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The Cubic to Trigonal Phase Transition in HoB_6 Measured on the New Powder Neutron Diffractometer HRPT at SINQ

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The new flexible high-resolution powder neutron diffractometer HRPT at the continuous spallation neutron source SINQ at the Paul Scherrer Institute (PSI) in Villigen, Switzerland, is introduced together with results of an early proposal experiment on HoB_6. Below the ferroquadrupolar ordering temperature $T_Q = 6.1$ K, the cubic crystal structure of HoB_6 (space group $Pm\bar{3}m$) is found to be rhombohedrically distorted (space group $R\bar{3}m$) with the angle α increasing from the cubic 90° to 90.264° at 2.1 K.

KEYWORDS: spallation neutron source SINQ, powder neutron diffractometer HRPT, germanium wafer monochromator, HoB_6, Jahn Teller effect

§1. Introduction

From the view of an external user the new flexible high-resolution powder neutron diffractometer HRPT[1,2] at the continuous spallation neutron source SINQ[3] at the Paul Scherrer Institute (PSI) in Villigen, Switzerland, is introduced in section 2. HRPT was designed by Peter Fischer. First neutron diffraction experiments were performed in 1999 and regular user operation has started in 2000. In section 3 the results of an early proposal experiment on HRPT are summarized (HoB_6, SINQ project II/99L-15). The excellent performance of HRPT is demonstrated by the successful measurement of the rather small distortion of the crystal structure of HoB_6 from cubic (space group $Pm\bar{3}m$) to trigonal (space group $R\bar{3}m$) below the ferroquadrupolar ordering temperature $T_Q = 6.1$ K.

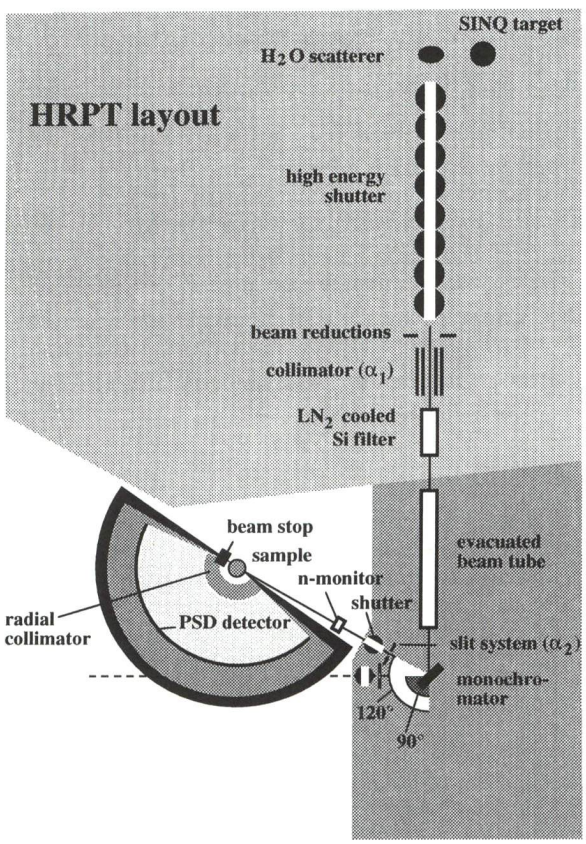

Fig. 1. Layout of HRPT diffractometer at SINQ.

§2. The Diffractometer HRPT at SINQ

The layout of HRPT is illustrated in Fig. 1. Thermal neutrons originate from a H_2O scatterer close to the SINQ target and pass a liquid nitrogen cooled Si filter of 20 cm length. An intensity gain up to a factor four is achieved by means of a 28 cm high, vertically fo-

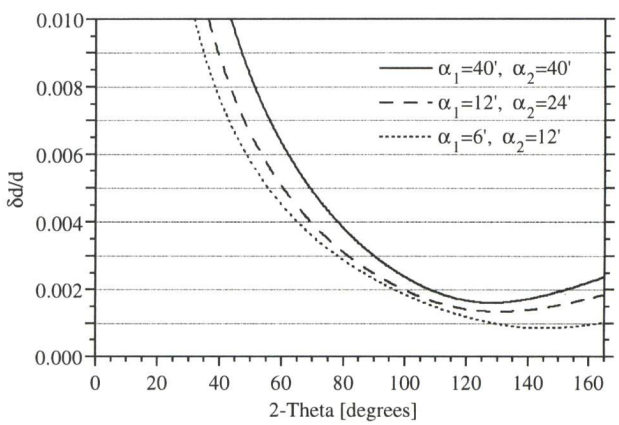

Fig. 2. Measured resolution functions of HRPT for monochromator take-off angle 120° and sample diameter 10 mm (Si powder standard).

