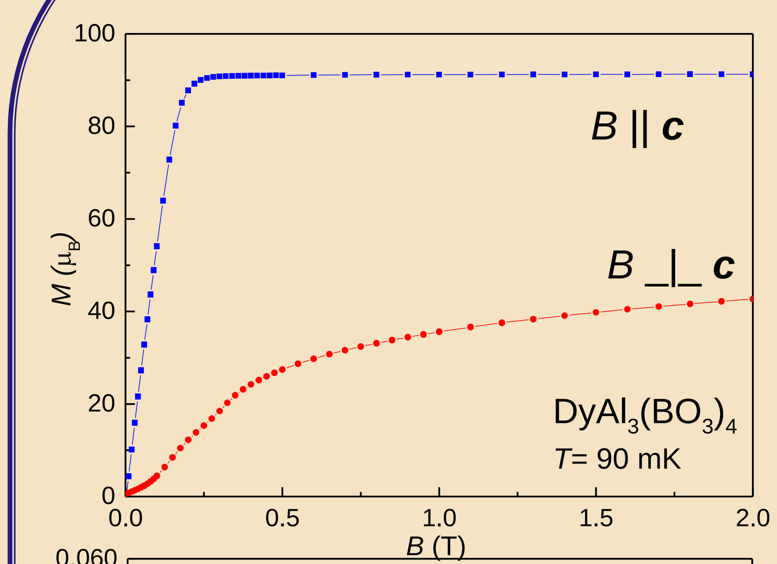
Low-temperature phase transition in *Dy* aluminoborate.

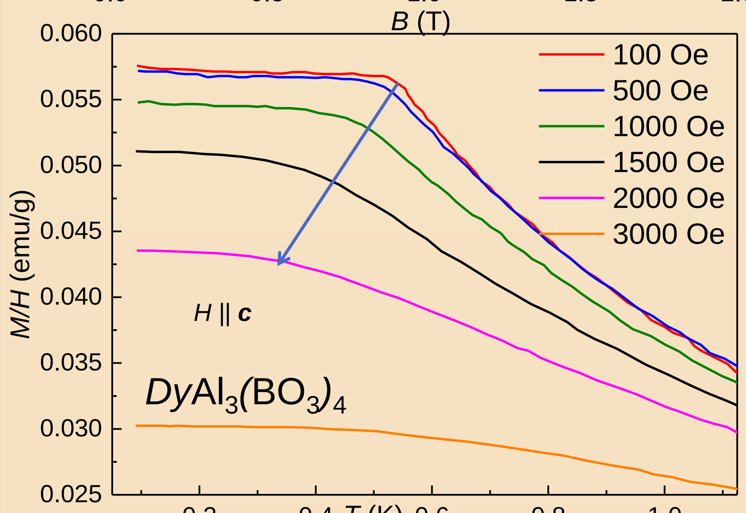
T. Zajarniuk*[1], A. Szewczyk[1], E. Lhotel[2], M.U. Gutowska[1], W. Szuszkiewicz[1], S. Petit[3], A. A. Prokhorov[4], R. Puźniak[1] and H. Szymczak[1].

1. Institute of Physics, Polish Academy of Sciences, Warsaw 02 668, Poland
2. Institut Néel, CNRS & Université Grenoble Alpes, Grenoble 38 042,
3. Laboratoire Leon Brillouin, CEA-Saclay 91 191, France
4. Institute of Physics, AS CR, Praha 182 21, Czech Republic

Introduction A magnetic phase transition below 1 K in the $DyAl_3(BO_3)_4$ aluminoborate single crystal was discovered by means of specific heat, C_B, measurements. It was found, that under influence of increasing external magnetic field, *B*, the temperature of the transition decreases, albeit the magnetization and neutron studies of the $DyAl_3(BO_3)_4$ compound showed that the magnetic order appearing below the transition point has a ferromagnetic character with magnetic moments directed along the threefold *c* axis.
Analysis of the dependence of specific heat and magnetization, near the transition point, that we performed, suggests these behaviors to be characteristic of the behaviors near the transition having a quantum nature, i.e. influenced by quantum fluctuations. The results were found to be consistent with those found for the $TbAl_3(BO_3)_4$ aluminoborate [1].

