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LOW-TEMPERATURE STRUCTURAL PHASE TRANSITION IN MONOCLINIC $RbDy(WO_4)_2$ CRYSTAL

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The ESR spectrum of Dy^{3+} ion in the low-symmetry $RbDy(WO_4)_2$ crystal has been studied in the temperature region of $T = 4.2 \div 30$ K. The ESR linewidth was found to increase from 130 mT up to the maximum value of 190 mT at $T = 9$ K and then to decrease down to 150 mT at 4.2 K. The components of the g-tensor change considerably without change of their spatial orientation in the temperature range from 12 K to 7 K: $g_z = 2.5$, $g_x \approx 0$, $g_y = 1.41$ at $T > 12$ K; $g_z = 1.53$, $g_x \approx 0$, $g_y = 1.2$ at $T < 7$ K. The observed λ-shaped behaviour of absorption linewidth and the decrease in the g-factor are assumed to be due to the low-temperature structural phase transition ($T_{\mathrm{SPT}} \approx 9$ K). The width of the transition area is of about 5 K. It is suggested that the symmetry of high- and low-temperature phases is identical.

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1. Introduction

The recently performed studies of specific heat, optical and ESR spectra in the double rare-earth tungstate $KDy(WO_4)_2$ have shown that in spite of low symmetry the structural phase transition of the Jahn–Teller type (SPT JT) is realized in this crystal [1–3]. This transition is due to the presence of the Dy^{3+} ions with closely spaced energy levels. As a result of the specific heat measurements the magnetic phase transition with the Néel temperature of 0.6 K has also been found in the $KDy(WO_4)_2$ tungstate [4]. In $KRe(WO_4)_2$ (where Re = Y or Gd)

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*fax: (48-22)430-926, e-mail:borow@ifpan.edu.pl, home e-mail: mkpbor@it.com.pl the anomalies connected with the SPT were not observed in the same temperature region [5].

The discovery of the SPT JT in the $KDy(WO_4)_2$ tungstate has stimulated a research for other rare-earth tungstates with low-temperature phase transitions. Hence we have undertaken studies of the $RbDy(WO_4)_2$ compound having an identical with $KDy(WO_4)_2$ crystalline structure. The replacement of alkaline ions in the related compounds, namely, the rare-earth molybdates $XDy(MoO_4)_2$, was shown to influence considerably the temperatures of both structural and magnetic phase transitions [6]. For example, the SPT temperatures in $CsDy(MoO_4)_2$, $RbDy(MoO_4)_2$ and $KDy(MoO_4)_2$ are equal to 42 K, 24 K and 14 K, respectively [2, 6].

In this work we present the results of ESR spectra study in low-symmetry crystal of $RbDy(WO_4)_2$. These results are used for elucidation of the features of Dy^{3+} ion ground state as well as of the changes of ESR spectra parameters due to the replacement of an alkaline ion. Until now the magnetic and resonant properties of the $RbDy(WO_4)_2$ compound were not investigated. The ESR measurements presented below are a part of complex physical studies of the family of the alkaline and rare-earth double tungstates — $MRe(WO_4)_2$.

2. Samples and experimental

The rubidium–dysprosium tungstate belongs to a set of double $MRe(WO_4)_2$ tungstates and crystallizes in a monoclinic α-$KY(WO_4)_2$ structure ($C_{2h}^6 = C2/c$) [7], which is typical of the Dy^{3+} ion tungstates. The elementary cell of $RbDy(WO_4)_2$ contains the four formula units. The lattice parameters are presented in Table I. The Dy^{3+} ion is surrounded by eight oxygen ions and has local symmetry C_2. In this crystallographic structure the oxygen and tungstate ions are located in common positions. The dysprosium and rubidium ions have twofold rotation axes.

TABLE I

Parameters of elementary cell for $KDy(WO_4)_2$ and $RbDy(WO_4)_2$ crystals.

Crystal	a, Å	b, Å	c, Å	β	Ref.
$KDy(WO_4)_2$	8.05	10.32	7.62	94°13′	[7]
$RbDy(WO_4)_2$	8.14	10.45	7.57	94°33′	[8]

Crystals were grown from melt of rubidium ditungstate ($Rb_2W_2O_7$) by a modified Czochralski method, using the [110] oriented seeds and the growth rate of 0.05 mm/h (the crystal dimensions were about $6 \times 6 \times 10$ mm^3). The low-temperature phase of the rubidium–dysprosium tungstate undergoes the polymorphic transition to a high temperature phase at 1098°C. Hence the $RbDy(WO_4)_2$ single crystals were grown in the temperature range of 1053–1098°C. An orientation of crystals was determined by X-ray method.

