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The phase transitions in double tungstate - in extremely low-dimensional and low-symmetry compounds with cooperative Jahn-Teller effect

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ABSTRACT

The rare earth double tungstates are of special interest because of manifestation of cooperative Jahn-Teller effect (CJTE) for low-dimensional and low-symmetry (monoclinic) crystallographic structure. The structural phase transition (SPT) as a result of the CJTE is unique one among large numbers of various SPT in solids. In the alkali-dysprosium double tungstates $ADy(WO_4)_2$ (A= K, Rb, Cs) in spite of monoclinic symmetry the SPT of CJTE type are realized because the presence of Dy^{3+} ions with closely spaced energy levels.

In alkali-dysprosium double tungstates the magnetically ordered structures possessing a number of features connected with low-dimensional interactions of Dy^{3+} ions were observed. Studies of specific heat in magnetic field and of magnetic susceptibility led to conclusion that the magnetic phase transitions (MPT) from paramagnetic to antiferromagnetic state take place at subkelvin temperature region.

Both MPT and SPT are very sensitive to magnetic field. In case of SPT this confirms its CJTE nature and allows to determine the type of the elastic ordering (SPT from para- to antiferroelastic states are observed). The external magnetic field induced the transitions from antiferro- to ferromagnetic states.

The alkali-dysprosium double tungstates belong to the more general class of magneto-elastics with interrelation between magnetic and elastic ordering.

Keywords: rare earth double tungstate; cooperative Jahn-Teller effect, structural phase transition, magnetic phase transition, elastic ordering, magnetic ordering

1. INTRODUCTION

Phase transitions, including structural phase transitions (SPT), are among the most pervasive phenomena in nature. They are intriguing because of the SPT manifest connections and interactions in a substance that determine the structure and properties of its stable states. The SPT, whether spontaneous or induced, can be used to establish the basic laws governing the formation of phase states and symmetry in real crystalline materials. Accordingly, the studies of SPT as a result of the cooperative Jahn-Teller effect (CJTE) are of major importance. As a rule, the SPT of the cooperative Jahn-Teller type (SPT CJTE) takes place in high symmetry compounds [1]. This kind of phase transitions is not very common for rare earth compounds. Particularly SPT CJTE has never been observed in rare-earth low-dimensional materials.

The dysprosium double tungstates with general formula $ADy(WO_4)_2$ (ADyW), where A is alkali metal ion, with low-symmetry (monoclinic) and with low-dimensional structures in the form of chain-layered atomic constructions are currently intensively studied [2-29]. Scientific interest in these compounds is mainly connected with the SPT CJTE which occurs in them at low temperature of order of several kelvins and with the complex magnetic ordering at subkelvins region.

One of the main purposes of this paper was to determine the character and mechanism of elastic ordering in ADyW compounds (where A = K, Rb, Cs). Studies of magnetic properties of the ADyW crystals are of interest because of the interrelation between magnetic and elastic ordering realized in these magneto-elastics. Main goal of these studies was to investigate peculiarities of magnetic ordering and character of spin-spin interactions in low-dimensional magnets as well as to establish the magnetic structure of the ground state.

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Elastic and magnetic ordering in the alkali-dysprosium double tungstates ADyW has been studied by means of several independent experimental methods, namely: specific heat (from 0.2 K); specific heat in magnetic field; index of refraction; optical absorption spectroscopy of electronic states (from 1.1K); photoluminescence, Raman scattering; optical absorption spectroscopy of phonon states; Electron Spin Resonance (ESR); magnetization; magnetization under pressure, magnetic susceptibility (from 0.6 K); neutron scattering (from 0.04 K) in wide interval of temperatures (T= 40 mK - 300 K) and magnetic fields (up to 3 T) including also studies under pressure up to 1.2 GPa. (the pressure for elastics plays the same role as the magnetic field for magnetics or the electric field for electrics). The details of used experimental methods are described in large number of papers[2-29].

