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Thermal properties of rare earth dodecaborides

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Abstract

We have measured heat capacity and thermal expansion of rare earth dodecaborides REB_{12} (RE = Y, Tb–Tm, Lu). YB_{12} and LuB_{12} are diamagnetics whereas the other dodecaborides are ordered antiferromagnetically. The amplitude of the heat capacity discontinuity at the Néel temperature and the shape of the heat capacity variation in the critical region for all these antiferromagnetics are characteristics for amplitude-modulated magnetic structures. In the ordered state TbB_{12} reveals two first-order phase transitions, most likely due to magnetic structure changes. The heat capacity of ErB_{12} just below the Néel point shows an anomaly of unclear origin. From the Schottky contribution to the heat capacity we have determined crystal field parameters. They are completely different than that is estimated from Point Charge Model.

Keywords: Rare earth dodecaborides; Heat capacity; Thermal expansion; Crystal electric field; Amplitude-modulated magnetic structure

1. Introduction

All rare earth dodecaborides, except ScB_{12}, crystallize in a face-centered cubic structure of the UB_{12}-type (sp.gr. $Fm3m$-O_h^5), which may be considered as a simple closest-packed lattice formed by rigid units-B_{12} cubooctahedrons with metal atoms located in cavities of this lattice. The crystal structure may also be deduced from the NaCl-type structure, where the Na-sites are occupied by RE-ions and the Cl-sites by B_{12} cubooctahedrons [1]. In this structure RE-ions form a *fcc* lattice.

Strong covalent bonds between boron atoms intra and inter B_{12} cages lead to very rigid boron sublattice. To compensate for the electron deficiency in the boron sublattice in order to reach the maximum stability two valence electrons per each rare earth atom are transferred to this sublattice. In three-valent rare earth dodecaborides the third valence electron enters the conduction band. So all dodecaborides studied in this work are good metals, in which conduction bands at the Fermi level have mainly a RE 5d-character with an admixture of B 2p [2,3]. As a consequence, an exchange interaction between spins of the 4f-shells is of the RKKY-type, which leads to the antiferromagnetic ordering [4–6] in TbB_{12}, DyB_{12}, HoB_{12}, ErB_{12}, and TmB_{12} with Néel temperatures equal to 22.05, 16.35, 7.38, 6.65 and 3.28 K, respectively. Diamagnetic LuB_{12} is a superconductor below 0.5 K [7].

On the ground of ^{169}Tm Mössbauer spectroscopy Gubbens et al. [8] have concluded that TmB_{12} is a crystal field (CF) singlet–triplet system, so the antiferromagnetic ordering is the result of induced magnetic moment into the ground state by closely spaced ($\Delta = 6 \pm 2$ K) Γ_4 triplet. The same CF ground state and overall CF splitting gives the Point Charge Model (PCM) ($W = -0.144$ K, $x = -0.97$) within the LLW parameterization scheme [9]. However, our studies of Schottky heat capacity yield $W = 1.09$ K and $x = -0.15$ and consequently the magnetic ground state $\Gamma_5^{(1)}$ [10]. The recently determined CF-parameters ($W = 1.19$ K and $x = -0.074$) by inelastic neutron scattering are in good agreement with them. Therefore one may reject the

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supposition on induced type of antiferromagnetism in TmB_{12} [10].

Among the dodecaborides a magnetic structure has been determined only for TmB_{12} [10] and TbB_{12} [11]. The magnetic structure of both compounds below the Néel temperature is a sinusoidally modulated one. The propagation vector is equal to $\mathbf{k} = (1/2 \pm \tau,\ 1/2 \pm \tau,\ 1/2 \pm \tau)$. The structure can be described as a modulation of magnetic moments (stacked parallel in (111) sheets but with antiparallel orientation of the neighboring sheets) which propagates along three crystallographic directions.

Except TmB_{12} [12] there is no direct information from inelastic neutron scattering on CEF-splitting in rare earth dodecaborides. Without this knowledge it is impossible to analyze quantitatively their physical properties. On the other hand low-temperature thermal properties such as a heat capacity as well as thermal expansion may serve as probes for crystal field determination. So we have undertaken this work, first of all, for the determination of crystal field parameters. However, this study may give also important information on magnetic ordering in rare earth dodecaborides. Blanco et al. in a series of papers [13–16] have shown that within the Periodic Field Model (PFM) the heat capacity behavior in the critical region of an antiferromagnetic transition is distinctly different for systems with amplitude-modulated (AM) magnetic structure in comparison to systems with equal moment (EM) magnetic structures.

2. Experimental details

We used high-purity TbB_{12} sintered samples and DyB_{12}, HoB_{12}, ErB_{12}, TmB_{12}, LuB_{12} single crystals grown by the crucible free inductive zone melting process in an atmosphere of pure argon. The details of sample preparation are described in Ref. [17].

The heat capacity (C_p) was measured by a pulse quasi-adiabatic method between 2.6 and 70 K using a calorimeter the details of which are described in Ref. [18]. Mass of the studied samples was no more than 750 mg. The calorimeter measures the heat capacity in comparison to the standard heat capacity data of copper with an error $\pm 1\%$ in the whole temperature range. The heat capacity of ErB_{12}, TmB_{12} and LuB_{12} in the temperature range 0.5–2.6 K was measured by using a similar method in Osaka University.

