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Bi-doping effect on the Jahn–Teller phase transition in CsDy(MoO$_4$)$_2$ crystal

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Using spectroscopic and visual optical methods the shift of the critical temperature ($T_{tr} \approx 42$ K) of the first-order phase transition of the Jahn–Teller type to the low-temperature side at doping the CsDy(MoO$_4$)$_2$ crystal with Bi^{3+} (concentration up to $x \approx 0.08$) was revealed. Effect of the doping is compared to the effect of uniaxial pressure. Using the result of the Zeeman effect we have calculated the critical value H_c of external magnetic field at which the spontaneous change of the sizes of crystal is suppressed under magnetic field and the high-temperature phase may be induced at $T = 0$ K. It is supposed that doping with Bi^{3+} leads to decrease of the critical magnetic field value for doped CsDy(MoO$_4$)$_2$.

Key words: *bi-doping, Jahn–Teller effect, uniaxial pressure*

1. Introduction

CsBi(MoO$_4$)$_2$ and CsDy(MoO$_4$)$_2$ crystallise in the D_{2h}^3 crystal structure with two molecules in the unit cell [1, 2]. Both crystals undergo different successions of phase transitions which take place at 325 and 125 K for CsBi(MoO$_4$)$_2$ and 50 and 42 K for CsDy(MoO$_4$)$_2$ [3–6]. The crystal structures below phase transition temperatures are not known. It was shown earlier that the doping of CsDy(MoO$_4$)$_2$ with various rare earth ions (Gd, Eu and others) shifted significantly the critical temperature (T_{tr} = 42 K) of the first-order Jahn–Teller type phase transition to the low-temperature side [4, 7, 8]. When Dy^{3+} ions concentration became less than critical [8, 9], the low-temperature phase was quite different from that found for $CsDy(MoO_4)_2$. The investigations of phase transitions of Jahn–Teller type in $CsDy(MoO_4)_2$ and in the mixed crystals $CsDy_{1-x}$ $Bi_x(MoO_4)_2$ with bismuth ions substituting dysprosium ones are of principal interest because bismuth is not a rare earth element and its ion radius is essentially different from that of dysprosium. Shift of the first-order type phase transition temperature to the low-temperature side was also observed under the external magnetic field: when magnetic field was oriented along axis a (H ψ a), the transition temperature decreased by 5 K from $H \approx 70$ kOe to 170 kOe [10]. Moreover, a small shift of T_{tr} towards lower temperature under external pressure was observed experimentally [11]. Therefore, the comparison of the pressure, magnetic field and doping effects is of special interest.

2. Experimental

The electronic absorption spectra in the NIR region were used to study the phase diagram (x–T_{tr}) of the $CsDy_{1-x}Bi_x(MoO_4)_2$ crystals. The spectra were recorded in the range of 13 000–13 500 cm^{-1} for which the phase transition is particularly well observed. The measurements of the absorption spectra of $CsDy(MoO_4)_2$ and $CsDy_{1-x}Bi_x(MoO_4)_2$ at the external magnetic field H ψ a in the low-temperature phase at $T = 6.5$ K ($T < T_{tr}$) were performed up to 6 T. The absorption spectra in the 13 000 –13 500 cm^{-1} range were recorded with the resolution of 0.5 cm^{-1} using the set-up with double monochromator. For the low-temperature measurements the samples in the form of very thin plates (c.a. 0.6 mm thick) were placed in a cryostat.

The crystals have been grown by the method of crystallization of the solution in melt with bismuth content x in the mixture ranging from 5% to 80%. Solubility of ingredients at crystal growing was not under control. The actual crystal composition was determined with the help of X-Ray dispersion methods based on the scanning electron microscope Philips SEM 515 and microanalyzer EDAX 9800. The phase diagram (x–T_{tr}) was also determined by visual method. Visual detecting of the temperature of the first-order Jahn–Teller phase transition was performed by observations of the typical domain structures forming near T_{tr} [9].

