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Single crystals of HoB_4 have been grown and used for synchrotron X-ray diffraction studies at pressures up to 23 GPa and temperatures down to 100 K. The experimental bulk modulus 195 ± 6 GPa is in good agreement with 188.4 and 198.2 GPa values calculated in the LSDA and LSDA + U approximations, indicating that mainly the boron sublattice determines the bulk modulus. The experimental c/a ratio decreases slightly with pressure, but the effect is small. An orthorhombic distortion begins at $T_c \approx 295$ K, *i.e.* at a temperature much higher than the Néel temperature $T_{N1} = 7.1$ K. The behavior is interpreted in terms of built-in strains and crystal mosaicity.

Keywords: X-ray diffraction; crystal structure; equation of state; density functional theory

1. Introduction

Yttrium and all the lanthanides, except Eu and Pm, form isostructural metallic tetraborides with a tetragonal unit cell with space group $P4/mbm$ (#127) and four molecules per unit cell. These compounds have unusual magnetic properties as a result of the competition between multipolar interactions and the geometrically frustrated lattice of the rare-earth ions [1]. In particular, HoB_4 orders antiferromagnetically with two successive Néel temperatures, $T_{N1} = 7.1$ K and $T_{N2} = 5.7$ K. Recent studies of the magnetic structures can be found in [2,3]. In the present work, we have studied the crystal structure, the bulk modulus and the evolution of the unit-cell parameters at low temperatures. The experimental results are supported by calculations using the density functional theory.

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2. Procedures

Single crystals of HoB_4 were prepared in a multistage process: synthesis of single-phase powder, compacting by sintering into rods, and single-crystal growth by the floating zone method. The final impurity content is less than 10^{-3} wt%. A crystal structure refinement was performed at room temperature using Mo Kα radiation.

High-pressure X-ray diffraction spectra of powdered crystals were recorded at HASYLAB-DESY, using synchrotron white radiation and a diamond-anvil cell of Syassen–Holzapfel type, the pressure-transmitting medium being 4:1 methanol:ethanol. The pressure was determined from Decker's [4] equation of state for NaCl mixed with the sample. The experimental bulk modulus was determined from a fit of the Birch–Murnaghan equation [5] to the experimental pressure-volume data points. A Huber four-circle single-crystal diffractometer equipped with an Oxford Cryojet was used for measuring the evolution of the unit-cell parameters at low temperatures using monochromatic synchrotron radiation ($\lambda = 0.7000$ Å). The unit-cell parameters were calculated by least-squares refinement using the setting angles of 28 high-angle reflections.

Electronic structure calculations were performed with the linear-muffin-tin-orbital method [6] in a full-potential (FP) implementation [7]. Exchange and correlation effects were treated in the local spin density approximation (LSDA), and the LSDA with local Coulomb correlation (LSDA + U) [7]. For the screened f–f Coulomb parameter, the value of $U = 8$ eV was used [1] with the double counting correction as given by the fully localized limit [8]. Experimental values of the c/a ratio and atomic coordinates were assumed.

3. Results and discussion

The main results of the crystal structure refinement at room temperature are shown in Table 1. The lattice parameters are in good agreement with the available literature data. Figure 1 shows the compression curve. It is seen that the LSDA and LSDA + U calculations agree almost equally well with those of the experiment, straddling the experimental curve. This is surprising, since the manifold of Ho f-electrons is highly correlated, and one would expect an improved description with the inclusion of the Coulomb correlation effects in the LSDA + U approach. This suggests that the compressibility is determined mainly by the boron p electrons, which are described similarly in the two approaches, apart from the difference in hybridization with Ho f-electrons. In passing, it may be mentioned that LSDA + U is indeed superior when it comes to describing the magnetic properties of HoB_4. Our measured and calculated values of the bulk modulus are listed in Table 2. To the best of the authors' knowledge, there are no published values with which to compare the present results. The experimental c/a ratio is found to decrease with increasing pressure, but the variation is less than 1% within the observed pressure range (≤ 23 GPa). Thus, no attempt has been made to optimize this parameter.

Table 1. Atomic positions in tetragonal HoB_4 (space group $P4/mbm$): $a = 7.0910$ (15) and $c = 4.0086$ (7) Å.

