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# Magnetostriction of rare earth double tungstates

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**Abstract.** The isothermal, longitudal and transverse magnetostriction of rare earth double tungstates $KDy(WO_4)_2$, $KHo(WO_4)_2$ and $RbNd(WO_4)_2$ has been measured at low temperatures along the crystallographic axes in a magnetic field up to 12 T. The measurements have been performed by the strain gauge method on single crystals. For all three axes, we observed anomalies connected to the structural phase transitions induced by a collective Jahn–Teller effect or by strong external field at temperatures near a spontaneous structural phase transition of Jahn–Teller nature. It was shown that all the studied phase transitions are of first order. The magnetostriction measurements in rare earth double tungstates are important and interesting, since: (i) in these objects, there is a Jahn–Teller spontaneous structural transition at low temperatures; (ii) information on the behaviour of an elastic subsystem in these samples is necessary for understanding the mechanism of this transition under the influence of an external magnetic field applied along the crystallographic axes; (iii) it allows us to form a conclusion on the anisotropy of the studied phenomenon.

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## Contents

## 1. Introduction

It is generally accepted that Jahn–Teller ions are strongly coupled to the lattice. The orbital degeneracy leads to a variety of instabilities such as structural or magnetic phase transitions and is responsible for the strong magnetoelastic coupling. As a rule, structural instabilities and resulting structural phase transitions induced by the collective Jahn–Teller effect take place in high-symmetry crystals [1]. However, it has been found experimentally, in the rare earth double tungstates, that the collective Jahn–Teller effect [2]–[4] exists also in low symmetry systems whose ground state consists of a system of closely spaced energy levels. In this case, the structural phase transitions occur as a result of pseudodegeneracy of the ground state levels: such a situation exists in monoclinic double tungstate $ARe(WO_4)_2$ crystals (where Re = rare earth, A = K, Rb). Double tungstate crystals are very interesting hosts for rare earth ions for realizing up-conversion laser output [5, 6]. The strong crystal field–ion interaction suggests that these materials may be sensitive to the applied stress, which may affect the spin configuration of the sample due to magnetoelastic interaction. In this paper, we report the studies of magnetostriction in $KRe(WO_4)_2$ (Re = Dy, Ho) and $RbNd(WO_4)_2$ single crystals. These studies are expected to confirm the strong ion–lattice coupling in these compounds and the Jahn–Teller mechanism of the observed structural phase transitions.

## 2. Samples and experimental details

The rare earth double tungstates are characterized by the space group C2/c [7, 8]. The unit cell contains four formula units. All four rare earth atoms are magnetically equivalent [2]. In the unit cell, the $Re^{3+}$ ions are arranged in two chains parallel to the [1 0 1] direction. The distance between the neighbouring ions inside the chain is equal to about 4 Å. The chains are shifted relative to each other by a half-period along the *b*- and *c*-axes. The growth procedure of large-sized high-quality single crystals, using the so-called modified Czochralski method (TSSG), is described in detail in [9, 10].

Magnetostriction was measured with a strain gauge used as a dilatometer [11]. We have used strain gauges from a wire (from the Central Aerohydrodynamic Institute, Russia) specially designed for cryogenic measurements in strong magnetic fields. One of the strain gauges was fixed onto the surface of the investigated sample and the second was glued onto quartz by polymer glue (Russia trade specification BF-2). The active grid area of the gauge was about $1.5 \times 5\,\mathrm{mm}^2$.

The sample length change was measured by gauge resistance changes using a resistance bridge. Two identical strain gauges were used in two arms of a 10 mA bridge supplied by direct current (dc). The resistance of the strain gauges was about 100 Ω. The sensitivity of our sensor was equal to $5 \times 10^{-7}$. The instrumental error of the determined magnetostriction value was about 10%.

To exclude the influence of internal strains appearing at the interface, we balanced the resistance bridge at each required temperature and only then switched on the external magnetic field and measure the signal which is proportional only to the magnetostriction of the sample. The experimental error for $T$ is about 0.1 K.

To characterize the behaviour of the tensor-sensor in different magnetic fields and at various temperatures, the magnetic field dependent magnetostriction at constant temperature was determined. This dependence is smooth.

The measurements were performed using a Cryogenics (Cryogenic Limited, London, UK) high field superconducting magnet system with a maximum attainable field of 12 T at 4.2 K. Above 4.2 K, the sample was cooled by helium vapour flow.

