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LOW-TEMPERATURE HEAT CAPACITY OF DYSPROSIUM DIBORIDE

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Heat capacity $C_p(T)$ of dysprosium diboride is experimentally investigated at the temperatures of 5–300 K. On the dependence $C_p(T)$ smooth anomaly at the temperatures of 15–20 K and sharp anomalies at T_{m1}=47.8 K and T_{m2}=178.8 K are revealed. Anomaly at T_{m1} is caused, obviously, by ferromagnetic phase transition in DyB_2. The lattice contribution to DyB_2 heat capacity is determined by comparison with heat capacity of non-magnetic YB_2. The estimation of Schottky contribution to DyB_2 heat capacity is made, the scheme of splitting of the ground state of Dy^{3+} ion is offered.

Keywords: *diborides, heat capacity, low temperatures, magnetic phase transitions*

Introduction

The diborides of rare-earth elements RB_2 represent the group of borides which is practically not investigated until recently. It is caused obviously by the difficulty of making single-phase samples of these compounds. It is known that diborides of neodymium, samarium, gadolinium are formed only at high pressures. The diborides of the heavier RE metals may be received by direct synthesis from elements at high temperatures [1].

The rare-earth diborides are crystallized in hexagonal structure D^1_{6h} – P6 / mmm, there is one atom of metal and two atoms of boron per elementary cell (Fig. 1). At low temperatures the majority of rare-earth diborides are ferromagnetics. Curie temperatures T_C of rare-earth diborides are in the interval 5–150 K ($T_{C_{TbB_2}}$ =151 K, $T_{C_{DyB_2}}$ =55 K, $T_{C_{HoB_2}}$ =15 K, $T_{C_{ErB_2}}$ =16 K) [1, 2].

The purpose of the present work is the experimental research of heat capacity of dysprosium diboride at the temperatures of 5–300 K.

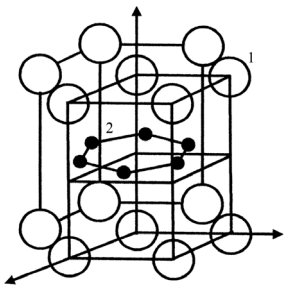

Fig. 1 Crystal structure of DyB_2: 1 – Dy atoms; 2 – B atoms

Experimental

Sample

DyB_2 sample was synthesized from elements through intermediate hydride phase. Synthesis was carried out according to reactions

$$2R+3H_2 \rightarrow 2RH_3$$

$$RH_3+4B \rightarrow RB_2+B_2H_6$$

$$RH_3+RB_4 \rightarrow RB_2+B_2H_6$$

The received hydride was mixed up stoichiometrically with amorphous boron, the mix was frayed in jasper mortar, was pressed at pressure 8t. The received tablet was placed in a molybdenum crucible and burnt in an atmosphere of argon in two stages.

The first stage of burn lasted 6 h at temperature T=1200°C. The X-ray spectrum of the created sample contained mainly diffraction maxima of RB_4 and also RB_2.

At the 2nd stage the hydride RH_3 was added to the frayed sample according the scheme: $RH_3+RB_4 \rightarrow RB_2+B_2H_6$. The received mixture was frayed in a jasper mortar and again pressed under pressure 8t, then was burnt at temperature T=1200°C during 3 h. The X-ray powder diffraction pattern of the synthesized sample is given on Fig. 2. The positions and amplitudes of reflexes of DyB_2 phase on the diffractogram are close to ASTM data. There is an insignificant quantity (less than 3%) of tetraboride phases and also the oxide of dysprosium in the sample. The lattice parameters are calculated from the X-ray data are: a=0.32915 nm, c=0.385182 nm (on the data [2] a=0.328 nm, c=0.3845 nm).

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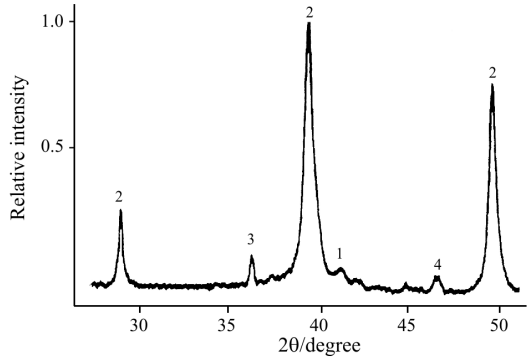

Fig. 2 X-ray powder diffraction pattern of DyB_2: 1 – Dy, 2 – DyB_2, 3 – Dy_2B_3, 4 – DyB_4

The heat capacity at constant pressure of DyB_2 was measured in an adiabatic calorimeter with puls heating [3]. At the temperatures of 5–15 K the temperature was measured with a germanium resistance thermometer with accuracy of 0.05 K. At higher temperatures the platinum thermometer was used whose accuracy of measurement was 0.01 K. The relative error of measurement in the temperature interval of 5–20 K equals 0.6%, at higher temperatures – 0.3%. Calibration of the calorimeter was done on a sample of electrolytic copper which was burnt in vacuum.

