

Specific features of the magnetic properties of RB_4 ($R = \text{Ce}, \text{Sm}$ and Yb) tetraborides. Effects of pressure

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(Submitted December 19, 2014)

Fiz. Nizk. Temp. **41**, 254–261 (March 2015)

The temperature dependence and the effect of pressure P up to 2 kbar on the magnetic susceptibility χ of the tetraborides SmB_4 and YbB_4 was studied. For the compound CeB_4 , the electronic structure and magnetic susceptibility were calculated from first principles as a function of the atomic volume. The results show that in the studied tetraborides, rare-earth ions (Ce^{4+} , Sm^{3+} and $\text{Yb}^{2.8+}$) exhibit different valence states, which determines the specific features of their magnetic properties. In particular, the obtained pressure derivatives of susceptibility $\text{dln}\chi/\text{d}P$ for cerium, samarium and ytterbium tetraborides are -2 , -0.6 and $+2.7$ (in units of Mbar^{-1}), respectively, which are characteristic for the exchange-enhanced itinerant paramagnetism, Van Vleck ionic paramagnetism with a stable f -shell, and the magnetism of rare-earth ions in the intermediate valence state. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4916067>]

Introduction

Rare-earth tetraborides RB_4 are isostructural compounds with a tetragonal lattice of the type UB_4 (space group $P4/m\bar{b}m$). Most of them are antiferromagnets with Neel temperatures T_N of 7–44 K, with the exception of the ferromagnet PrB_4 (Curie temperature $T_C \simeq 25$ K) and the compounds CeB_4 and YbB_4 with a paramagnetic ground state.^{1–4} An unusual feature of heavy rare-earth metals ($R = \text{Tb–Tm}$) tetraborides is the presence of stepwise plateaus in the magnetization plotted as a function of magnetic field.^{5–11} This is characteristic to a particular dimeric structure, which is topologically equivalent to the Shastry-Sutherland lattice.¹² A wide variety of magnetic ordering types combined with the associated structural transitions^{13–16} forms a large field for experimental and theoretical studies of this tetraboride family.

On the other hand, the magnetic properties of the tetraborides RB_4 with $R = \text{Ce}, \text{Sm}$ and Yb , which show signs of $4f$ -shell instability, are much less studied. One of these signs is the deviation of the lattice parameters from the monotonic trend in the sequence of the lanthanide isostructural compounds RB_4 in which the rare earth ion is in the trivalent state. As seen in Fig. 1, these deviations are most pronounced in cerium and ytterbium tetraborides, whereas the data on the lattice parameters for samarium are ambiguous and require clarification. Since the volume of the R-ion is closely related to its valence, it can be assumed that in the compounds CeB_4 , SmB_4 and YbB_4 , the valence of the R-ions deviates from $3+$ and an intermediate valence state may be formed.

Most sensitive to the valence of the R-ion in rare-earth compounds are their magnetic properties. An effective indicator of the intermediate valence state is a large effect of pressure in the magnetic susceptibility, which is observed, for example, in the compounds of cerium, samarium and ytterbium.^{19–22} The main objective of this work is a detailed

study and analysis of the behavior of the magnetic susceptibility of CeB_4 , SmB_4 and YbB_4 tetraborides under pressure, aimed to elucidate the nature of magnetism and the valence state of the R-ion in these compounds. The magnetic properties of CeB_4 and their dependence on the atomic volume are presented as the results of theoretical calculations within the local spin density approximation (LSDA). These data are supplemented by the results of experimental studies of the magnetic susceptibility and the effect of hydrostatic pressure on it in SmB_4 and YbB_4 tetraborides.