In this paper, we present for the first time the results of magnetostriction investigation of rare earth double tungstates (the magnetostriction of terbium molybdate was studied in [12]). The measurements of magnetostriction of the $KDy(WO_4)_2$ double tungstate single crystal were performed in an external magnetic field parallel to the $a$-, $b$- or $c$-axes of the monoclinic cell over a temperature range from 4.2 to 16.8 K. The two samples measured were cut from a large single crystal and had the shape of plates with dimensions $3\times5\times1$ mm$^3$. A strain gauge placed onto the $3\times5$ mm$^2$ surface of the sample measured the change of the longest sample dimension.

## 3. Magnetostriction

The measured magnetostriction was defined as $\lambda = (l(\mathrm{H}) - l(0))/l(0)$, where $l(\mathrm{H})$ is the field-dependent sample length. In the temperature interval from 7.5 to 16.8 K and in the external magnetic field up to 11 T, all the magnetostriction curves are smooth, which is evidence for the lack of structure changes in the investigated crystal in this temperature and magnetic field range.

The isotherms of magnetostriction recorded at $T = 4.2$ K and $T = 6.5$ K have an anomalous character independent of the magnetic field and measured deformation directions.

In figure 1, the isotherm of longitudinal magnetostriction along the $b$-axis measured in the magnetic field up to $H = 5.49$ T at $T = 4.2$ K is shown. The magnetostriction is seen to be positive. In low magnetic fields, the magnetostriction curve can be well approximated by a straight line. The magnetostriction decreases sharply in magnetic field $H_{\mathrm{cr}} = 3.6$ T which is accompanied by a relative change of the sample size along the $b$-axis of about $\Delta b/b = -7.8 \times 10^{-6}$. After the jump down, the magnetostrictive curve continues to increase linearly with the same slope up to $H = 5.49$ T. When the magnetic field decreases, the magnetostriction decreases nearly linearly down to the field $H = 0.6$ T. On further decreasing the magnetic field down to $H = 0$, the crystal size along the $b$-axis remains constant. The lack of magnetostriction jump with decreasing field means that the performed cycle with change of magnetic field up and then down is accompanied by an appearance of permanent crystal strains along the $b$-axis, $\Delta b/b = -8.1 \times 10^{-6}$. After reversal of the magnetic field direction, the magnetostriction curve was recorded when the field was increased and then again was decreased to zero. One should note the absence of any anomalies in the magnetostrictive curves. The obtained curves practically coincide.

