Published in final edited form as:

J Magn Magn Mater. 2016 February 15; 400: 125–129. doi:10.1016/j.jmmm.2015.07.066.

Magneto-elastic coupling across the first-order transition in the distorted kagome lattice antiferromagnet $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$

M.S. Henriques^{1,2,*}, D.I. Gorbunov^{1,3}, D. Kriegner⁴, M. Vališka⁴, A.V. Andreev¹, and Z. Matijević⁴

¹Institute of Physics, Academy of Sciences, Na Slovance 2, 182 21 Prague, Czech Republic

²CCTN, IST/CFMCUL, University of Lisbon, Nuclear and Technological Campus, P-2695-066 Bobadela, Portugal

³Dresden High Magnetic Field Laboratory (HLD-EMFL), Helmholtz-Zentrum Dresden-Rossendorf, D-01314 Dresden, Germany

⁴Charles University in Prague, Faculty of Mathematics and Physics, Department of Condensed Matter Physics, Ke Karlovu 5, 121 16 Prague, Czech Republic

Abstract

Structural changes through the first-order paramagnetic-antiferromagnetic phase transition of $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ at 7 K have been studied by means of X-ray diffraction and thermal expansion measurements. The compound crystallizes in a hexagonal crystal structure of $\text{Gd}_3\text{Ru}_4\text{Al}_{12}$ type ($P6_3/mmc$ space group), and no structural phase transition has been found in the temperature interval between 2.5 and 300 K. Nevertheless, due to the spin-lattice coupling the crystal volume undergoes a small orthorhombic distortion of the order of 2×10^{-5} as the compound enters the antiferromagnetic state. We propose that the first-order phase transition is not driven by the structural changes but rather by the exchange interactions present in the system.

Keywords

first-order transition; magneto-elastic coupling; thermal expansion; low-temperature X-ray diffraction

1 Introduction

Geometrical frustration leads to a competition of exchange interactions and usually has profound influence on the magnetism of the underlying material (for review see, e.g., Refs. [1,2]). Perhaps the most typical example is an antiferromagnet on a triangular lattice [3]. Triangles of antiferromagnetic interactions can be built into a crystal lattice from stacked triangular lattices, kagome lattices and lattices of corner-sharing tetrahedra. As a result of frustration, e.g., the kagome-lattice compound $\text{SrCr}_8\text{Ga}_4\text{O}_{19}$ enters a spin glass state [4,5]. Similarly, for pyrochlores $A_2B_2O_7$ where the spins are located on two lattices of corner-sharing tetrahedra, a spin-glass state was also found [6–8].

*Corresponding author: henriques@fzu.cz.

Recently, $R_3\text{Ru}_4\text{Al}_{12}$ (R is a rare-earth element or uranium) compounds have received much attention with respect to this matter. They crystallize in a hexagonal crystal structure of $\text{Gd}_3\text{Ru}_4\text{Al}_{12}$ type (space group $P6_3/mmc$). The R atoms occupy one crystallographic site ($6h$) and form planar triangular nets parallel to the (ab) plane (Fig. 1). The Ru atoms are located in two Wyckoff positions ($6g$ and $2a$) and Al in four ($12k$, $6h$, $4f$ and $2b$) [9–11]. The layers containing the Dy and Al atoms are planar, whereas those containing the Ru and Al atoms are slightly puckered. In addition, Fig. 1b also shows that the R atoms are arranged in distorted kagome nets. Due to this feature, geometrical frustration is likely one of the factors that influence electronic properties of $R_3\text{Ru}_4\text{Al}_{12}$.

$R_3\text{Ru}_4\text{Al}_{12}$ display different ground states depending on the R element. The compounds with $R = \text{La}$ and Ce were reported to be paramagnets [12]. $\text{Nd}_3\text{Ru}_4\text{Al}_{12}$ and $\text{Pr}_3\text{Ru}_4\text{Al}_{12}$ are ferromagnets [12], whereas the systems with $R = \text{Tb}$, Dy , Yb and U display an antiferromagnetic order [13–17]. Thus, the presence of a magnetic R element lifts the geometrical frustration, at least partially, and leads to long-range magnetic order.