Methods and results of calculations of the electronic structure and magnetic properties of the compound CeB_4

Electronic structure calculations for CeB_4 were conducted using a modified relativistic full-potential linear-muffin-tin orbitals (FP-LMTO, implementation RSPt) method.^{23–25}

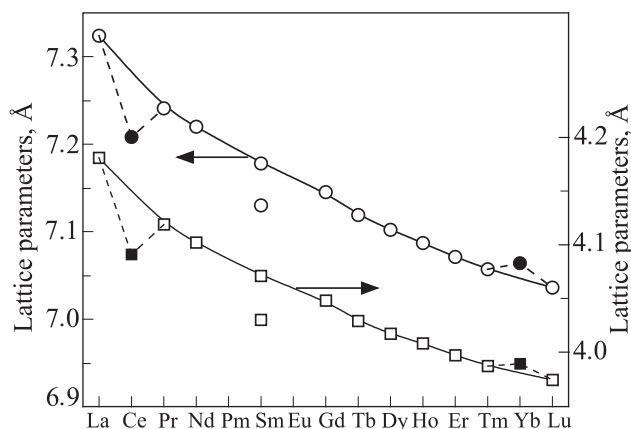


FIG. 1. Experimental values of the lattice parameters in the compounds RB_4 for $R = \text{La–Lu}$ from Ref. 17. The solid lines connect the data for tetraborides in which the R-ion is in the trivalent state. Lower values for SmB_4 were taken from Ref. 18.

Exchange-correlation potential was taken into account both in the framework of LSDA²⁶ and in the generalized gradient approximation (GGA)²⁷ in the density functional theory (DFT). In the course of self-consistent calculations of the crystal potential, the states of the ion core were calculated at each iteration, i.e., the “frozen-core” approximation was not used. No restrictions on the charge density or the potential of the system under study were applied within the FP-LMTO method. This is especially important for the anisotropic layered structure of CeB₄. The maximum value of the orbital quantum number l (l_{\max}) was assumed to be 3 for cerium. The semi-core $5p$ -states of Ce were also included in the band-structure calculation.

Like other RB₄ tetraborides, CeB₄ compound crystallizes into a tetragonal structure of the UB₄ type; detailed data on its lattice parameters are given in Refs. 1, 28, and 29. In this paper, calculations of the electronic structure of CeB₄ and the total energy E as a function of the unit cell volume V were carried out for a set of lattice parameters that were selected to be close to those found experimentally ($a = 7.2034 \text{ \AA}$ and $c = 4.1006 \text{ \AA}$). The lattice parameter a was varied, while the ratio c/a for the tetragonal lattice of CeB₄ was set to the experimental value: $c/a = 0.5693$. The theoretical values for the equilibrium volume ($V_0 = 203.25 \text{ \AA}^3$) and the bulk modulus ($B \simeq 2.03 \text{ Mbar}$) were determined from the calculated equation of state $E(V)$ using the well-known Murnaghan equation.²⁵

The calculated electron density of states $N(E)$ for the compound CeB₄ is shown in Fig. 2. The total density of states as well as the partial contribution of the $4f$ -states of cerium to the $N(E)$ are indicated. It can be seen that the contribution of $4f$ -electrons to the density of states at the Fermi level $N(E_F)$ is dominant in CeB₄. Generally, the $4f$ -states form a narrow band due to the hybridization with $5d$ -states of cerium and $2p$ -states of boron. It should be noted that there is an energy gap at $E \simeq 0.44 \text{ eV}$ above the Fermi level, whereas in the vicinity of E_F , $N(E)$ grows smoothly.

In the present paper we also calculated the electronic structure of the compound CeB₄ in an external magnetic field B , taking into account the spin-orbit interaction according to Refs. 23 and 24. The influence of an external magnetic

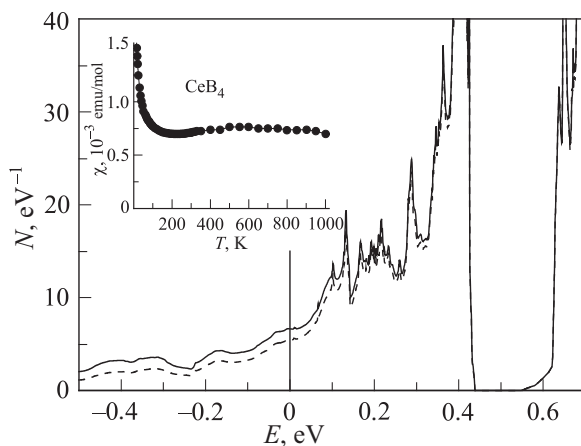


FIG. 2. Calculated density of states for CeB₄ (per formula unit). The dotted line shows the contribution of cerium $4f$ -states. The Fermi level E_F is denoted by a vertical line at $E = 0$. The inset shows the experimental temperature dependence of the magnetic susceptibility taken from Ref. 29.