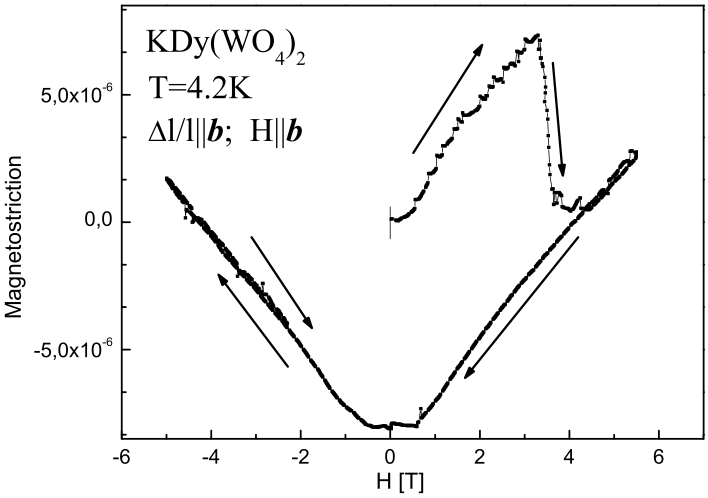

**Figure 1.** Magnetostriction of KDy(WO$_4$)$_2$ for $H||b$, $\Delta l||b$ at 4.2 K.

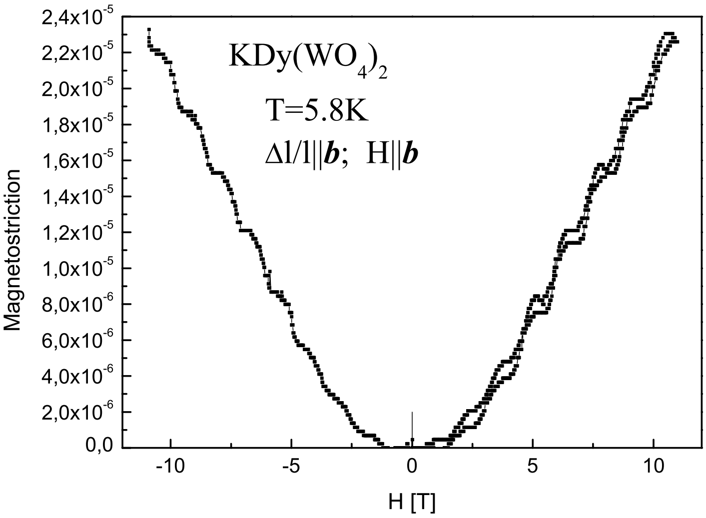

**Figure 2.** Magnetostriction of KDy(WO$_4$)$_2$ for $H||b$, $\Delta l||b$ (at 5.8 K, up to 11 T).

In figure 2, the magnetostriction along the $b$-axis at $T = 5.8$ K measured when the magnetic field was changed from $H = -11$ T to $H = +11$ T and then again to $-11$ T (the total loop) is shown. Any jumps of magnetostriction are absent; however, some characteristic steps on the magnetostriction curves are observed with both increasing and decreasing magnetic field. These magnetostriction steps show some hysteretic behaviour.

Along with the longitudinal magnetostriction along the $b$-axis, the transverse magnetostriction was measured at $T = 4.2$ K. The magnetic field was directed along the $b$-axis and the magnetostriction was studied along the $a$-axis. In figure 3, the recorded magnetostriction curve is shown. One can see that the main peculiarities of this curve are very similar to that shown in figure 1. When the increasing magnetic field reaches some critical value, a jump down of magnetostriction takes place, while a decrease in the magnetic field is not accompanied by any anomalies. Hence, on reversal to zero magnetic field, the sample is in the strain state. The

