Pulsed magnetic field synchrotron X-ray powder diffraction of the Jahn-Teller distortion in TbVO₄

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Abstract. X-ray powder diffraction experiments under pulsed magnetic fields were carried out at the DUBBLE beam line at the ESRF. A mobile generator delivered 110 kJ to the load coil, which was sufficient to generate peak fields of 30 T. A liquid He flow cryostat allowed us to vary the sample temperature accurately between 8 K and 300 K. Powder diffraction patterns of TbVO₄ were recorded in a broad temperature range using 21 keV monochromatic X-rays and an on-line image plate detector. We present results on the suppression of the Jahn-Teller structural distortion in TbVO₄ by to the magnetic field.

1. Introduction

X-ray diffraction is the by far the dominant method for the determination of crystal structures. Classical laboratory X-ray sources have however a rather low X-ray flux, and are therefore not compatible with the short pulse duration of pulsed magnetic fields (1 ms – 1 s). For this reason, the use of synchrotron sources, as available at the European Synchrotron Radiation facility (ESRF), is a suitable X-ray source. Since, however, a synchrotron is in general a bigger installation than a capacitor driven pulsed field equipment, the Laboratoire National des Champs Magnétiques Pulssés (LNCMP) has developed a mobile pulsed field apparatus with a flow cryostat, which can be transported to the ESRF when a (non dedicated) beam line is available for high field structural characterization. Before that, X-ray diffraction has so far been combined only with moderate (12 T) steady fields produced by split-pair superconducting magnets (with the exception of very recent developments [1]).

The scientific interest in diffraction under high magnetic fields is reflected in the number of large scale projects worldwide: Two independent Japanese groups are developing pulsed field
installations for synchrotron experiments at Spring-8, Japan [1,2]. Both groups employ split pair coils in Voigt geometry, i.e. with the incident beam perpendicular to the magnetic field, which is preferable for single crystal diffraction experiments. Projects exist to construct a facility for resistive DC fields at the Hahn-Meitner Institute (HMI), Berlin, and are included in the long-term strategy of the European Synchrotron Radiation Source (ESRF), Grenoble and the Institute Laue Langevin (ILL), Grenoble. Here we present the results of the first European pilot experiments on X-ray powder diffraction under pulsed magnetic fields up to 30 T.

2. Experimental setup

The experiment was performed on the DUBBLE CRG beamline [3] (BM26B) at the European Synchrotron Radiation Facility. The radiation hutch EH2 of this beamline is large enough to hold the entire setup, including the generator and the high field magnet/sample cryostat assembly, as shown in figures 1 and 2. Magnetic fields up to 30 T can be generated in the magnet coil.

![Figure 1. The generator is composed of the three subunits, containing the storage (left and right) and control units (center). The magnet/sample cryostat and x-ray detector are seen on the far right.](image)

2.1. Generator

The pulsed field generator used for the experiments presented here was developed at the LNCMP, Toulouse. It consists of three subunits (figure 1): two identical storage units contain the capacitor banks, crowbar diodes, resistors, and inductive current limiters. The third (control) unit houses the charger, thyristor stack, dump resistors and relays, and the current and voltage monitors. The generator can be charged up to 130 kJ. Charging up to full voltage (16 kV) takes less than 1 min. The energy of the capacitor bank is released into the coil through an optically triggered thyristor switch. Consecutive charging operations can be easily done by operating the charger continuously and firing as soon as the voltage reaches the selected value. In this way we have triggered up to 15 pulses at maximum charge within 15 min. Each subunit is mounted in a steel frame so that it can be transported using a fork lift or an overhead crane. The capacitor modules weigh approximately 1200 kg each and have dimensions (h x d x w) 1.25 x 1.30 x 0.95 m³. The control unit has the same size, but weighs only 400 kg. For our synchrotron experiments the generator was linked to the personal safety system of the radiation hutch such that it could be charged only after the hutch had been searched and interlocked. As an additional safety measure the generator and magnet/sample cryostat assembly were hard wired to the site ground.

2.2. High field magnet

The generator was connected to the high field magnet by a high voltage-high current coaxial cable. The magnet coil was designed and manufactured at the LNCMP in Toulouse. It was wound with
Glidcop wire (type C15720; proof strengths of 450 MPa at room temperature and 500 MPa at 77 K). The inductance of the coil was L = 8.6 mH and the resistance at liquid nitrogen temperature amounted to 70 mΩ. Its bore was ~22 mm. The external diameter of the coil was 124 mm and the height was 74 mm. The coil was horizontally mounted in a cryostat with separate magnet and sample spaces (figure 2). The beam axis was along the bore of the magnet (Faraday geometry). In normal operation the magnet was immersed in liquid nitrogen; this reduced the electrical resistance of the coil and also acted as a thermal screen for the sample volume.