2. EXPERIMENTAL TECHNIQUES

The double tungstates of the general formula $ARe(WO_4)_2$, where A is an alkaline ion, Re - rare-earth ion, undergo irreversible structural phase transitions at temperatures slightly below their melting points. This phenomenon does not allow obtaining low temperature phases of these compounds by means of the Czochralski technique despite their congruent melting. To lower the temperature of crystallization below the temperature of the phase transition High Temperature Solution Growth (HTSG) technique is used. The single crystals of $ADy(WO_4)_2$, where A= K, Rb, were grown by the TSSG technique on [110] oriented $KDy(WO_4)_2$ seeds (in some paper this technique is called the modified Czochralski method), which were obtained by means of spontaneous crystallization from solutions of $KDy(WO_4)_2$ in $K_2W_2O_7$ as solvent. The single crystals grow in form of cylinder bounded by {110} and {011} prisms and by {100}, {010}, and {001} pinacoids. The dimensions of the homogeneous single crystals reached about 20x20x60 mm for $KDy(WO_4)_2$ and about 6x6x10 mm for $RbDy(WO_4)_2$. The microcrystals of $CsDy(WO_4)_2$ grown by the method of spontaneous crystallization reached of about 300 μm in diameter. The $CsDy(WO_4)_2$ microcrystals were pressed to form of pellets. Density is equal: 7.47g/cm^3 for $KDy(WO_4)_2$ and 7.79g/cm^3 for $RbDy(WO_4)_2$. The Mohs hardness (pinacoid {100}) was approximately five. The energy gap is of about 3.8 eV. The color of single crystals is connected with optical absorption of rare earth ions: for the $ADy(WO_4)_2$ is light yellow, for the $AEr(WO_4)_2$ is pink.

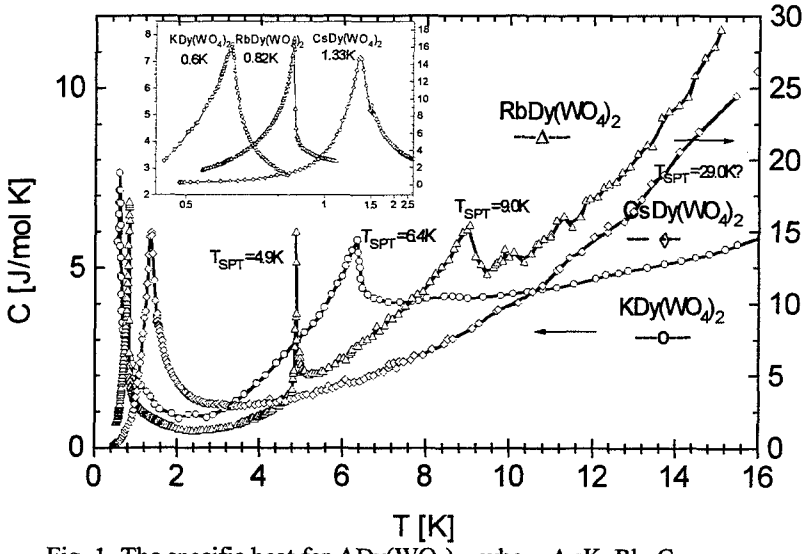

Fig. 1. The specific heat for $ADy(WO_4)_2$, where A=K, Rb, Cs.

The alkali-dysprosium double tungstates crystallize at room temperature in α-$KY(WO_4)_2$ structure and they are characterized by the space group $C^6_{2h} = C2/c$ [30]. The unit cell contains four formula units. The lattice parameters are a=8.05A; 8.14A, b=10.32A; 10.45A, c=7.52A; 7.57A, β=94°13'; 94°34' for $KDy(WO_4)_2$ and $RbDy(WO_4)_2$ respectively. The structure is characteristic for several others rare earth double tungstates and belongs to the chain-layered systems. The unit cell consists of layers of $(DyW_2O_8)^-$ spaced parallel to the *ac* plane and separated by layers of K^+ ions. Eight oxygen ions surrounding the dysprosium ion form a dodecahedron in which two oxygen ions are spaced at a greater distance from the rare earth ion than the other six. The dodecahedrons of oxygen are located in chains parallel to **a** axis. The oxygen and tungstate ions are located at common positions. The dysprosium and alkali metal ions are placed on C_2 point symmetry site.

The chain-layered crystallographic structure is a reason of anisotropy of many physical properties (for example mechanical anisotropy observed in processes of cutting and polishing of single crystals). In the system characterized by $C^6_{2h} = C2/c$ the symmetry point exists. For systems with this symmetry point any Jahn-Teller distorsions cannot lead to state with spontaneous electrical polarization but they can lead to state with spontaneous deformation of lattice. That means the alkali-dysprosium double tungstates can be elastics (ferro- or antiferroelastics) but they cannot be electrics (ferro- or antiferroelectrics).