The temperature dependence of a relative length change ($\Delta L/L$) was measured in the range 5–200 K with a resolution of 1×10^{-9} by a three-terminal capacitance method. The used capacitance cell was similar to that described by Brandli and Griessen [19]. The thermal expansion of the investigated sample $\Delta L/L$ was approximated by cubic splines after subtraction of the cell contribution. Then the linear thermal expansion coefficient $\alpha = (\partial \ln Z/\partial T)_P$ was easily determined. The relative experimental error $\Delta L/L$ by standard copper is no more than $\pm 1\%$ below 20 K and decreases down to 0.3% near 200 K. The samples were cylinders or parallelepipeds ($L = 4$–6 mm) with plane-parallel basis (precision ± 1 μ).

3. Results and discussion

3.1. Heat capacity

Temperature dependencies of the heat capacity of all studied dodecaborides are shown in Fig. 1 in log-log scale. The heat capacity of TbB_{12} and ErB_{12} in the ordered range is shown in Fig. 2. The observed behavior of the heat capacity in the critical region of all antiferromagnetic dodecaborides is intrinsic for amplitude-modulated magnetic systems. Namely, (1) the heat capacity maximum (T_M) lies below the Néel temperature (T_N) determined from the magnetic susceptibility (Table 1) and (2). As we show later in this paper the heat capacity at T_M is equal to that expected for amplitude-modulated magnetic systems. In the ordered state TbB_{12} reveals two first-order transitions due to magnetic structure changes [11]. Just below the Néel temperature ErB_{12} shows a small anomaly of unclear origin.

Our recent neutron diffraction studies have shown that TmB_{12} [10] and TbB_{12} [11] indeed order within sinusoidally modulated magnetic structures. Magnetic structure of terbium dodecaboride remains modulated down to 4 K the lowest temperature, at which the neutron scattering experiment has been performed.

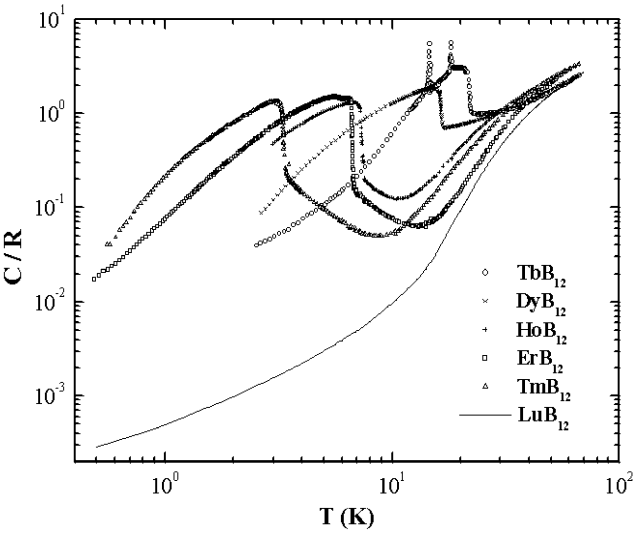

Fig. 1. Temperature dependence of the heat capacity of rare earth dodecaborides.

It is well known that only if the crystal field ground state is a nonmagnetic state or a many-body singlet (attributed to Kondo effects) the modulated magnetic structure can remain stable down to 0 K. In the opposite case, due to entropy effects associated with the modulation of the magnetic moment amplitude, the magnetic system should either (1) suddenly jump through a first-order transition to an equal magnetic moment structure or (2) evolve to an antiphase structure at 0 K through a progressive squaring up of the modulation. This latter process is accompanied by growing of higher order harmonics of the propagation vector.

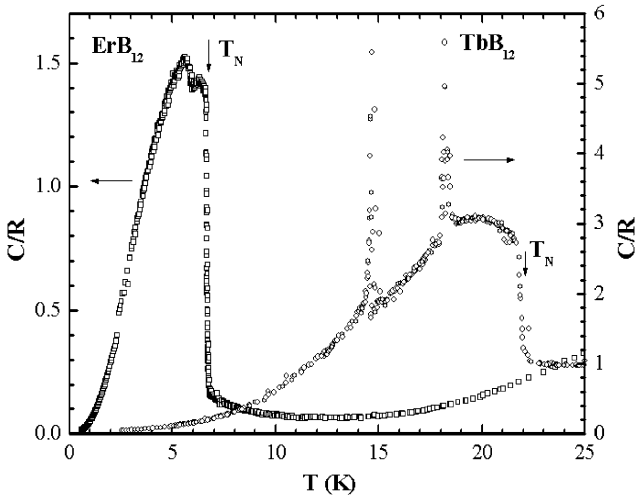

Fig. 2. Temperature dependencies of the TbB_{12} and ErB_{12} heat capacities in expanded low-temperature range.