3. Results and discussion

The absorption spectra in the energy region 13 000–13 500 cm^{-1} were obtained at c.a. 42 K ($>T_{tr}$) and at c.a. 6.5 K ($<T_{tr}$) temperatures (Fig. 1). The absorption bands are due to transitions inside f-shells of Dy^{3+} ions from the components of the ground multiplet $^6H_{15/2}$ to the excited $^6F_{3/2}$ state split by low-symmetry crystal field into 8 and 2 components, respectively. The phase transition for the crystal studied occurs at about 42 K. At $T > T_{tr}$ two wide components with the energy interval of approximately

41 cm^{-1} were observed in the spectra. For this phase the low-energy satellite appears due to the transition from the first excited level of $^6H_{15/2}$.

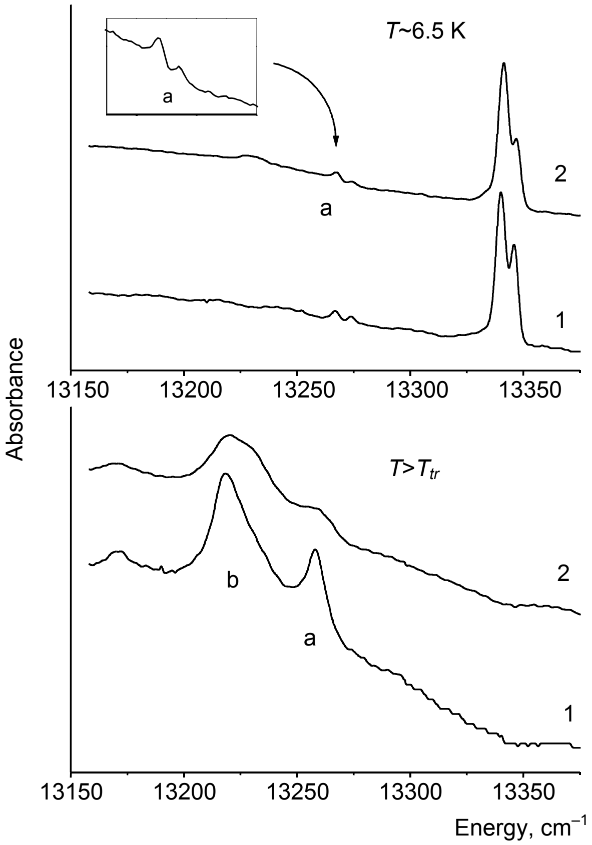

Fig. 1. Absorption spectra of the CsDy$_{1-x}$Bi$_x$(MoO$_4$)$_2$ crystals with $x = 0.01$ (1) and $x = 0.06$ (2) at the temperature higher than T_{tr} and at 6.5 K (transition from $^6H_{15/2}$ to $^6F_{3/2}$)

In Figure 1 one may notice only one doublet band observed at 6.5 K, the energy gap between doublet components is 8 cm^{-1}. The resolved doublet structure of the band was observed owing to the small bandwidth of lines at low temperatures. However, at $T > T_{tr}$ the expected doublet structure of the band is not observed because bandwidths of the lines are too large comparing to the interval between the doublet components.

Similar as for CsDy(MoO$_4$)$_2$ [3], all doped crystals in the low-temperature phase show shifts of the discussed doublet by at least 80 cm^{-1} to the high energy side in comparison with the initial phase at $T > T_{tr}$. This behaviour of the absorption spectra proves that in all crystals of the series the co-operative Jahn–Teller effect results in the lowering of the ground state by the same value of about 80 cm^{-1} and permits us to use the spectral methods for testing the low-temperature phase.

Additionally, at 6.5 K one can also observe a few other spectral features (see the inset in Fig. 1). This spectrum is inherent for the high temperature phase ($T > T_{tr}$). In this phase the 41 cm^{-1} energy distance between band peaks *a* and *b* corresponds to the distance between ground and the nearest excited levels of the $^6H_{15/2}$ ground multiplet at $T > T_{tr}$.