The measurements of ESR spectra were carried out in an X-band spectrometer with a high-frequency modulation in the temperature region of $T = 4.2 \div 30$ K on the crystals with a size of about 3 mm. Magnetic field was valued between 0 and 1 T. The magnetic component of a high-frequency field was perpendicular to an external magnetic field. The sample was rotated in the *ac* plane. The temperature was stabilized by a gas helium flow.

3. Results and discussion

The Dy^{3+} ion has $4f^9$ electronic configuration. The multiplet $^6H_{15/2}$ is split into eight Kramers doublets by a low-symmetry crystal field. The ESR spectrum consisting of one line was observed as a transition between two levels of the lowest spin-doublet. Figure 1 shows the angular dependence of the resonance field in the *ac* plane. The difference between resonance field values at $T = 14$ K and $T = 4.2$ K is clearly visible in Fig. 1. According to the measurements of the angular dependence of the ESR spectrum in various crystalline planes two main axes of the g-tensor (g_{max} and g_{min}) were established to lie in *ac* plane. It should be noted that the g_{max} direction has a deviation of 12° from the crystallographic c-axis, unlike the $KDy(WO_4)_2$ compound, where this angle is equal to 20°. The third main axis of the g-tensor (g_{b}) is parallel to the second order axis C_2 and coincides with the crystallographic b-axis. The values of spectroscopic parameters for two rare-earth tungstates are listed in Table II.

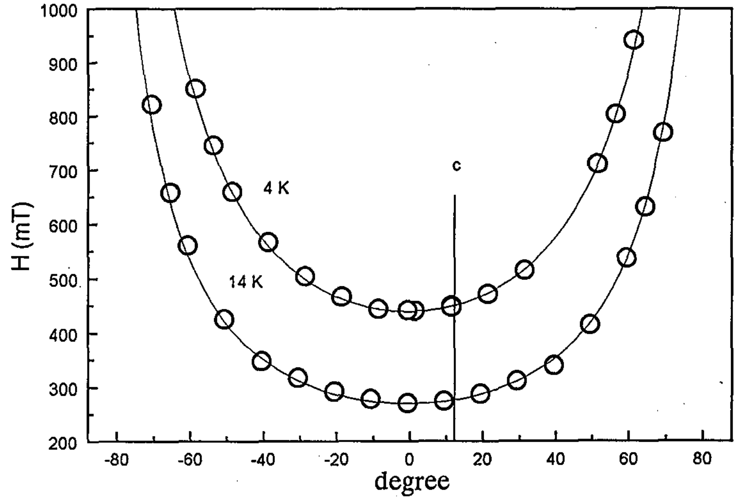

Fig. 1. Angular dependence of the position of ESR line of Dy^{3+} ion in $RbDy(WO_4)_2$ compound in *ac* plane in high-temperature ($T > 12$ K) and low-temperature ($T < 7$ K) phases. The g_{max} direction is deviated of 12° from the c-axis.

The temperature dependence of the g-factor along the direction of its maximum value in *ac* plane is shown in Fig. 2. It can be seen from Table II and Fig. 2 that the g-tensor components are changed significantly in the temperature region of $T = 12 \div 7$ K.

TABLE II

Spectroscopic parameters for $KDy(WO_4)_2$ and $RbDy(WO_4)_2$ compounds in high- and low-temperature phases crystal.

Crystal	$T_{\rm SPT}$,K	$g_{\rm max}$	$g_{\rm min}$	$g_{\rm b}$	ΔH, mT	Ψ_0
$T = 4.2$ K						
$KDy(WO_4)_2$	7	1.98	0	1.19	190	20
$RbDy(WO_4)_2$	9	1.53	0	1.2	150	12
$T > 12$ K						
$KDy(WO_4)_2$	7	3.13	0	0.82	170	20
$RbDy(WO_4)_2$	9	2.5	0	1.41	130	12

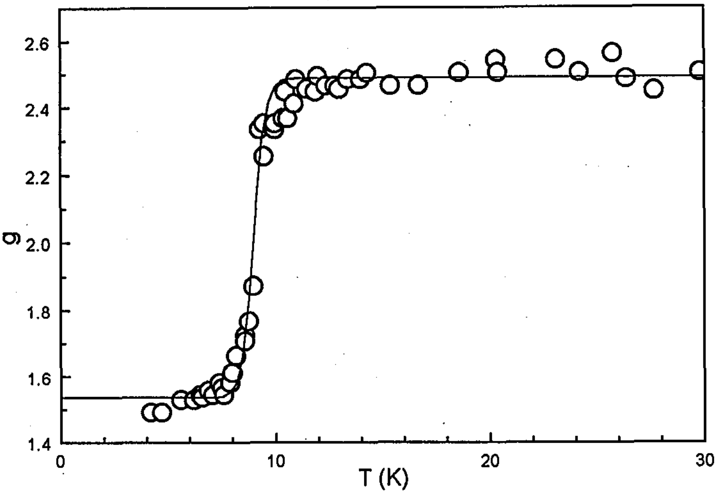

Fig. 2. Temperature dependence of the g-factor along the direction of its maximum value (z axis) in the ac plane (12° from the c-axis).