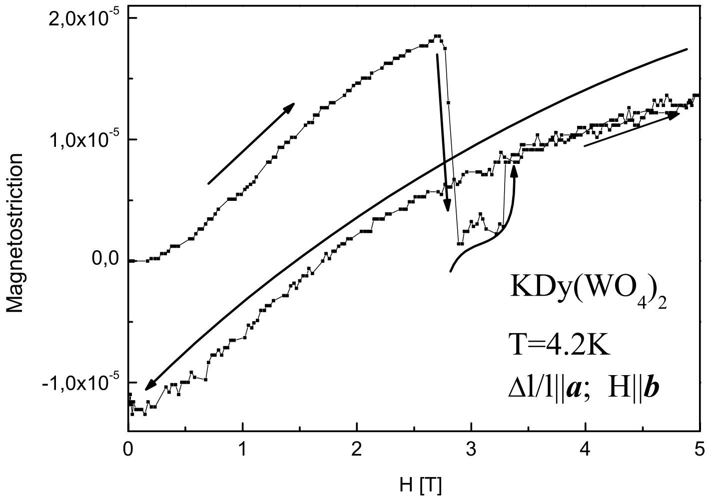

**Figure 3.** Magnetostriction of KDy(WO$_4$)$_2$ for $H||b$, $\Delta l||a$ at 4.2 K.

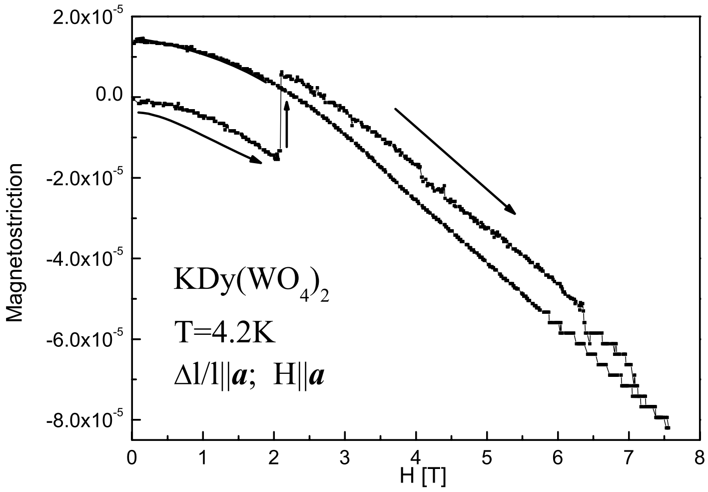

**Figure 4.** Magnetostriction of KDy(WO$_4$)$_2$ for $H||a$, $\Delta l||a$ at 4.2 K.

remanent strain along the *a*-axis is negative, and its value, $\Delta a/a = -12.9 \times 10^{-6}$, is higher than the remanent strain value along the *b*-axis. Unlike the longitudinal case, the field dependence of the relative strains along the *a*-axis has strongly non-monotonic character. Some differences between the magnetic field values at which the jumps of magnetostriction occur (see figures 1 and 3) are probably caused by the fact that the measurements have been performed on different samples. It seems that the process in the magnetic field directed along the *b*-axis, which is accompanied by the observed magnetostriction anomaly, has strong field direction dependence. It should be emphasized that, in both cases, the anomalies observed have a sharp character.

It was interesting to clarify whether the magnetic field directed along other axes than the *b*-axis has also an effect on the magnetic properties of KDy(WO$_4$)$_2$. Therefore, the magnetostriction for different magnetic field geometries was measured. In figure 4, the longitudinal magnetostriction along the *a*-axis as a function of magnetic field at $T = 4.2$ K when the magnetic field was also directed along the *a*-axis, is shown. It is seen that, unlike the case of

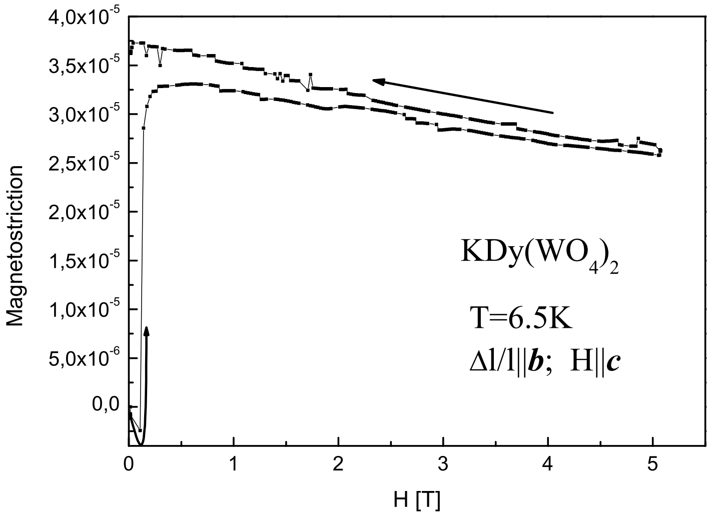

**Figure 5.** Magnetostriction of $KDy(WO_4)_2$ for $H||c$, $\Delta l||b$ at 6.5 K.

$H||b$, an increase in magnetic field is accompanied by sample shortening and the magnetic field dependence of magnetostriction is strongly nonlinear. As in the case of $H||b$, when the increasing magnetic field reaches some critical value, the smooth trace of the magnetostriction is disturbed by a jump down with the strain of $\Delta a/a = +17.8 \times 10^{-6}$. A decrease in external magnetic field was expected not to be accompanied by any anomaly. In zero field, the sample has a remanent strain value of $+17.8 \times 10^6$. The value of the critical field $H||a$, in which the magnetostriction jump was observed, was equal to 2.04 T at $T = 4.2$ K.

In figure 5, the transverse magnetostriction of $KDy(WO_4)_2$ single crystal at $T = 6.5$ K, when the external magnetic field was directed along the $c$-axis and the strains were measured along the $b$-axis, is shown. It is seen that a smooth magnetostrictive curve recorded as the field increases is also disturbed by a sharp anomaly characterized by the strain $\Delta b/b = +31.1 \times 10^{-6}$. In this case, the jump up is observed in a relatively weak magnetic field, $H \sim 0.1$ T. A further increase in magnetic field is accompanied by a linear decrease of the sample size along the $b$-axis with a small inclination relative to the $x$-axis. A decrease in magnetic field down to zero allowed us to evaluate the sample permanent strain along the $b$-axis which is equal to $\Delta b/b = +32.2 \times 10^{-6}$.