The real Bi^{3+} content determined by X-Ray methods was quite different from the concentration value in the melt. It appeared that for the crystals with $x = 0.95$ for Dy^{3+} and $x = 0.05$ for Bi^{3+} in the melt, the real Bi^{3+} content in the crystals is $x = 0.03–0.04$.

For the crystals with the real Bi^{3+} content $x \approx 0.01$ and $x = 0.035$ the transition temperatures were determined visually and were equal to c.a. 36–39 K at cooling and c.a. 34–36 K at heating (see Fig. 2 – centred circles). For the crystals with the highest Bi^{3+} content in the melt the transition temperature is near 26 K. Assuming that the transition temperature depends linearly on *x* for the crystals with low Bi^{3+} concentrations (dashed line in Fig. 2), one can estimate the real Bi^{3+} content. It may be concluded that in our crystals the Bi^{3+} ion concentration does not exceed $x = 0.08$, i.e. the maximal Bi^{3+} content in crystals is nearly ten times lower than in the melt.

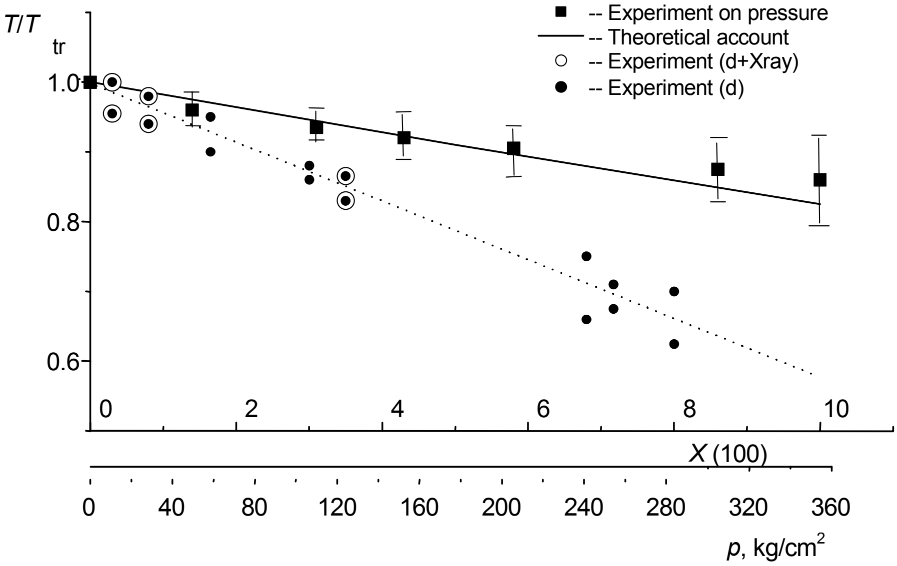

Fig. 2. Dependence of the temperature of phase transition of Jahn–Teller type on concentration in the $CsDy_{1-x}Bi_x(MoO_4)_2$ crystals. The dark squares correspond to the averaged data [11], solid line shows the theoretical estimation, and centred circles correspond to the transition temperatures determined by visual method in the crystals with concentrations taken from X-Ray data. Dashed line goes through these points. The dark circles correspond to the reduced temperature of phase transition, T/T_{tr}. Lower circles (cooling) and higher ones (heating) are shown symmetrically relative to the dashed line

Observation of the domain structure formation allowed us also to conclude that in the mixed crystals the temperature region of coexistence of the initial and low-temperature phases is widened. For some crystals the mixed phase may be observed till temperatures as low as 15 K. This result is confirmed by the absorption spectra investigations (Fig. 1).

Therefore, it was found out that Bi^{3+} doping lowers the temperature of transition without changing the character of transition and also widens the temperature region of coexistence of the initial and low-temperature phases. Besides, the phonon spectra in the mixed crystals as well as electronic spectra does not differ substantially from those in $CsDy(MoO_4)_2$. By contrast, an external magnetic field changes the low-energy electronic spectra essentially due to the large g-factor components of g-tensor of the spectroscopic splitting for dysprosium ion ground state. To examine the external magnetic field effect on the electronic spectra we have measured the absorption spectra at magnetic field up to 60 kOe ($H \parallel a$).

