiltonian of the form:

$$H_s = \mu_B B g S + D [S_z^2 - I/3 S(S+I)] + E (S_x^2 - S_y^2) \quad (2)$$

Best results we obtained for axial local symmetry of Mo^{5+} ions with g-factor values: $g_{\perp}=4.0, g_{\parallel}=2.8, D=312$ mT, $E \sim 0$. It agrees with local symmetry of $\text{Gd}^{3+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ ions substituted for W^{6+} in similar compounds. These compounds seem to be promising luminescent materials (Tomaszewicz et al., 2010b).

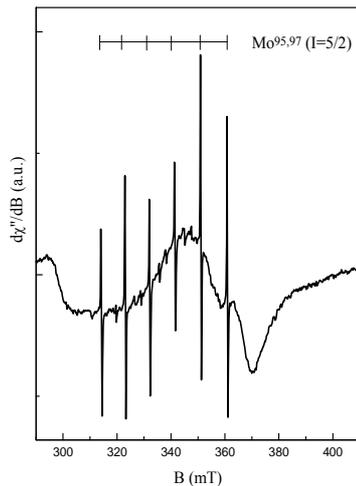


Fig. 3. Hyperfine structure of odd Mo^{5+} isotopes observed in $\text{Cd}_x\text{Gd}_{2-2x}(\text{MoO}_4)_x(\text{WO}_4)_{3-3x}$ solid solutions with $x=0.995$ at a temperature of 220 K.

According to the crystal structure of typical double tungstates and molybdates, they nominally could

consist of two kinds of paramagnetic centres: RE^{3+} ions with C_2 or lower point symmetry, located at distorted dodecahedra and/or reduced transition metal Me^{5+} ($\text{Mo}^{5+}, \text{W}^{5+}$) ions located at octahedral sites (Fuks et al., 2010, Kaczmarek et al., 2010, Tomaszewicz et al., 2010a-c).

The tungsten or molybdate center is expected to undergo two subsequent one-electron reductions from Me^{6+} to Me^{4+} . The intermediate Me^{5+} is paramagnetic and shows a typical $S=1/2$ signal with all g values usually below 2.0, which is still observable at temperatures as high as 100 K (Tomaszewicz et al. 2010b). In case of some praseodymium tungstates ($\text{II-Pr}_2\text{W}_2\text{O}_9$ and $\text{II-Pr}_2\text{WO}_6$, Kaczmarek et al., 2010), besides main EPR line centered at about $g=2.07$ attributed to W^{5+} ion we have observed hyperfine structure of W^{4+} ions. The 4-fold signal of hyperfine interaction, centered at $g = 1.210, 1.110, 1.007$ and 0.932 seem to be a hyperfine structure of ^{183}W isotope ($\sim 14\%$ abundance) with an electron spin $S = 1$ and nuclear $I = 1/2$.

The resonance spectra of the $\text{ZnGd}_2\text{MoWO}_{10}$ compound observed in the range of 79-250 K show a wide, asymmetric and intense EPR line due to the Gd^{3+} paramagnetic centers (Tomaszewicz et al., 2010c). The line requires analysis in negative fields. The shape of this line seems to be more Gaussian type (G) than Lorentzian one (L), and best fitting of the experimental line we obtained for the formula: 66% G + 34% L. Significant share of the Gaussian line indicates on dominating dipole-dipole interaction between gadolinium ions. The temperature dependence of the EPR integrated intensity, χ_{EPR} , of $\text{ZnGd}_2\text{MoWO}_{10}$ complex is presented in Fig. 4. Unexpectedly, in the high-temperature range ($T > 100$ K) the integrated intensity increases with temperature increase. In case of the $\text{ZnGd}_2\text{MoWO}_{10}$ complex the C-W law (second term, monomers) was not sufficient to give good enough agreement with experimental points, so we add Bleaney-Bowers (Bleaney & Bowers, 1952) term containing the contribution of dimers (first term) of the following form:

$$\chi_{EPR} = \frac{C_1}{T - \theta_{BB}} \left[1 + \frac{1}{3} \exp\left(-\frac{2J}{kT}\right) \right]^{-1} (1 - \rho) + \frac{C_2}{T - \theta_{CW}} \rho + C_3 \quad (3)$$

where ρ is the fraction of monomeric gadolinium centers, k – Boltzmann constant, J – exchange interaction constant, $C_i, i=1, 2, 3$ – constants. Eq. 3 is generally valid for the paramagnetic ions with effective spin $1/2$, nevertheless it gave very good approximation to our experimental points. So we adopted the approach of $S_{eff}=1/2$. In Fig. 4 the results of the least-squares fit to the experimental points, χ_{EPR} , are presented. The value of the Curie-Weiss

temperature obtained from $1/\chi_{EPR}$ dependence for temperatures below 100 K was $\theta_{CW} = 20$ K. For higher temperatures it takes a value of -30 K. As one can see from Fig. 4 the percentage of monomeric paramagnetic gadolinium ions is as high as 72% (dominating dipole-dipole interaction). The temperature dependence of the product of a temperature and integrated intensity, $T \cdot \chi_{EPR}$, for $ZnGd_2MoWO_{10}$ compound reveals that it decreases with temperature decrease in high-temperature range ($T > 100$ K), but increases in low-temperature range, below 100 K. Thus the dominating antiferromagnetic interaction at high temperature changes to the ferromagnetic interaction at low temperatures. The switch of magnetic interaction type is usually interpreted in terms of two-component system. The first is a paramagnetic one, present as a monomeric gadolinium. The second component is an antiferromagnetic one, formed as a result of an intermolecular indirect exchange interaction between gadolinium centers. The fit gave the following value of the interaction constant $-2J = 220$ (cm^{-1}) confirming antiferromagnetic kind of interactions in high temperature region.

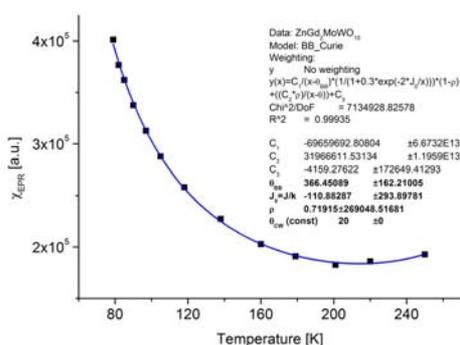


Fig. 4. Integrated intensity and its fit to Curie-Weiss and Bleaney-Bowers mixed curve for $ZnGd_2MoWO_{10}$

PERSPECTIVES AND CONCLUSIONS

Another step in our researches includes study of tungstates and molybdates or mixed tungstato-molybdates with Nd^{3+} and Dy^{3+} ions (Tomaszewicz et al., 2010b). Recently obtained low temperature spectra revealed existence of the EPR signal of both ions at high symmetry (axial like) position and the same hyperfine structure without central line attributed to Mo^{5+} ions as observed in the above compounds. Due to high interval between ground and excited states both of RE^{3+} ions could be treated as Kramers type magnetic centers with effective spin $S=1/2$. Analysis with employing of the SIMPOW procedure is possible in this case (Tomaszewicz et al., 2010b).

At low temperatures some extra lines are visible at magnetic field below 300 mT. These lines could be

ascribed to complex magnetic system developed in this group of materials.

Presented tungstates and molybdates could melt congruently in some conditions. So, in next future, crystal growth of the materials using the Czochralski method seems to be possible.

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