The change of ESR linewidth, measured for the inflection points of absorption line, is shown in Fig. 3. The linewidth is equal to 130 mT in the temperature region of $T > 12$ K and it increases to its maximum value of 190 mT at $T \approx 9$ K. Further temperature decreasing causes the linewidth narrowing to 150 mT at $T = 4.2$ K.

The behaviour of the ESR line is described by the following spin Hamiltonian with spin $S = 1/2$:

$$H = g_x \beta H_x S_x + g_y \beta H_y S_y + g_z \beta H_z S_z, \qquad (1)$$

written in such coordinate axes that $g_x = g_{\rm min}$, $g_y = g_{\rm b}$ and $g_z = g_{\rm max}$. In Eq. (1) β is the Bohr magneton.

In the vicinity of the phase transition a smooth change of the g-factor with temperature is observed. This dependence, shown in Fig. 2, is well described by the following function:

$$g = a \tanh[(1/2)b(T - T_0)] + d, \qquad (2)$$

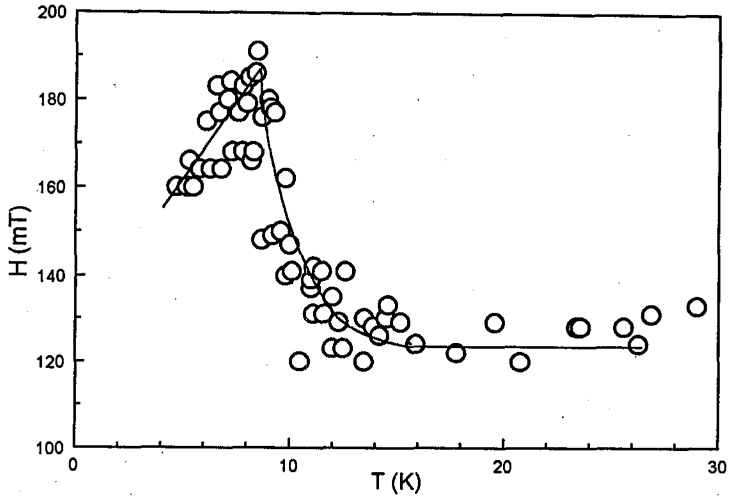

Fig. 3. Temperature dependence of width of ESR line obtained by the inflection points of absorption line. The permanent magnetic field is directed along the $g_{\max}$.

where $a = 0.48$, $b = 3.62$ K^{-1}, $T_0 = 9$ K, $d = 2.01$. The parameters T_0 and d characterize the inflection point of $g(T)$ curve.

It should be noted that the $g(T)$ and $\Delta H(T)$ dependences, obtained for the RbDy$(WO_4)_2$ compound at low temperatures, are identical to these observed in the KDy$(WO_4)_2$ tungstate. The λ-shaped temperature dependence of the linewidth is also qualitatively similar to the specific heat temperature dependence [1]. In KDy$(WO_4)_2$ crystal these anomalies of thermal and resonant properties were shown to be connected with the structural phase transition ($T_{\mathrm{SPT}} = 6.38$ K). The ESR spectrum measurements have shown that the RbDy$(WO_4)_2$ compound is a paramagnet with the strong anisotropy of the g-factor down to helium temperatures. It is also known that the magnetic phase transitions in the rare-earth tungstates occur at very low temperatures (for example, in KDy$(WO_4)_2$ at 0.6 K [4]). Hence, by analogy with KDy$(WO_4)_2$, we suggest that the RbDy$(WO_4)_2$ compound undergoes the structural phase transition at $T \approx 9$ K.

Note that the directions of main axes of the g-tensor did not change, within the experimental error, at SPT. The significant extension of absorption line, in the vicinity of the phase transition, is most probably connected with the fluctuation of the order parameter, leading to a spread of crystal field parameters describing the rare-earth ion.