The cooperative Jahn-Teller effect is a phase transition which is driven by the interaction between the electronic states of one of the constituent species of ions in a solid and the collective lattice vibrations (phonons). The phase transition may be of first or second order and in both these cases a symmetry-lowering distortion of the crystal lattice is involved. As a result the splitting of all electron energy levels is observed. This short description of the cooperative Jahn-Teller effect indicates that we must consider thermodynamical properties (for example specific heat) to find a phase transition, and then (next) the electron states, the lattice vibrations and finally we must find a change of the space symmetry (point or translational; the phase transition is proper if point symmetry is changed and it is improper if only translational symmetry changes).

3. SELECTED EXPERIMENTAL RESULTS

3.1. Specific heat

Fig. 1 presents globally the results of specific heat measurements in zero magnetic field for the ADyW crystals, where A= K, Rb, Cs. The subkelvins region is presented in details in the insert of Fig. 1. Several anomalies can be observed. For the $KDy(WO_4)_2$ crystal the temperature dependence of specific heat C(T) has a broad maximum with peak at $T_{SPT} = 6.38$ K. For the $RbDy(WO_4)_2$ crystal the zero-field specific heat as a function of temperature C(T) was found to exhibit the peculiarities at the following temperatures: 4.9 K; 9.0 K and about 18 K. The results of measurements of specific heat in the $CsDy(WO_4)_2$ powder pellets have shown that anomaly takes place at T= 29 K. All above anomalies were attributed to the structural phase transitions. In subkelvins region the anomalies at 0.6 K, 0.82 K and 1.34 K for KDyW, RbDyW, CsDyW, respectively are clearly seen. These anomalies are shown to be related to the magnetic phase transitions.

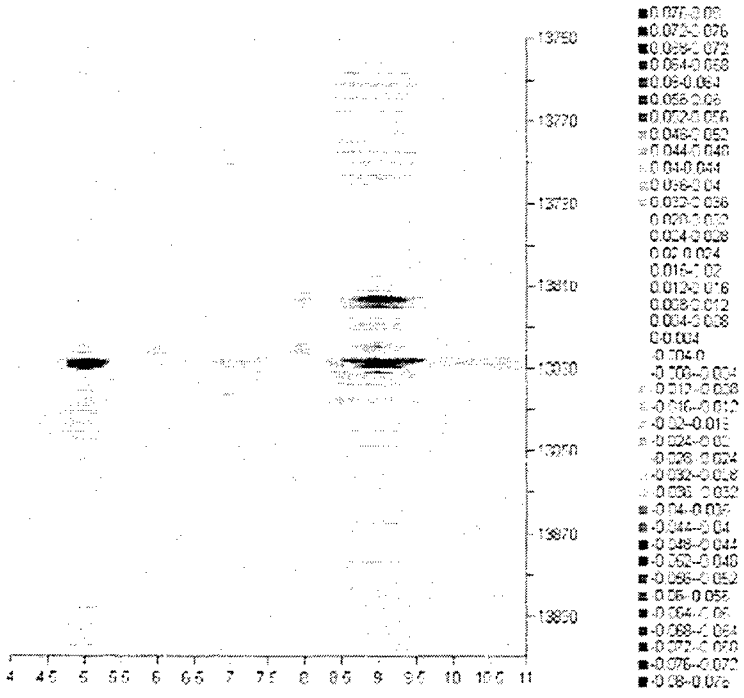

Fig. 2 Derivative of optical absorption coefficient for $RbDy(WO_4)_2$ (as example) in arbitrary selected spectral region 13750cm^{-1}-13900cm^{-1} (optical transition from $^6H_{15/2}$ to $^6H_{1/2}$ and $^6F_{3/2}$) at temperature from 4.0K to 11K in maep representation.

3.2. Optical spectroscopy of electron states

Because of low symmetry (C^6_{2h}-C2/c) of the $ADy(WO_4)_2$ single crystals its optical properties are highly anisotropic. In particular, the alkali-dysprosium double tungstates belong to the optical class of biaxial crystals. The orientations of optical axes (main axes of indicatrix) and the crystallographic axes are different with one exception of the optical axis **y** which is identical with the crystallographic axis **b**. The angle between the optical axis **x** and the crystallographic axis **a** is of order of 20 degrees.

The trichroism (pleochroism) of $ADy(WO_4)_2$ was found experimentally, that means the optical absorption is characterized by three different, independent spectra attributed to three optical axes (so called main optical spectra). The spectra are composed of several groups of narrow lines in the same spectral regions (and in the same order) similarly to the spectrum of free dysprosium ion. The absorption spectra are attributed to the electronic transitions between ground state and excited states of Dy^{3+} ion with f^9 electron configuration. The ground multiplet $^6H_{15/2}$ in crystal field of low monoclinic symmetry is split into 8 Kramers doublets. The energy separations between the lowest Kramers doublets of ground multiplet are following 10 cm^{-1}, 135 cm^{-1} and 350 cm^{-1}. Specially important is the system of two lowest Kramers doublets separated by only 10 cm^{-1}. This two level system is nearly degenerated.

