Direct Observation of the High Magnetic Field Effect on the Jahn-Teller State in $TbVO_4$

C. Detlefs,[1] F. Duc,[2] Z. A. Kazeĭ,[3] J. Vanacken,[4] P. Frings,[2] W. Bras,[5] J. E. Lorenzo,[6] P. C. Canfield,[7] and G. L. J. A. Rikken[2]

[1]*European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble Cedex, France*
[2]*Laboratoire National des Champs Magnétiques Pulsés, CNRS-INSA-UPS, Université de Toulouse, 143 Avenue de Rangueil, F-31400 Toulouse, France*
[3]*Moscow State University, Leninskye Gory, Moscow, 119992 Russia*
[4]*Pulsveldengroep, Institute for Nanoscale Physics and Chemistry, Clestijnenlaan 200D, B-3001 Leuven, Belgium*
[5]*Netherlands Organisation for Scientific Research (NWO), DUBBLE CRG at the ESRF, BP220, F-38043 Grenoble, France*
[6]*Institut Néel, CNRS, BP 166X, F-38043 Grenoble, France*
[7]*Ames Laboratory, USDOE and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA*

(Received 19 November 2007; published 8 February 2008)

We report the first direct observation of the influence of high magnetic fields on the Jahn-Teller (JT) transition in $TbVO_4$. Contrary to spectroscopic and magnetic methods, x-ray diffraction directly measures the JT distortion; the splitting between the (311)/(131) and (202)/(022) pairs of Bragg reflections is proportional to the order parameter. Our experimental results are compared to mean-field calculations, taking into account all possible orientations of the grains relative to the applied field, and qualitative agreement is obtained.

DOI: 10.1103/PhysRevLett.100.056405 PACS numbers: 71.70.Ej, 75.10.−b, 75.25.+z

Phase transitions induced by quadrupolar interactions have recently received much attention, mostly due to their influence on the magnetic properties of the sample, e.g., in the giant-magnetoresistive effect of manganite compounds [1] and the magnetoelectric effect in multiferroic materials [2,3]. The cooperative Jahn-Teller (JT) effect arises from the same quadrupolar interactions [4], and may indeed be interpreted as ferro-quadrupolar order. In JT compounds, the balance between magnetic and quadrupolar effects can be tuned by varying the strength of an externally applied magnetic field. To date, however, only a small amount of experimental evidence has been reported [5], as the required magnetic fields tend to be rather large.

In this Letter we present the first direct experimental evidence for the modification of the JT effect by a external magnetic field. This effect was predicted by both qualitative [6,7] and quantitative [8,9] theories, but previous experiments [5,9–12] observed only indirect signatures of this behavior.

Terbium ortho-vanadate, $TbVO_4$, along with $DyVO_4$, is a textbook example for a JT transition [4] induced by quadrupolar interactions between the Tb $4f$ moments, mediated through phonons. At high temperatures, $TbVO_4$ crystallizes in the tetragonal zircon structure with space group $I4_1/amd$ [13], with lattice parameters $a_t = b_t = 7.1831(3)$ Å and $c = 6.3310(4)$ Å. Upon lowering the temperature through $T_Q \approx 33$ K, it undergoes a cooperative JT transition: The crystal spontaneously distorts along the [110] direction (B_{2g} strain, δ-symmetry distortion) to the orthorhombic space group $Fddd$ with lattice parameters $a_o = 10.239(2)$ Å, $b_o = 10.029(2)$ Å, and $c = 6.3154(13)$ Å at 22 K. The distortion is surprisingly large, reaching $\epsilon^\delta = 2(a_o - b_o)/(a_o + b_o) = 2\%$ at 22 K [13], and increasing further toward lower temperatures.

The JT transition has been studied extensively, both experimentally and theoretically. The early studies, however, focused on the sample's properties in the absence of applied magnetic fields [4]. The effect of large external magnetic fields on $TbVO_4$ was studied only recently. Quantitative mean-field calculations [8] found that the JT distortion is suppressed when fields above $\approx$29 T are applied along the c axis of the sample, in good agreement with susceptibility measurements [9]. Diffraction experiments have so far not been carried out, as the required combination of high magnetic fields and x-ray diffraction equipment has only recently become available [14–16].

