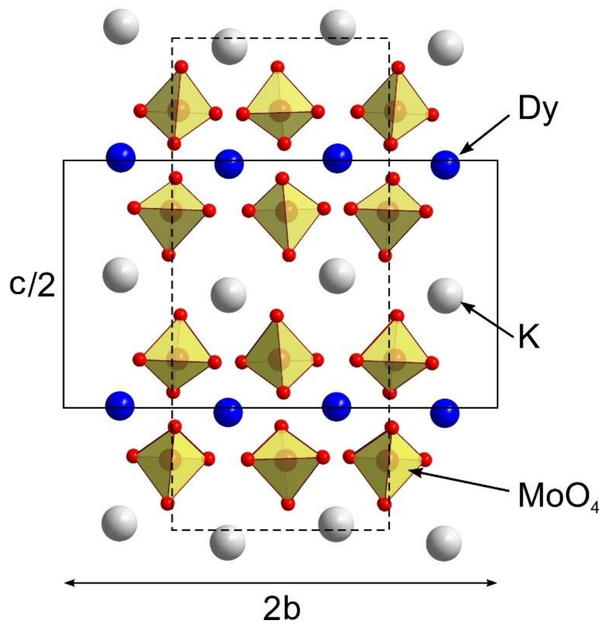
About the nature of incommensurate phase in double Jahn-Teller rare-earth molybdates

Yu.M. Kharchenko, K.V. Kutko, N.M. Nesterenko

B.Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, 47 Nauky Ave., Kharkiv, 61101 Ukraine.
e-mail: nesterenko@ilt.kharkov.ua

The subject of investigation is the cooperative Jahn-Teller effect (CJTE) type phase transition in $KDy(MoO_4)_2$ at T ~15K [1]. The aim of the work is to defend the possibility of existence of the incommensurate phase (IP) by symmetry approach in $KDy(MoO_4)_2$ and others isostructural double molybdates ($MRe(MoO_4)_2$) at the CJTE processes.

Cooperative Jahn-Teller effect in $KDy(MoO_4)_2$.

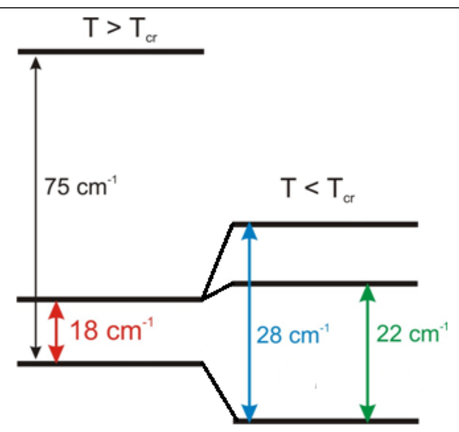


Crystal structure of $KDy(MoO_4)_2$ consist two *Re* layers in unit cell [2].

D_{2h}^{14} (P_{bcn})
(T=100K)
z = 4
a = 0.507 nm,
b = 0.795 nm,
c = 1.802 nm.
T_N = 0.9 K

Table 1. The IR-active lattice vibrations observed in $KRe(MoO_4)_2$ [3]

Compound	$E_\omega \| a\ (B_{3u})$	$E_\omega \| b (B_{1u})$
	ω_{1a} (cm^{-1})	ω_{1b} (cm^{-1})
$KY(MoO_4)_2$	18.9	28.6
$KDy(MoO_4)_2$	17.5	26.5
$KEr(MoO_4)_2$	17.0	26.0
$KTm(MoO_4)_2$	16.7	25.5

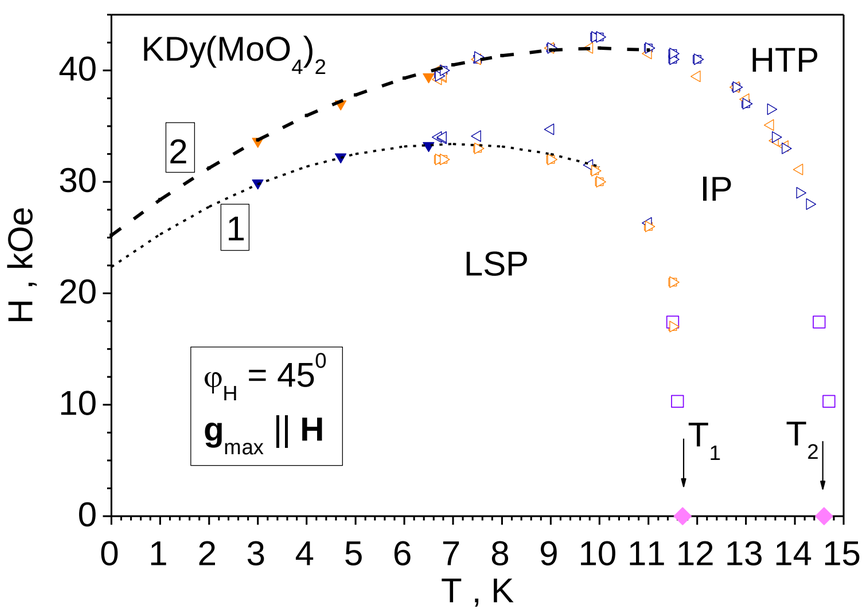


The scheme of Dy^{3+} electronic levels in vicinity of CJTE type phase transition [4].