Table 1
The temperatures of the REB_{12} phase transitions

REB_{12}	T_M (K)	$T_N(\chi)$ (K) [6]	Remarks
TbB_{12}	19.87	22.05	Two phase transitions of the first-order at 18.19 and 14.61 K
DyB_{12}	15.20	16.35	
HoB_{12}	6.61	7.38	
ErB_{12}	6.38	6.65	Anomaly at 5.59 K
TmB_{12}	3.08	3.28	

We emphasize, in order to understand the observed behavior as well as other physical properties of the dodecaborides we have to know their crystal field. Because of the lack of this information from direct experiment, i.e. inelastic neutron scattering, we tried to determine CF-parameters from Schottky contribution to entropy (S) and heat capacity (C_{Sch}):

$$S = -\left(\frac{\partial F}{\partial T}\right) = R(\ln Z + \langle E\rangle/k_B T), \quad (1)$$

$$C_{Sch} = -T\left(\frac{\partial^2 F}{\partial T^2}\right) = \frac{R}{k_B^2 T^2}(\langle E^2\rangle - \langle E\rangle^2), \quad (2)$$

where $\langle X\rangle = \frac{\sum_{i=1}^{n} f_i X_i \exp(-E_i/k_B T)}{\sum_{i=1}^{n} f_i \exp(-E_i/k_B T)}$—statistical average; $Z = \sum_{i=1}^{n} f_i \exp(-E_i/k_B T)$—partition function; F—Helmholtz free energy; E_i—energy of CEF level with degeneracy f_i.

In order to extract a magnetic contribution C_m from the full heat capacity C_p of the magnetic dodecaborides we use the heat capacity of nonmagnetic reference compound LuB_{12} as a sum of electronic and lattice contribution to the total heat capacity. The heat capacity of LuB_{12} is characterized by Sommerfeld coefficient $\gamma = 4.14 \pm 0.02$ mJ/(mol K^2) and Debye temperature $\Theta_D = 1110 \pm 80$ K. In further analysis we neglect the electronic heat capacity because it yields the main contribution to C_p in the low temperature range (up to 10 K), where the magnetic part is several orders of magnitude greater than C_p of LuB_{12}.

Next, because of a difference in molar masses of the studied compounds we should appropriately renormalize the heat capacity of LuB_{12}

$$C_{ph}(REB_{12}) = k\, C_p(LuB_{12}). \quad (3)$$

Table 2
The schemes of the splitting of the RE-ions ground multiplet by REB_{12} crystal electric field

TbB_{12}				DyB_{12}				HoB_{12}		ErB_{12}		TmB_{12}	
I		II		I		II		I		I		I	
$W = -0.38$ K, $x = 0.44$		$W = -0.29$ K, $x = -0.017$		$W = -0.18$ K, $x = 0.66$		$W = 3.92$ K, $x = -0.47$		$W = 0.73$ K, $x = 0.42$		$W = -0.85$ K, $x = 0.37$		$W = 1.25$ K, $x = -0.12$	
Γ_i	E_i (K)	Γ_i	E_i (K)	Γ_i	E_i (K)	Γ_i	E_i (K)	Γ_i	E_i (K)	Γ_i	E_i (K)	Γ_i	E_i (K)
Γ_2	0	Γ_2	0	$\Gamma_8^{(3)}$	0	Γ_7	0	$\Gamma_5^{(1)}$	0	$\Gamma_8^{(3)}$	0	$\Gamma_5^{(1)}$	0
$\Gamma_5^{(2)}$	20.6	$\Gamma_5^{(2)}$	24.1	Γ_6	7.1	Γ_6	24.7	$\Gamma_3^{(1)}$	63.3	Γ_6	115.0	Γ_3	78.7
Γ_3	39.7	Γ_1	45.2	$\Gamma_8^{(2)}$	54.3	$\Gamma_8^{(1)}$	75.3	$\Gamma_4^{(1)}$	135.0	$\Gamma_8^{(2)}$	217.0	Γ_4	170.0
Γ_4	62.6	Γ_4	47.7	Γ_7	61.4	$\Gamma_8^{(2)}$	1182	$\Gamma_5^{(2)}$	149.0	$\Gamma_8^{(1)}$	288.0	Γ_1	183.0
Γ_1	65.9	Γ_3	64.9	$\Gamma_8^{(1)}$	68.2	$\Gamma_8^{(3)}$	1227	Γ_1	284.0	Γ_7	360.0	$\Gamma_5^{(2)}$	243.0
$\Gamma_5^{(1)}$	78.1	$\Gamma_5^{(1)}$	88.6					$\Gamma_4^{(2)}$	393.0			Γ_2	329.0
								$\Gamma_3^{(2)}$	416.0				

We accept the most frequently used expression for the renormalization factor k:

$$k = \frac{C_{\mathrm{ph}}(RE\mathrm{B}_{12})}{C_{\mathrm{ph}}(\mathrm{LuB}_{12})} = \left(\frac{\Theta_{\mathrm{D}}(\mathrm{LuB}_{12})}{\Theta_{\mathrm{D}}(RE\mathrm{B}_{12})}\right)^3 = \left(\frac{M(RE\mathrm{B}_{12})}{M(\mathrm{LuB}_{12})}\right)^{3/2}, \quad (4)$$

where Θ_{D}—Debye temperature, M—molar mass.