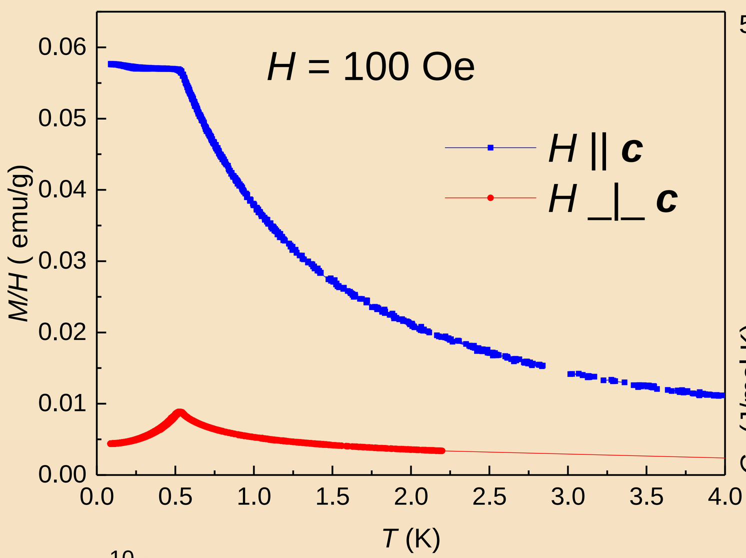
Magnetic measurements

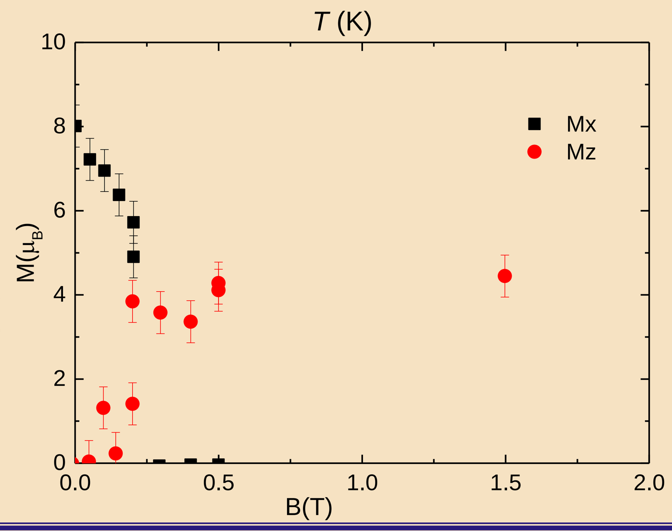




Magnetization process at 90 mK

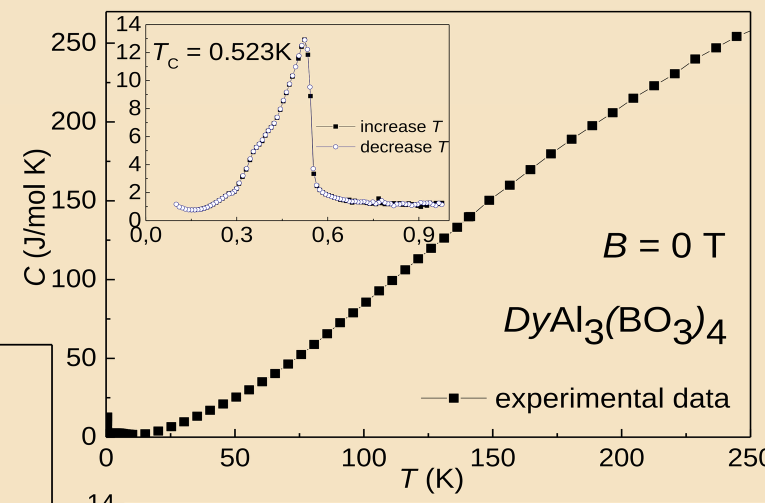
In *B* **||** *c* the magnetisation curve is typical of strongly uniaxial ferromagnets, which proves the magnetic structure to have a large ferromagnetic component along ***c***