What happens with electronic states of dysprosium ions, and in consequence with optical absorption, at temperature of structural phase transitions? For potassium and rubidium dysprosium double tungstates some small changes

were found, but enough small, that in usual representation of optical absorption curves they would be difficult to observe. In contrary to usual representation, Fig. 2 presents derivative of optical absorption coefficient on temperature for $RbDy(WO_4)_2$ single crystals as example. It is clearly seen in Fig. 2, that in this representation of optical absorption there can be found spectacular changes on temperature strongly correlated to the anomalies in specific heat at 4.9 K and 9.0 K. Similar results can be obtained for potassium dysprosium double tungstates at 6.4 K. The explanation of the optical result is following: at temperatures of structural phase transitions the energy separations between two nearly degenerated lowest Kramers doublets increase: for KDyW of about 2-3 cm^{-1} (at 6.4 K), for RbDyW of about 1-2 cm^{-1} (at 4.9 K) and 1 cm^{-1} (at 9.0 K). Change of energy separations between two lowest Kramers doublets is the biggest for mixed single crystals with cesium: for $Cs_xK_{1-x}DyW$ the change is of about 4 cm^{-1} (for SPT at 14.0 K and 19.0 K for x=0.05 and x=0.1 respectively). The increase of separation between two lowest Kramers doublet strongly indicates on mechanism of Jahn-Teller effect type.

3.3. ESR

The smooth change of g-factors with temperature in the KDyW crystal has been observed in the vicinity of the SPT (for example, g_z is equal to 3.13 at T>12 K and 1.98 at 4.2 K). The transition region has sufficiently wide temperature interval of about 8 K. The ESR linewidth increases from 0.17 T (at T>12 K) to maximum value of 0.24 T at T_{SPT} = 7 K. A narrowing of resonance line to 0.19 T takes place at T= 4.2 K. Similar behavior has been observed in the RbDyW crystal. The g-tensor components change considerably from: g_z= 2.5; $g_x \approx 0$; g_y= 1.41 for T>12 K to: g_z= 1.53; $g_x \approx 0$; g_y= 1.2 for T< 7 K. The ESR linewidth increases from 130 mT for T>12 K up to maximum value of 190 mT at $T_{SPT} \approx 9$ K and then it decreases monotonously to 150 mT at 5 K.

The change of gyroscopy factor at temperature of the structural phase transition, the width of ESR line of specific shape near the SPT are simple interpreted in frame of change of energy separation between two lowest Kramers doublets. That means the interpretation of ESR results are in full agreement with the interpretation of the optical absorption results.

Partially summarizing, at SPT the changes of electronic state are observed, the electron ground state energy has lower energy below the temperature of the SPT. To confirm of manifestation of the cooperative Jahn-Teller effect one should consider now the behavior of the atomic system.

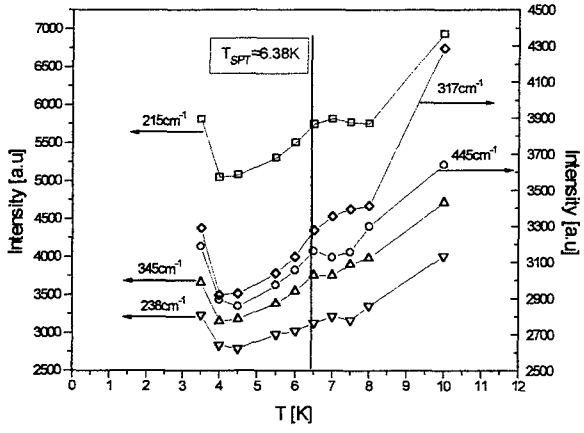

Fig. 3 The Raman scattering results for XX polarization for selected phonon modes in function of temperature.

3.4. Raman scattering

Raman scattering is unusual complicated. However, the good explanation (at room temperature) made by Hanuza [31] is known in world literature. The phonon modes, mainly these ones, which are connected with dysprosium ions in Hanuza interpretation, behaves anomaly at temperature of structural phase transition - Fig. 3. The irregularities of the behavior of the atomic system which where serched for and found strongly suggest that the structural phase transitions observed in specific heat are related to the cooperative Jahn-Teller effect.

