



Research articles

Peculiarities of a magnetic transition in a quasi-one-dimensional ferromagnet PbMnBO₄A. Pankrats^{a,b,*}, M. Kolkov^{a,b}, S. Martynov^a, S. Popkov^{a,b}, A. Krasikov^a, A. Balaev^a, M. Gorev^{a,b}^a Kirensky Institute of Physics, Federal Research Center KSC SB RAS, Krasnoyarsk, Russia^b Siberian Federal University, Krasnoyarsk, Russia

A B S T R A C T

Near the Curie temperature $T_C = 30.3$ K, the temperature dependences of the magnetization and heat capacity of a single-crystal ferromagnet PbMnBO₄ in the magnetic fields of 1, 3, 10 and 30 kOe are studied. In the strong magnetic fields, both the magnetic contribution to the specific heat and the nonlinearity of the field dependences of the magnetization are maintained up to the temperatures exceeding T_C more than twice. It is assumed that in PbMnBO₄ the difference between T_C , the paramagnetic Curie temperature $\theta = 49$ K and the broad temperature region above T_C where the magnetic contribution to the specific heat is significant is due to the quasi-one-dimensional character of the magnetic structure of this ferromagnet. Using both the estimation of T_C from the Ginzburg-Landau field theory and the θ value, the total exchange interaction parameters $2J \approx 40.4$ K (intrachain) and $z'J' \approx 8.8$ K (interchain) are determined, with $z' = 4$ being the number of neighboring chains. The estimation shows that the Ginzburg-Landau field theory describing the quasi-one-dimensional behavior of PbMnBO₄ is well applicable in the temperature range from $T = S^2J \approx 80$ K. Above this temperature, the mean field approximation with the exchange parameter λ_θ based on the paramagnetic Curie temperature θ describes well the experimental temperature dependences of the magnetization in the strong magnetic field and the specific heat is determined by the lattice contribution.

1. Introduction

The search for and synthesis of new magnetic materials, as well as the investigation of their physical properties, are the priority tasks in solid-state physics. Such studies allow one to find promising materials for technical applications, and also provide experimental data for studying new physical effects arising at the intersection of magnetic, electrical, elastic, and other properties of solid state physics. The crystal classes which admit the existence of a family of isomorphous magnets with different magnetic ions in one of the crystallographic positions attract particular interest. This property can lead to a variety of physical properties, in particular, to different magnetic structures in the family of isomorphous crystals.

Orthoborate crystals with the general formula PbABO₄ are representatives of such an interesting family. Their structure for A = Ga, Al was first studied by H. Park et al. [1] where the orthorhombic structure with the space group *Pnma* was established. Later the same group of authors investigated the magnetic properties of polycrystalline compounds with A = Fe, Cr, and Mn [2] and found that the type of magnetic order depends on the paramagnetic ion A. The anti-ferromagnetic order was established for Fe and Cr with the Néel temperatures of 125 K and 8.3 K, respectively. The compound with A = Mn showed the ferromagnetic order with the Curie temperature $T_C = 31$ K.

Magnetic studies on single crystals have a number of advantages.

Single crystals have a higher quality than polycrystalline samples which often contain extraneous phases. It is also important that the studies on single crystals provide more information allowing one to study the anisotropic properties of matter. The magnetic studies of the PbFeBO₄ single crystals which were grown by spontaneous crystallization allowed us [3] to explain them as typical of the three-dimensional anti-ferromagnetic order and to refine the Neel temperature as $T_N = 115$ K. We also investigated the dielectric properties of PbFeBO₄ and found anomalies for both polycrystalline and single-crystal samples, which indicates the correlation between the magnetic and electrical subsystems in the crystals.

The PbMnBO₄ single crystals were also first grown using spontaneous crystallization by a flux technique [4]. The analysis of its magnetic and resonance properties showed [4] that the static Jahn-Teller effect characteristic of the Mn³⁺ ion leads to the ferromagnetic exchange interaction in the PbMnBO₄ crystal. The same effect apparently causes the strong magnetic anisotropy in the crystal. The significant effective anisotropy fields of the crystal determine the energy gap in the FMR spectrum which is extraordinarily large for ferromagnets (112 GHz at $T = 4.2$ K). Another unusual property of the PbMnBO₄ crystals was observed when studying the temperature dependences of the magnetization and resonance fields. In the external magnetic field, the induced ferromagnetic ordering is retained in the crystal above the Curie temperature up to the temperatures much higher than T_C . Thus, the aim of

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this work is to study in detail the transformation of the ferromagnetic state to a paramagnetic one in the presence of the external magnetic field.

A detailed study of the magnetic and thermophysical properties of PbMnBO_4 shows that the nonlinearity of the field dependences of the magnetization inherent to the ordered ferromagnetic state and the magnetic contribution to the specific heat actually remains in this crystal up to temperatures exceeding more than twice the Curie temperature which is 30.3 K in accordance with the specific heat data. It is suggested that the main reason for this is the quasi-one-dimensional character of the magnetic structure of the crystal. The parameters of intra- and interchain exchange interactions are estimated using the experimental values of the magnetic ordering temperature and paramagnetic Curie temperature. The peculiarity of the magnetic structure of PbMnBO_4 is that these parameters differ significantly less than in classical quasi-one-dimensional magnets. Above ~ 80 K, the specific heat of this ferromagnet is determined by the lattice contribution, and the magnetic properties are well described within the framework of the mean field theory with the exchange parameter calculated using the paramagnetic Curie temperature.

2. Experimental details

The studies were carried out on PbMnBO_4 single crystals grown by spontaneous crystallization using the technique described in [4]. The magnetic measurements were performed using an original vibrating sample magnetometer in the temperature range from 4.2 to 300 K and magnetic fields of up to 70 kOe. PPMS-9 (Quantum Design) was used to measure the specific heat in the temperature range 2–300 K and in magnetic fields up to 30 kOe.