Among the $R_3\text{Ru}_4\text{Al}_{12}$ compounds studied up to date, $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ represents a special case in the sense that the phase transition into the magnetically ordered state at the Néel temperature, $T_N = 7 \text{ K}$, is of first order [14], whereas the other materials display a second-order phase transition. The first-order type of the transition is evident from the temperature dependence of the specific heat (Fig. 2) that displays a sharp symmetrical anomaly at T_N . The antiferromagnet $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ exhibits a complex non-collinear magnetic structure, which can be regarded as a fingerprint of the geometrical frustration. A set of other unusual electronic properties were observed: field-induced magnetization jumps along all crystallographic directions, large positive magnetoresistance at the jumps and high magnetic entropy that can be seen in the inset in Fig. 2 from a comparison between $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ and the isostructural compound with non-magnetic Y.

The reason for the first-order transition of $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ remains unexplained. In the present work we study the crystal structure and thermal expansion of $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ through the first-order phase transition and put forward a possible reason for its first-order type. Several systems are known to exhibit pronounced anomalies in elastic properties at first-order phase transitions upon entering a magnetically-ordered state (see, e.g., Refs. [18–22]). The magnetoelasticity provides information whether changes in the crystal structure drive the formation of magnetic order or the establishment of long-range magnetic ordering distorts the crystal lattice.

2 Experimental part

A single crystal of $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ was grown by a modified Czochralski method in a tri-arc furnace on a water-cooled copper crucible under protective argon atmosphere. A piece of the single crystal was ground into a fine powder and loaded homogeneously onto the Cu cold finger. The XRD study was performed in Bragg-Brentano focusing geometry and θ – θ configuration (fixed sample) in a refurbished Siemens D500 diffractometer equipped with a He-cryostat. Cu radiation and a straight linear detector [23] were used to enable the fast recording of the temperature dependent XRD data. The sample temperature was measured

on the cold finger and thermal isolation was ensured by an evacuated sample environment and a cold shield covered by a metalized Mylar foil.

Diffraction patterns were collected upon cooling and heating in the temperature interval from 2.5 to 300 K in the angular range $5^\circ \leq 2\theta \leq 150^\circ$. Between 2.5 and 12 K, the data collection was performed in steps of 0.5 K. The temperature was stabilized at each step in order to keep the thermal equilibrium between the sample and its holder during the measurements. All the patterns were fully refined by the Rietveld method using the Jana2006 program [24]. As magnetoelastic effects are usually very small, the errors in our data analysis were minimized by considering the instrumental contribution to the profile width and shape of the diffracted peaks. To this end, the numerical parameters describing the line broadening and displacement were estimated from the fitting of the experimental patterns collected at room temperature on Si and LaB₆ powder standard materials supplied by the National Institute of Standards & Technology (NIST640d and NIST660b, respectively). Pseudo-Voigt peak-shape functions were used to fit the patterns. The background was refined using Legendre polynomials and the asymmetry of the diffractometer was accounted for by the Berar-Baldinozzi correction, which proved to be best when dealing with the refinement of the standards' data. The uncertainty in the determination of the lattice parameters was found to be 1×10^{-4} Å at 300 K.

The single crystal was oriented along the principal crystallographic directions by the back-scattered Laue diffraction. The thermal expansion of Dy₃Ru₄Al₁₂ along the [100], [120] and [001] axes was measured on an oriented parallelepiped-shaped single crystal of dimensions $1.23 \times 1.56 \times 1.58$ mm³. A Vienna-type microdilatometric capacitance cell [25] was used with three terminal connections to the ultra-precision capacitance bridge (Andeen Hagerling 2500 A, 1 kHz). The method provides a high resolution and makes it possible to cover a large temperature range (2–300 K) in one measurement. The cell was inserted into a PPMS-14 system (Quantum Design).