field on the electronic structure of the paramagnetic phase was treated self-consistently within the LSDA by including the Zeeman operator in the FP-LMTO Hamiltonian:

$$\mathcal{H}_Z = \mu_B B \cdot (2\hat{s} + \hat{\mathbf{I}}), \quad (1)$$

where \hat{s} is the spin operator and $\hat{\mathbf{I}}$ is the operator of the orbital angular momentum. Induced spin and orbital magnetic moments calculated in an external field $B = 10 \text{ T}$ yielded the corresponding components of the magnetic susceptibility tensor χ_{spin} and χ_{orb} (Table 1) by differentiating the field-induced magnetization. It should be noted that the spin contribution to the susceptibility χ_{spin} calculated for CeB₄ directly involves exchange and correlation effects. The magnitude of these effects, which is characterized by the Stoner factor $S \simeq 2.7$, is determined by the ratio of the calculated χ_{spin} and the unperturbed Pauli spin susceptibility $\chi_P = \mu_B^2 N(E_F)$.

As can be seen from Table 1, the spin contribution χ_{spin} dominates in the magnetic susceptibility of the compound CeB₄ and is mainly determined by the $4f$ -states of cerium. These states also determine a noticeable orbital contribution χ_{orb} , which should be taken into account when quantitatively comparing the calculations and the experiment. Experimental data for CeB₄ from Ref. 29, which are shown in the inset of Fig. 2, indicate a relatively weak dependence of the susceptibility on temperature in the temperature range 100–1000 K. At low temperatures, there is a significant contribution of Ce³⁺ ionic impurity to $\chi(T)$. Accounting for this has allowed the authors of Ref. 29 to estimate the intrinsic susceptibility of the compound at $T = 0 \text{ K}$ as $\chi(0) \simeq 0.7 \times 10^{-3} \text{ emu/mol}$. This estimate agrees quite well with results of our calculation of the paramagnetic susceptibility of CeB₄ (see Table 1) reported here if small contributions due to the diamagnetism of ion-cores and the orbital Landau diamagnetism of conduction electrons are taken into account. Note that the smooth behavior of the dependence $N(E)$ near E_F (Fig. 2) suggests a weak temperature dependence of spin susceptibility, which is also in qualitative agreement with experiment.

To determine the effect of hydrostatic pressure on the electronic structure and magnetic properties of the compound CeB₄, calculations of the electron spectrum and the field-induced magnetic moment as functions of the unit cell volume were carried out within the framework of the above approaches. The obtained values of the volume derivatives of the density of electron states at the Fermi level and the paramagnetic susceptibility are given in Table 1. In general, the large magnitude of the volume derivative $d \ln \chi / d \ln V \simeq 4$ is consistent with similar data for other intermetallic compounds of cerium (CeCo₂,³⁰ CeNi₅³¹), the magnetic properties of which are related to the band properties of the

TABLE 1. Calculation results for CeB₄: the electron density of states at the Fermi level, $N(E_F)$ (in eV^{-1} per formula unit), the spin χ_{spin} and orbital χ_{orb} contributions to the magnetic susceptibility (10^{-3} emu/mol), and the logarithmic derivatives of $N(E_F)$ and total susceptibility $\chi_{\text{total}} = \chi_{\text{spin}} + \chi_{\text{orb}}$ with respect to volume.

$N(E_F)$	$\frac{d \ln N(E_F)}{d \ln V}$	χ_{spin}	χ_{orb}	χ_{total}	$\frac{d \ln \chi_{\text{total}}}{d \ln V}$
6.63	2.8	0.577	0.173	0.750	4.1

4*f*-states of cerium due to their strong hybridization with valence electrons. It should be also noted that the DFT calculations carried out in the present study give a good description of the CeB₄ lattice parameters (with an accuracy of 1.5%) specifically under the condition of delocalization of cerium 4*f*-states and their participation in the chemical bond.