The calculated k values for TbB_{12}, DyB_{12}, HoB_{12}, ErB_{12} and TmB_{12} are equal to 0.921, 0.938, 0.950, 0.962 and 0.970, respectively. Now we can analyze CF contribution to the heat capacity of dodecaborides. In Fig. 3 this analysis is shown for TbB_{12}. Best agreement between the experimental Schottky contribution and calculated one we obtained for two sets of CF parameters: (1) $W = -0.38$ K, $x = 0.44$ and (2) $W = -0.29$ K, $x = -0.017$. Both sets give the singlet Γ_2 as the ground state and the triplet $\Gamma_5^{(2)}$—as the first excited level (Table 2). For both CF parameter sets the overall CF-splitting is rather small and does not exceed 90 K. However, the magnetic entropy calculated for these parameters exceeds clearly the experimentally determined one S_{m} (insert in Fig. 3).

Similar situation as in the case of TbB_{12}, we found for DyB_{12} (Fig. 4). Here also for two sets of CF-parameters—(1) $W = -0.18$ K, $x = 0.66$ and (2) $W = 3.92$ K, $x = -0.47$—the calculated Schottky heat capacity (C_{Sch}) agrees quite well with the experimental one but calculated entropy disagrees with the experimentally determined one (insert in Fig. 4). At the Néel temperature the experimental S_{m} reaches $R \ln 4$. Thus the ground state should be either a quartet, or a pseudo-quartet.

The failure in univocal determination of CF-parameters for these two compounds is, first of all, due to the restricted range of temperatures, where measurements have been done, and with their high temperatures of the magnetic ordering. Therefore, we plan to measure terbium and dysprosium dodecaborides to higher temperatures as well as the heat capacity of their solid solutions with lutetium dodecaboride.

For holmium, erbium and thulium dodecaborides the analysis gives the excellent agreement between the experimental and calculated C_{Sch} as well as between the experimental entropy and the calculated one. For illustration the results of such analysis for TmB_{12} are shown in Fig. 5. For HoB_{12} we obtained $W = 0.73$ K

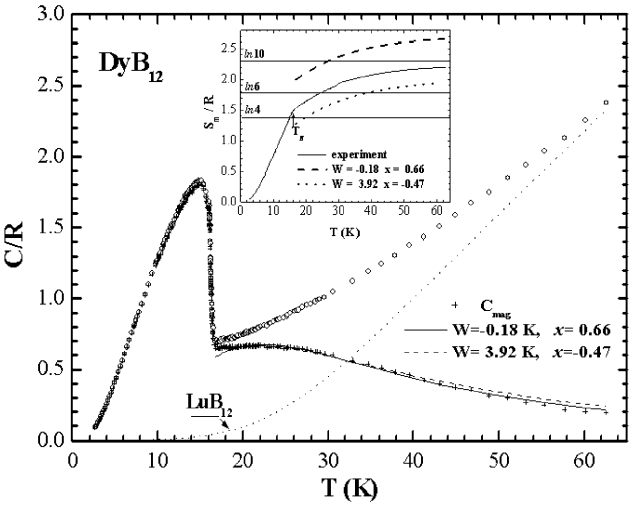

Fig. 4. Temperature dependencies of the full heat capacity C_p, its magnetic part C_{m} and fitting Schottky heat capacities C_{Sch} for different W and x for DyB_{12}. Insert: temperature dependencies of the DyB_{12} experimental and calculated entropies.

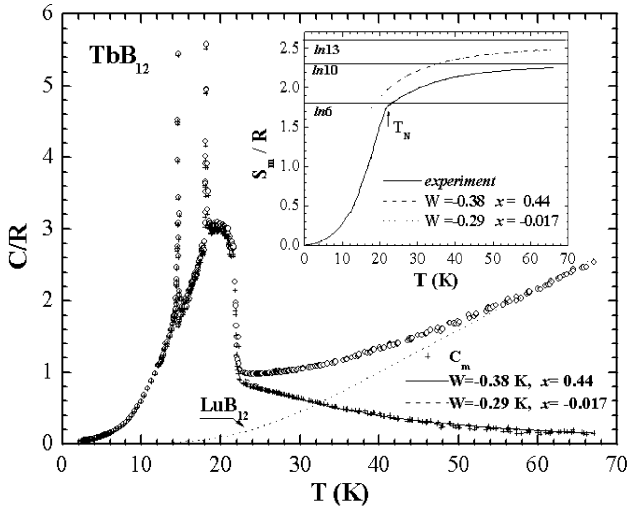

Fig. 3. Temperature dependencies of the full heat capacity C_p, its magnetic part C_{m} and fitting Schottky heat capacities C_{Sch} for different W and x for TbB_{12}. Insert: temperature dependencies of the TbB_{12} experimental and calculated entropies.