![Figure 2](image)

**Figure 2.** Schematic overview of the experimental setup. The beam is supplied by the ESRF beam line (DUBBLE, BM26B), and delivers photons of 21 keV. The LNCMP Pulsed Field Controller opens two consecutive shutters, allowing the beam to pass only when the desired field is reached. In a sequence of pulses, all diffracted photons are detected by an image plate with automatic readout. The flow cryostat and magnet construction is shown in detail as well as the capacitor bank diagram.

### 2.3. Flow cryostat

A He flow cryostat, custom designed and built at the LNCMP in Toulouse, was inserted from the upstream side into the bore of the magnet (figure 2). A Lakeshore model 332 temperature controller was used to vary the sample temperature between T = 7.5 and 300 K. Samples can be loaded and in situ, using a load lock and transfer stick. The access on the upstream side was restricted by the cryostat and amounted to \( \varnothing \sim 3 \text{ mm} \) over a length of half a meter. After proper alignment this opening was largely sufficient to allow the entrance of the incoming beam. Downstream of the sample, the assembly was optimized for the largest possible optical access. However, X-ray scattering angles were limited to 14° in order to stay within a well proven classical coil design. The sample space is evacuated. Kapton foil (120 \( \mu \text{m} \) thickness) was used for the entrance and exit windows. The powdered samples were prepared and mounted as follows: single crystals of TbVO\(_4\) grown by the flux method were ground into a fine powder and embedded in low molecular weight polyvinylpyrrolidon (PVP) in order to inhibit field-induced motion of the powder particles, while at the same time...
improving thermal contact. The resulting pellets were mounted in a sample holder that was screwed into the cryostat by means of an actuator. Magnetic fields up to 30 T can be generated in the magnet with the present capacitor bank. This limit, however, was imposed by safety considerations of this design. It is relatively straightforward to upgrade the system for fields of the order of 50 T, or to a split-pair magnet configuration where the magnetic field direction is perpendicular to the x-ray beam.

2.4. Limiting stray magnetic fields
Synchrotron beamlines employ large numbers of computers, detectors, and other sensitive electronic instruments, which in general are not shielded against magnetic fields. The electron beam of the ring is sensitive to magnetic fields on the order of one-tenth of the earth’s magnetic field. Despite the peak field of 30 T, the stray magnetic fields of the pulsed field system presented here are much smaller than those observed in a 10 T superconducting split-pair magnet. The dipolar moment of the magnet at maximum field amounted to 12250 Am². From this the field in the horizontal plane at moderate distances amounts to between 1.25 and 2.5 mT at a distance of 1 m and eight times less (2³) at a distance of 2 m. The order of magnitude of these values was confirmed by measurements.

2.5. Timing issues and synchronized data acquisition
The time structure of the magnetic field pulse is shown in figure 3. The field rises from zero to maximum within 4 ms. The full width at half maximum (FWHM) of the magnetic fields pulses is 18 ms. Due to the restrictions of magnetic pulse length and x-ray beam intensity, the experiment requires the accumulation of some tens of magnetic field shots to acquire statistically relevant data. After several tests we have run the experiment in the fast-pulse mode, triggering 10-20 pulses as fast as the charger permitted, before allowing the coil to cooldown back to liquid nitrogen temperature.

The detector was read out after such an accumulated series of pulses. In this way we reduced the noise introduced by the readout process (compared to reading out after each pulse) and reduced the total background, as the detector was read after 15 min (compared to 1h). During these sequential pulses the magnet heats up gradually so that the cooldown period after a series of experiment pulses has to be extended—after 15 pulses at the maximum field of 30 T, the coil had heated up to 260 K, and 45 min of cooldown time were required. Furthermore, the electrical resistance of the wire material increases with temperature and a progressively larger part of the energy dissipates into the coil. Consequently, the peak field and the pulse length obtained for a given energy both decrease, as shown in figure 3. At this point of our studies the decrease of the peak field is not problematic. The effect can be controlled by limiting the number of pulses per series before cooldown, or by adapting the capacitance of the
generator such that the pulse length corresponds to the maximum admissible temperature increase in one single pulse.