The experiments were performed on the DUBBLE CRG beam line, BM26B, at the ESRF [17], using the experimental configuration described in [16]. Flux-grown single crystals of $TbVO_4$ [18,19] were ground into a fine powder and embedded in low molecular weight polyvinylpyrolidone in order to prevent movement of the powder grains due to magnetic forces, while at the same time improving the thermal contact. The sample was then mounted in a pulsed magnet and cryostat assembly [16].

The data shown here were taken by accumulating $\approx$45 magnetic field pulses per spectrum. For each field pulse a mechanical shutter exposed the image plate detector for 4.9 ms centered around the maximum field. Representative powder diffraction spectra are shown in Fig. 1.

The JT transition manifests itself as splitting of some, but not all, powder lines (see Table I). For small distortions, $\epsilon^\delta \ll 1$, the orthorhombic lattice parameters can be approximated as $a_o \approx (1 + \frac{1}{2}\epsilon^\delta)\bar{a}$ and $b_o \approx (1 - \frac{1}{2}\epsilon^\delta)\bar{a}$, where $\bar{a} = \frac{1}{2}(a_o + b_o) \approx \sqrt{2}a_t$. To first order in ϵ^δ, the splitting of a pair of Bragg reflections $(H, K, L)_o$ and $(K, H, L)_o$ is then given by

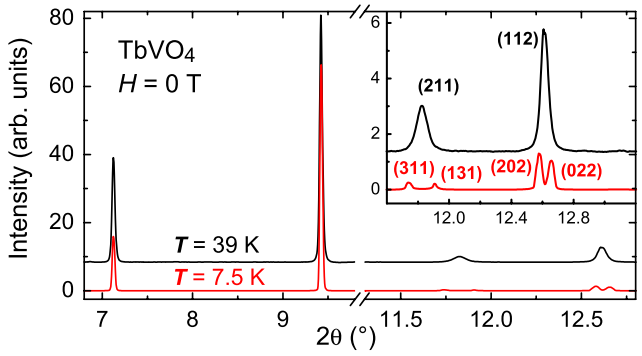

FIG. 1 (color online). X-ray powder diffraction spectra of $TbVO_4$. The inset shows the (311)/(131) and (202)/(022) pairs of reflections that are sensitive to the orthorhombic distortion, ϵ^δ.

$$\delta(2\theta) \approx \frac{\lambda^2}{\bar{a}^2}\frac{K^2-H^2}{\sin(2\theta)}\epsilon^\delta = 2\tan(\theta)\frac{K^2-H^2}{H^2+K^2+\frac{\bar{a}^2}{c^2}L^2}\epsilon^\delta. \quad (1)$$

Our experimental configuration, with photon energy $E = 21$ keV ($\lambda = 0.59$ Å), allowed us to observe scattering angles up to $2\theta = 12.8°$, covering the reflections, in the orthorhombic notation, (111), (220), (311), (131), (202), and (022). Within this range, only the (311)/(131) and the (202)/(022) pairs are sensitive to the JT distortion.

In samples with large magnetocrystalline (MC) anisotropy, such as $TbVO_4$, the phase diagram depends not only on the magnitude of an applied magnetic field, but also on its orientation relative to the crystal symmetry axes. The grains in a powder sample are aligned randomly, so that for a macroscopic measurement, e.g., magnetic susceptibility, the direction of the field has to be averaged over the full solid angle of 4π.

In a diffraction experiment, however, the orientation is constrained: Any grain contributing to the diffraction signal at the angle 2θ must be oriented such that the Bragg planes of the corresponding reflection (H, K, L) form the angle θ with the incident beam. The powder averaging must then be taken only over the azimuthal angle, ψ, i.e., rotation about the scattering vector $\boldsymbol{Q} = (H, K, L)$.

TABLE I. Bragg reflections of $TbVO_4$, scattering angle at $E = 21$ keV, and the splitting due to the JT-effect. Values are based in the lattice parameters given in Ref. [13] for $T = 22$ K.