Experimental details, results for SmB₄ and YbB₄ and discussion

For the synthesis of RB₄ (R = Sm, Yb) tetraborides, pure samarium and ytterbium and their hexaborides were used as starting materials. The process was carried out at temperatures of about 800–1000 °C in view of high vapor pressure of these metals in vacuum and the thermodynamic activity of gas molecules according the reaction



where (s) and (g) denote a solid reactant and a gaseous phase, respectively. The preparation was carried out in several stages until the final product weight was close to the calculated value. The final homogenizing annealing at a temperature of 1300–1350 °C yielded single-phase tetraboride samples in the form of fine-grain powder. X-ray structural analysis confirmed the tetragonal type of crystal structure with the lattice parameters close to those known from literature.

The temperature dependence of the magnetic susceptibility of the samples was measured in the temperature range 4.2–300 K using a superconducting quantum interference device (SQUID) in a magnetic field of 0.05 T. Samples were prepared by filling the raw powder into an aluminum foil capsule. They had cylindrical shape with a diameter of approx. 3 mm and roughly the same height. The contribution of the aluminum foil to the susceptibility was taken into account, based on the weak and temperature-dependent paramagnetism of aluminum $\chi \simeq 0.7 \times 10^{-6}$ emu/g.

Magnetic susceptibility measurements of the samples under helium gas pressure *P* of 2 kbar were carried out at constant temperatures of 78 and 300 K using a pendulum magnetometer, which was placed directly inside the pressure chamber.³² In this case the aluminum-foil capsule, which was filled with the tetraboride powder, had a parallelepiped shape with dimensions of about $2.4 \times 10 \times 4$ mm. The measurements were carried out in a magnetic field of 1.7 T and the relative error did not exceed 0.05%, taking into account the contribution of the capsule material.

Figure 3 shows the temperature dependence of the intrinsic magnetic susceptibility of SmB₄ which was obtained by correcting the measurement data for the small low-temperature impurity contribution ($\sim 1\%$) due to free Sm³⁺ ions. The observed maximum in $\chi(T)$ at $T_N \simeq 23$ K, which corresponds to the antiferromagnetic transition temperature, is in good agreement with the reported literature values of $T_N \simeq 25$ K (Ref. 33) and $T_N \simeq 26$ K.⁵ Generally, the overall shape of the $\chi(T)$ dependence is also close to known literature data.^{5,33}

It is well-known³⁴ that specific features of the magnetic properties of samarium and related compounds are due to the fact that in Sm³⁺ ions (as well as Eu³⁺) the nearest excited multiplets are separated from the ground state

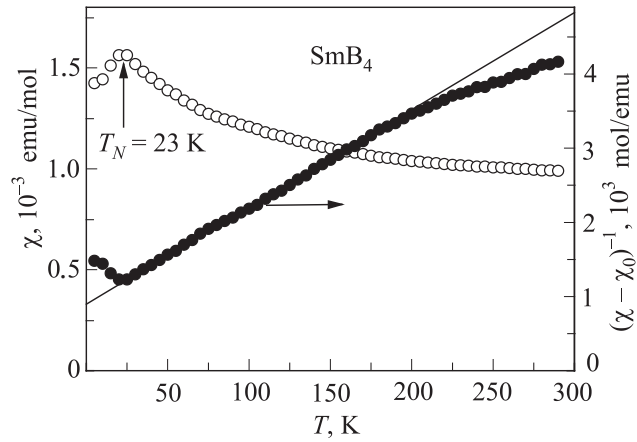


FIG. 3. Temperature dependence of the magnetic susceptibility SmB₄ and its approximation by the Curie-Weiss law (solid straight line; see the text for details).

multiplets by a relatively small energies, which leads to a significant paramagnetic contribution to the susceptibility χ_{VV} , which was first considered by Van Vleck and Frank.³⁵ In particular, the contribution of Sm³⁺ ions can be estimated using an equation presented in Ref. 36:

$$\chi_{VV} = N_A \frac{2\mu_B^2(L+1)S}{3(J+1)\Delta} \simeq 0.68 \times 10^{-3} \text{ emu/mol}, \quad (3)$$

where N_A is the Avogadro's number, μ_B is the Bohr magneton, L , S and J are the quantum numbers for the orbital, spin and total angular momentum, Δ is the difference between the energies of the ground ⁶H_{5/2} and excited ⁶H_{7/2} multiplets of Sm³⁺ ions, which amounts to 1100 cm⁻¹.³⁷