Now the summary is following: the anomalies in specific heat, strongly correlated with lowering of energy of the electron state and the irregularities in behavior of the atomic systems suggests: our SPTs are type of the cooperative Jahn-Teller effect.

3.5. Elastic ordering

The information about the type of elastic ordering bases on the experimental results of specific heat in magnetic field. Generally magnetic field diminishes the structural phase transitions. Interpretation of dependences on magnetic field in the frame of molecular field theory, with interaction between Jahn-Teller active ions in formalism of pseudo-spin [32], with magnetic field and magnetoelastics coupling included to the formalism indicates that for all dysprosium double tungstates the antiferroelastic ordering is realized.

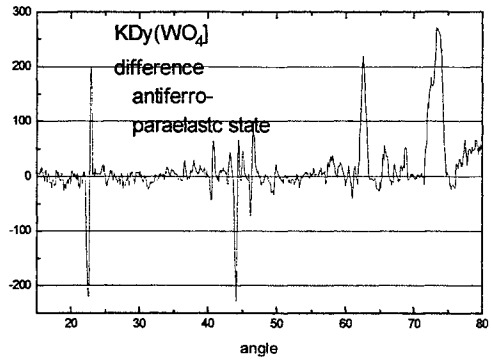

Fig. 4 The neutron scattering results for powdered potassium dysprosium double tungstate

3.6. Neutron structural investigations

Fig. 4 presents the preliminary results of the neutron scattering for powder of potassium dysprosium double tungstate. Figure presents the difference between the neutron scattering for antiferroelastic and paraelastic states. The difference is composed from shifts of some lines and additional lines for higher angles. However, because of high coefficient of neutron absorption of dysprosium ions the errors are enough high that the results must be confirm with used the independent or high sensitivity method. But it is clear that results present additional information about the symmetry of the atomic system and they will be very important to understand of mechanism of the SPT in double tungstates.

3.7. Magnetic phase transitions

The magnetic phase transitions (MPT) in alkali-dysprosium double tungstates have been studied using the temperature dependence of the specific heat C(T) measured in magnetic field and the results of the magnetization and magnetic susceptibility experiments. The results indicate that the alkali-dysprosium double tungstates ADyW crystals are good paramagnets with strong anisotropy of magnetic properties up to helium temperatures.

The main feature of C(T) dependences at subkelvin temperature is an anomaly connected with the magnetic ordering of Dy^{3+} ions with the peak at T_N= 0.6 K; 0.82 K; 1.34 K, respectively for the KDyW, RbDyW, CsDyW. The C(T) dependences above and below T_N were analyzed using the theoretical models for both 3D Ising and 2D Ising lattices and XY model. Data of the analysis give no single-valued answer as to what model well describes the specific behavior near T_N. The temperature dependences of the specific heat at $T > T_N$ can not be well described by 2D and 3D Ising models. The C(T) dependences below T_N are 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.

In magnetic field the C(T) peaks shift to lower temperatures. The C(H,T) dependences strongly depend on magnetic field orientation. For example for KDyW crystals the decreasing of T_N by 0.04 K takes place in field of 240 mT along the *c*-axis while field H = 60 mT applied along the ***a***-axis is enough to obtain the same shift. The experimental and theoretical H - T_N diagrams also show that T_N depends strongly on magnetic field direction. The experimental phase boundary between the magnetic (antiferromagnetic) and paramagnetic phases is in a reasonable agreement with the theoretical $T_N(H)$ dependence for 2D Ising antiferromagnet that suggest the magnetic ordering of Dy^{3+} sublattice has a two-dimensional character. The comparison of the calculation with the experiment data shows that a part of the expected Rln2 entropy is missing. The experimental value of the effective exchange parameter was obtained. 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 Dy^{3+} ions interactions. The experimental J/k value was shown to correlate with theoretical value for 2D Ising model better than for 3D one.

4. CONCLUSIONS

The rare earth double tungstates are unique one among large numbers of various SPT in solids because of manifestation of cooperative Jahn-Teller effect (CJTE) as the reason of structural phase transition for low-dimensional and low-symmetry (monoclinic) crystallographic structure. To this time, the structural phase transitions (SPT) of the cooperative Jahn-Teller type from paraelastic to antiferroelastic state were observed at 6.38K, 4.9K and 9.0K, ~29K for KDyW, RbDyW and CsDyW, respectively.