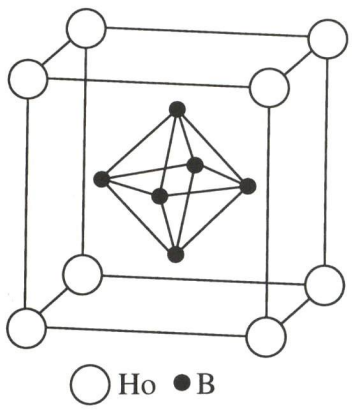

Fig. 3. The simple cubic crystal structure of HoB_6.

cusing wafer-type Ge (h,k,k) monochromator with variable curvature.[4] The neutron wavelength can be easily changed in the range from 1.2 to 2.5 Å by turning of the monochromator around the vertical axis. HRPT uses high monochromator take-off angles $2\Theta_M$ of 90° or 120°. Resolution and intensity can be tuned to the experimental needs by appropriate choices of the primary collimation α_1 (6', 12', 40') and the variable slit system α_2. Even for fairly large samples of 10 mm diameter, excellent resolution with lattice spacing d reaching $\delta d/d < 10^{-3}$ may be obtained, as shown in Fig. 2. HRPT is equipped with a large position sensitive ^{3}He multidetector (radius: 1.5 m, active height: 15 cm) with 1600 channels of angular 2Θ separation 0.1°. It was produced by Cerca at Romans, France, and allows simultaneous measurements within a scattering angle range of 159.9° with angular step 0.1° (e.g., for real-time experiments). Measurements of the complete neutron diffraction pattern ($4.95° \leq 2\Theta \leq 164.90°$, angular step: 0.05°) are performed at two angular positions with the first detector at $2\Theta = 4.95°$ and at 5.00°.

For standard measurements, powder samples are enclosed under helium gas atmosphere into cylindrical vanadium tubes (diameters: 5 to 10 mm, usable height: up to 50 mm) and are mounted in an evacuated aluminium pot which is equipped with a cooling machine (8 K $\leq$ T $\leq$ 300 K). Bragg peaks from the sample environment, such as for cryostats and furnaces, are removed by an oscillating radial collimator consisting of individually stretched mylar foils coated with Gd-O. It was fabricated by J. Linderholm (JJ X-Ray) at Risø, Denmark.

§3. Experiments on HoB_6

The binary compound HoB_6 adopts the very simple CaB_6-type crystal structure (cubic space group $Pm\bar{3}m$, No. 221, with sites 1a (0, 0, 0) occupied by holmium and 6f (x_B, 0.5, 0.5) by boron). This structure, illustrated in Fig. 3, can be viewed as two interpenetrating simple cubic lattices of B_6-octahedra and Ho ions, which are set apart by the vector (0.5, 0.5, 0.5). HoB_6 has a Γ_5 triplet as crystal-field ground-state and undergoes two successive phase transitions at $T_Q = 6.1$ K (ferroquadrupolar ordering) and $T_N = 5.6$ K (antiferromagnetic ordering).[5–7] Single crystals of incongruently melting HoB_6 were grown at Tohoku University by a crucible-free vertical floating zone method under 1 MPa pressurized high-purity (99.995%) argon.[6] For the neutron diffraction experiments on HRPT, 4.2 grams of $Ho^{11}B_6$ sample (prepared with 99.5 at% enriched ^{11}B isotope) was powderized and enclosed under helium gas atmosphere into a cylindrical vanadium container of 7.5 mm diameter and 30 mm height.

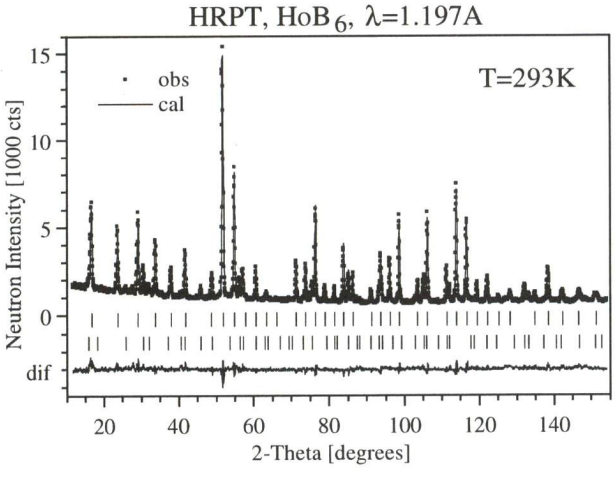

Fig. 4. Observed, calculated and difference HRPT neutron diffraction patterns (λ = 1.197 Å, high-intensity mode) of HoB_6 at 293 K. Vertical bars indicate positions of nuclear Bragg peaks for HoB_6 (upper row) and for the impurity phase HoB_{12} (lower row).