3. Experimental results

To correctly compare the results of the magnetic and thermophysical studies, the temperature dependences of the magnetization and specific heat were measured in the same applied magnetic fields. Fig. 1 shows the temperature dependences of the magnetization measured in the temperature range 4.2–80 K in the magnetic field of 3, 10 and 30 kOe applied in the direction of easy magnetization (the orthorhombic axis a). In the figure, the magnetization is given as normalized to the maximum in the experimental value of the magnetization measured at $T = 4.2$ K and field of 70 kOe (taken from our previous study [4]). At low temperatures, the magnetization dependence

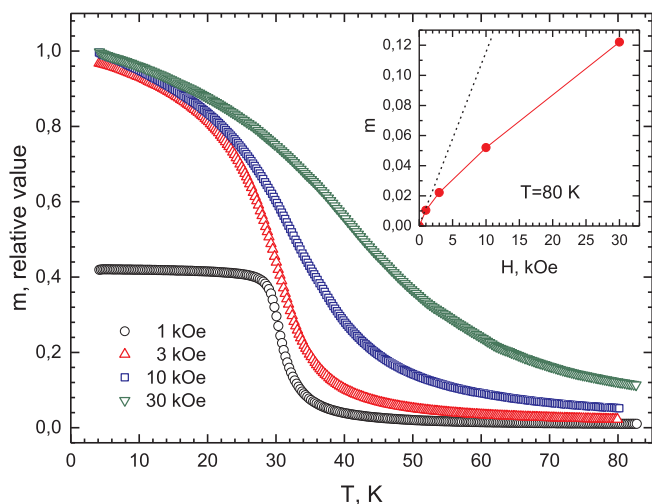


Fig. 1. Temperature dependences of the relative magnetization of PbMnBO_4 measured in the easy direction in the magnetic fields of 1, 3, 10 and 30 kOe. The inset shows the field dependence of the relative magnetization at $T = 80$ K.

measured at 3 kOe goes slightly below the other curves. Taking into account the field dependences of the magnetization [4], this feature can be explained by the fact that the magnetization is not yet fully saturated in this measuring field due to the domain structure.

The magnetization dependence measured in the field of 1 kOe is also given here for comparison. An unusual form of this temperature dependence can easily be understood from the field dependences of the magnetization given in [4]. Due to the domain structure, saturation of the magnetization at low temperatures occurs in the field just above 3 kOe. The initial parts of the magnetization isotherms corresponding to the rearrangement of the domain structure in fields up to 1 kOe coincide at all temperatures up to $T = 25$ K. Therefore, the magnetization remains almost constant at all temperatures below the Curie temperature and decreases sharply only with the approach to $T_{c^{***}}$.

The larger the measuring field, the slower the magnetization decreases at temperatures above T_C . As the inset in Fig. 1 shows, the field dependence of the magnetization based on the temperature dependences remains nonlinear even at $T = 80$ K. The direct measurements of the field dependences of the magnetization in PbMnBO_4 given in [4] also demonstrate a nonlinear character at temperatures above T_C up to the maximum in the experiment temperature of 77 K.

The specific heat was also measured on the single crystal in the magnetic fields of 0, 3, 10, and 30 kOe (Fig. 2) applied in the orthorhombic axis a . In the absence of the field, the specific heat has a pronounced λ -peak at the Curie temperature whose refined value is $T_C = 30.3$ K. In the presence of the magnetic field, as it should be, the jump of the specific heat disappears; the λ -peak transforms into a hump which broadens and shifts towards the higher temperatures as the magnetic field increases.

4. Discussion

The Debye-Einstein model was used to calculate the contribution of the crystal lattice to the specific heat; this contribution is shown by the solid red line in Fig. 2. The Debye and Einstein temperatures are fitted as $\theta_D = 245.6$ K and $\theta_E = 609.6$ K. The inset shows the temperature dependence of the specific heat measured in zero magnetic field in the temperature range up to 200 K. It can be seen that the lattice contribution is decisive at high temperatures. In zero magnetic field, the deviation of the experimental data from the lattice contribution appears at temperatures slightly above 60 K and increases when approaching the Curie temperature. It is obvious that these deviations are caused by fluctuations due to the establishment of the magnetic order.

The experimental specific heat can be represented by the sum of the lattice C_{lat} and magnetic C_{mag} contributions. The temperature

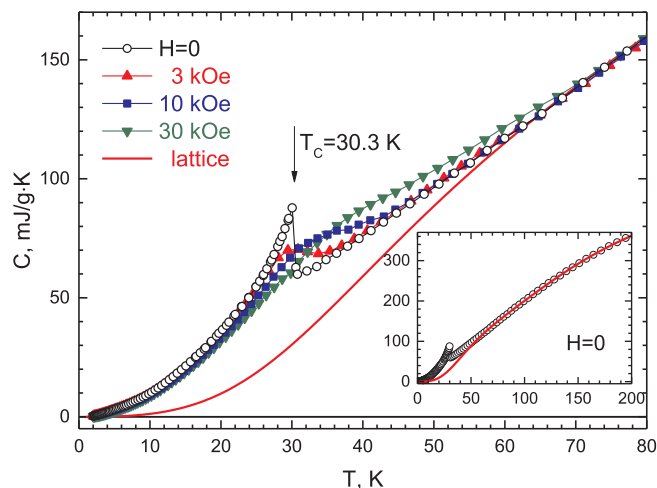


Fig. 2. Temperature dependences of the specific heat measured in different magnetic fields.