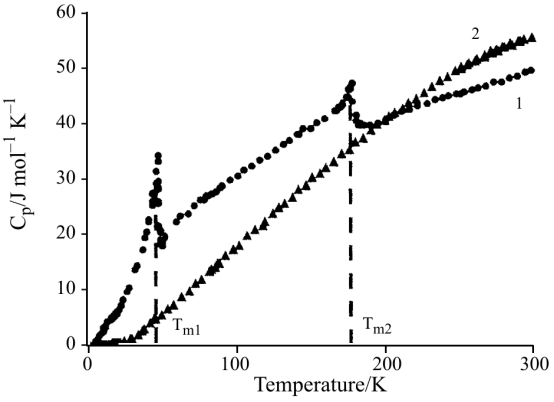

Fig. 3 Heat capacity of 1 – DyB_2 and 2 – YB_2

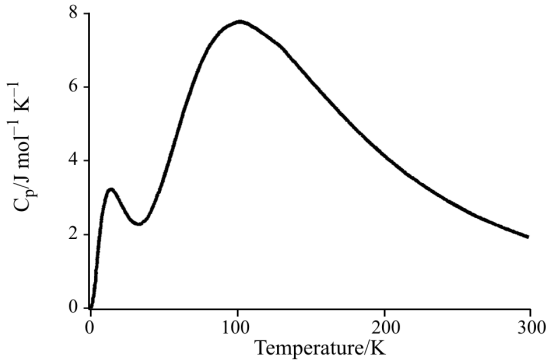

Fig. 4 Schottky contribution to heat capacity of DyB_2

Experimental values of heat capacity $C_p(T)$ of DyB_2 and YB_2 plot of temperature are given on Fig. 5. Practically in all investigated temperature interval the heat capacity of DyB_2 is greater than appropriate values of the non-magnetic YB_2 which are also given on Fig. 3.

On a curve $C_p(T)$ of dysprosium diboride a number of anomalies is clearly shown: a smooth maximum in the field of 20 K and two sharp maxima at temperatures T_{m1}=47.8 K and T_{m2}=178.8 K.

Results and discussion

Lattice component of heat capacity $C_{lat}(T)$ of dysprosium diboride was determined by the method of conformity of lattice heat capacities of isostructural compounds by comparison with non-magnetic yttrium diboride [4]. Thus it is considered, that near to room temperature isobaric and isochoric heat capacities of diborides are approximately identical, $C_p \cong C_v$, and the full heat capacity of diborides consists only of lattice component. In this case it is possible to believe, that heat capacities of isostructural substances are identical functions of absolute temperature and characteristic temperature inherent to every compound. Therefore

$$\frac{\Theta_{DyB_2}(T)}{\Theta_{YB_2}(T)} = \frac{\Theta_{DyB_2}(300\ \mathrm{K})}{\Theta_{YB_2}(300\ \mathrm{K})}$$

Using formula (1) and tables of Debye's function the first approximation of lattice contribution to DyB_2 heat capacity C_{lat_1} was calculated. After separation of lattice component of heat capacity and integration of the given excess heat capacity $\Delta C_1(T)/T=(C-C_{lat_1})/T$ the value of DyB_2 excess entropy $\Delta S_1(T)$ was received. It equals 44.6 J mol^{-1} K^{-1} at the temperature 300 K. This value considerably surpasses the theoretical value of entropy change $\Delta S_m = R\ln(2J+1)$ during infringement of magnetic ordering. For Dy^{3+} ions J=15/2 and ΔS_m equals 23.04 J mol^{-1}. Obviously other mechanisms besides processes of magnetic ordering also contribute to the full heat capacity of dysprosium diboride. Such additional contribution may be the heat capacity caused by Schottky's effect which is characteristic for compounds of the majority of rare earths.