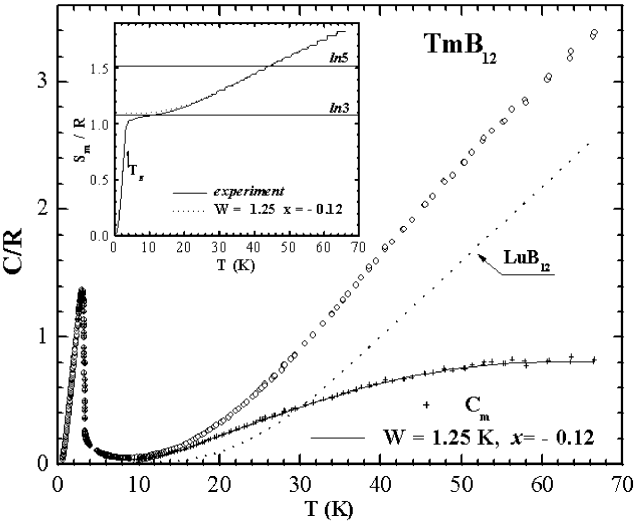

Fig. 5. Temperature dependencies of the full heat capacity C_p, its magnetic part C_m and fitting Schottky heat capacity C_{Sch} of TmB_{12}. Insert: temperature dependencies of experimental and calculated entropies.

and $x = 0.42$, which give the triplet $\Gamma_5^{(1)}$ as the ground state, the doublet $\Gamma_3^{(1)}$ at 63 K as the first excited level and overall CF-splitting about 420 K; for ErB_{12}—$W = -0.85$ K and $x = 0.37$ and as a consequence the quartet $\Gamma_8^{(3)}$ as the ground state, the doublet Γ_6 at 115 K as the first excited level and the overall splitting about 360 K, and for TmB_{12}—$W = 1.25$ K and $x = -0.12$, which give the triplet $\Gamma_5^{(1)}$ as the ground state, the doublet Γ_3 at about 80 K and full splitting about 330 K.

For the last three compounds CF parameters $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$ are, for sure, negative. The sixth-order term is nearly constant $[-(22\pm4)$ K]. The fourth-order term changes strongly and nearly linearly with the number of the $4f$-electrons of REE. Assuming that this behavior holds also for TbB_{12} and DyB_{12} we have estimated for them new CF parameters. However, they also do not give an agreement with the experiment.

We may compare these CF-parameters with those determined from the Point Charge Model (PCM) [20]. Taking into account five nearest coordination spheres and assuming a charge $+3|e|$ of *RE*-ions and $-2|e|$ of B_{12} complexes we obtain the CF-parameters, which are completely different in comparison with the parameters determined from analysis of Schottky heat capacity. First, both terms—$A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$—are positive and smoothly decreasing with increase of *RE* atomic number, second, the PCM gives a prevailing contribution from fourth-order term and third—overall CF-splitting does not exceed 35 K.

The PCM is a very crude approximation and the model usually does not work in metallic RE compounds. It is well known that important contribution to the CF arises from interactions with the conduction band: the classical Coulomb's contribution and the exchange contribution. In cubic systems, conduction electrons which have a d-like character can give a contribution only to the fourth-order CF parameters and those, which have an f-like character, can give a contribution to the fourth- and sixth-order CF parameters. In a cubic crystal the d-band is split into e_g and t_{2g} sub-bands. The Coulomb interaction depends on the e_g and t_{2g} characters of the conduction electrons and these two types of contribution to fourth-order CF parameters have opposite signs. The exchange contribution to the CF parameters keeps the same sign with the e_g and t_{2g} electrons. The band structure calculations [2,3] indicate that the conduction bands in the dodecaborides have mainly $5d$-character. One may therefore think that conduction band electrons give a prevailing contribution to crystal field of *RE* dodecaborides.

According to inelastic neutron scattering experiments on $Tm^{11}B_{12}$ the distances between the ground state and the excited levels are equal to about 83, 160 and 223 K [21] that agrees with our results on CF determination from Schottky heat capacity (Table 2). Also calculated ordered magnetic moment of Tm^{3+} ion using CF parameters is in agreement with the experiment [8]. This confirms correctness of the used procedure of CF determination for all REB_{12}.

Now we consider the critical region of the antiferromagnetic ordering. We have shown earlier that temperature of the heat capacity maximum T_M lies below the Néel temperature (Table 1). The second important feature is a magnitude of the heat capacity discontinuity ΔC at the antiferromagnetic transition. In the framework of the PFM, the ΔC_{AM} of a system which orders within amplitude-modulated magnetic structure, is equal to 2/3 of the ΔC_{EM} expected for a system, which orders within an equal magnetic moment structure.

In the absence of contribution connected with crystal field ΔC_{AM} is described by [14]

$$\Delta C_{AM}/R = \frac{10}{3}\frac{J(J+1)}{2J^2+2J+1}, \tag{5}$$

where J is an angular moment.

The first excited CF level in HoB_{12}, ErB_{12} and TmB_{12} is located too high that practically only the ground state is thermally populated at temperatures near the antiferromagnetic transition. In this case HoB_{12} and TmB_{12} may be characterized by effective spin $S_{eff} = 1$ and $\Delta C_{AM} = 11.09$ J/mol K, ErB_{12}—by $S_{eff} = 3/2$ and $\Delta C_{AM} = 12.23$ J/mol K; the experimental ΔC_{AM} values are equal to 10.75, 11.36 and 12.14 J/mol K respectively (Table 3). The agreement is quite good.