Atom	Site symmetry	Atomic position	$U_{11} = U_{22}$	U_{33}
Ho	$4g$ $(x, 1/2 + x, 0)$	$x = 0.18197$ (3)	4.6 (1)	8.9 (2)
B1	$4e$ $(0, 0, z)$	$z = 0.2062$ (21)	7.2 (19)	9.6 (29)
B2	$8j$ $(x, y, 1/2)$	$x = 0.1773$ (7), $y = 0.0391$ (7)	5.9 (18)	7.2 (17)
B3	$4h$ $(x, 1/2 + x, 1/2)$	$x = 0.0859$ (8)	4.5 (17)	9.2 (24)

Note: The anisotropic thermal displacements U_{ii} are in Å$^2 \times 10^3$. Uncertainties are in units of the last decimal place.

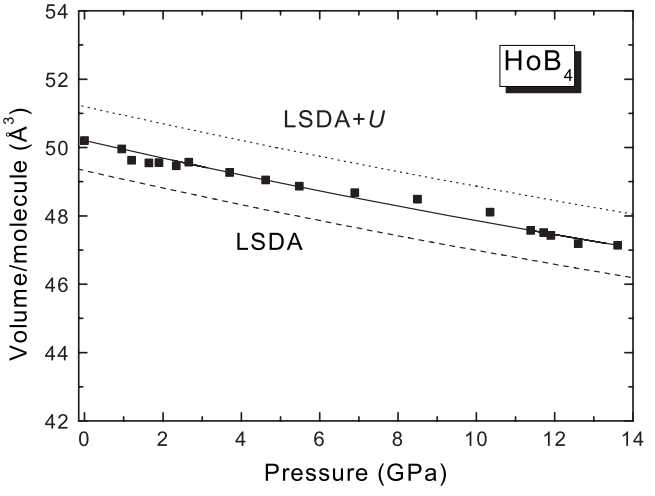

Figure 1. Volume per formula unit as a function of pressure. The full curve is the fit to the experimental data points, the dashed curve is the LSDA calculation and the dotted curve the LSDA + U.

Table 2. Unit-cell volume V_0, bulk modulus B_0 and pressure derivative B'_0 of HoB_4.

V_0 (Å^3)	B_0 (GPa)	B'_0
201.6 (1)	195 (6)	4.0 Experiment
197.4	188.4	3.7 Theory (LSDA)
204.8	198.2	3.3 Theory (LSDA + U)

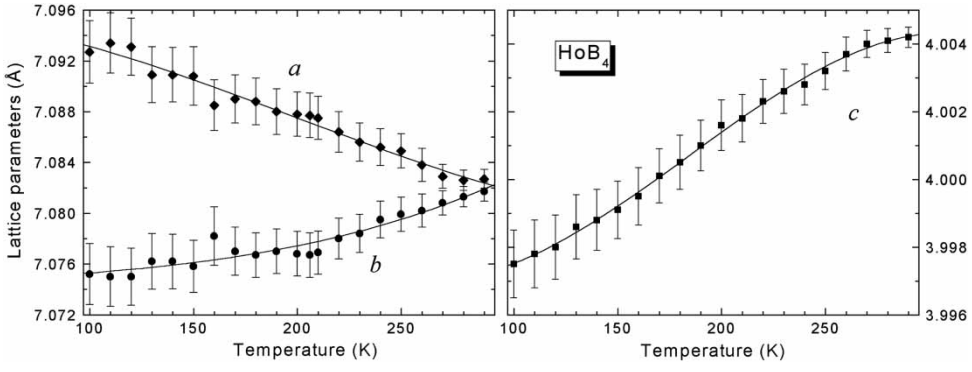

Figure 2. Temperature-dependent evolution of the lattice parameters.

Figure 2 shows the evolution of the lattice parameters a, b and c with temperature. A spontaneous distortion in the (a, b) plane appears below a critical temperature $T_c \approx 295$ K. The distortion is nearly symmetrical with respect to the tetragonal c-axis without saturation effects. The continuously growing distortion, lowering symmetry from tetragonal to orthorhombic, can be interpreted as a Landau-type phase transition [9]. Unexpectedly, the distortion begins at a temperature much higher than T_{N1}. Therefore, its physical mechanism cannot be directly related to the magnetic order. We consider the behavior be connected with individual features of the sample, determined by inherent built-in static strains generated by geometric frustration in the Ho^{3+} sublattice and by crystal mosaicity. Heiba et al. [10] have reported a similar situation for TbB_4 ($T_c = 80$ K, $T_N = 43$ K). The present experiments show that the paramagnetic phase of HoB_4 is not truly

tetragonal when cooled from room temperature to T_{N1}, as hitherto supposed. In fact, it consists of micro-clusters of orthorhombic symmetry, the generally assumed tetragonal cell being a macroscopic volume-average of those clusters.

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