The absorption spectra originating from the optical transition $^6H_{15/2}$–$^6F_{3/2}$ were measured at different values of external magnetic field at 6 K (see Fig. 3). The intensity of the low-frequency component of the absorption band is decreased. This fact results from the decrease of the population of the upper level of the split ground state when magnetic field increases. Therefore, we may conclude that splitting of the absorption band is defined by g-factor of the ground state. A similar behaviour was observed for the absorption band of the "frozen" high-temperature phase in $CsDy(MoO_4)_2$ with 0.1% of Bi^{3+} .

Basing on the measured absorption spectra we have constructed the frequency-field dependence of the $^6H_{15/2}$–$^6F_{3/2}$ optical transition and defined g-factor of the spectroscopic splitting of the ground state for the low- and high-temperature phases. These g-factor values occurred to be $g_1 = 10.8$ and $g_2 = 11.5$ for the low- and high-temperature phase, respectively (Fig. 3).

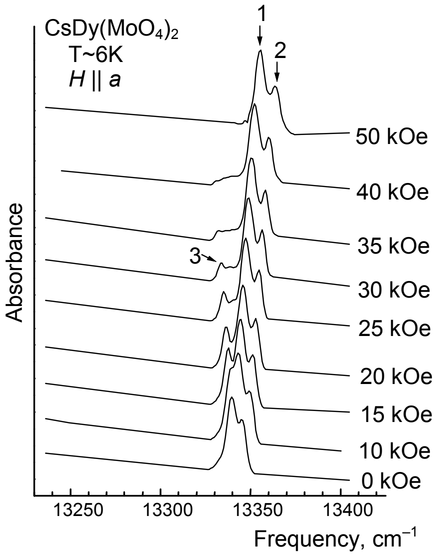

Fig. 3. The bands originating from the optical transition $^6H_{15/2}$–$^6F_{3/2}$ in the absorption spectrum of the $CsDy(MoO_4)_2$ crystal measured at different magnetic field values (for the low-temperature phase)

We can conclude that magnetic field in the geometry of experiment does not shift the critical temperature but leads only to the splitting of the energy level, i.e. the value of magnetic field available in our experiment is not high enough to turn the low-temperature phase into the high-temperature one.

At the temperature $T_{tr} \approx 42$ K the $CsDy(MoO_4)_2$ crystal undergoes the structural phase transition of the co-operative Jahn–Teller effect type (CJTE) accompanied by significant distortion of the crystal lattice as well as lowering of the ground state of the electron subsystem of Dy^{3+} ions by the value $\Delta E \approx 80$ cm^{-1} [3].

From all results presented it follows that the Jahn–Teller phase transition temperature moves to the low-temperature region for the mixed crystals. The transition temperature is also lowered under external pressure applied along *a* direction [11]. Taking into account that parameter *a* for the $CsBi(MoO_4)_2$ crystal is less than the corresponding parameter for the $CsDy(MoO_4)_2$ crystal, one may assume that doping of the dysprosium crystal results in effective crystal compression along *a* direction. In other words, impurity effect is qualitatively similar to the effect of uniaxial pressure. We have compared our data with those from Ref. [11].

For further considerations the Clausius–Clapeyron equation in the form $(\Delta P \cdot \Delta V)/L = \Delta T/T_{cr}$ was used. Here $\Delta P \cdot \Delta V = U$, where U is elastic deformation energy emerging at phase transition, L is latent heat at phase transition (jump of enthalpy $L = 0.64$ kJ/mol was earlier determined [13]), T_{cr} is the critical temperature of phase transition without the elastic deformation and ΔT is the change of T_{cr} at the corresponding U deformation.