In the case of TbB_{12} and DyB_{12} the Schottky heat capacity at their Néel points is large. This means that excited CF levels are at these temperatures considerably populated. Then for a determination of the ΔC_{AM}, we have to use the more complicated formula given in Ref. [16] which takes into account a full CF splitting. Because of the lack of well-determined CF parameters we have

Table 3
The most important HoB_{12}, ErB_{12}, TmB_{12} characteristics defined from their heat capacity

REB_{12}	W (K)	x	The ground state	$A_4\langle r^4\rangle$ (K)	$A_6\langle r^6\rangle$ (K)	T_M (K)	ΔC_{AM} (J/mol K)	
							Experiment	Theory
HoB_{12}	0.73	0.42	$\Gamma_5^{(1)}$	−153.45	−23.61	6.61	10.79	11.08
ErB_{12}	−0.85	0.37	$\Gamma_8^{(3)}$	−118.06	−18.67	6.35	12.14	12.23
TmB_{12}	1.25	−0.12	$\Gamma_5^{(1)}$	−15.51	−25.79	3.06	11.36	11.08

not performed the analysis of the ΔC_{AM} in these two compounds.

Nevertheless, it seems nearly sure that all $4f$-open shell dodecaborides order within amplitude-modulated magnetic structures. The AM structures in TbB_{12} [11] and TmB_{12} [10] have been confirmed by elastic neutron scattering. In the case of the terbium compound the modulation persists well below the lower first-order transition. In this temperature range two magnetic phases, which are described by the same type of propagation vector $\mathbf{k} = (1/2 \pm \tau,\ 1/2 \pm \tau,\ 1/2 \pm \tau)$ but with somewhat different values of τ ($\tau_1 = 0.022$ and $\tau_2 = 0.059$), coexist. The phase transition at 14.6 K is due to the disappearance of additional magnetic phase and the simultaneous rearrangement of the τ-components of the $\mathbf{k}$ vector describing the sine-wave modulation of magnetic moments. In spite of careful examination of neutron data no difference has been found in the temperature range at which the second ($T_2 = 18.2$ K) first-order transition in heat capacity is observed.

Most likely the terbium compound conserves the sine-wave ordering down to 0 K. Therefore, the CF ground state has to be a nonmagnetic singlet. In fact, the Γ_2 singlet ground state we have obtained from an analysis of the Schottky heat capacity. In the other dodecaborides the CF ground state is the magnetic one. Therefore, their AM structures have to be an antiphase at 0 K. Because first-order transition down to temperatures well below their Néel points is not seen; the antiphase structures are reached most likely through the progressive squaring.

Now we analyze the magnetic heat capacity of TbB_{12} DyB_{12}, ErB_{12} and TmB_{12} well below their Néel temperatures. It contains a nuclear, spin-wave and linear (γ^*T) terms

$$C = \alpha/T^2 + \gamma^* T + \delta T^3 \exp(-\Delta/T), \tag{6}$$

where Δ is an energy gap in a spin-wave spectrum.

Results of this multi-component fitting are shown in Table 4. The nuclear contribution we have found only in TbB_{12}; according to it the hyperfine magnetic field H_{hf} on Tb^{3+} nucleus is equal to 2.502 MG. An energy gap in spin-wave spectrum for TbB_{12}, DyB_{12} and TmB_{12} is equal to zero, and one is very small ($\Delta \approx 0.5$ K) for ErB_{12}. The energy gap is $\Delta = (2H_E H_A + H_A^2)^{1/2}$, where H_E and H_A are exchange and magnetocrystalline anisotropy fields, respectively. Therefore, the gapless spin-wave spectrum means that the magnetocrystalline anisotropy is small.

For all compounds the large linear contribution is obtained. The estimated linear coefficients γ^* are much higher (Table 4) than the electron heat capacity coefficient for the diamagnetic LuB_{12}—$\gamma = 4.14$ mJ/(mol K^2). XPS studies of TmB_{12} [22] have shown that the $4f$-shell is well localized and lies 5 eV below the Fermi energy. We may, therefore, expect in this compound as well as in other dodecaborides, a negligible hybridization between $4f$ and conduction electron states. In consequence there is no enhancement of the electronic heat capacity coefficient γ. Similar phenomenon, i.e. an appearance of the large linear term in the heat capacity of UP_xSe_{1-x} has been qualitatively explained as a result of the RKKY-type interaction between disoriented magnetic moments [Ref. [23] and references therein].

3.2. Thermal expansion

Thermal expansion of magnetic dodecaborides, HoB_{12}, ErB_{12}, and TmB_{12}, has been measured on single crystals along the $\langle 001 \rangle$-axis. The thermal expansion of diamagnetic LuB_{12} has been analyzed in detail [24], and here we use it as a nonmagnetic reference for the magnetic REB_{12}.

Since Helmholtz free energy F of a system is an additive function of free energies of phonons F_{ph}, conduction electrons F_e and $4f$-electrons F_m subsystems, the thermal expansion coefficient is

$$\beta = (\partial \ln V/\partial T)_P = -(\partial^2 F/\partial V \partial T)/B_T, \tag{7}$$

where B_T is the isothermal bulk modulus, is also an additive function of thermal expansion coefficients of corresponding subsystems

$$\beta = \beta_{ph} + \beta_e + \beta_m. \tag{8}$$

The thermal expansion coefficient and heat capacity at constant volume C_V are related by Grüneisen expression

$$\beta = \gamma_{Gr} C_V / B_T V, \tag{9}$$

where C_V is the heat capacity at constant volume; γ_{Gr} is the generalized Grüneisen function. A sign of the β is given by a sign of γ_{Gr}.