In the tungstates (K,Rb,Cs)DyW in spite of monoclinic symmetry the SPT of CJTE type are realized because the presence of Dy^{3+} ions with closely spaced energy levels. According to our conceptions they are accompanied by the distortions of ligand environment of Dy^{3+} ions as a result of effective interaction of rare-earth ions. The interactions of rare earth ions change the distance between two lowest Kramer's doublets of Dy^{3+} ions. The following values of increase of the energy distance were noticed: of about 2.5 cm^{-1}, 2 cm^{-1} (4.9K) and 1 cm^{-1} (9.0K), 4 cm^{-1} (from of about 10 cm^{-1}) for KDyW, RbDyW and $K_{0.9}Cs_{0.1}DyW$, respectively.

In rare earth double tungstates the magnetically ordered structures possessing a number of features connected with low-dimension interactions of Dy^{3+} ions were observed at very low temperatures (because of a weak exchange interactions and of essential role of dipole-dipole coupling). Studies of specific heat in magnetic field and of magnetic susceptibility led to conclusion

that the magnetic phase transitions from paramagnetic to antiferromagnetic state take place at 0.6K, 0.82K and 1.34K for KDyW, RbDyW, CsDyW, respectively.

Table 1. Phase transitions of $ADy(WO_4)_2$, where A= K, Rb, Cs

double tungstates	magnetic phase transition	structural phase transitions
$KDy(WO_4)_2$	0.60 K	6.38 K
$RbDy(WO_4)_2$	0.82 K	4.9 K; 9.0 K;~18 K?
$CsDy(WO_4)_2$	1.34 K	29 K?
$K_{0.95}Cs_{0.05}Dy(WO_4)_2$		14.0 K
$K_{0.9}Cs_{0.1}Dy(WO_4)_2$		19.0 K

The temperature dependence of specific heat near the magnetic phase transition (MPT) can not be properly described in frames 2D and 3D models. The phase H-T diagram of RbDyW has a complicated shape indicative of the occurrence of different magnetic phases in magnetic field H parallel to c-axis. This allows to suppose that a complicated (two sublattice and more) structure with exchange interactions of different signs along various axes as well as with different orientation of magnetic moments in various sublattices can be realized.

Both MPT and SPT transitions are very sensitive to magnetic field. In case of SPT this confirms its CJTE nature. The external magnetic field induced the transitions from antiferro- to ferromagnetic states

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REFERENCES

1. M.D.Kaplan, B.G.Vekhter, *Cooperative Phenomena in Jahn-Teller crystals*, Plenum Press, New York, London, 1995
G.A.Gehring, K.A.Gehring "Cooperative Jahn-Teller effects", *Rep.Prog.Phys.* **38**, 1-89, 1974
2. M.T.Borowiec, V.P.Dyakonov, A.Jędrzejczak, V.I.Markowicz, H.Szymczak, "Low temperature specific heat of the tungstate $KDy(WO_4)_2$", *Phys.Solid.State* **38(7)**, pp.1229-1232, 1996.
3. M.T.Borowiec, V.P.Dyakonov, A.Jędrzejczak, V.I.Markovicz, A.Nabiałek, A.A.Pavluk, S.Piechota, A.D.Prochorov, H.Szymczak, "Jahn-Teller type structural transition in $KDy(WO_4)_2$", *Sol.St.Commun.* **102(8)**, pp.627-630, 1997.
4. M.T.Borowiec, V.P.Dyakonov, A.Nabiałek, A.A.Pavluk, S.Piechota, A.D.Prochorov, H.Szymczak, "ESR study of low temperature phase transition in $KDy(WO_4)_2$", *Physica B* **240(1-2)**, pp.21-25, 1997.
5. M.T.Borowiec, A.Jędrzejczak, A.Nabiałek, S.Piechota, H.Szymczak, M.Załęski, V.P.Dyakonov, V.I.Markovich, A.D.Prokhorov, A.A.Pavlyuk, " The Jahn-Teller type structural phase transition for dysprosium-potassium double tungstate", *Proc. SPIE* **3178**, pp.270-272, 1997.
6. M.T.Borowiec, V.P.Dyakonov, E.E.Zubov, E.N.Khatsko, H.Szymczak, "Magnetic properties of $KDy(WO_4)_2$ monoclinic magnet", *J.de Physique I* **7(12)**, pp.1639-1644, 1997.
7. M.T.Borowiec, V.P.Dyakonov, A.Jędrzejczak, V.I.Markovich, A.A.Pavlyuk, H.Szymczak, E.E.Zubov, M.Załęski, "Magnetic ordering of Dy^{3+} ions in $RbDy(WO_4)_2$ single crystal", *J.Low Temp.Phys.* **110(5-6)** , pp.1003-1011, 1998.
8. V.P.Dyakonov, V.I.Markovich, V.L.Kovarskii, A.V.Markovich, M.T.Borowiec, A.Jędrzejczak, H.Szymczak, "Low-temperature structural phase transition in a monoclinic $KDy(WO_4)_2$ crystal", *Phys. Solid State* **40(4)**, pp.691-698, 1998.
9. M.T.Borowiec, V.P.Dyakonov, A.Jędrzejczak, V.I.Markovich, A.A.Pavlyuk, H.Szymczak, E.E.Zubov, M.Załęski, "Magnetic phase transition in $KDy(WO_4)_2$ single crystal", *Phys.Lett. A* **243(1-2)** , pp.85-90, 1998.
10. M.T.Borowiec, V.P.Dyakonov, V.I.Kamenev, A.Nabiałek, A.D.Prokhorov, H.Szymczak, M.Załęski, "Low temperature structural phase transition in monoclinic $RbDy(WO_4)_2$ crystal", *Acta Phys.Polon. A* **94(1)** , pp.71-77, 1998.
11. M.T.Borowiec, V.P.Dyakonov, V.I.Kamenev, I.N.Krygin, S.Piechota, A.D.Prokhorov, H.Szymczak, "Pressure effect on the Gd^{3+} ion ground state in the $KY(WO_4)_2$+ 0.5%Gd crystal", *Phys.Stat.Solidi B* **209**, pp.443-448, 1998.