The comparison of the magnetostriction measurements results of the $KDy(WO_4)_2$ single crystal for $H||b$, $H||a$ at $T = 4.2$ K and for $H||c$ at $T = 6.5$ K allows us to conclude that the magnetostriction jumps are found for all the crystallographic axes when the magnetic field increases after zero field cooling. The samples after the application of magnetic field are characterized by permanent strains along different axes (table 1).

The critical field values, at which the jumps of magnetostriction were found, are shown in table 2 for different field directions.

The data shown in tables 1 and 2 verify the anisotropic response of the $KDy(WO_4)_2$ single crystal to the application of external magnetic field. We found a large difference between the critical field values measured along different crystallographic axes; the smallest value of the critical field was found for $H||c$.

According to [2], the measurement results of heat capacity of the $KDy(WO_4)_2$ single crystal indicate the structural phase transition of the antiferrodistortion type at $T \sim 6.4$ K. The influence

**Table 1.** Magnetostriction of $KDy(WO_4)_2$.

| | $\Delta l/l$, $10^{-6}$ | |
|---|---|---|
| $H$ | $b$-axis | $a$-axis |
| $H\|\|b$ | $-8.1$ | $-12.9$ |
| $H\|\|a$ | – | $+17.8$ |
| $H\|\|c$ | $+32.2$ | – |

**Table 2.** Critical points on $H$–$T$ diagram for $KDy(WO_4)_2$.

| | $H$, $T$ | | |
|---|---|---|---|
| $T$ (K) | $H\|\|b$ | $H\|\|a$ | $H\|\|c$ |
| 4.2 | 2.7; 3.6 | 2.04 | – |
| 6.5 | – | – | 0.1 |

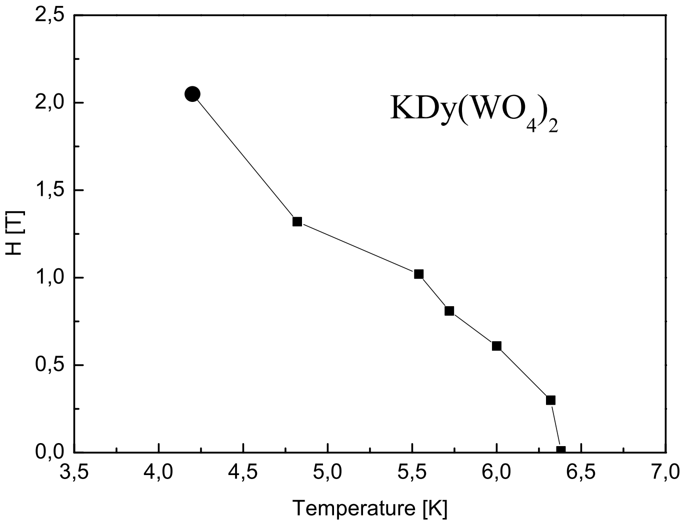

**Figure 6.** $H$–$T$ diagram of $KDy(WO_4)_2$ for $H||a$. The value (●) was evaluated from magnetostriction measurement, while the values shown by ■ were obtained from the specific heat measurement [2, 9].

of external magnetic field on this transition was studied and the magnetic $H$–$T$ phase diagram for $H||a$-axis was constructed (figure 6). This phase diagram allows us to conclude that the structural phase transition shifts towards low temperatures with increasing magnetic field. The data for $H||a$ (full circle in figure 6) and $H||c$ are in agreement with heat capacity measurement data (see figures 4 and 5). The data for $H||b$ verify that the magnetic field along the $b$-axis shifts the structural phase transition also, and at $T = 4.2$ K, the value of the critical field is of 2.7–3.6 T.