Table 4
The characteristic values obtained from REB_{12} heat capacity analyses in ordered range ($T \leqslant T_N/4$)

REB_{12}	α (mJ K/mol)	γ^* (mJ/mol K^2)	δ (mJ/mol K^4)	Δ (K)	H_{hf} (MG)
TbB_{12}	96	104.4	2.92	0	2.502
DyB_{12}	0	73.2	29.38	0	—
ErB_{12}	0	130.9	465.0	0.51	—
TmB_{12}	0	54.3	1788.0	0	—

The expressions for β_{ph}, β_e, β_m are similar to Eq. (9) but with respective Grüneisen functions ($\gamma_{ph}, \gamma_e, \gamma_m$) and heat capacity components (C_{ph}, C_e, C_m). The generalized Grüneisen function γ_{Gr} is an average of the individual γ_r weighted by the respective heat capacities C_r:

$$\gamma_{Gr} = \sum_r \gamma_r C_r \Big/ \sum_r C_r. \quad (10)$$

For cubic compounds as in our case β is equal to the triple coefficient of linear thermal expansion α.

The linear expansion coefficient α of diamagnetic LuB_{12} is a sum only of two components—phonon α_{ph} and electron α_e, and the first one dominates in the studied temperature range. Below 120 K the thermal expansion of this compound has two negative ranges. This behavior is most likely connected with peculiarities of the phonon spectra of the rare earth dodecaborides (Fig. 6) [24].

Temperature dependencies of the linear thermal expansion coefficient α of HoB_{12}, ErB_{12} and TmB_{12} are shown in Fig. 6. In the ErB_{12} ordered state an extra anomaly of α occurs at temperature, at which the heat capacity reveals a similar anomaly.

Magnetic contribution to the thermal expansion α_m we have separated using the thermal expansion of LuB_{12} as a nonmagnetic reference with the same factor k as for heat capacity (Eq. (3)). Determined in such a way the temperature variation of the TmB_{12} α_m is shown in Fig. 7. In the paramagnetic state a magnetic contribution to the thermal expansion is determined by CF [25]:

$$\alpha_{CF} = -\frac{1}{3B_T}\frac{\partial^2 F}{\partial V \partial T} = \frac{1}{3B_T V k_B T^2} \times (\langle E^2\gamma\rangle - \langle E\gamma\rangle\langle E\rangle), \quad (11)$$

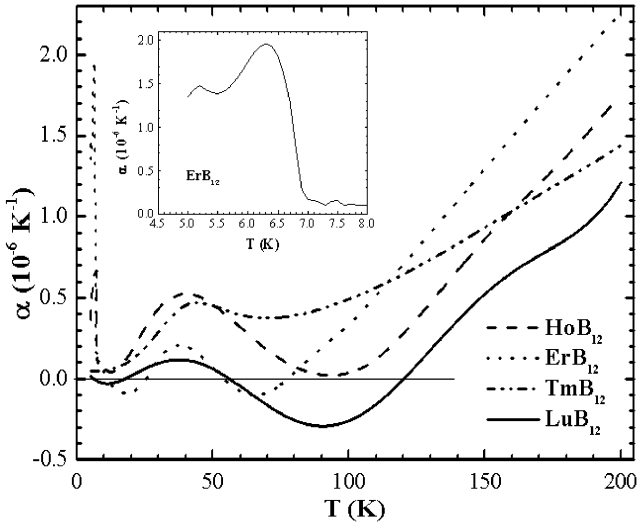

Fig. 6. Temperature dependencies of the thermal expansion coefficients α for REB_{12}. Insert: α vs. T for ErB_{12} in expanded temperature scale.

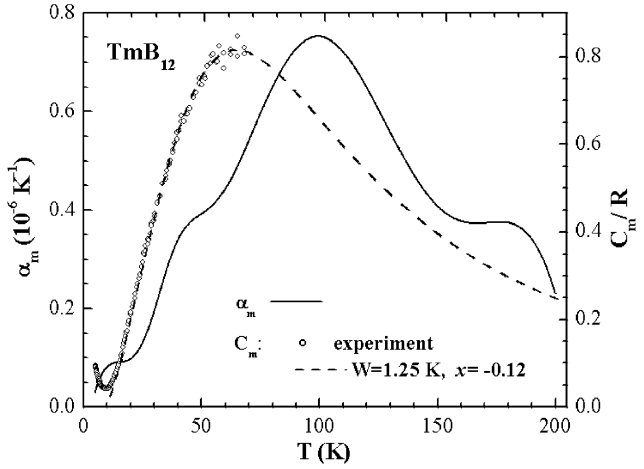

Fig. 7. Temperature dependencies of the magnetic thermal expansion α_m and magnetic heat capacity C_m of TmB_{12}.

where $\gamma \equiv \gamma_{CF}^i = -\partial \ln E_i / \partial \ln V$ is the CF Grüneisen parameter of the CF energy level E_i with respect to the ground state level.