For evaluation of the temperature T_{cr} we use the fact that *a* parameter changes in $CsDy(MoO_4)_2$ at T_{tr} (*a* parameter increases abruptly at T_{tr}, $\Delta a/a \approx 0.68\%$ [14]). The related *stretch* lattice deformation along *a* parameter is 0.3 kJ/mol [15]. It was determined using the simplified model of crystal consisting of alternating $[Dy(MoO_4)_2]^-$

layers and Cs^+ ions as well as data obtained for elastic modules from the spectra in Ref. [15]. Assuming that the phase transition occurs at $T_{tr} = T_{cr} - \Delta T = 42$ K, we estimate from Clausius–Clapeyron equation $\Delta T = 35$ K and therefore $T_{cr} = 77$ K. Supposing further that the averaged parameter a in the mixed crystals linearly changes when concentration x increases, we may construct the $T_{cr}(x)$ dependence.

The data from Ref. [11] do not contradict the evaluations presented. After our considerations the effective decrease of the a at Bi^{3+} content $x = 0.1$ is equivalent to the a parameter decrease under the external pressure about $3.6\cdot10^2$ kg/cm^2. For comparison the data from Ref. [11] are shown in Fig. 2. The dependence obtained in our experiments is steeper than that from Ref. [11]. It may be caused by action of the other mechanisms lowering the phase transition temperature. The limited dissolving of bismuth as we suppose is the result of the tendency of bismuth ions to change their valence at high temperatures during the crystal growing.

So we have shown that the external pressure and Bi^{3+} doping stabilize the high-temperature phase. Doping with Bi has little effect on the low-energy phonon spectra as well as on the low-energy electron levels position, though it essentially shifts the transition temperature. Note that the effect of uniform pressure does not explain in full the lowering of the phase transition temperature at Bi^{3+} doping. The additional mechanism of the effective shift of the T_{tr} to the low-temperature side is the result of *percolation* of the low dimension crystal structure with the bismuth ions.

It is well known that the transition temperature of the CJTE type phase transitions is rather sensitive to the action of the external magnetic field. Magnetic field effect on CJTE is possible due to rather strong magnetoelastic coupling between the Jahn–Teller centres; in our case Jahn–Teller centres are dysprosium ions surrounded by oxygen ligands. The transition temperature shift depends on the direction of applied magnetic field because of g-factor anisotropy of the Jahn–Teller centres ground state [16].

Experimental investigations of the external magnetic field influence on the cooperative Jahn–Teller ordering in $KDy(MoO_4)_2$ ($T_{tr} \approx 14$–15 K) (orthorhombic compound with a similar structure) have shown that at the definite value and direction of external magnetic field the Jahn–Teller ordering is destroyed and transition to non-ordered, or high-temperature phase takes place [16, 17]. Such investigations were undertaken for the $CsDy(MoO)_2$ crystal [10], but the critical magnetic field was not achieved in the experiments.

For further discussion of the magnetic field effect on the spectra we would take into account the feature of the crystal structure. It is known that the crystals consist of the $[Dy(MoO_4)_2]^-$ layered blocks weakly coupled by the alkali ion layers $[Cs]^+$ [18]. The Dy^{3+} ions chains, including two Dy^{3+} ions coupled by inversion, are considered as arrays formed inside the layers and therefore we take into account only one magnetically equivalent paramagnetic JT centre.

Our investigations as well as the former ones [19] allowed us to determine the values of g-factors of the ground state spectroscopy splitting. They turned out to be $g_a = 11$, $g_b = 1$, $g_c = 13$ for the low-temperature phase, where a, b, c are the orthorhombic cell parameters. One can see that *g*-factor tensor for the low-temperature phase resembles the structure of *g*-factor tensor of the ground state for the high-temperature phase of KDy$(MoO_4)_2$ [16].