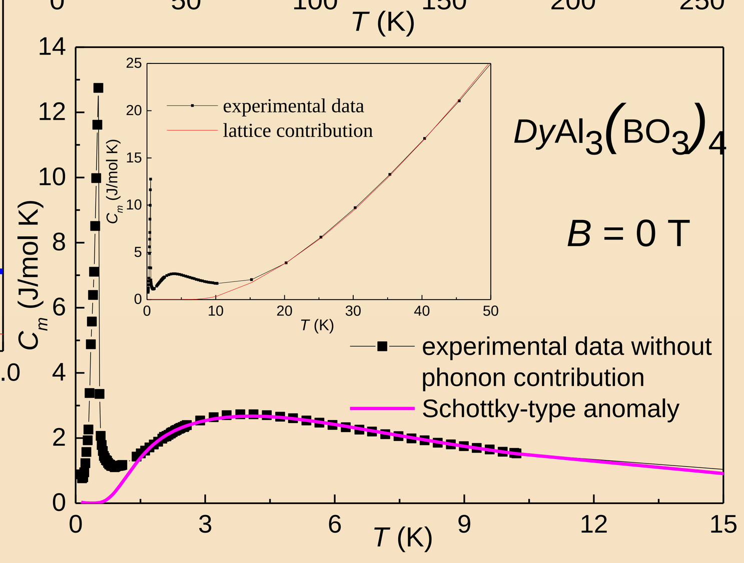




Neutron diffraction: a kind of transition induced by the field above 0.2 T, the ferromagnetic structure with moments along the ***c*** disappear while a field induced moment rises along the ***b***. The order of magnitude of this moment is in agreement with *M(H)* at low temperature.

Specific heat studies





The sharp λ-type anomaly of specific heat at T_C = (0.523 ± 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.

$$C_{total} = C_m + C_{ph}(T) + C_{Sch}(T)$$

Phonon specific heat was described by mixing the Debye and the Einstein models [1]:

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

The best fit was achieved for the parameters: *α* = 0.001329, n_D = 3 (n_D is the number of modes described within the Debye model), θ_D =380 K (θ_D is the Debye temperature), Θ_1=107K, Θ_2=170K, Θ_3=312K, Θ_4=472K, Θ_5=525K, Θ_6=580K, 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).

$$C_{Sch}(T) = \frac{k_B N_A}{T^2}\left[\frac{\sum_{i=1}^{n}E_i^2 e^{-\frac{E_i}{T}}}{\sum_{i=1}^{n}e^{-\frac{E_i}{T}}} - \left(\frac{\sum_{i=1}^{n}E_i e^{-\frac{E_i}{T}}}{\sum_{i=1}^{n}e^{-\frac{E_i}{T}}}\right)^2\right]$$

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.

The crystal field of D_3 symmetry splits the ground multiplet of the Dy^{3+} ($^6H_{15/2}$) into 8 doublets.