From comparison of Eqs. (2) and (11) for C_{Sch} and α_{CF} respectively it is seen that they are proportional when the Grüneisen parameters γ_{CF}^i for all thermally populated energy levels are the same. For two-level system this requirement is fulfilled automatically.

In Fig. 7 the temperature dependence of the TmB_{12} magnetic heat capacities—experimental (C_m) and calculated with crystal field parameters (C_{Sch})—are also presented. In paramagnetic region only for HoB_{12} the proportionality between α_m and C_{Sch} is observed from 12 up to 100 K, for ErB_{12} and TmB_{12} $\alpha_m \propto C_{Sch}$ in a very narrow range—20–30 and 20–40 K, respectively. These three magnetics are multilevel systems (Table 2), so the proportionality between α_m and C_{Sch} is possible only at the above-mentioned conditions: when it may neglect by contribution of second and consequent excited levels or the partial parameters γ_{CF}^i for all levels are the same.

We have calculated contributions from the individual CF excited levels to Schottky heat capacity to evaluate the temperatures, at which the contribution from each CF level in C_{Sch} begins to manifest. For illustration results of calculations are shown for TmB_{12} (Fig. 8). It appears that for REB_{12} the region of the pseudo two-level system is very narrow and the contribution of the second excited level is necessary to take into account from 15 K for HoB_{12}, 20 K for ErB_{12} and TmB_{12}.

4. Conclusion

1. On the basis of Schottky heat capacity analysis the CF parameters and realistic schemes of CEF levels splitting for RE-ions in HoB_{12}, ErB_{12} and TmB_{12} are established. The RE^{3+} ground states in these

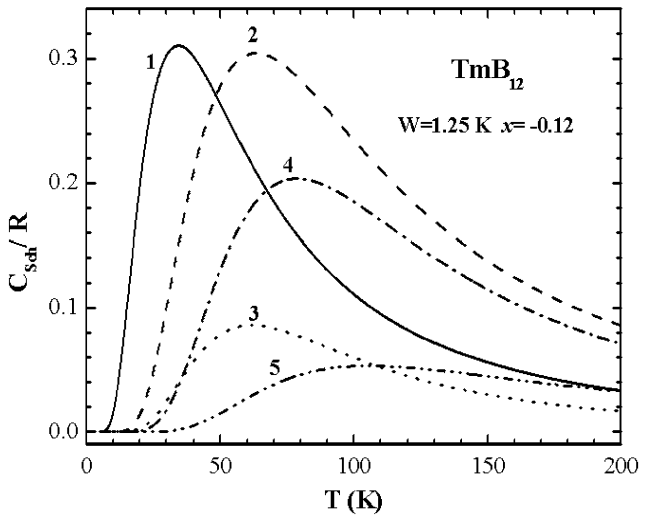

Fig. 8. Temperature dependencies of the individual contributions of CEF excited levels to TmB_{12} Schottky heat capacity. Numbers at curves corresponds to transitions from the ground level to 1st, 2nd, etc. excited levels.

compounds ($\Gamma_5^{(1)}$, $\Gamma_8^{(3)}$ and $\Gamma_5^{(1)}$ correspondingly) are magnetic and responsible for their magnetic ordering. Apart from the magnetic moment the $\Gamma_5^{(1)}$ and $\Gamma_8^{(3)}$ states have also intrinsic quadrupolar moments, which should manifest in magnetic as well as in transport properties of these compounds.

2. CF parameters for TbB_{12} and DyB_{12} should be taken with caution.

3. Heat capacity behavior in the critical region of REB_{12} is characteristic for amplitude-modulated magnetic structure. The first excited CF state of HoB_{12}, ErB_{12} and TmB_{12} is located so highly that practically only the ground state is thermally populated in the vicinity of the AF transition. The "jump" of the heat capacity ΔC_{AM} at the AF transition, which has been calculated for HoB_{12}, ErB_{12} and TmB_{12} in the framework of Periodic Field Model, agrees very well with ΔC_{AM} determined experimentally. This fact additionally confirms correctness of the determined CF parameters for these compounds and simultaneously the adequacy of used Periodic Field Model. For TmB_{12} and TbB_{12} the hypothesis has been confirmed experimentally by elastic neutron study [10,11].

4. Most likely, the amplitude-modulated magnetic structures of DyB_{12}, HoB_{12}, ErB_{12} and TmB_{12} reach antiphase ones at 0 K through squaring up of the modulation.

5. The small anomaly in the heat capacity of ErB_{12} below T_N most likely is connected with reorientation within the AM structure. Similar effect was observed in other erbium compound—$ErGa_3$ [26].

6. The magnetic heat capacity analysis for TbB_{12}, DyB_{12}, ErB_{12} and TmB_{12} at temperatures $T \leqslant T_N/4$ revealed suddenly large linear contribution by temperature to C_m, the nature of which is rather obscure.

7. The HoB_{12}, ErB_{12} and TmB_{12} magnetic thermal expansion coefficients α_m demonstrate the complex behavior stipulated in paramagnetic region by CF effect. The proportionality between α_m and C_{Sch} is observed in limited temperature range that is determined by the very narrow region of existence of a pseudo-two-level system.

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