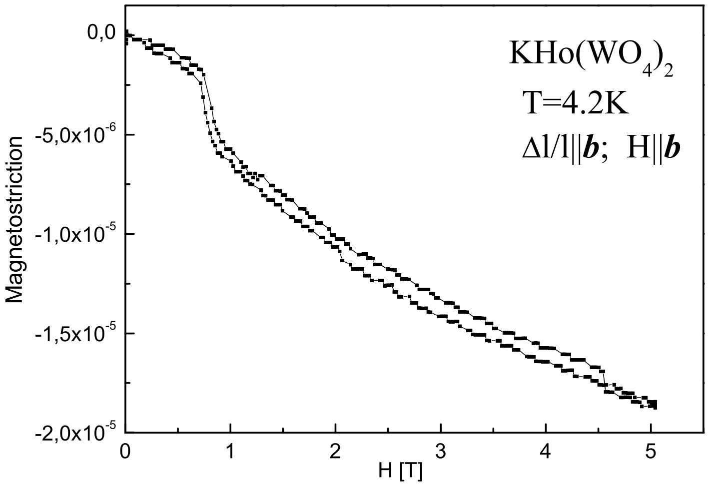

**Figure 7.** Magnetostriction of KHo(WO$_4$)$_2$ for $H||b$, $\Delta l||b$ at 4.2 K.

On the basis of heat capacity measurements in the magnetic field, the conclusion was made that the magnetic field induced phase transition is of second order. However, the magnetostriction measurements show that the anomalies observed are very sharp. This is characteristic of first order phase transitions.

The experimental curves with the magnetostriction anomalies presented in figures 1, and 3–5 were measured with both increasing and decreasing magnetic field. This behaviour was observed only at the first measurement at fixed temperature. The jumps are not observed at repeated measurements. The first magnetostriction curve can be reproduced after the sample heating to a temperature higher than that of the spontaneous structural phase transition ($T = 6.4$ K). We heated the samples up to liquid nitrogen temperature. Then the temperature was decreased down to the desired value. As a result, we obtained the anomalous magnetostriction curve. The inversion of magnetic field did not restore the initial state of the sample.

We explain the sharp changes of the magnetostriction by the lattice deformation as being the result of a spontaneous structural phase transition induced by external magnetic field at nearly the temperature of the Jahn–Teller structural phase transition.

The magnetostriction has been also measured for KHo(WO$_4$)$_2$ and RbNd(WO$_4$)$_2$ single crystals. Since data on magnetic properties of these crystals are not available, we have restricted ourselves to a brief presentation of the performed measurement results without their detailed analysis.

In figure 7, the magnetostriction for KHo(WO$_4$)$_2$ single crystal is presented. The field dependence of the longitudinal magnetostriction indicates the phase transition near $H = 1$ T at $T = 4.2$ K. In contrast to the Dy$^{3+}$ ion, the Ho$^{3+}$ ion ground state is a nonmagnetic singlet. The magnetic properties of these compounds are due to a singlet–singlet coupling. This is a reason for the specific behaviour of these compounds, in comparison with those having Kramers doublet as a ground state.

Another type of low-field phase transition was observed in RbNd(WO$_4$)$_2$ in the low temperature range (figure 8). It is similar to that observed for KDy(WO$_4$)$_2$ (figure 1). This first order phase transition is expected to be due to the collective Jahn–Teller effect, in analogy to KDy(WO$_4$)$_2$.

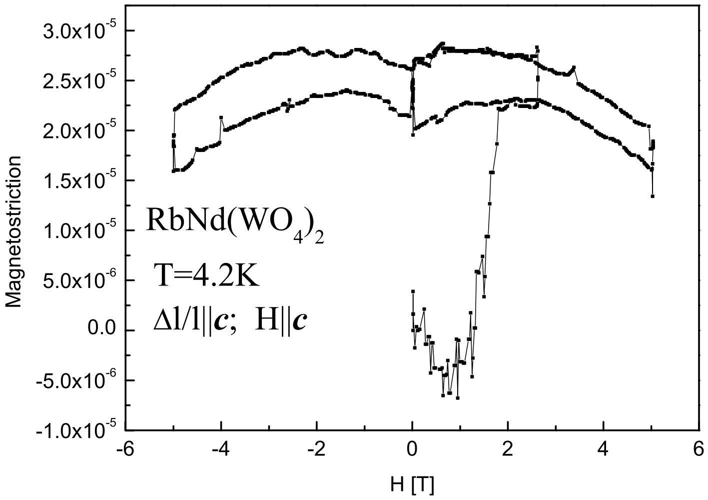

**Figure 8.** Magnetostriction of $RbNd(WO_4)_2$ for $H||c$, $\Delta l||c$ at 4.2 K.

## 4. Conclusion

The magnetostriction measured in rare earth double tungstates is shown to be very high (of the order of $10^{-4}$). These measurements confirm the hypothesis on the strong ion–lattice coupling in these crystals. The strong coupling between $Re^{3+}$ ions and the lattice is responsible for the first order structural phase transitions observed at low temperatures. The sharp jumps and hysteresis of magnetostriction near the transition points prove unequivocally the first order character of these transitions.

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