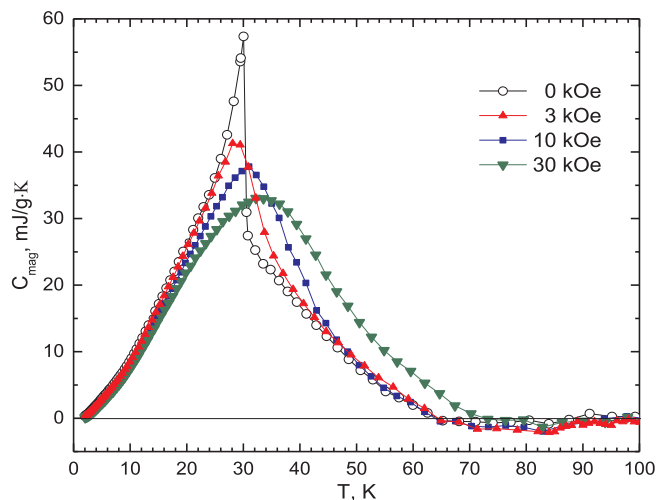


Fig. 3. Temperature dependences of the magnetic contribution to the specific heat measured in different magnetic fields.

dependences of the magnetic contribution to the specific heat are shown in Fig. 3. In the zero field, the magnetic contribution to the specific heat appears upon cooling below 65 K and increases abruptly at the Curie temperature. With the application of the magnetic field, this sharp jump transforms into a smooth hump which broadens and shifts towards higher temperatures with the increasing magnetic field.

The magnetic contribution to the specific heat allows one to calculate the entropy associated with the transition in the magnetic subsystem. It should be noted that for all magnetic fields the entropy tends to a level determined by the quantity $\Delta S_{mag} = R \ln(2S + 1) = 39.71 \text{ mJ/g.K}$, confirming a purely magnetic character of the transition. But the rate of approaching this level depends on the applied magnetic field. Thus, in the zero magnetic field the relative contribution to the entropy of the transition at the Curie temperature reaches ~ 0.8 of the maximum level ΔS , and in the magnetic field of 30 kOe it is only ~ 0.6 . Accordingly, the maximum entropy of the transition in such a magnetic field reaches saturation at temperatures above 70 K while in the zero field this level is reached even at 60 K.

Thus, both the thermophysical and magnetic properties of the PbMnBO_4 crystal indicate that the field-induced ferromagnetic order is partially retained at temperatures much greater than T_C . However, even in the absence of the magnetic field some features of the ordered state also persist in a wide temperature range above T_C . Judging from the magnetic contribution to the specific heat (Fig. 3), this contribution even in the zero magnetic field vanishes only at $T \approx 65 \text{ K}$ which is twice as T_C . A detailed comparison of such contributions measured in the external magnetic fields shows that the relatively weak field (3 and 10 kOe) leads only to the smearing of the jump in the temperature range near T_C , and with further heating the temperature dependences of the magnetic contribution coincide with the curve for the zero field at temperatures above $\sim 40 \text{ K}$ for 3 kOe and $\sim 48 \text{ K}$ for 10 kOe. But in the stronger field of 30 kOe, the magnetic contribution to the specific heat remains substantially higher than the curve for zero field at all temperatures above T_C up to the disappearance of this contribution at $T \approx 72 \text{ K}$. The same features can also be noticed in the temperature dependence of the magnetic contribution to the entropy (Fig. 4).

Another important peculiarity of the magnetic properties of PbMnBO_4 is the considerable discrepancy between T_C and the paramagnetic Curie temperature θ obtained from the high-temperature part of the magnetic susceptibility in the paramagnetic region. In PbMnBO_4 , the paramagnetic Curie temperature observed here for the direction of easy magnetization is equal to $\theta \approx 49 \text{ K}^1$ exceeding T_C by more than a

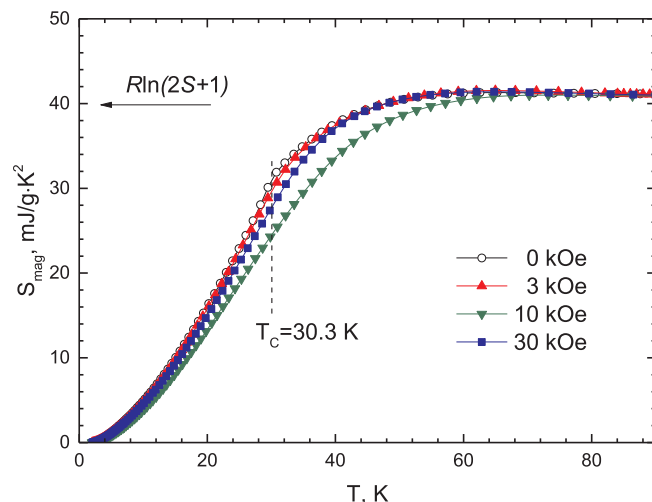


Fig. 4. Temperature dependences of the magnetic contributions to the entropy.

factor of 1.5.

In ferromagnetic metals and alloys, a similar temperature difference gave rise to the term “smeared magnetic transition” [5], the degree of smearing was usually characterized by the temperature interval $\Delta T_{sm} = \theta - T_C$. It is usually assumed that the short-range magnetic order is retained above T_C within this interval due to the fluctuations of the magnetic order. One of the possible reasons of fluctuations in such compounds can be the inhomogeneities of the crystal structure. As an example, one can mention ferromagnetic nickel [5] with $T_C = 631 \text{ K}$ for which $\Delta T_{sm} \approx 14 \text{ K}$, with $\Delta T_{sm} \ll T_C$ [5]. In metal alloys with a random distribution of atoms in the crystal structure, the value of ΔT_{sm} can reach 70 K [5] remaining anyway significantly lower than T_C . Obviously, the great difference between T_C and θ in PbMnBO_4 is of different physical nature which will be discussed below.