Another manifestation of the smallness of the parameter Δ is the appearance of appreciable contribution of the magnetic states of the excited multiplet already at room temperature. In view of the above, the magnetic susceptibility of SmB₄ can be approximately represented as

$$\chi(T) \simeq \chi_0 + \frac{C_0}{(T - \Theta)} + \frac{8}{6} \frac{C_1}{T} e^{-\Delta/kT}, \quad (4)$$

where χ_0 , C_0 and Θ are the parameters of the Curie-Weiss law, describing the contribution of the ground state of Sm³⁺ ions to the susceptibility, C_1 is the Curie constant of the excited state, and the coefficient of (8/6) is the ratio of multiplicities $2J + 1$ for the excited and ground multiplets. As can be seen in Fig. 3, for $T_N \leq T \leq 200$ K, the temperature dependence of the susceptibility is well described by the first two terms on the right hand side of Eq. (4) calculated with the following parameters: $\chi_0 \simeq 0.75 \times 10^{-3}$ emu/mol, $\Theta \simeq -70$ K, and $C_0 = 0.0763$ K·emu/mol (straight line in Fig. 3). The obtained value of C_0 corresponds to the magnitude of the effective magnetic moment of Sm³⁺ ion in the ground state $\mu_{\text{eff}} \simeq 0.78\mu_B$. These results are close to the data of Ref. 18 which were obtained using a single-crystal sample SmB₄: $\chi_0 \simeq 0.84 \times 10^{-3}$ emu/mol, $\Theta \simeq -103$ K and $\mu_{\text{eff}} \simeq 0.82\mu_B$.

As can be seen in Fig. 3, already for $T \geq 200$ K the contribution of the excited multiplet starts to manifest itself in the temperature dependence of the susceptibility. Based on an estimate for the magnitude of this contribution at $T = 300$ K, we find the value of $C_1 = (1.2 \pm 0.1)$ K·emu/mol,

which coincides within the experimental error with the value of 1.115 K·emu/mol reported in Ref. 18. The corresponding magnitude of the effective moment of the first excited multiplet of a Sm^{3+} ion is about $3 \mu_B$.

Reasonable agreement of the above values of the parameters describing the temperature dependence of the magnetic susceptibility of SmB_4 in Fig. 3 with the literature data obtained on single-crystals¹⁸ indicates good quality of the polycrystalline sample used in this study. It should be noted that the obtained value of χ_0 is almost identical to the estimated value of χ_{VV} according to Eq. (3). This indicates the dominant role of the Van Vleck paramagnetism in the magnetic susceptibility of the compound SmB_4 .

Unlike samarium tetraborides, in YbB_4 the Van Vleck contribution is virtually non-existent and its magnetic properties are determined by a relatively large magnitude of the effective moment of ytterbium ions μ_{eff} , which is equal to $4.54 \mu_B$ for Yb^{3+} . The temperature dependence of the magnetic susceptibility of YbB_4 is shown in Fig. 4. As can be seen, the behavior of $\chi(T)$ for our polycrystalline sample is in agreement with the data of Ref. 5, which were also obtained on polycrystalline samples. At the same time, at low temperatures, these results are markedly different from the averaged data of Ref. 33 obtained on a monocrystalline sample. Presumably, this difference is due to the contribution of free Yb^{3+} impurity ions, which were present at about 1.5 at. % in both polycrystalline samples.

One important feature of the compound YbB_4 is strong anisotropy of its magnetic susceptibility in the absence of magnetic ordering down to the lowest temperature attained experimentally.³³ A similar anisotropy has been observed in a paramagnetic phase of the related compound TmB_4 ,⁸ which is due to the effect of crystal field. In the case of strong anisotropy, an attempt to analyze the temperature dependence of the susceptibility in a polycrystalline sample (Fig. 4) within the framework of the Curie-Weiss law leads to incorrect values of its parameters. We shall therefore discuss the results of such an analysis using the data obtained for a single-crystal sample of YbB_4 in Ref. 33 for the $\chi_{||}(H||c)$ component of the susceptibility, which is dominant at low and moderate temperatures. Based on the