$(HKL)_o$	2θ [deg]	$\delta(2\theta)/\epsilon^\delta$ [deg/%]
(111)	7.14	0
(220)	9.45	0
(311)/(131)	11.78/11.94	0.076
(202)/(022)	12.61/12.69	0.036
(400)/(040)	13.24/13.52	0.134
(222)	14.32	0
(331)	15.19	0
(113)	16.81	0

In our experiment, the external field $\mu_0\boldsymbol{H}$ was aligned along the incident beam axis; the angle between the field and the Bragg planes is therefore the Bragg angle, θ.

For systems with substantial MC anisotropy any simulation of the powder diffraction spectrum must thus be carried out peak by peak: For each Bragg reflection the magnetic field direction and the corresponding influence on the phase diagram and the lattice parameters must be calculated as a function of ψ, yielding, in this case the distortion $\epsilon^\delta(\psi)$, and the corresponding scattering angle, $2\theta_{\text{calc}}(HKL, \epsilon^\delta(\psi))$. The resulting diffraction patterns are then averaged over the azimuthal angle, taking into account the instrumental resolution.

In order to quantitatively describe the effect outlined above for $TbVO_4$ we have performed comprehensive mean-field calculations of the magnetoelastic distortion of $TbVO_4$ as a function of the strength and direction of the externally applied magnetic field. Our calculations closely follow those of [8,9] and will be published in full detail elsewhere. In particular, we have used crystal field parameter set 2 of [8], and a quadrupolar constant $G^\delta = 130$ mK.

The order parameter (OP), ϵ^δ, is proportional to the expectation value of the quadrupole operator $Q_{xy} = \langle P_{xy}\rangle$,

$$\epsilon^\delta = \frac{B^\delta}{C_0^\delta}Q_{xy}, \quad (2)$$

where $P_{xy} = \frac{1}{2}(J_xJ_y + J_yJ_x)$[20]. The coefficient $B^\delta/C_0^\delta = 13.9 \times 10^{-4}$ was determined from the zero-field, low-temperature value of the spontaneous deformation ϵ^δ.

We first consider the influence of the applied magnetic field on the quadrupole moment Q_{xy}. Two effects must be taken into account: Changes in the magnitude of the distortion will result in variations of the splitting between the pairs of peaks, whereas (for a given grain) the preferential population of domains with positive or negative distortion will lead to a magnetically induced texture that manifests itself in a shift of spectral weight from one partner to the other.

A magnetic field along the c axis leads to a nonvanishing expectation value of $\langle J_z\rangle$ in competition with the OP. A magnetic field along a_o or b_o, on the other hand, will induce a magnetization $\langle J_x \pm J_y\rangle$ along the corresponding axis. Above the JT transition a magnetostrictive orthorhombic distortion of δ-symmetry is induced. In the ordered state, $T < T_Q$, however, one has to distinguish between a field applied along a_o and b_o: Along the two axes, the susceptibility will be of slightly different value, thus breaking the degeneracy of $\pm\epsilon^\delta$. Crossing the phase boundary in the presence of such a magnetic field will then lead to the preferential population of one of these domains. Fields along the $[110]_o$ directions should lead to a distortion with γ-symmetry (B_{1g}-type), as observed in $DyVO_4$ [21,22]. Finally, if the external field is applied along an arbitrary direction, then both δ and γ strains are induced

simultaneously, lowering the symmetry of the crystal to monoclinic. Fortunately, the γ magnetostrictive distortion in $TbVO_4$ is 2 orders of magnitude smaller than the δ distortion and can therefore be neglected.

Typical theoretical results for the (311) diffraction peak at $T = 7.5$ K and 39 K are shown in Fig. 2. The (311) partner of the (311)/(131) pair corresponds to a positive quadrupole moment, $Q_{xy} > 0$ [see Eq. (1)].