The comparison of the temperature dependence of the magnetization curves for PbMnBO_4 in the external magnetic field H_0 directed along the easy axis of magnetization with the calculation in the framework of the mean field approximation was carried out on the basis of the Hamiltonian for the spin $S = 2$:

$$H = g\mu_B H_0 \sum_i S_i^z + \sum_{i>j} J_{ij} S_i S_j + K_1 \sum_i S_i^z{}^2 + K_2 \sum_i S_i^{x2}, \quad (1)$$

where the parameters of the two-axis anisotropy K_1 and K_2 (both < 0) obtained from the FMR data [4] are used.

In this approximation, the relative magnetization of one ion has the form

$$\frac{\langle S_i \rangle}{S} = \sigma = \frac{e^{-\beta K} \sinh(\beta g\mu_B H_{\text{eff}}) + 2e^{-4\beta K} \sinh(2\beta g\mu_B H_{\text{eff}})}{0.5 + e^{-\beta K} \cosh(\beta g\mu_B H_{\text{eff}}) + 2e^{-4\beta K} \cosh(2\beta g\mu_B H_{\text{eff}})},$$

$$H_{\text{eff}} = H_0 + H_E, \quad K = K_1 - \frac{K_2}{2}, \quad (2)$$

where the exchange field has the form $H_E = \lambda S\sigma/g\mu_B$ and the secular part of the single-ion anisotropy $K/g\mu_B = -11 \text{ kOe}$ is taken into account. The non-secular part of the anisotropy of the Hamiltonian (1)

$$H_{ns} = \frac{K_2}{4} (S^{+2} + S^{-2})$$

gives a small correction to the magnetization in the considered temperature and field regions and can be rejected.

The mean field coefficient λ was determined from the experimental values of both the paramagnetic Curie temperature $\theta = 49 \text{ K}$ and the

(footnote continued)

axis a , for the other two axes the values are 51 K (axis b) and 47 K (axis c). All values were defined here more exactly than in [4] from the susceptibility data for $T > 175 \text{ K}$.

¹ This value of the paramagnetic temperature θ is given for the orthorhombic

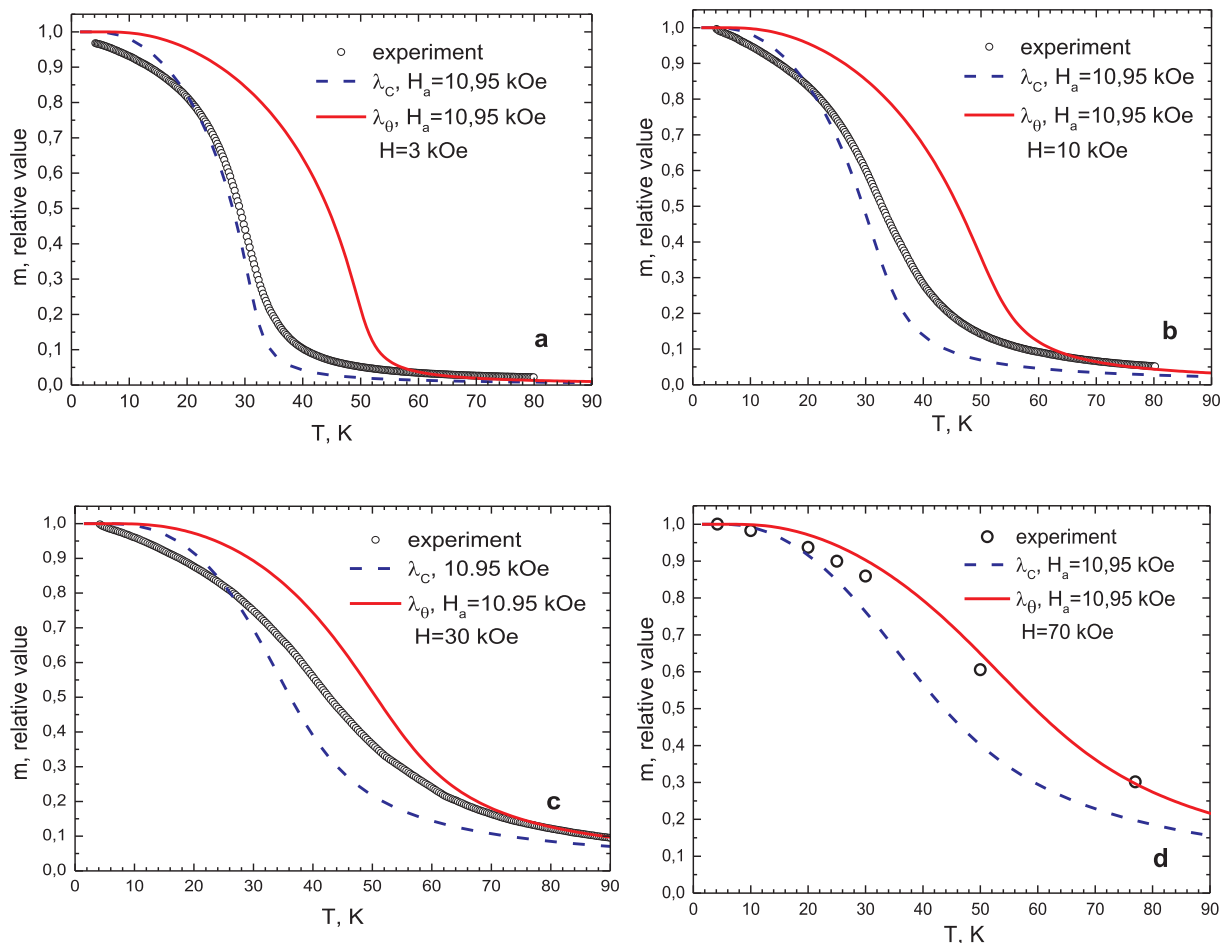


Fig. 5. Comparison of the theoretical and experimental temperature dependences of magnetization measured in different magnetic fields.