$$C_m = C_N + C_{cr}$$

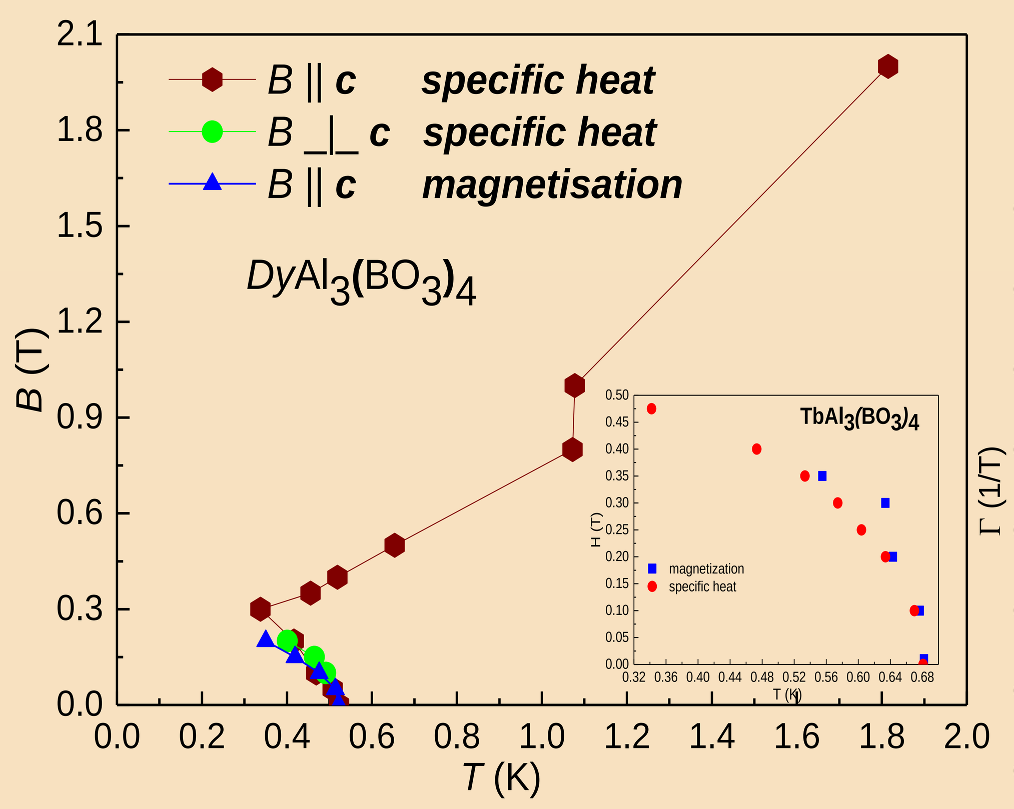
$$C_N = DT^{-2} - ET^{-3} - FT^{-4} \quad [2]$$

$$\frac{D}{R} = \frac{1}{3}á^2 I(I+1) + \frac{1}{45}P^2 I(I+1)(2I-1)(2I+3) \qquad \frac{E}{R} = \frac{1}{15}á^2 PI(I+1)(2I-1)(2I+3) \qquad \frac{F}{R} = \frac{1}{30}á^4 I(I+1)(2I^2+2I+1)$$

where *á* is magnetic hyperfine constant, *P* is quadriupol coupling constant

Quantum 2nd order phase transition

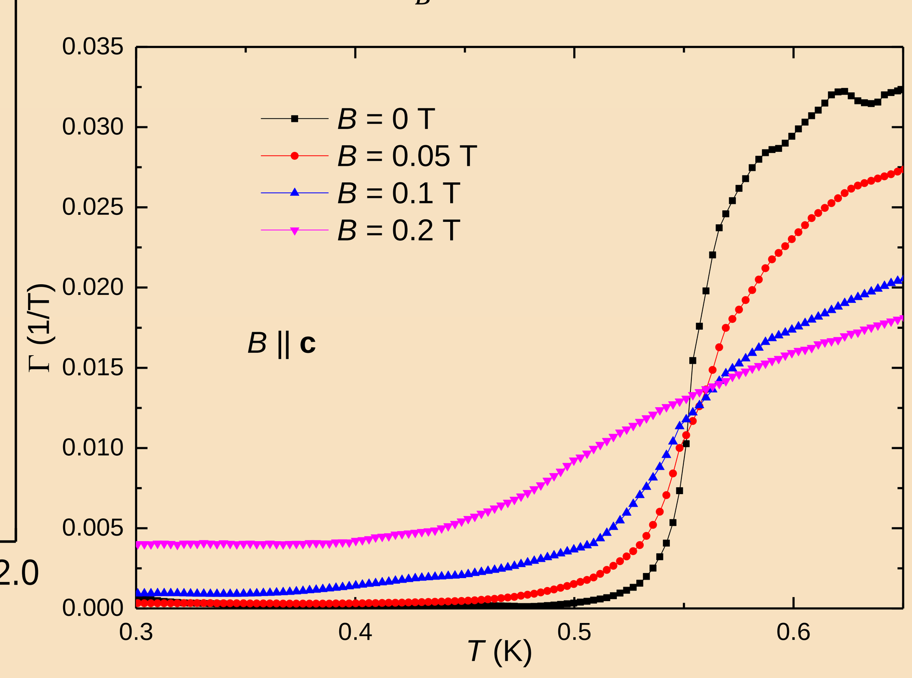
T-B phase diagram for *Dy* aluminoborate