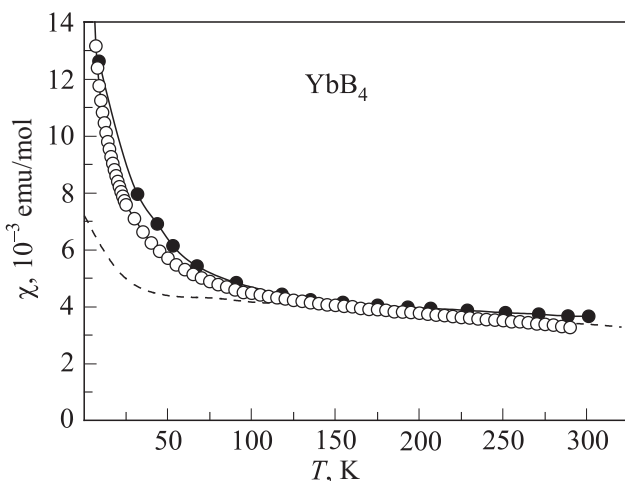


FIG. 4. Temperature dependence of the magnetic susceptibility of YbB_4 : (○)—our data, (●)—data from Ref. 5. The dotted line shows average data for a single-crystal sample from Ref. 33.

experimental data of Ref. 33, for $70 \text{ K} \leq T \leq 350 \text{ K}$, the dependence $\chi_{||}(T)$ can be described as $\chi_{||}(T) \simeq C/(T - \Theta)$ with the parameters $C \simeq 2.05 \text{ K}\cdot\text{emu/mol}$ and $\Theta \simeq -140 \text{ K}$. The magnitude of the effective magnetic moment $\mu_{\text{eff}} \simeq 4.05 \mu_B$, which follows from the value of the Curie constant C , is significantly lower than that for the trivalent ytterbium ion ($4.54 \mu_B$). This fact, along with a noticeable deviation of the lattice parameters of YbB_4 in the sequence of R^{3+}B_4 compounds (Fig. 1) indicates the intermediate-valence state of the ytterbium ion in this tetraboride, arising due to fluctuations between the states with ion configurations $4f^{13}5d(\text{Yb}^{3+})$ and $4f^{14}(\text{Yb}^{2+})$. Since the magnetic moment of the ion in the state Yb^{2+} is zero, the magnetic properties of the compound are determined by the relative residence time of the ion in the state Yb^{3+} , i.e., its occupation n . The value of n can be found from the relation $C = nC_0$ (C_0 is the Curie constant for Yb^{3+} ion) and is equal to 0.8. Thus, the estimated valence of the ytterbium ion in YbB_4 is $\text{Yb}^{2.8+}$.

Now let us discuss the effect of pressure on the magnetic susceptibility of the compounds SmB_4 and YbB_4 . Figure 5 shows typical experimental pressure dependences of the susceptibility, which demonstrate the scale and sign of the effect, as well as its linear behavior within the experimental error. The respective values of the derivatives $d\ln\chi/dP$ are shown in Table 2. They indicate a weak dependence of the effect of pressure on the temperature.

The observed effect of pressure on the magnetic susceptibility of SmB_4 is mainly determined by the pressure dependence of the Van Vleck paramagnetism since this contribution to the susceptibility is dominant, i.e., $d\ln\chi/dP \simeq d\ln\chi_{VV}/dP$. According to Eq. (3), χ_{VV} is determined by the parameter Δ , which, in turn, is closely related with the screening constant of the nuclear charge σ :³⁸