temperature of the ferromagnetic ordering $T_C = 30.3$ K using the following expressions:

$$\begin{aligned} \lambda_\theta &= 3k\theta/S(S+1) \\ \lambda_C &= 3kT_C/S(S+1) \end{aligned} \quad (3)$$

The theoretical dependences of the magnetization (2) for both cases are shown in Fig. 5 in comparison with the experimental ones measured in various external magnetic fields applied in the direction of easy magnetization. For the field $H = 70$ kOe (Fig. 5c), the experimental dependence is presented using the magnetization isotherms given in [4]. When the parameter λ_θ corresponding to the paramagnetic Curie temperature (the solid red lines in Fig. 5) is used, good agreement with the experiment is achieved in the high-temperature region $T \geq 2.5T_C$ and in the relatively large magnetic fields $H_0 \geq 10$ kOe. For the parameter λ_C , the mean field approximation does not give a satisfactory agreement with the experiment both below and above the ordering temperature in any magnetic field (the dashed blue lines in the Figures).

The significant difference between the magnetic ordering temperature T_C and the paramagnetic Curie temperature θ is a sign either of the frustration of the exchange bonds or of the quasi-low-dimensional spatial distribution of the exchange interactions. For ferromagnetic ordering, the first reason is absent since the mutual orientations of the spins below the ordering temperature coincide with their orientations in the external magnetic field in the high-temperature limit. At the same time, the crystal structure of PbABO_4 creates the prerequisites for the formation of a quasi-one-dimensional magnetic structure. The crystal structure of this crystal and its role in the formation of the magnetic structure of PbMnBO_4 were considered in detail in [4]. The main

fragments of the structure are linear MnO_4 chains made up of edge-sharing MnO_6 octahedra; the chains are linked by the BO_3 and PbO_4 groups. This peculiarity of the structure can lead to the fact that the exchange interaction between the Mn^{3+} ions in the chain is stronger than the interaction between them, which can lead to a difference between T_C and θ . With the strong difference between the intra- and interchain interactions, other features are observed in such structures: as a rule, the temperatures of the establishment of the long-range magnetic order are sufficiently low, and in the paramagnetic region, a broad peak of the specific heat is observed² which is due to the establishment of short-range magnetic correlations in the chains. Similar features were observed in quasi-one-dimensional magnets formed from the ferromagnetic chains ($\text{C}_6\text{H}_{11}\text{NH}_3$) CuCl_3 , ($\text{C}_6\text{H}_{11}\text{NH}_3$) CuBr_3 [6,7], RbFeCl_3 [8] and CsNiF_3 [9].

Currently, there is no consensus on the dimensionality of the magnetic structure of the crystals of the PbABO_4 group with $A = \text{Fe, Mn}$ and Cr . In [2], these crystals are classified as quasi-low-dimensional magnets, since the authors found broad peaks of the magnetic susceptibility when studying the polycrystals with $A = \text{Fe}$ and Cr . In addition, the study of polarized Raman scattering in the PbFeBO_4 crystal shows [10] that the intrachain exchange interaction is dominant, which evidences the quasi-low-dimensional character of the magnetic structure of this antiferromagnet. The results of the calculation of the exchange parameters for this crystal [11] obtained by the density functional (DFT) method $J_0/k_B = -21$ K (intra-) and $J_2/k_B = -3.9$ K (inter-) also

² In quasi-low-dimensional antiferromagnets, a broad peak of the magnetic susceptibility appears also in the same temperature region, but such a peak of the susceptibility is absent in quasi-low-dimensional ferromagnets.

indicate the dominant character of the intrachain exchange.

However, our measurements [3] performed on the single-crystal PbFeBO_4 show the absence of a broad peak of the magnetic susceptibility in the paramagnetic region; the temperature dependence of the susceptibility in the paramagnetic region follows the Curie-Weiss law. Most likely, the broad peak of the susceptibility observed in [2] is not due to the correlations of the short-range magnetic order but is rather induced by the contribution of the $\alpha\text{-Fe}_2\text{O}_3$ hematite phase present in the polycrystalline sample. In addition, the PbFeBO_4 crystal has a relatively high Neel temperature $T_N = 114$ K, which is not typical of most quasi-low-dimensional magnets. Based on these data, it is concluded [3] that the PbFeBO_4 crystal is most likely a three-dimensional antiferromagnet.

A similar situation is observed in the ferromagnet PbMnBO_4 . The DFT calculations of the exchange parameters for this crystal [11] also show the difference between the inter- and intrachain exchange parameters. However, there is no pronounced wide peak on the temperature dependence of the specific heat in the paramagnetic region which is smooth and well described by the lattice contribution (see the inset in Fig. 2).