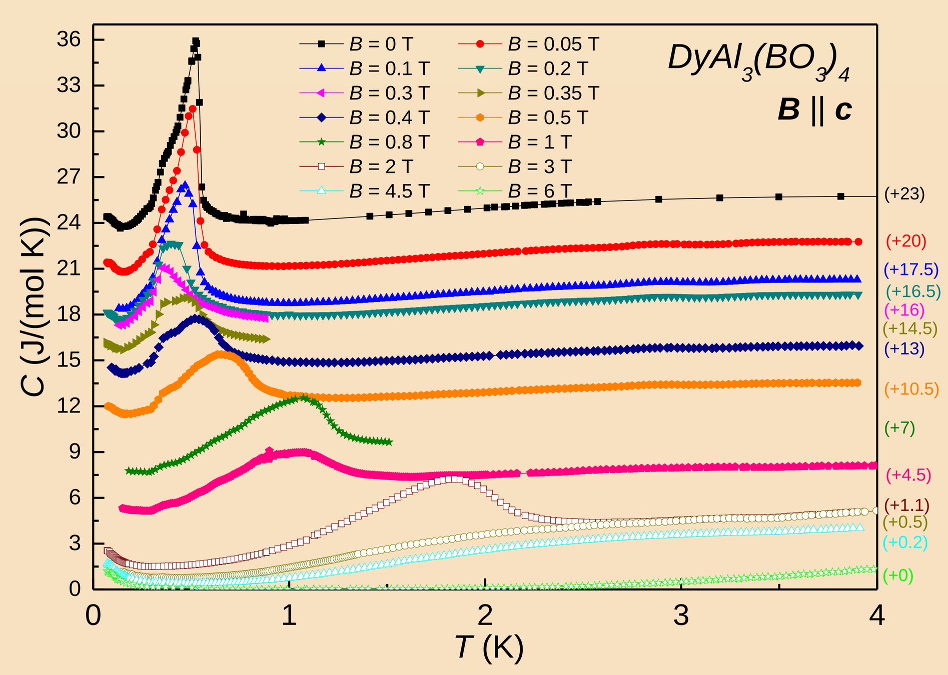


Grüneisen parameter

$$\Gamma = -\frac{1}{T}\frac{\left(\frac{\partial S}{\partial B}\right)_T}{\left(\frac{\partial S}{\partial B}\right)_B} = -\frac{\left(\frac{\partial M}{\partial T}\right)_B}{C_B(T)} = \frac{1}{T}\left(\frac{\partial T}{\partial B}\right)_S$$

