The thermal properties and the nature of the interaction in $DyAl_3(BO_3)_4$ aluminoborate of rare earths

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Introduction Rare earth aluminoborates $RAl_3(BO_3)_4$ (R - rare earth ion) demonstrate interesting physical properties, e.g., a very strong magnetoelectric effect [1]. They are promising materials for the laser techniques [2].

The $DyAl_3(BO_3)_4$ crystal studied, crystallizing in a trigonal symmetry, described by the $R32$ space group, was grown by spontaneous solution-melt crystallization method. Magnetic properties of $DyAl_3(BO_3)_4$ originate from the 4*f*-electrons of the Dy^{3+} ions which sit in a trigonal lattice. According to the Hund's rules the dysprosium ion has a $^6H_{15/2}$ ground state, which splits into doubles under influence of the crystal electric field in aluminoborates.

The phase diagram of the dysprosium aluminoborate was constructed for $2\ K > T \geq 50\ mK$. It was found that, under influence of increasing external magnetic field, B, the temperature of the transition decreases, albeit the studies of the magnetization of the $DyAl_3(BO_3)_4$ compound showed that the appearing order has a ferromagnetic character with magnetic moments directed along the ***c*** axis.

Apparatus

PPMS system equipped with

- ***9T magnet***
- ***Dilution Refrigerator (DR) option*** (minimum temperature 50mK)
- ***Specific heat option*** (50mK- 400K)

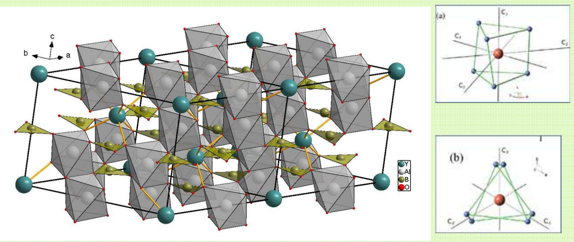
High-field low temperature SQUID-magnetometer

- with ***DR option*** (temperature down to 90 mK)
- ***magnetic field up to 8.5T***

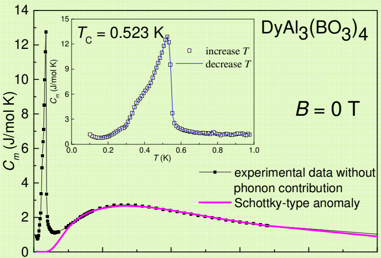
Crystalline structure

$RAl_3(BO_3)$ crystals have a trigonal symmetry, the $R32$ space group.

- The $\mathbf{Al^{3+}}$ **ions** are located within edge sharing octahedra formed by O^{2-} ions.
- The magnetic $\boldsymbol{R^{3+}}$ **ions** are located inside the deformed prisms formed by six O^{2-} ions (Fig. (*a*) and (*b*)).
- Particular ***R*-O6** prisms are separated with **B-O3** triangles and **Al-O6** octahedra.



Specific heat studies



The sharp λ-type anomaly of specific heat at $T_C = (0.523 \pm 0.2)$ K accompanies **the second order magnetic phase transition:**

- **no hysteresis**
- **lambda-like shape**

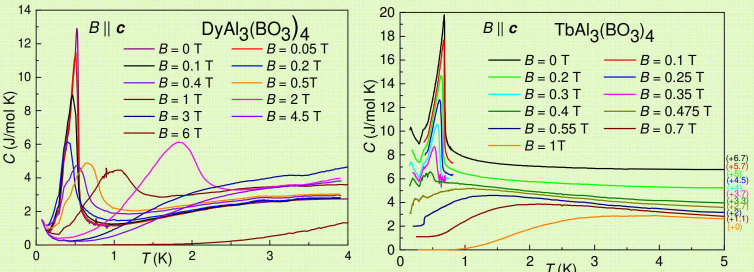
We interpret it as the appearance of a long range ordering of Dy^{3+} magnetic moments.

Phonon specific heat was described by mixing the Debye and the Einstein models, i.e. by formula:

$$C_{ph}(T) = \frac{1}{(1-\alpha T)}\frac{k_B N_A}{2}\left[3n_D\left(\frac{T}{\theta_D}\right)^3\int_0^{\frac{\theta_D}{T}}\frac{x^4e^x}{(e^x-1)^2}dx + \sum_{i=1}^{n_O} n_i\left(\frac{\Theta_i}{T}\right)^2\frac{e^{\frac{\Theta_i}{T}}}{\left(e^{\frac{\Theta_i}{T}}-1\right)^2}\right]$$

The best fit was achieved for the parameters: $\alpha = 0.001329$, $n_D = 3$ (n_D is the number of modes described within the Debye model), $\theta_D = 380$ K (θ_D is the Debye temperature), $\Theta_1 = 107$ K, $\Theta_2 = 170$ K, $\Theta_3 = 312$ K, $\Theta_4 = 472$ K, $\Theta_5 = 525$ K, $\Theta_6 = 580$ K, $n_1 = 1$, $n_2 = 3$, $n_3 = 3$, $n_4 = 2$, $n_5 = 6$, and $n_6 = 7$ (Θ_i are energies, in temperature units, of the optical phonon modes described within the Einstein's model and n_i are the number of optical modes, assigned to the Θ_i energies).

By subtracting the phonon contribution from the measured specific heat C, the magnetic contribution, C_m, was determined. C_m contains, among others, the Schottky contribution, C_{Sch}, coming from excitations of R ions to energy levels split by the crystalline electric field. The best fit was achieved for the energies: $E_1 = 0$ K, $E_2 = 0.0164$ K, $E_3 = 5.56$ K, and $E_4 = 14.91$ K.