3 Results and Discussion

3.1 Low temperature X-ray diffraction

The XRD patterns collected at 300 and 3 K for Dy₃Ru₄Al₁₂ are displayed in Fig. 3. The X-ray data were refined into the hexagonal space group $P6_3/mmc$ yielding the lattice parameters $a = 8.7764$ Å and $c = 9.5291$ Å at room temperature and $a = 8.7488$ Å and $c = 9.5002$ Å at 3 K. The final Rietveld refinement factors were $R_p = 2.06$ and 2.43 , $R_{wp} = 3.49$ and 3.75 at 300 K and 3 K respectively. The lattice parameters found at room temperature compare well to those reported previously [14]. As can be seen in the insert of the upper panel in Fig. 3, besides those of Dy₃Ru₄Al₁₂ there are a few small unindexed Bragg reflections attributed to the Cu sample holder, resulting in positive differences between the observed and calculated patterns (blue line at the bottom of both panels). There is no evidence of any structural change or lowering of the space group symmetry in the whole temperature interval. A clear proof of it is given by Fig. 4, which shows the evolution of the X-ray patterns taken between 3 and 300 K upon heating the sample. In the planar projection of the peak positions as a function of temperature it can be observed that for $2\theta \approx 135^\circ$ the

peaks bend slightly to lower angles for temperatures above 50 K as a manifestation of the natural lattice expansion with increasing temperature.

The changes of the lattice parameters, a and c , and the volume V of the unit cell as a function of temperature are depicted in Fig. 5. For temperatures above 8 K, the XRD shows normal expansion of the lattice up to 300 K (Fig. 5a and 5b). Below 6 K the lattice parameters and the volume of $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ are practically constant, within the error of the technique. By contrast, around the Néel temperature of $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$, $T_N = 7$ K, a small step is seen in both lattice constants, being reflected more noticeably in the volume. It is worth noting that the step is found in the structural parameters on heating and cooling (Fig. 5c and 5d), best observed in the temperature evolution of the volume between 2.5 and 12 K (Fig. 5d). Nevertheless, it must be emphasized that all the data are affected by non-negligible error bars since for the X-ray diffraction measurements we assumed that the minimum change in the lattice constants that can be detected is 1×10^{-4} Å. The c/a ratio remains practically constant in the whole temperature range, which is consistent with the conservation of the hexagonal symmetry. Additionally, the shortest distances between Dy atoms in the unit cell, $d_{\text{Dy-Dy}}$, are plotted in the inset of Fig. 5b as a function of temperature. The distance between the Dy atoms decreases steadily when lowering the temperature down to 10 K and exhibits a minimum at around 6 K.

3.2 Thermal expansion

The upper panel in Fig. 6 presents the temperature dependence of the thermal expansion, $(\Delta l/l)_i$, of the $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ single crystal along the lattice directions $i = [100]$, $[120]$ and $[001]$. $\Delta l/l$ displays pronounced anisotropy, similarly to other physical properties [14]. All relative length changes exhibit a step-wise contraction with decreasing temperature around 7 K. Overall, the thermal expansion is hysteretic between cooling and heating, which is characteristic of first-order phase transitions. The thermal expansion jump is approximately two times larger along $[100]$ than along the other two directions.

The difference between $\Delta l/l_{[100]}$ and $\Delta l/l_{[120]}$ gives information about an orthorhombic distortion due to the magnetic ordering. The appearance of the distortion is not surprising since the Dy magnetic moments have projections onto the three orthogonal axes [14]. Above T_N the crystal is hexagonal, therefore, the ratio of the lattice dimensions in orthorhombic coordinates along $[120]$ (“ b ”) and $[100]$ (“ a ”) is $\sqrt{3}$. Since “ a ” drops by 3×10^{-5} and “ b ” by 1×10^{-5} , the ratio becomes larger by 2×10^{-5} , which is a measure of the orthorhombic distortion induced by magnetostriction. Such a small value of the orthorhombic distortion is likely due to the large angle between the Dy magnetic moments and the basal plane as follows from the neutron-diffraction study [14].