After comparing the obtained results with the ESR data in KDy$(WO_4)_2$ [3], it is apparent that in RbDy$(WO_4)_2$ the structural transition temperature is increased and the absorption linewidth is diminished. The increase in SPT temperature can be connected with an increase in the spin–lattice interaction of Dy^{3+} ions and changes of the energy of the spin-doublet states. According to optical studies, the difference of the SPT temperatures in RbDy$(MoO_4)_2$ ($T_{\mathrm{SPT}} = 24$ K) and KDy$(MoO_4)_2$ ($T_{\mathrm{SPT}} = 14$ K) is due to the difference of the splitting values of the two lowest-energy Kramers doublets both in high-(Δ_∞) and in low-temperature phases (Δ_0). The suitable values are equal $\Delta_\infty \approx 17$ cm^{-1}, $\Delta_0 \approx 36$ cm^{-1} and $\Delta_\infty \approx 14$ cm^{-1}, $\Delta_0 \approx 19$ cm^{-1} for RbDy$(MoO_4)_2$ and KDy$(MoO_4)_2$ [2, 9], respectively.

By analogy, we suggest that the increase in T_{SPT} in RbDy$(WO_4)_2$, in comparison with KDy$(WO_4)_2$ ($\Delta_\infty \approx 10$ cm^{-1}, $\Delta_0 \approx 18$ cm^{-1}), can be due to an increase in the splitting value of the two lowest spin-doublet states (taking into account that the symmetry of these crystals is the same).

It is known that the width of ESR line is mainly determined by spin–spin interactions of Dy^{3+} ions. A certain contribution can also introduce a spread of parameters of the crystal field forming a ground state. Measurements of pair spectra in diluted KY$(WO_4)_2$ + 0.5% Dy^{3+} single crystal [unpublished] have shown that this contribution is negligible. The linewidth in the diluted crystal did not exceed 20 Oe. Hence the decreasing of spin–spin interactions undoubtedly causes the linewidth narrowing.

The spin–spin interactions are determined by magnetic dipole–dipole and exchange interactions. As it is seen from Table I, the lattice constants of the parent compounds differ insignificantly. The increase in lattice parameters in RbDy$(WO_4)_2$ is because the Rb^+ ion radius (1.47 Å) is slightly greater than the K^+ one (1.33 Å). Hence the distance between the Dy^{3+} ions in these two crystals does not differ significantly and the above factor cannot result in the change of these interactions. The most essential changes in the ESR spectrum of RbDy$(WO_4)_2$ are connected with the decrease in the g-factors in high- and low-temperature phases as well as with the decrease in the angle between the c-axis and the direction of maximum g_z-factor.

An estimate of the contribution of the dipole–dipole interaction to the width of the ESR line shows that it decreases by a factor of about 1.6. This explains the decrease in absorption linewidth.

Both the absence of jumps of spectrum parameters and the large temperature interval of the SPT suggest that the observed SPT is the second-order phase transition.

The studies of ESR spectra give no possibility of making a single-valued conclusion about symmetry of a crystal lattice in low-temperature phase. However, both the absence of inequivalent positions of Dy^{3+} ions and the preservation of directions of main axes of the g-tensor testify that the monoclinic structure of initial high-temperature phase is not changed at structural phase transition and the smooth distortion of lattice occurs at some directions.

4. Conclusion

In conclusion we have presented the results of the Dy^{3+} ion ESR spectra study in monoclinic RbDy$(WO_4)_2$ crystal in the temperature region of $T = 4.2 \div 30$ K. The ESR linewidth increases from 130 mT at $T > 12$ K up to the maximum value of 190 mT at $T \approx 9$ K and then it decreases to 150 mT at 4.2 K. The components of the g-tensor change noticeably, without any change of their spatial orientation in the temperature range from 12 K to 7 K. The observed λ-shaped behaviour of absorption linewidth and the smooth decrease in the g-factor are caused by the low-temperature structural phase transition. The width of the transition area is of about 5 K. Both the absence of jumps of ESR spectra parameters and the large temperature interval of the SPT suggest that the SPT is the second-order phase transition. The symmetry of high- and low-temperature phases is suggested to be identical. The observed decrease in absorption linewidth in the process of phase transition is mainly connected with the decrease in the dipole–dipole interactions.

It should be noted that the substitution of Rb^+ ion in $MDy(WO_4)_2$ for K^+ ion causes the increase in SPT temperature by a factor of about 1.5. The replacement of $(WO_4)_2^{2-}$ complex for $(MoO_4)_2^{2-}$ one, which realizes the connection between rare-earth and alkaline ions in rubidium–dysprosium compounds, results in the decrease in T_{SPT} by a factor of about 2.

Unfortunately, an X-ray measurement of the low-temperature structure of the $RbDy(WO_4)_2$ crystal has not been carried out at the present time. Hence a detailed consideration of the structural phase transition mechanisms in the low symmetry $RbDy(WO_4)_2$ compound could not be carried out.

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