The opening of the x-ray beam shutter must be synchronized with the magnetic field pulse. The shutter opened and closed after predefined delays (figure 3), adjusted such that the average magnetic field during the exposure is within 90% of the maximum. This corresponds to time frames of 4.9 ms. To obtain enough diffraction counts in the detector, sequences of pulses were required. Each pulse added 4.9 ms measuring time for a spectrum at one given field value and the detector integrates the x-ray signal over this exposure time. This process was repeated until the data were statistically relevant. In this mode of data acquisition a separate series of field pulses is required for each value of the magnetic field. The software package FIT2D [4, 5] was used to extract 20 scans from the raw images. A background spectrum derived from an unexposed raw image was subtracted before the data of several series of magnetic field pulses were averaged in order to improve the counting statistics. The diffracted intensity as function of scattering angle, $2\theta$, was obtained by angular integration of the Debye rings. Figure 4 shows the raw image and corresponding 20 scan for a 45 times 5 ms exposure at $T = 7.5$ K without applied magnetic field (the quality of the experiment is only dependent on the exposure time, no degradation of the signal is apparent in field).

Figure 4. 45 shots of 5 ms in zero magnetic field collected on the MAR image plate. The diffracted rings are from TbVO$_4$ at $T = 7.3$ K. The $I$-$2\theta$ graph is obtained by $2\pi$ circular integration of the 2D image. The observed peaks are the 311, 131, 202 and 022 reflections (ordered by increasing angle).

3. Observation of a field induced phase change in TbVO$_4$

3.1. Why should one expect a structural phase transition?
Terbiumvanadate, TbVO$_4$, is a textbook example for a cooperative Jahn-Teller transition (JT) mediated by quadrupolar interactions between the 4f moments [6]. At high temperatures TbVO$_4$ crystallizes in the tetragonal zircon structure with space group $I4_1/amd$ and lattice parameters [7] $a=b=7.1841(3)$ Å and $c=6.3310(4)$ Å. Upon lowering the temperature through $T_{JT}=33$ K, it undergoes a cooperative JT transition: the crystal spontaneously distorts along the [110] direction to the orthorhombic space group $Fddd$ with lattice parameters [7] $a=10.239(2)$ Å, $b=10.029(2)$ Å, and $c=6.3154(13)$ Å. As order parameter we use the normalized difference of the orthorhombic $a$ and $b$ lattice parameters, $\varepsilon=2(a-b)/(a+b)$. It is surprisingly large, reaching 2% at 22 K, and increasing further towards lower temperatures. Antiferromagnetic ordering of the Tb moments occurs [8] at 0.6 K, but it is of no relevance in this study. The JT transition has been studied extensively both experimentally
and theoretically (see [6]). Early, qualitative theories already suggested that the JT effect should be quenched by a magnetic field [9,10]. Recently, the suppression of the JT distortion was observed [11] indirectly through changes in the differential magnetization, dM/dH(H). Demidov and Kolmakova [12] used mean-field theory to quantitatively study the effect of a large magnetic field applied along the c axis of the crystal and found that fields above B = 29 T suppress the JT distortion, in good agreement with the experimental data [11]. Despite these long-standing predictions, the suppression of the JT distortion by an external field has never been observed directly, due to the lack of a suitable experimental method.

3.2. Pulsed Field Spectra
Powder x-ray diffraction diagrams were recorded as described above, using an X-ray photon energy of 21 keV. Figure 5 shows the I-2θ results in magnetic fields ranging from 0 T to 30 T, using a 15 x 5 ms shots integration at T = 7.5 K. As can be seen from the raw data integrated over the angle, the diffraction peaks from TbVO₄ are clearly observed (311, 131, 202 and 022 reflections, ordered by increasing angle). Zero field spectra recorded before and after magnetic field pulses showed weak variations in the total intensity and the intensity ratio of various peaks. We attribute these to tiny shifts in sample position or grain orientation due to the magnetic forces on the powder grains.

![Figure 5](image)

Figure 5. 15 shots of 5 ms in various magnetic fields at T=7.5K. The I-2θ graph is obtained by 2π circular integration of the 2D MAR image. All images have been corrected for the MAR background.