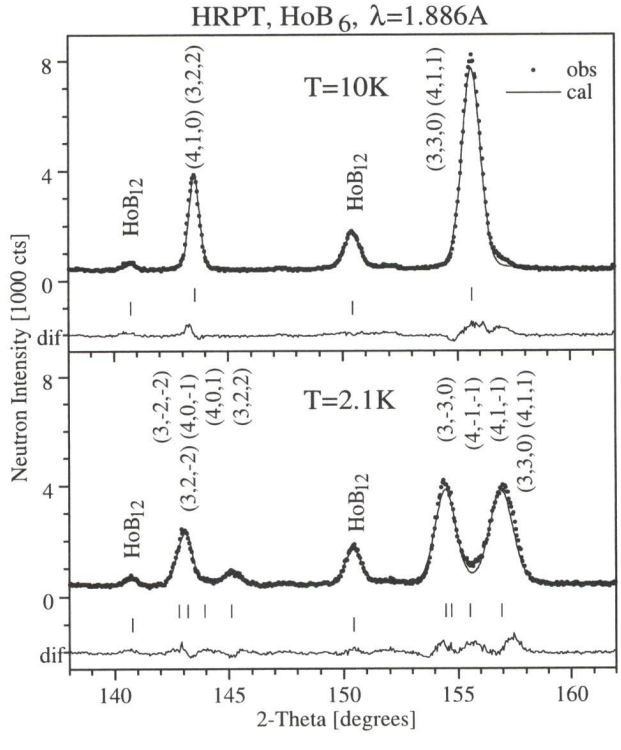

Fig. 5. High-scattering angle part of observed, calculated and difference HRPT neutron diffraction patterns (λ = 1.886 Å, high-resolution mode) of HoB_6 at 10 and 2.1 K. Vertical bars indicate positions of nuclear Bragg peaks for HoB_6 (upper row) and for the impurity phase HoB_{12} (lower row).

Fig. 4 displays the neutron diffraction pattern of the HoB_6 sample at room temperature. HRPT was operated in the high-intensity mode (collimations: $\alpha_1 = 40'$, $\alpha_2 = 40'$) and the neutron wavelength $\lambda = 1.197$ Å was obtained from a Ge (7,3,3) monochromator at the take-off angle $2\Theta_M = 120°$. The profile refinement of this diffraction pattern confirms the CaB_6-type crystal structure of HoB_6 with the lattice parameter $a = 4.097$ Å and the positional parameter $x_B = 0.199$. Moreover, it revealed the presence of a 11 volume% fraction of the impurity phase HoB_{12} in the sample.

In HoB_6, the Jahn-Teller effect for the crystal-field ground-state Γ_5 gives rise to a huge softening of the elastic constant C_{44} (80% just above T_Q) and to ferroquadrupolar ordering with Γ_5 symmetry ($\langle O_{yz}\rangle = \langle O_{zx}\rangle = \langle O_{xy}\rangle \neq 0$) below T_Q.[5] To study the change of the crystal structure of HoB_6 below T_Q (characterized by the spontaneous strain ($\langle \varepsilon_{yz}\rangle = \langle \varepsilon_{zx}\rangle = \langle \varepsilon_{xy}\rangle \neq 0$), HRPT was operated in a high-resolution mode ($\alpha_1 = 12'$, $\alpha_2 = 24'$, $\lambda = 1.886$ Å, $2\Theta_M = 120°$).

The HRPT neutron diffraction data shown in Fig. 5 provide experimental evidence for a distortion of the cubic crystal structure below $T_Q = 6.1$ K. Note that, in contrast to HoB_6, the Bragg peaks of the impurity phase HoB_{12} do not exhibit significant positional shifts in the same temperature range. According to profile refinements, based on the cubic space group $Pm\bar{3}m$ at 10 K and on the trigonal space group $R\bar{3}m$ at 2.1 K, the trigonal angle $\alpha = \beta = \gamma$ changes from the cubic 90° at 10 K to 90.264° at 2.1 K. The order parameter θ of this structural phase transition at T_Q can be determined from the angle α by using the relation $\alpha = 90° + 2\theta$. The angle $\alpha > 90°$ corresponds to a shrinking of the cubic crystal structure along a [1,1,1] direction. A similar effect has been observed in DyB_6 below $T_Q = 32$ K.[8]

Below $T_N = 5.7$ K, in the magnetically ordered state of HoB_6, antiferromagnetic Bragg peaks are observed in the low scattering angle part of the HRPT neutron diffraction patterns. The magnetic phase transition in HoB_6 has been studied in more detail on the neutron diffractometer DMC[2] at SINQ and results will be reported elsewhere.

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