Thus, one can summarize the following. All the crystals of the PbABO_4 group with $A = \text{Fe, Mn and Cr}$ have structural prerequisites for the formation of the quasi-one-dimensional magnetic structure. In these crystals, the exchange intrachain interactions are stronger than the interchain ones, which is qualitatively confirmed by the theoretical DFT calculations as well as in the experimental Raman studies of the PbFeBO_4 crystal. However, in the crystals with $A = \text{Fe and Mn}$ this difference between the interactions is apparently not so great; and in these crystals, the temperature ranges for the formation of the short-range magnetic order are close enough to the corresponding temperatures of the magnetic phase transitions. As a result, in the paramagnetic regions of both crystals there are no pronounced maxima of the thermodynamic characteristics which are associated with the establishment of the short-range magnetic order. On the other hand, the difference between the intra- and interchain exchange interactions in PbMnBO_4 leads to the fact that the paramagnetic Curie temperature $\theta \approx 49$ K which is found from the high-temperature susceptibility and determined by the sum of both exchange interactions considerably exceeds the transition temperature T_C . And it is the difference in the exchange interactions which leads to the fact that the magnetic contribution to the specific heat is observed over a wider temperature range above T_C than in three-dimensional magnetic materials with isotropic exchange interaction.

A similar situation seems to be observed in PbFeBO_4 where the difference between the intra- and interchain exchange interactions leads to the fact that the paramagnetic Néel temperature in its absolute value (≈ 260 K) is more than twice than that of T_N . But this difference between the exchange parameters is also insufficient to resolve the broad maximum of the susceptibility in the paramagnetic temperature range.

Apparently, only in PbCrBO_4 the interaction between the chains is quite small as compared to the intrachain one, which leads both to the small value of the Néel temperature $T_N = 8$ K and the well pronounced maximum of the magnetic susceptibility at $T(\chi_{\text{max}}) \approx 13$ K.

Having the experimental values of T_C and θ for PbMnBO_4 and using their theoretical expressions (3), one can determine the parameters of the spin Hamiltonian – both the exchange between the spins within the chain J and the total interchain exchange $z'J'$ (for the structure PbMBO_4 , the number of the neighboring chains $z' = 4$). The single-ion anisotropy parameter K used for the analysis of the temperature behavior of magnetization (2) is small compared both to the temperatures at which the determination of θ was carried out and the ordering temperature T_C , with the latter being increased by 4%. Therefore, it was not taken into account when estimating the exchange parameters of the Hamiltonian (1).

The paramagnetic Curie temperature θ is obtained using the

asymptotic limit $T \rightarrow \infty$ in the expression for the relative magnetization (2) using the exchange field parameter for both exchange interactions in the Hamiltonian (1) [12]

$$\lambda = \frac{k}{2} \sum_{mn} J_{ij} = k \left(J + \frac{z'}{2} J' \right), \quad (4)$$

which gives

$$\theta = \frac{S(S+1)}{6} (2J + z'J'). \quad (5)$$

An analytical expression for the temperature of the quasi-one-dimensional magnet ordering is obtained for the chain of classical spins $S = 1$ in the mean field of neighboring chains in the continuum approximation of the Ginzburg-Landau field theory [13] and is used to describe the magnetic properties of CsNiF_3 [14]. Applying the transition from the exchange integral in the system of classical spins of the unit length to the integral in the system of quantum spins $SJ_{\parallel}(J_{\perp}) = S^2J(J')$ [15] and using the second term (4) as the coefficient of the interchain exchange field, we obtain an expression for the temperature of ordering

$$T_C \cong S^2 \sqrt{\frac{z'}{3}} J'J. \quad (6)$$

Substituting the experimental values of T_C and θ in (5) and (6), one obtains an estimate of the exchange parameters of the Hamiltonian (1):

The obtained value of the exchange within the chain almost coincides with the result of describing the susceptibility of PbMnBO_4 as the susceptibility for the one-dimensional chain [2] obtained using the classical Fisher approach [15] ($J_S = 11$ K for the Hamiltonian $H = -2J_S \sum_i \mathbf{S}_i \mathbf{S}_{i+1}$). Thus, the parameters of the spin Hamiltonian (1) obtained from the experimental values of T_C and θ confirm the chain character of the spatial distribution of the exchanges in PbMnBO_4 . The theoretical DFT calculation of the exchange parameters for this magnet [11] yields $J = 37$ K, $J_1' = 0.5$ K and $J_2' = 3.0$ K where J_1' and J_2' describe the interchain exchange interactions with $z_1' = 4$ and $z_2' = 8$, respectively. These values of the exchange parameters can only be regarded as a qualitative confirmation of the quasi-one-dimensional character of the magnetic structure of PbMnBO_4 since the estimate of the paramagnetic Curie temperature using these parameters is twice as high as the experimental value of θ .

The temperature interval in which the Ginzburg-Landau field theory is applicable was obtained in [16]; in the notation of the Hamiltonian (1) this interval has the form

$$S^2J > T > S^2 \sqrt{\frac{z'}{3}} J'J = T_C. \quad (7)$$

$H_0 \geq 10$ kOe Thus, the upper limit of this interval $T \approx 80$ K quantitatively corresponds to the temperature above which the mean field approximation with the parameter λ_0 well describes the experimental temperature dependences of magnetization measured in the magnetic fields.

At low temperatures $T < T_C$, the magnetization of PbMnBO_4 rapidly decreases with the increasing temperature. The same decrease is observed for the sublattice magnetization in CsNiF_3 [17]. Such a behavior can be explained by the existence in the ordered phase of nonlinear excitations of the sin-Gordon type [18] in a chain magnet with small anisotropy in the easy plane of magnetization. In PbMnBO_4 , the value of anisotropy is much smaller than the above-mentioned temperature of the magnetic measurements, which provides the conditions for the existence of such excitations decreasing the magnetization.