Observation of field-induced structural changes
In the high temperature phase (T = 39 K) we observed two Bragg reflections with Miller indices (using the high temperature tetragonal unit cell, subscript tet) (211)tet near 11.8° and (112)tet near 12.6°. The low temperature (T = 7.5 K) distortion due to the Jahn-Teller effect is observed as a splitting of these peaks: (211)tet → (311)ortho+(131)ortho and (112)tet → (202)ortho+(022)ortho, where the subscript ortho signifies indexing with respect to the orthorhombic unit cell. The splitting can then be used to determine the orthorhombic lattice parameters and the order parameter $\varepsilon = 2(a-b)/(a+b)$, as shown in Figure 6. Let us return to figure 5, and investigate the evolution of the spectra as function of applied
field at low temperature $T=7.5$ K. Immediately visible is a change of the relative amplitude of the high- and low-angle partners. We attribute this to the preferential population of domains, due to an in-plane ($a_{\text{ortho}}$ vs $b_{\text{ortho}}$) magnetocrystalline anisotropy of TbVO$_4$. The splitting decreases with increasing field, indicating that the Jahn-Teller effect is suppressed. It should be noted that this slight difference in preferential domains does not affect the determination of the peak positions.

In the high temperature spectra (not shown, more details in [13]), we observed that upon applying the magnetic field a splitting ((202)/(022)$_{\text{ortho}}$ pair) appears, and that a preferential domain population develops [(311)/(131)$_{\text{ortho}}$ pair], i.e., the magnetic field induces the Jahn-Teller state.

At $B=30$ T the magnitude of the distortion is similar for both temperatures, as shown in figure 6. At all temperatures the peaks broaden as the field is applied. This is due to the strong dependence of the phase diagram on the angle between the magnetic field and the sample's $c$ axis.

Our experiment thus clearly shows that the magnetic field modifies the Jahn-Teller distortion in TbVO$_4$, and that these changes can be detected using x-ray powder diffraction at a synchrotron source.

![Figure 6. Field dependence of the orthorhombic distortion $\varepsilon = 2 (a-b)/(a+b)$ at $T=7.5$ K and $T=39$ K.](image)

4. **Possible Technological Improvements**

The final goal of this project is to provide the highest magnetic fields possible within the constraints imposed by the synchrotron x-ray beam line. Main concerns are as follows: (1) magnetic pulse duration and optimization of the detection system; (2) repetition rate needed to ensure reasonable counting statistics and efficient use of the synchrotron beam time; (3) the opening angle of the coil, as these techniques are photon-in photon-out experiments; and (4) lifetime, reliability, and safety of the installation. Based on the preliminary results obtained with the present generator and magnet, we estimate that fields in excess of 40 T should be feasible.

The following improvements are envisaged:

(i) Increasing the maximal field: The state-of-the-art for 60 T pulsed field magnets have a life expectancy on the order of 200 shots, whereas our 30 T coil is still operational after over 1000 shots.

(ii) Increasing the opening angle in the Faraday geometry to 45°, while simultaneously lowering the magnet coil cooldown time required in between shots. As a second step we envisage a split-pair coil with the field perpendicular to the beam (Voigt geometry).

(iii) The cryostat will be upgraded to reach lower temperatures with better temperature control.

(iv) A qualitative gain is possible with a fast x-ray detection system: With a fast x-ray detector (frame rate of 1 kHz or better), it would be possible to follow the variation of the x-ray
signal as the magnetic field pulse evolves, recording a hysteresis curve as a function of time.

(v) Other measuring techniques besides diffraction:
- Matsuda et al have already demonstrated single crystal diffraction and absorption spectroscopy in fluorescence detection. Several other spectroscopic techniques could also be carried out under pulsed magnetic fields.
- Dispersive x-ray absorption spectroscopy, where an entire absorption spectrum can be measured in one shot, holds great potential. This technique requires only a narrow optical access and is thus compatible with classical solenoid coil designs, and spectra can be recorded with high enough frame rates to track the evolution of the signal as function of field strength during the pulse.
- Single crystal diffraction could also be performed in the Laue mode. By using a quasi-white high energy beam, where the low energy spectrum has been filtered out, the heat load on the sample is reduced to acceptable levels.

Summary

Using the 21 keV x-ray synchrotron beam, in combination with an 18 ms (FWHM) pulsed field magnet and a custom designed flow cryostat, we have successfully measured the field dependence of the TbVO₄ powder diffraction peaks at T=7.5 K and 7=39 K. We have observed that on increasing magnetic field the orthorhombic splitting is strongly suppressed, showing that the phase transition observed in differential magnetization experiments [12] is actually related to a structural change from the orthorhombic to the tetragonal phase. More details are in press elsewhere [13].

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