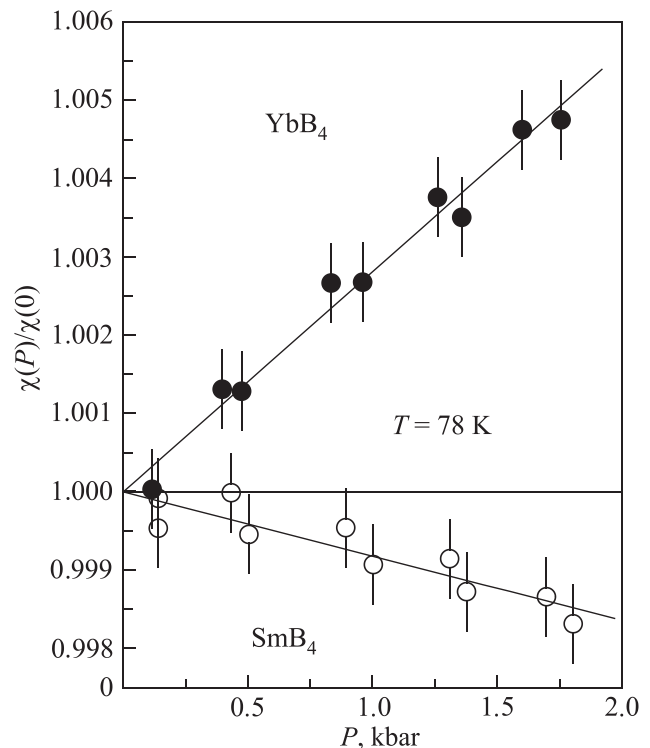


FIG. 5. Pressure dependence of the magnetic susceptibility for SmB_4 and YbB_4 at $T = 78 \text{ K}$.

TABLE 2. Derivative of the magnetic susceptibility in compounds SmB₄ and YbB₄ with respect to pressure $d\ln\chi/dP$ at T = 78 K and 300 K

T (K)	$d\ln\chi/dP$ (Mbar ⁻¹)	
	SmB ₄	YbB ₄
78	-0.8 ± 0.3	+2.7 ± 0.3
300	-0.6 ± 0.3	+2.5 ± 0.3

$$\Delta \propto (Z - \sigma)^4. \quad (5)$$

As a result, given Eqs. (3) and (5), we find the pressure derivative for the screening constant:

$$\frac{d\ln\sigma}{dP} \simeq \frac{d\ln\chi}{dP} \frac{Z - \sigma}{4\sigma} = (-0.15 \pm 0.05) \text{ Mbar}^{-1}, \quad (6)$$

where we took $Z = 62$, $\sigma = 33$,³⁸ and the mean value of $d\ln\chi/dP = (-0.7 \pm 0.3) \text{ Mbar}^{-1}$ for SmB₄ as follows from Table 2. This result indicates a slight weakening of the nuclear-charge screening upon applying hydrostatic pressure

$$\frac{dv}{dP} = (2.1 \pm 0.3) \text{ Mbar}^{-1}. \quad (7)$$

The magnitude and the sign of dv/dP found in YbB₄ is typical for the whole family of compounds with intermediate valence, including not only the ytterbium compounds,^{19,39} but also those of samarium^{20,39,40} and cerium.^{22,41} This reflects the general pattern of increase in the valence of rare-earth ions in such compounds under high pressure due to the partial delocalization of 4*f*-electrons and their transition to the conduction band.

Conclusion

The experimental and theoretical studies of the magnetic properties of cerium, samarium and ytterbium tetraborides allowed us to specify the valence state of the rare-earth ions and the related behavior of the magnetic susceptibility of these compounds as a function of temperature and hydrostatic pressure.

The results of *ab initio* calculations show that CeB₄ is an exchange-enhanced itinerant paramagnet in which the cerium ion does not have a magnetic moment due to the complete delocalization of 4*f*-electrons and is characterized by the valence state Ce⁴⁺. Moreover, the calculated magnitude of the effect of pressure on the susceptibility is characteristic for the itinerant paramagnets in terms of both magnitude and sign.

The experimental temperature dependence of the magnetic susceptibility of SmB₄ is adequately described within the concept of a trivalent samarium ion and the dominant role of the Van Vleck paramagnetism. The stability of the 4*f*-shell of Sm³⁺ ion is supported by the smallness of the observed effect of pressure.

One of the important results of the work is the confirmation of the existence of an intermediate valence state of ytterbium ion in the compound YbB₄, which is based on the magnitude and the positive sign of the observed effect of pressure on the susceptibility. This finding is consistent with the estimate of ytterbium valence $v \sim 2.8$, resulting from the

analysis of the published data on the temperature dependence of the susceptibility.

It should be noted that the valence of cerium and ytterbium ions in CeB₄ and YbB₄ are in reasonable agreement with the deviation of the crystal lattice parameters of these compounds from the general trend in the sequence R³⁺B₄ (Fig. 1). At the same time for SmB₄, where the samarium ion is trivalent, the lattice parameters from Ref. 18, shown in Fig. 1, assume significantly higher values of the valence and are apparently incorrect.

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Translated by L. Gardt