At $T = 39$ K $> T_Q$ there is no spontaneous quadrupole moment at $H = 0$. For azimuthal angles ψ below $\approx 22°$ a positive quadrupole moment is induced, whereas for larger azimuthal angles the induced quadrupole moment is negative, i.e., corresponding to the (131) partner. We thus expect the magnetic field to induce a magnetoelastic splitting with unequal domain populations of $\approx 33\%$ $Q_{xy} > 0$ [contributing to the (311) diffraction peak]) and $\approx 67\%$ $Q_{xy} < 0$ [contributing to the (131) diffraction peak] when averaging over the full interval (0–360°).

At $T = 7.5$ K $< T_Q$ the situation is different: A sizable spontaneous quadrupole moment is present, and in a zero-field cooled sample domains with positive and negative Q_{xy} will be populated almost equally. Upon applying an external field the quadrupole moment is reduced, and the degeneracy of $\pm Q_{xy}$ is lifted, so that (depending on their azimuthal angle) domains may invert their quadrupole moment. This transition is first order and therefore subject to pinning on defects, grain boundaries, surfaces, and elastic interactions between twinned domains [13].

The calculated dependences $Q_{xy}(H)$ for fixed T and different azimuthal angles ψ allow us to simulate the x-ray powder diffraction data. For the (202)/(022) pair the values were averaged over the interval $0° < \psi < 180°$ since the twofold symmetry persists. For the (311)/(131) pair the averaging was performed over $0° < \psi < 360°$. The parameters of the resolution function were fitted to the experimental data at $T > T_Q$ and $H = 0$. Different parameter sets were used for the (311)/(131) and (202)/(022) pairs, and the intensity parameter had to be adjusted to match the data at low temperature and high field.

At $T > T_Q$, calculations for the (202)/(022) pair adequately reproduce the almost symmetric splitting of the line by the magnetic field observed in the data (Fig. 3). The calculated magnitude of the splitting, however, is $\approx 25\%$ larger than the experimental one (Fig. 4). The origin of this discrepancy remains unclear. In particular, it does not seem to be related to the value of the interaction parameters used in the calculations since the value of the spontaneous splitting at $H = 0$ is correctly described (Fig. 4). Similar deviations between theory and experiment are observed at the (311)/(131) pair. Calculations describe the shape of the (311) line in different fields: the intensity ratio for two components of the split peak is about 1:2. But again the calculated value of the splitting is larger than the experimental one by about 25% (see Fig. 3). The OP may be decreased by sample heating, e.g., due to the magnetocaloric effect. A reasonable temperature increase of about 8–10 K, however, cannot fully explain the observed discrepancy.

The experimental observations at $T > T_Q$ and $H = 30$ T are well described by our calculations when the coefficient B^δ/C_0^δ is reduced by 25%; this value, however, is too small for the spontaneous deformation. This may be interpreted as the variation of the quadrupolar constant G^δ under high magnetic field, as was observed for the quadrupolar constant G^γ of $DyVO_4$ and considered within an improved "compressible Ising model" [22,23]. However, for $TbVO_4$ no dependence of G^δ was observed when the OP increases as the temperature decreases, and its low field behavior is described adequately by the mean-field theory [4].

For the quadrupole ordered phase the results of the numerical calculations for the (202) and (311) peaks are compared with the experimental data in Fig. 3. For both peaks the averaging were performed for two domains (ϵ^δ and $-\epsilon^\delta$) for $0 < \psi < 360°$, in steps of $\Delta\psi = 5°$. For the (202)/(022) pair the calculations do not reveal a noticeable decrease of the splitting under external field of 30 T, while

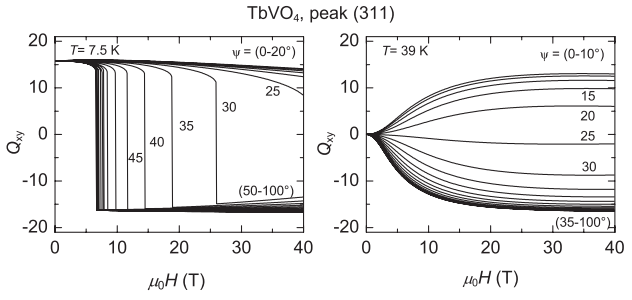

FIG. 2. Calculated dependence of the quadrupole moment Q_{xy} on the external magnetic field for different azimuthal angles in the interval (0–100°) at the diffraction peak (311). Left: $T = 7.5$ K, Right: $T = 39$ K.