12. A.Szewczyk, M.U.Gutowska, K.Piotrowski, M.Gutowski, M.T.Borowiec, V.P.Dyakonov, V.L.Kovarskii, H.Szymczak, L.Gładczuk, "Specific Heat and the Cooperative Jahn-Teller effect in $KDy(WO_4)_2$", *J.Phys.Cond.Matter* **10(47)**, pp. 10539-10548, 1998.
13. M.T.Borowiec, A.Majchrowski, H.Szymczak, M.Załęski, J.Żmija, "Structural Phase Transitions in $K_{1-x}Cs_xDy(WO_4)_2$", XXth International Conference on Crystal Growth, Jerusalem 1998.
14. V.P.Dyakonov, M.T.Borowiec, A.Jędrzejczak, V.I.Markovich, H.Szymczak, E.E.Zubov, M.Załęski, "Magnetic ordering of Dy^{3+} ions in $ADy(WO_4)_2$ single crystals", series Phys.Chem.Sol. 1998, pp.80-83, ed. M.Kazimierski, Proc. XIth Seminar on Phase Transitions and Critical Phenomena, May 4-7, 1998, Wrocław, Polanica Zdrój.
15. M.T.Borowiec, V.P.Dyakonov, A.Jędrzejczak, V.I.Markovich, A.D.Prokhorov, H.Szymczak, M.Załęski, "Elastic ordering in double tungstates", series Phys.Chem.Sol. 1998, pp.71-74, ed. M.Kazimierski, Proc. XIth Seminar on Phase Transitions and Critical Phenomena, May 4-7, 1998, Wrocław, Polanica Zdrój.
16. V.P.Dyakonov, V.I.Markovich, V.L.Kovarskii, A.V.Markovich, M.T.Borowiec, A.Jędrzejczak, H.Szymczak, "The effect of a magnetic field on Jahn-Teller ordering in the monoclinic crystal $RbDy(WO_4)_2$", *Phys. Solid State* **40(12)**, pp. 2017-20, 1998.
17. M.T.Borowiec, H.Szymczak, M.Załęski, V.P.Dyakonov, A.Majchrowski, J.Żmija, M.Ceremuga, "Optical properties of $ADy(WO_4)_2$ single crystal (A=K,Rb,Cs)", *Proc. SPIE* **3724** , pp.292-295, 1999.
18. M.T.Borowiec, M.Załęski, V.P.Dyakonov, A.Majchrowski, H.Szymczak, J.Żmija "Pleochroism (trichroism) of dysprosium-alkali metal double tungstates", *Proc. SPIE* **3724** , pp.283-287, 1999
19. M.T.Borowiec, H.Szymczak, M.Załęski, P.Kaczor, L.Adamowicz, J.Strzeszewski, A.Watterich, L.Kovacs, "Raman and IR spectroscopy investigations of double tungstates", *Proc. SPIE* **3724** , pp.288-291, 1999.
20. M.T.Borowiec, V.P.Dyakonov, I.M.Fita, A.Nabiałek, A.A.Pavlyuk, H.Szymczak, M.Załęski, E.E.Zubov, "Magnetization of the $KDy(WO_4)_2$ single crystal in paramagnetic phase", *Proc. SPIE* **3724** , pp.318-322, 1999.
21. M.T.Borowiec, V.P.Dyakonov, I.M.Fita, A.Nabiałek, A.A.Pavlyuk, A.Szewczyk, H.Szymczak, M.Załęski, E.E.Zubov, "Magnetic structure of ground state of the $KDy(WO_4)_2$ single crystal", *JMMM* **195**, pp.119-124, 1999.
22. M.T.Borowiec, A.Hoser, „Structural and magnetic phase transition of potassium- and rubidium-dysprosium double tungstates", *BENSC Experimental Reports 1998*, p.42, 1999; *BENSC Experimental Reports 1999*, p.44 , 2000.