$$\Gamma(T\to 0, B) = \frac{G_B}{B-B_C}, with\ G_B = \frac{\nu(d-y_0 z)}{y_0}$$

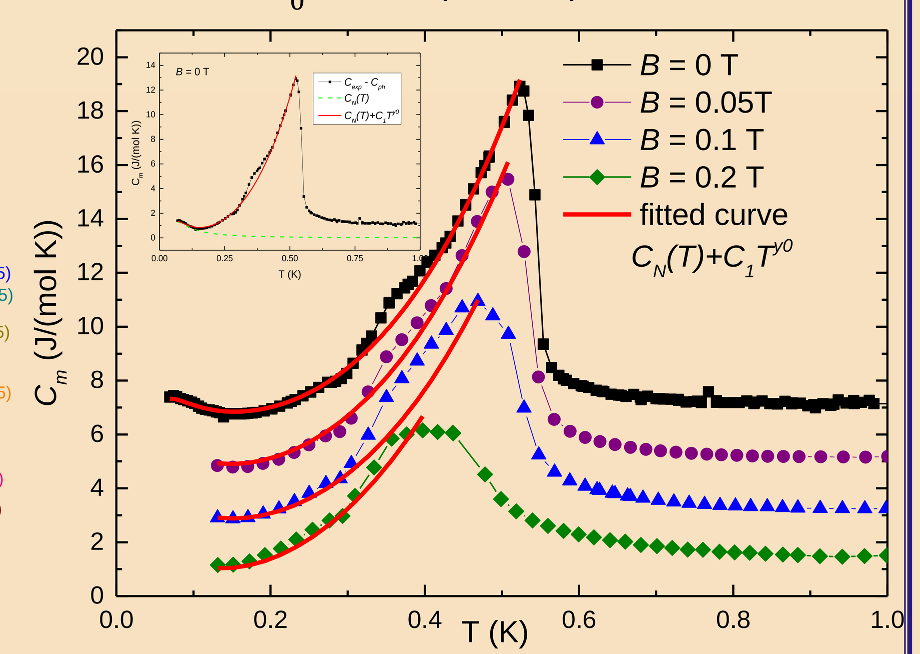




Specific heat

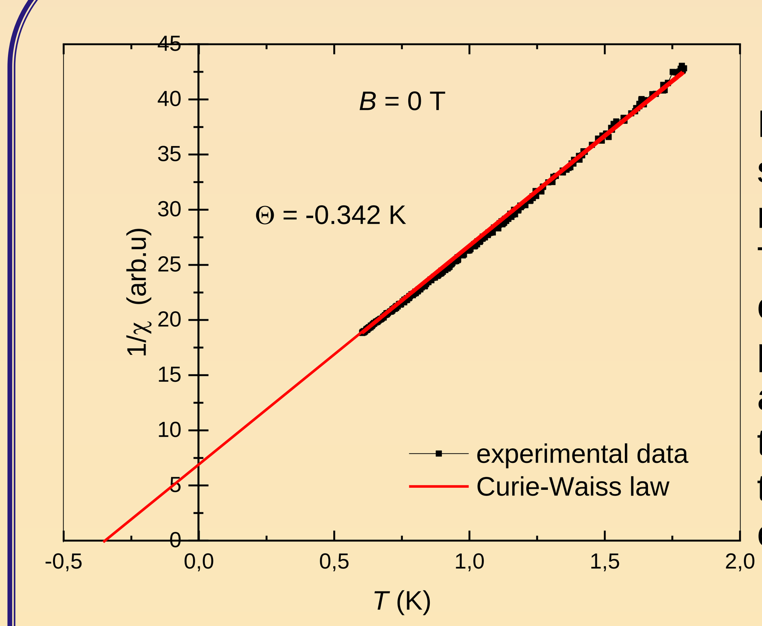
$$C_{cr}(T\to 0, B) = T\frac{\partial S}{\partial T} = C_1(B)T^{y_0}$$

$$C_1 = R\frac{\rho_0 c y_0(y_0+1)}{T_0^{y_0+1}}\left|\frac{B-B_C}{B_C}\right|^{\nu(d-y_0 z)}$$