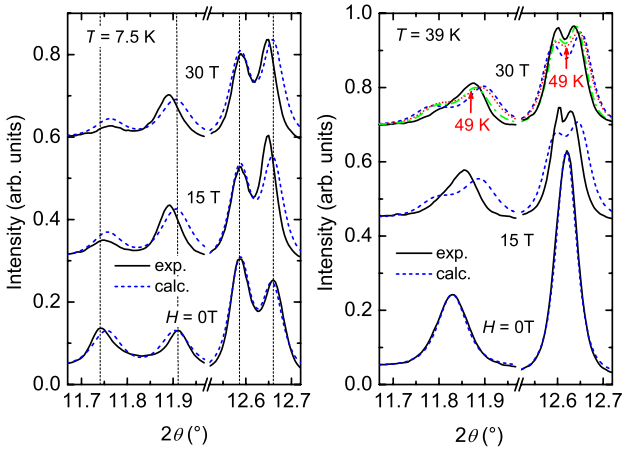

FIG. 3 (color online). Comparison between calculated and measured spectra for different temperatures and fields. Left: $T = 7.5$ K. Right: $T = 39$ K. At $T = 39$ K and 30 T, the dotted curve (in red) corresponds to the calculations including the magnetocaloric effect, and the green line to the calculations with the coefficient B^δ/C_0^δ reduced by 25%.

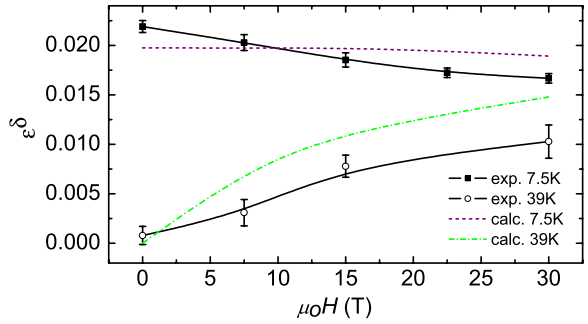

FIG. 4 (color online). Average order parameter as a function of applied magnetic field for selected temperatures. Continuous lines: Experimental data. Dashed lines: Theory.

for the (311)/(131) pair a small shift is expected for the low-angle component.

We examined, and refuted, several possible explanations for the discrepancy between the theoretical and experimental results. First, we ascertained that various weak pair interactions (bilinear, quadrupole of γ-, α-, and ϵ- symmetry) which were omitted in our calculations do not change the results noticeably. Then we estimated the effect of the sample heating due to the magnetocaloric effect in our experiment. In the adiabatic regime, the temperature change is large enough (about 25 K at 7.5 K) for the magnetic field orientation close to the easy magnetization axis. Additional studies are necessary to elucidate the influence of the magnetocaloric effect in our experiments.

In summary, we have directly observed for the first time the effect of magnetic fields on the Jahn-Teller distortion of $TbVO_4$, and compared the experimental data to a detailed mean-field theory. Because of the polycrystalline nature of the sample and its strong MC anisotropy the calculated spectra had to be averaged over all possible orientations of the powder grains relative to the applied magnetic field. The applied magnetic field was found to influence both the magnitude of the OP, as observed in the splitting of the (311)/(131) and (202)/(022) pairs of Bragg peaks, and the relative domain populations, reflected in the intensity ratio between the partners of a pair. Our theory is in qualitative agreement with the experimental results, even though small quantitative discrepancies persist.

This new technique was found to be a powerful tool to study JT systems, and allows us to observe new aspects of magnetic behavior of the classical and well studied JT compound $TbVO_4$. These high magnetic field data may be used both to revise known theoretical models and to develop new, improved ones.