The calculation of the temperature dependence of the magnetic contribution to the specific heat in the external field can be performed both below and above T_C similarly [19–21]:

$$C_m = \frac{dE_m}{dT} = \frac{d}{dT} H_{\text{eff}} M, \quad (8)$$

where E_m is the magnetic energy and H_{eff} is determined in (2). In this

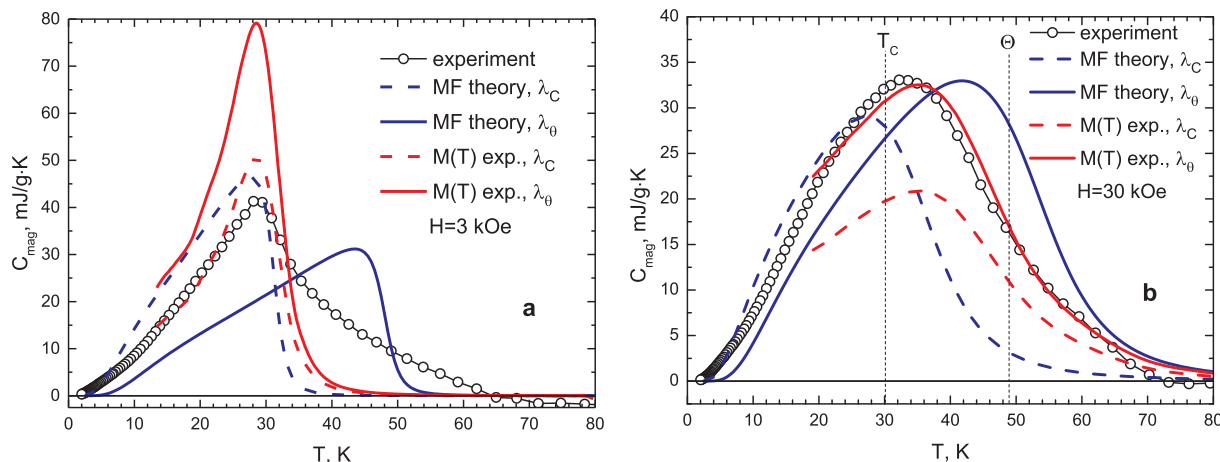


Fig. 6. Temperature dependences of the magnetic contributions to the specific heat measured in magnetic fields of 3 kOe (a) and 30 kOe (b). Points – experiment, lines – calculations (see text).

case, both the temperature dependence of magnetization (2) calculated in the framework of the mean field approximation and the experimentally measured dependence (Fig. 1) can be used for the calculation. In both cases, the exchange field is written as $H_E = \lambda M / g^2 \mu_B^2$. The substitution of this expression in (8) gives

$$C_m = \left(H_0 + \frac{2\lambda M}{g^2 \mu_B^2} \right) \frac{d}{dT} M. \tag{9}$$

The 1/2 multiplier for the exchange term of the effective field in [18–20] should be taken into account in the transition from the Hamiltonian of the exchange interaction to the exchange field $H_{E1,2}$ from each exchange coupling

$$JS_1 S_2 \rightarrow g\mu_B (H_{E2} S_1 + H_{E1} S_2), \quad H_{E1} = H_{E2} = \frac{\lambda \langle S \rangle}{g\mu_B}, \tag{10}$$

which is necessary to avoid doubling the total exchange energy of the spins. Taking this into account leads to the appearance of this factor for a number of magnetic neighbors when the parameter λ and exchange integrals (4) are compared.

Fig. 6 shows the results of the comparison of the theoretical dependences of the magnetic contribution to the specific heat (9) with the experimental ones measured in the magnetic fields of 3 and 30 kOe. The figures show the results of the calculations using both the experimental dependences of magnetization (the red lines) and mean field approximation (the blue lines). In the Figure, the dotted and solid lines correspond to the use in (9) of either λ_C or λ_θ , respectively, as an exchange parameter. The comparison shows that the best agreement with the experiment is obtained in the strong magnetic field $H_0 \geq 30$ kOe when using both the experimental temperature dependence of magnetization and mean field coefficient λ_θ . Moreover, in this case a good description of the experimental data is obtained not only in the high-temperature region, but also in the vicinity of T_C . In the weak magnetic field $H = 3$ kOe, the agreement with the experimental data is unsatisfactory for any methods of calculation of the theoretical dependence: neither for the mean field approximation nor for the experimental dependence $M(T)$. Apparently, in the weak magnetic fields, in the expression for the effective field H_{eff} in (8) it is necessary to take into account the magnetic anisotropy comparable with H_0 .

Although the intrachain exchange in PbMnBO_4 exceeds the interchain one by an order of magnitude the complete interchain exchange $z'J'$ is comparable to $2J$ which leads to the temperature of ordering T_C which differs by a factor of 1.5 from the paramagnetic temperature θ . In addition, because of the relatively small difference between the intra- and interchain interactions in this crystal, the influence of the short-range magnetic order in the chains has its own peculiarities.

In classical quasi-one-dimensional magnetic materials in which the ratio of exchanges is $J'/J \sim 10^{-2} - 10^{-3}$, the wide maximum of the specific heat due to the formation of the short-range magnetic order in the chains is in the paramagnetic region far from the temperature of the magnetic phase transition and is clearly visible, as in the systems already mentioned [6–9]. In the other limiting case of three-dimensional magnetic materials with an isotropic exchange interaction, the magnetic contribution to the specific heat does not fall to zero at the temperature of the phase transition, and a “tail” is observed in a certain temperature interval (usually small) above T_C , due to the disruption of the 3D short-range magnetic order.

The PbMnBO_4 crystal refers to the intermediate case when there is only a 5-fold difference between the complete inter- $z'J'$ and intrachain $2J$ exchanges. Therefore, the wide peak of the magnetic heat capacity due to the short-range order in the chains is superimposed on this “tail” and is poorly discernable against its background.