Low energy phonon excitations are formed by transversal shear vibrations of $\{Re(MoO_4)_2\}^-$ and K^+ layers along crystallographic directions *a* and *b* [3]. CJTE in $KDy(MoO_4)_2$ is accompanied with the lowering of the ground state of rare earth ions as a result of interaction of their lowest excited levels with the low energy phonon excitations.

D_{2h}^{14}, k_{23} = 1/2(b_2 + b_3), D_{2h}^{14} to C_{2h}^5, C_2 II ***a***, T_{CJTE} ~ 15K., absence IP [5]

The symmetry analysis of the existence of an incommensurate phase in the CJTE process.



(H-T) phase diagram of $KDy(MoO_4)_2$, obtained as a result of birefringence experiment (**E || (*ac*)**, ***k* || H || g_{max}**, magnetic field applied with the angle $\varphi_H = 45^0$ to the *c*-axis). The dashed lines represent approximations of the phase boundaries: 1- between the antiferrodistortion (low symmetry phase (LSP)) and the incommensurate phase (IP); 2- between the IP and the high-temperature phase (HTP). Solid triangles represent data obtained from magnetization measurements, magenta symbols – from absorption spectra. Different colors of open symbols shows measurements for different samples.

Symmetry considerations. The expansion of mechanical representation on the irreducible ones gives us

$$\Gamma_N = 17A_g+19B_{1g}+19B_{2g}+17B_{3g}+17A_u+19B_{1u}+19B_{2u}+17B_{3u},$$

here A_g, B_{1g} and so on are the irreducible representations of D_{2h} factor-group, and coefficients show the number of the optical phonon modes, whose symmetry coordinates transform as the corresponding representations. Lattice modes which correspond to A_u modes are active neither in Raman nor IR spectrum. Wave functions transformed by A_u matrix may be constructed as direct productions of B_g and B_u - types rotation or translation modes:

$$A_u = B_{3g}*B_{3u} \text{ or } = B_{2g}*B_{2u} \text{ or } = B_{1g}*B_{1u}$$

Introduce the shifts (x_I - x_{II}) of neighboring layers along *x*||***a*** with the numbers I and II. These displacements belong to B_{1u} representation, because two-fold axis C_2||*x* is conserved, when alternative shifts of the layers take place. The symmetry coordinates constructed as a direct production of (x_I - x_{II}) and u_{yz} ,

E	$2_x(\tau_x,\tau_y,0)$	$2_y(\tau_x,\tau_y,0)$	2_z	$i(\tau_x,0,\tau_z)$	$\sigma_x(0,\tau_y,\tau_z)$	$\sigma_y(0,\tau_y,\tau_z)$	$\sigma_z(\tau_x,0,\tau_z)$	
1 0	1 0	1 0	1 0	-1 0	-1 0	-1 0	-1 0	ξ
0 1	0-1	0 1	0 -1	0 1	0 1	0 -1	0 -1	p

First line ξ corresponds to A_u representation, B_{2g} - p – correspond to the second line. The rotations of the molecular complexes $(MoO_4)^{2-}$ around axis *y* transforms by this representation. Let us include pseudo-degenerate parameter (ξ, p), and construct the invariant

$$p*d\xi/dx - \xi*dp/dx,$$

here ξ transforms as A_u, x – as B_{2u}, p – as B_{2g}. This form is invariant form for D_{2h} point group and must be added to the thermodynamic potential P(ξ, p). Note, that the gradient terms

$$p*d\xi/dy - \xi*dp/dy,\ p*d\xi/dz - \xi*dp/dz$$

are possible for D_{2h} group by formal reason too. Because of the existence of the gradient invariants, the two-dimensional order parameter (ξ, p) induces the incommensurate phases (IP), which "precedes" the commensurate (monoclinic, for example) ones, determined above. The question is more complicate, however, and the structural data about the low-temperature phases are necessary.

The proposed symmetry analysis allows us to describe the possible nature of the IP in the rare-earth double molybdates. The main supposition which permit us to prove the IP existence is taking into account the weak rotations of the rigid tetrahedral anions $(MoO_4)^{2-}$ in the process of shifting layers $\{Dy(MoO_4)_2\}^-$. The special interest is the addition consideration of the low-frequency vibrations of the rare-earth layers as for the establishing of the behavior of structure under the external magnetic fields (magnetoelastic behavior), so as for the low temperature phase symmetry determination [6].

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