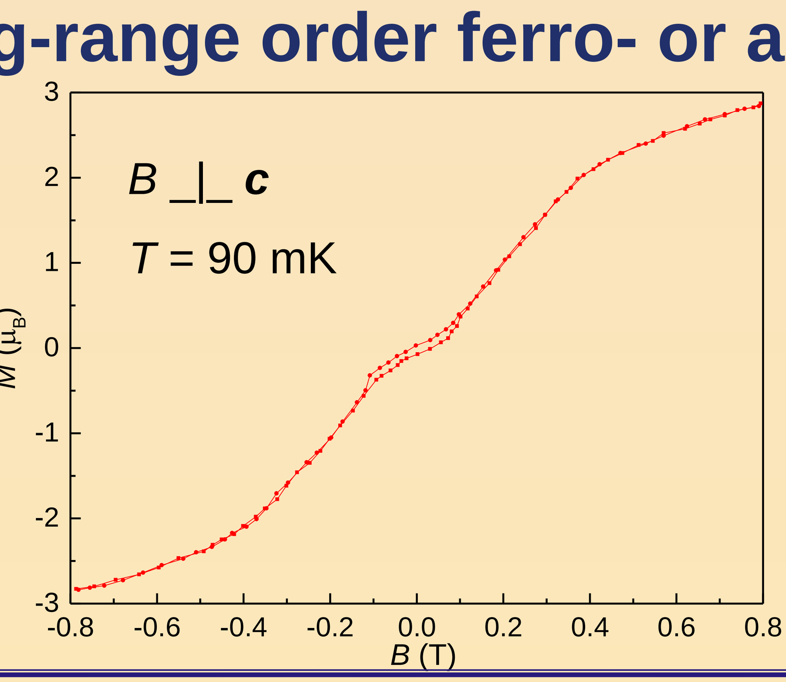


- The **T-B phase diagram** was constructed on the basis of experimental data. It suggests that in *Dy* aluminoborane, as in *Tb* aluminoborane, the phase transition shifts under the influence of the magnetic field in the direction of QCP.
- Experimental data of the **specific heat** are characteristic of such systems, in which the line of phase transitions under the influence of a change in the parameters of the control field tends to the quantum critical point.
- The behavior of the temperature dependence of the **Grüneisen parameter** could not be determined, through insufficient amount of experimental data.

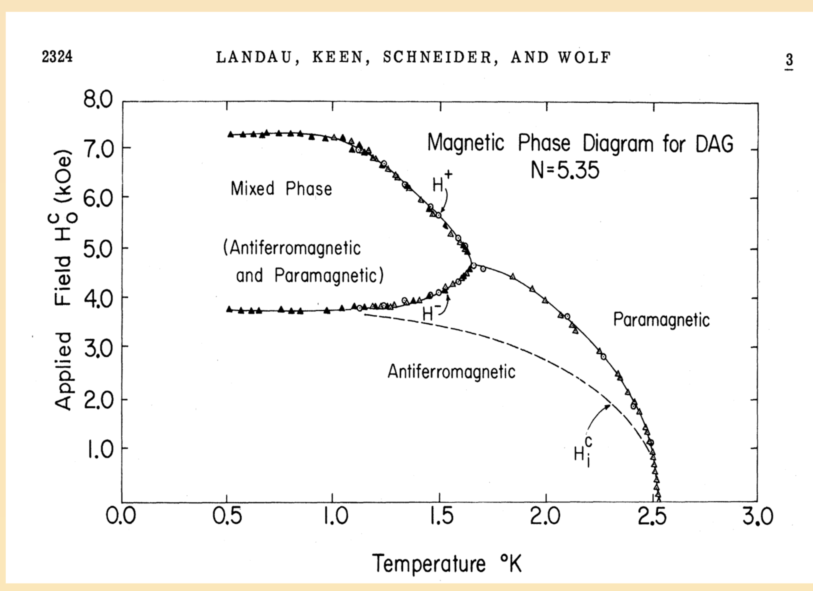
Nature of the long-range order ferro- or antiferromagnetic?



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.



Considering the complex behavior of the temperature dependence of specific heat and magnetization, and the inconsistencies of the experimental data, we can suggest that the case described in the article [5] is observed in the material under study. We assume that the phase diagram for *Dy* aluminoborate will be more complex, similar to the diagram on the right.



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 0.25 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.**
- **The physical mechanism of this transition is not clear [5]. We suggest that an antiferromagnetic-paramagnetic transition is observed in this material. At a certain value of the magnetic field, there is a change in ordering (ferromagnetic).**

Acknowledgments This work was supported partially by the National Science Centre, Poland, under project No.2018/31/B/ST3/03289

References
[1] T. Zajarniuk *et al.*, Phys. Rev. B **105**, 094418 (2022). [2] O.V..Lounasmaa *et al.*, Phys.Rev **126** 1357 (1962)
[3] L. Zhu, *et al.*, Phys. Rev. Lett. **91** (2003) 066404 [4] M. Garst *et al.*, Phys. Rev. B **72** (2005) 205129 [5] D.P. Landau *et al.*, Phys.Rev B. 3, 2310 (1971)

corresponding author e-mail: zayar@ifpan.edu.pl