Since energy levels of ions with even number of electrons are split by crystal field to singlets and doublets [5] the statistical sum of energy levels of a dysprosium ion (Fig. 4) corresponding to the simplified three-level scheme of splitting is given by the formula:

$$Z = \xi_1 + \xi_2 e^{-\delta_1/kT} + \xi_2 e^{-\delta_2/kT}$$

where ξ_i is degeneration of i^{th} sublevel, δ_i is size of splitting.

Proceeding from the best conformity to the data of experiment the following characteristics of splitting are

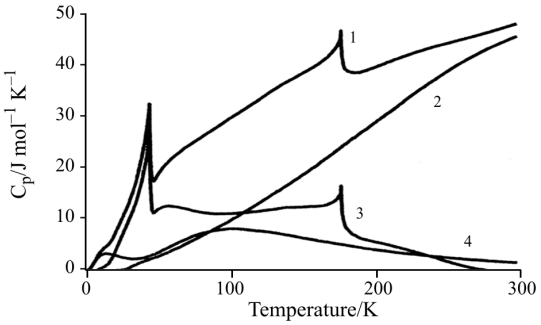

Fig. 5 Components of low-temperature heat capacity of DyB_2: $1 - C_{DyB_2}$, $2 - C_{lat_2}$, $3 - \Delta C_2$, $4 - C_{Sch}$

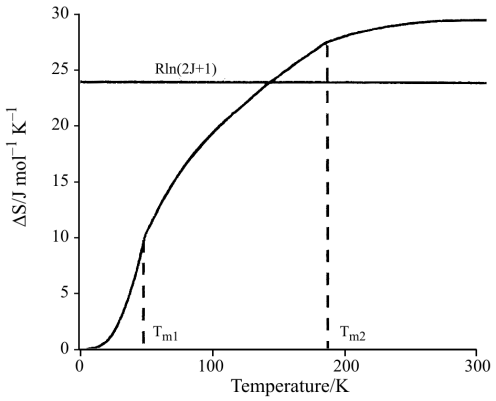

Fig. 6 Excess entropy of DyB_2, $\Delta S = \int_0^T \frac{\Delta C}{T} dT$ ($\Delta C = C - C_{lat} - C_{Sch}$) *vs*. temperature

offered: ξ_1=2, ξ_2=2, ξ_3=12, δ_1=50 K, δ_2=340 K. Here values of ξ_i may comprise united closely located sublevels. Schottky heat capacity $C_{Sch}(T)$ corresponding to this parameters is given on Fig. 4. The calculated value C_{Sch}(300 K) is 2.5 J mol^{-1} K^{-1}.

The account of this value at calculation of DyB_2 lattice heat capacity allowed to determine the corrected temperature dependence of lattice component $C_{lat_2}(T)$ given on Fig. 5. In the same figure dependences $C_{Sch}(T)$ and $\Delta C_2(T) = C - C_{lat_2} - C_{Sch}$ are given.

Temperature dependence of excess dysprosium diboride entropy $\Delta S(T)$ determined from dependence $\Delta C_2(T) = C_{DyB_2} - C_{lat_2} - C_{Sch}$ is given on Fig. 6. As you can see from the figure it turns out that the value ΔS(300 K) is close to ΔS_m, but nevertheless it surpasses ΔS_m at temperatures higher than 140 K. The X-ray investigation of DyB_2 has shown that at the temperature below 180 K reflexes of another phase appear on the X-ray powder diffraction patterns. This allows to consider that in dysprosium diboride besides magnetic transition a structural transition takes place. The effect of this transition is the maximum of heat capacity at the temperature T_{m2} and nonzero value of excess heat capacity at the temperatures of 50–180 K.

Conclusions

Calorimetric investigation of low-temperature properties of dysprosium diboride has allowed to reveal the series of new, earlier unknown characteristics of its lattice and magnetic subsystems.

- The characteristic temperatures of YB_2 and DyB_2 are quite big (Θ_{DyB_2} (300 K)=987 K, Θ_{YB_2} (300 K)= 774 K). This is characteristic for refractory substances. So the values of isochoric and isobaric heat capacities of diborides in the investigated interval of temperatures differ insignificantly.
- It follows from the analysis of temperature dependencies of excess entropy and X-ray data that besides ferromagnetic transition at the temperature T_{m1} in DyB_2 a structural phase transition also takes place at higher temperatures.
- Determined in this work parameters of splitting of Dy^{3+} ion ground level by crystal electric field and corresponding to them Schottky contribution to DyB_2 heat capacity were determined from the best correspondence to experimental data and have estimated character.

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