To illustrate this effect, we subtracted the contribution of a one-dimensional Heisenberg chain for $S = 1/2$ [22] from the experimental temperature dependence of the magnetic heat capacity for $H = 0$. In Fig. 7 this contribution is constructed for $J = 20$ K and is shown by the dashed line. Subtraction is meaningful at temperatures $T > T_C$ since there is a long-range magnetic order in the ordered region. The result of the subtraction marked by the red solid line in the figure is the contribution of 3D correlations and above T_C its form corresponds to the

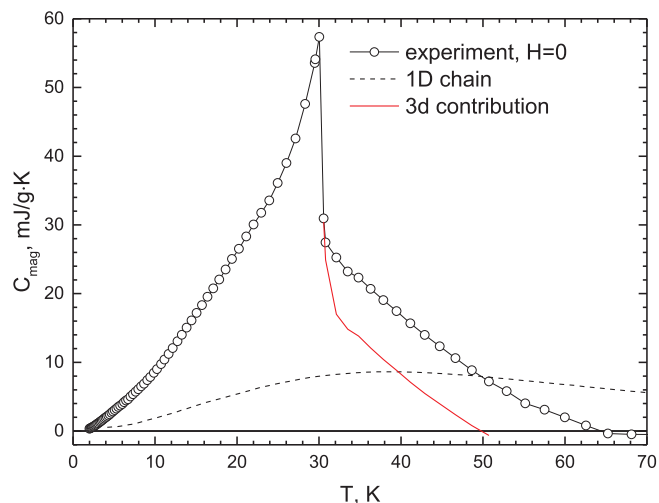


Fig. 7. Magnetic contribution to the specific heat for $H = 0$ as a sum of 1D and 3D contributions (see text).

usual behavior of the magnetic heat capacity for magnets with isotropic exchange.

Yet, such an illustration is only qualitative since here, the contribution of one-dimensional chains with $S = 1/2$ is used. However, it clearly demonstrates that in quasi-one-dimensional magnets with a relatively small difference in intra- and interchain interactions, the short-range order correlations in the chains do not lead to the formation of the well-discernible broad maximum of the specific heat in the paramagnetic region, but increase the temperature interval above T_C in which an appreciable magnetic contribution to the heat capacity is observed. This allows us to classify PbMnBO_4 as a chain magnet with an intermediate magnetic dimension between the quasi-one-dimensional and three-dimensional ones.

In this case, the correct application both of the quasi-one-dimensional approach and the mean field approximation allows one to correctly quantitatively describe the experimental data within the framework of the relatively simple Hamiltonian (1). Nevertheless, it should be noted that the Hamiltonian used is a very rough approximation. It does not take into account a number of features of the crystal structure, namely, the nonequivalence both of the magnetic chains and environments of the spins in the chains. These features lead to the rotation of the local anisotropy axes for Mn^{3+} ions both in the neighboring positions in the chain and in the neighboring chains. Moreover, the anisotropy of the paramagnetic Curie temperature indicates the presence of additional anisotropy mechanisms apart from the single-ion mechanism. Therefore, its description within the framework of Hamiltonian (1) should be considered only as the first approximation.

5. Conclusion

In the PbMnBO_4 single crystal, the temperature dependences of the magnetization and specific heat were measured in the external magnetic fields of 3, 10, and 30 kOe. The magnetic contribution to the specific heat measured in the zero magnetic field shows a sharp jump at the Curie temperature $T_C = 30.3$ K. When measured in the magnetic field, this jump is smeared into a smooth hump which broadens and shifts towards higher temperatures with the increasing magnetic field. For all the magnetic fields, the calculated transition entropy corresponds to the value $R \ln(2S + 1)$, confirming the purely magnetic character of the transition. It was found that even in the zero magnetic field, the temperature region in which the magnetic contribution to the heat capacity is maintained above T_C was significant, the magnetic contribution to the specific heat associated with the phase transition was observed up to ~ 65 K, and in the magnetic field of 30 kOe this contribution disappeared only at temperatures above 70 K.

The temperature and field dependences of the magnetization also indicate that in the strong magnetic field the magnetization decreases with the increasing temperature much slower than in classical three-dimensional ferromagnets, and the field dependences of the magnetization remain nonlinear up to the temperatures exceeding T_C more than twice. The experimental temperature dependences of the magnetization were compared with the theoretical ones calculated in the mean field approximation. The mean field coefficient λ used in this approximation was calculated either using the Curie temperature T_C or paramagnetic Curie temperature $\theta = 49$ K obtained from the high-temperature part of the magnetic susceptibility at $T > 175$ K. It is established that the

mean field approximation well describes the experimental data only in the high-temperature region and in relatively large magnetic fields with the exchange parameter λ_θ .

It is assumed that in PbMnBO_4 , the difference between T_C and θ and the wide temperature region above T_C in where the magnetic contribution to the specific heat is significant are due to the quasi-one-dimensional character of the magnetic structure of this ferromagnet. Using both the value of T_C from the Ginzburg-Landau field theory and the θ value, the intrachain exchange interaction parameter $2J \approx 40.4$ K and total interchain exchange interaction parameter $z'J' \approx 8.8$ K are determined, with $z' = 4$ being the number of the neighboring chains. The estimation shows that the Ginzburg-Landau field theory describing the quasi-one-dimensional behavior of PbMnBO_4 is well applicable in the temperature range from T_C to $T = S^2J \approx 80$ K. Above this temperature, the mean field approximation with the parameter λ_θ well describes the experimental temperature dependences of the magnetization in the strong magnetic field and the specific heat is determined by the lattice contribution.

The established difference in the parameters of the intra- and interchain exchange interactions is much smaller than in the traditional quasi-one-dimensional magnets. As a result, the short-range order correlations in the chains do not lead to the formation of the well-discernible broad maximum of the specific heat in the paramagnetic region but increase the temperature interval above T_C in which the magnetic contribution to the heat capacity is significant.

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