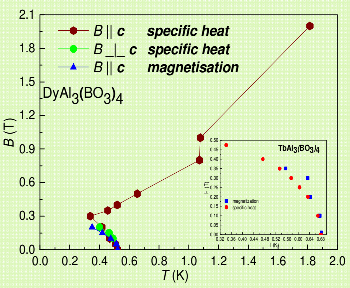
Evolution of the specific heat anomaly, in the magnetic field B parallel to the c axis for $DyAl_3(BO_4)_3$ and $TbAl_3(BO_4)_3$. We suppose that such phase transition behavior, is similar to $TbAl_3(BO_4)_3$[4], and as characteristic of systems in which the line of classical transitions is directed by the magnetic field to the quantum critical point. And dipole-dipole interactions are responsible for the nature of this transition [5].

Common properties:

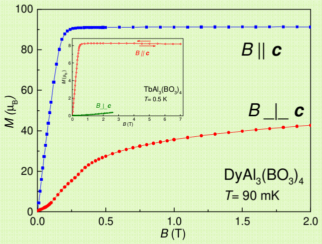
On increase of the external magnetic field parallel and perpendicular to the ***c*** -axis, there were observed:

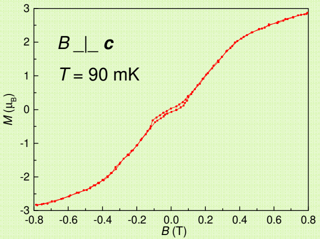
- *lowering the transition temperature,*
- *damping the λ anomaly,*
- *appearance of a wide maximum shifting towards higher temperatures.*

T-B phase diagram for Dy aluminoborate



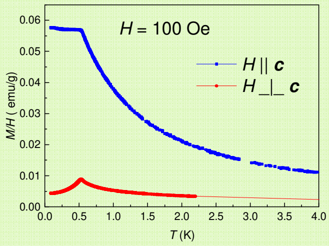
Magnetic measurements





Magnetization process at 90 mK

- In *B* || *c* the magnetisation curve is typical of strongly uniaxial ferromagnets, which proves the magnetic structure to have a large ferromagnetic component along *c*;
- In *B* _|_ *c* an inflection point and a small hysteresis appear on the magnetization curve for *B* ~ 0.2 T. This suggests that the magnetic order in the direction perpendicular to the *c* axis has an antiferromagnetic component and that B _|_ *c* induces a phase transition, related to reorientation of the magnetic moments. In conjunction with the trigonal symmetry of the crystal, this fact suggests that a frustration of interactions, influencing the magnetic order, can be present in the planes perpendicular to the *c* axis.

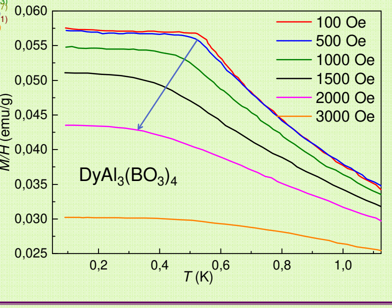


DC magnetic susceptibility vs temperature in $B = 0.01$ T

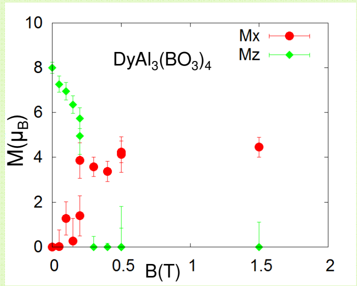
The anomaly observed for B perpendicular to the ***c*** confirms the hypothesis that the phase transition to the magnetically ordered phase, at $T = 530$ mK, is the transition to a spin canted phase with the large ferromagnetic component parallel to the ***c*** and an antiferromagnetic component perpendicular to the ***c*.**

DC magnetic susceptibility vs temperature for different B values

Evolution of the magnetic transition with increase of B || c is consistent with the specific heat data.



Neutron diffraction



Neutron diffraction: a kind of transition induced by the field above 0.2 T, the ferromagnetic structure with moments along the ***c*** disappear while a field induced moment rises along the ***b***. The order of magnitude of this moment is in agreement with *M*(*H*) at low temperature.

RESULTS for $DyAl_3(BO_3)_4$

The phase transition to the magnetically ordered phase, at 0.53 K, was discovered and the *T-B* phase diagram was constructed.

It was found that:

- **The magnetic field shifts the transition towards lower temperatures, when smaller than 0.35 T.**
- **The magnetic structure appearing is noncollinear. It has a large ferromagnetic component along the *c* axis and an anitferromagnetic one in the planes perpendicular to this axis.**
- **The phase transitions to the magnetically ordered state appears at very low temperature and behave atypically for ferromagnetic materials under influence of the magnetic field, which suggests that the transition can be modified by quantum fluctuations .**
- **Physical mechanism of the transition is not clear. Possibly, the magnetic dipole-dipole interactions are very important [5]**

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References
[1] K.-C.Liang et al., Phys. Rev. B 83 (2011) 180417(R). [2] S. Garcia-Revilla et al., Optical Materials 34 (2011) 461 [3] P. Goldner *et al*., Phys. Rev. B **76**, 165102 (2007). [4] T. Zajarniuk *et al*., Phys. Rev. B **105**, 094418 (2022). [5] G. Mennenga *et al.,* J. Magn. Magn. Mater. 44, 59 (1984)