To evaluate the critical value of external magnetic field H_{cr} at which the high-temperature phase may be induced in the crystal at temperatures $T < T_{tr}$, we used the following model. In Figure 4, the positions of the ground levels are shown at $T > T_{tr}$ and $T < T_{tr}$ without external magnetic field (left side). The right side shows magnetic filed effect on the levels. Here $\varDelta$ is the energy of the Jahn–Teller stabilization [15]. If the *g*-factors are strongly different for the ground and excited electronic states, which are Kramers doublets, the mutual approaching of the levels starts when the external field is switched on. On the other hand, if the *g*-factors for the ground states of the low-temperature and high-temperature phases are strongly different, we can evaluate the effect of magnetic field on the ground state energy position. When the energy interval between the ground states in the external magnetic field equals to the sum of the spontaneous elastic energy originating in the crystal as a result of the phase transition and additional energy corresponding to the splitting of the ground state, the crystal changes its state and the high-temperature phase spectrum is observed. Taking into account that elastic energy U is about $U \approx 0.3\varDelta$ [15] and the maximal *g*-factor difference for the ground states $\Delta g \approx 18 - 1 = 17$, we can evaluate the critical field H_c:

$$H_c = \frac{\varDelta - U}{0.5\Delta g \mu_b}, \qquad \mu_b = 9.2 \cdot 10^{-24}\ \text{J/10 kOe}$$

Here $\varDelta - U \cong 50\ \text{cm}^{-1} = 50 \cdot 1.99 \cdot 10^{-23}$ J, and we have $H_c = 128$ kOe.

So we have shown that at H_{cr} the high-temperature phase may be induced in the low-temperature phase at $T \approx 0$. When magnetic field suppresses the elastic deformation accompanied with Jahn–Teller phase transition in CsDy$(MoO_4)_2$, it gives rise to the high-temperature phase in crystal. The maximal difference in the *g*-factor tensor components for the ground states in the low- and high-temperature phases was found for the magnetic field applied at 14° in *ab* plane [19].

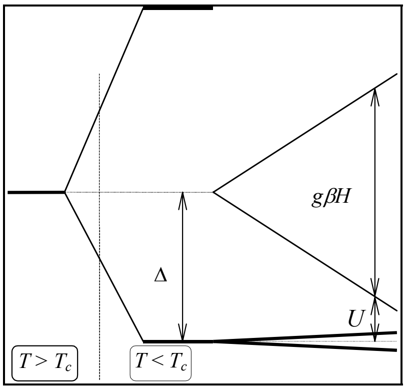

Fig. 4. Scheme of the Dy^{3+} ions energy levels splitting under external magnetic field for CsDy(MoO$_4$)$_2$

Note that by results of Ref. [15] the critical field at $T \approx 0$ was found for $H \approx 170$ kOe. The difference in the value reflects the fact that the magnetic field was applied in two cases at different directions according to the orthorhombic axes. But the value of the field which may destroy the low-temperature phase at a finite temperature, namely at $T \approx T_{tr}$, is much lower than H_c. The experimental shift of the external magnetic field value from 70 kOe to 170 kOe, when temperature is lowered from 42 K to 4.2 K, is not discussed in this paper, but is the question for the future work.

4. Conclusions

The comparison of the concentration dependence of the temperature of Jahn –Teller ordering type phase transition in CsDy$_{1-x}$ Bi$_x$(MoO$_4$)$_2$ at low x with P–T phase diagram [11] allowed us to suppose that the effect of impurity compressing the [Dy$_{1-x}$Bi$_x$(MoO$_4$)$_2$} layers correlates with the effect of the uniaxial pressure. We have observed the shift of T_{tr} to the low-temperature side without changing spectra of the low-temperature phase although the change of the crystal *average* size along *a* direction took place.

We can also suppose that in CsDy(MoO$_4$)$_2$ phase transition from the low-temperature phase to the high-temperature one may be induced by magnetic field. Estimated value of H_c corresponds to the magnetic field which leads to the transition of the crystal from the low- to the high-temperature phase when the crystal temperature T is about 0 K. The estimation that is based on the molecular field representations gave the value of the external magnetic field that induces this transition. The assumption concerning the lowering of the H_c critical value in the crystals doped by bismuth is quite realistic. Similar effect of the external magnetic field and pressure on the Jahn–Teller ordering in CsDy(MoO$_4$)$_2$ is the question to be necessarily studied further in more details.

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