The authors acknowledge the NWO/FWO Vlaanderen and ESRF for granting the beamtime for these experiments, and thank the staff of DUBBLE CRG and the ESRF for help in setting up these experiments. We thank M. Nardone, J. Billette, and A. Zitouni for their excellent work on the pulsed field coil and cryostat. Work at the Ames Laboratory was supported by the Department of Energy, Basic Energy Sciences under Contract No. DE-AC02-07CH11358. Z. A. K. acknowledges financial support from the RFBR (Project No. 07-02-01043). Part of this research was funded by the ANR (No. ANR-05-BLAN-0238) and EuroMagNet (EU Contract No. 506239).

[1] E. Dagotto, *Nanoscale Phase Separation and Colossal Magnetoresistance: The Physics of Manganites and Related Compounds*, Springer Series in Solid-State Sciences Vol. 136 (Springer, New York, 2003).
[2] N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, and S.-W. Cheong, Nature (London) **429**, 392 (2004).
[3] L. C. Chapon, G. R. Blake, M. J. Gutmann, S. Park, N. Hur, P. G. Radaelli, and S.-W. Cheong, Phys. Rev. Lett. **93**, 177402 (2004).
[4] G. A. Gehring and K. A. Gehring, Rep. Prog. Phys. **38**, 1 (1975).
[5] B. W. Mangum, J. N. Lee, and H. W. Moos, Phys. Rev. Lett. **27**, 1517 (1971).
[6] J. Sivardière and M. Blume, Phys. Rev. B **5**, 1126 (1972).
[7] J. Sivardière, Phys. Rev. B **6**, 4284 (1972).
[8] A. A. Demidov and N. P. Kolmakova, Physica (Amsterdam) **363B**, 245 (2005).
[9] Z. A. Kazei, V. V. Snegirev, J.-M. Broto, and H. Rakoto, JETP Lett. **82**, 609 (2005).
[10] E. Pytte, Phys. Rev. B **9**, 932 (1974).
[11] R. T. Hartley, C. H. Perry, and W. Richter, J. Phys. C **10**, L187 (1977).
[12] V. I. Kut'ko and M. I. Kobets, Czech. J. Phys. **46**, Suppl. 5, 2555 (1996).
[13] K. Kirschbaum, A. Martin, D. A. Parrish, and A. A. Pinkerton, J. Phys. Condens. Matter **11**, 4483 (1999).
[14] Y. Matsuda, Y. Ueda, H. Nojiri, T. Takahashi, T. Inami, K. Ohwada, Y. Murakami, and T. Arima, Physica (Amsterdam) **346–347B**, 519 (2004).
[15] Y. Narumi, K. Kindo, K. Katsumata, M. Kawauchi, C. Broennimann, U. Staub, H. Toyokawa, Y. Tanaka, A. Kikkawa, and T. Yamamoto *et al.*, J. Synchrotron Radiat. **13**, 271 (2006).
[16] P. Frings, J. Vanacken, C. Detlefs, F. Duc, J. E. Lorenzo, M. Nardone, J. Billette, A. Zitouni, W. Bras, and G. L. J. A. Rikken, Rev. Sci. Instrum. **77**, 063903 (2006).
[17] W. Bras, I. P. Dolbnya, D. Detollenaere, R. van Tol, M. Malfois, G. N. Greaves, A. J. Ryan, and E. Heeley, J. Appl. Crystallogr. **36**, 791 (2003).
[18] S. H. Smith and B. M. Wanklyn, J. Cryst. Growth **21**, 23 (1974).
[19] B. M. Wanklyn, J. Cryst. Growth **43**, 336 (1978).
[20] Note that for consistency with the existing literature [8,9] we have defined the quadrupole operator P_{xy} in the high-temperature, tetragonal coordinate system. In the low-temperature, orthorhombic basis $\epsilon^\delta \propto \langle O_2^2 \rangle$, with $O_2^2 = J_x^2 - J_y^2$.
[21] Z. A. Kazei, N. P. Kolmakova, and O. A. Shishkina, Physica (Amsterdam) **245B**, 164 (1998).
[22] A. A. Demidov, Z. A. Kazei, N. P. Kolmakova, J.-M. Broto, and H. Rakoto, Phys. Rev. B **70**, 134432 (2004).
[23] J. H. Page, S. R. P. Smith, D. R. Taylor, and R. T. Hartley, J. Phys. C **12**, L875 (1979).