23. V.P.Dyakonov, E.E.Zubov, A.A.Pavlyuk, M.T.Borowiec, H.Szymczak, "Magnetic structure of a $RbDy(WO_4)_2$ single crystal", *Phys. Solid State* **41(4)**, pp.605-609, 1999.
24. V.P.Dyakonov, V.I.Markovich, V.L.Kovarskii, A.V.Markovich, M.T.Borowiec, A.Jędrzejczak, H.Szymczak, "Characteristic features of the magnetic ordering of Dy^{3+} ions in a monoclinic $RbDy(WO_4)_2$ single crystal", *Phys. Solid State* **41(3)**, pp.440-444, 1999.
25. M.T.Borowiec, V.P.Dyakonov, A.D.Prokhorov, H.Szymczak, "Peculiarities of EPR spectrum in the $KY(WO_4)_2$ +Dy^{3+} single crystal", *Phys.Rev. B* **92(9)**, pp.5834-5838, 2000.
26. M.T.Borowiec, A.Majchrowski, H.Szymczak, M.Załęski, J.Żmija, „Structural Phase Transition in $K_{1-x}Cs_xDy(WO_4)_2$ Single Crystals", *Cryst.Res Technol.* **35(11-12)**, pp.1343-1346, 2000.
27. V.P.Dyakonov, M.T.Borowiec, A.Jędrzejczak, E.E.Zubov, T.Zayarnyuk, H.Szymczak, „Magnetic ordering of Dy^{3+} ion in low-dimensional $CsDy(WO_4)_2$ double tungstates", ICSSC 2000, Zakopane.
28. T.Zayarnyuk, M.T.Borowiec, V.P.Dyakonov, H.Szymczak, E.E.Zubov, A.A.Pavlyuk, M.Barański, „Optical properties of potassium erbium double tungstate $KEr(WO_4)_2$", ICSSC 2000, Zakopane.
29. A.Majchrowski, E.Michalski, J.Żmija, M.T.Borowiec, V.P.Dyakonov, H.Szymczak, T.Zayarnyuk, M.Barański, „Growth and properties of potassium holmium double tungstate $KHo(WO_4)_2$", ICSSC 2000, Zakopane (abstract only).
30. S.V.Borisov, R.F.Klevtsova, "Kristalicheskaya struktura $KY(WO_4)_2$", *Kristalografija* **13(2)**, pp. 517-519, 1968
E.N.Ipatova, R.F.Klevtsova, L.P.Soloveva "Crystal structure of the double rubidium dysprosium tungstate $RbDy(WO_4)_2$", *Sov. Phys.-Crystallogr. (USA).* **21(6)**, pp. 648-651, 1976.
P.V.Klevtsov, L.P.Kozeeva, R.F.Klevtsova, "Kristalograficheskie izuchenie kalii-ittrievykh volframata i molibdata", *Izv. AN SSSR Neorg.Mater.* **4(7)** , pp. 1147-1151, 1968.
31. J. Hanuza, „Vibtational characteristics of oxygen bonds in $KDy(WO_4)_2$ single crystal", *Acta Phys.Pol. A* **70(5)**, pp.585-602, 1986.
32. R.B.Stinchcombe, „Pseudo-spin approach to structural phase transitions", in *Electron-Phonon Interactions and Phase Transitions*, ed. T.Riste, Plenum Press, New York and London, pp.209-244.
33. M.T.Borowiec, bibliographical database *"The Double Tungstates and Double Molibdates"*, WWW page on Internet adress: http://info.ifpan.edu.pl/PERSONAL/borow/baza.htm.