It follows that the relative volume change, $\Delta V/V = (\Delta l/l)_{[100]} + (\Delta l/l)_{[120]} + (\Delta l/l)_{[001]}$, is estimated to be 6×10^{-5} at the phase transition. by our XRD data is higher, of the order of 1×10^{-4} . The discrepancy might be related to the different accuracy of the two methods we used, although the agreement between the two values is rather good.

The coefficient of linear thermal expansion, $\alpha = (1/l)(dl/dT)$, along $[100]$ is shown in the lower panel of Fig. 6. It displays sharp maxima of about $6 \times 10^{-5} \text{ K}^{-1}$ at the phase transition

upon cooling and heating. The coefficients of linear thermal expansion are of the same order along the [120] and [001] directions (not shown for clarity of presentation). This finding might also be explained taking into account the non-collinear magnetic structure found for $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$, with magnetic moments projected along all the lattice directions [14].

3.3 Discussion

The present study has demonstrated well-defined anomalies in the lattice parameters and the thermal expansion of $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ through the first-order phase transition at the Néel temperature. The compound undergoes lattice contraction as the long-range antiferromagnetic order sets in at $T_N = 7$ K. No structural phase transition has been found, except a very small orthorhombic distortion due to anisotropic magnetostriction. It leads us to assume that the first-order transformation is driven either by the decrease of the inter-atomic Dy-Dy distances (see inset in Fig. 5b) without altering the symmetry of the crystal lattice or by exchange interactions present in the system.

Several systems are known to display first-order transitions from a magnetically disordered into an antiferromagnetic state that originate from magnetoelastic coupling [22,26]. Such transitions in Eu and in EuSn_3 were shown to be due to the strain-induced exchange interactions, although the relative thermal expansion at the phase transformation was found to be relatively low, $\sim 1 \times 10^{-4}$, for both systems [22,26]. A somewhat larger $\Delta l/l \sim 5.6 \times 10^{-4}$ was reported for the compound MnSe where the strong dependence of the net exchange interaction from the lattice parameters also plays the principal role [27]. For $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ the linear thermal expansion at the phase transformation was found to be several times lower (see Fig. 6) and its effect is probably too small to drive the first-order transition.

The exchange interactions might explain the transition more convincingly. A rather unusual feature of $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ is the large magnetic entropy, $S_{\text{mag}} = 95 \text{ J mol}^{-1} \text{ K}^{-1}$, that cannot be accounted for by the Dy atoms alone whose contribution should be $S_{\text{mag,Dy}} = 3R \ln(2J+1) = 69 \text{ J mol}^{-1} \text{ K}^{-1}$ (R is the gas constant, $J = 15/2$ is the quantum number of the total Dy momentum) [14]. The inset in Fig. 2 compares the temperature-linear terms for the specific heat of $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ and non-magnetic $\text{Y}_3\text{Ru}_4\text{Al}_{12}$. The additional contribution to S_{mag} of the compound with Dy is attributed to spin fluctuations that arise from the Ru subsystem. Although the Ru 4*d* electronic band is not expected to be spin-split, it may be involved in exchange interactions due to the polarization produced by the Dy 4*f* shells. Similar effects were reported for $R_3\text{Rh}$, $R\text{Ni}$ and $R\text{Ni}_2$ compounds where the *f-d* exchange interaction makes an additional contribution to the temperature-linear specific heat [28–35].

We propose that the Ru 4*d* electrons play the decisive role in the first-order phase transition at T_N of $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$. Typically, for such a system one would expect that the exchange interactions are of the Ruderman-Kittel-Kasuya-Yosida type. Their oscillatory long-range character arises due to the polarization coming from the Dy 4*f* shells of the 5*d* conduction electrons. Just as the Dy 5*d* band, the Ru 4*d* band is also polarized and maintains the exchange interactions among the Dy atoms. The higher the temperature, the lower the Dy 4*f* magnetic moment and the lower the polarization field produced on the conduction electrons. Under these circumstances, the first-order transition may occur if the Ru 4*d* polarization abruptly collapses at T_N . The instability of the Ru sublattice may be the driving force for the

first-order phase transformation at the antiferromagnetic-paramagnetic phase transition of $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$. In addition, the Al $3p$ states might be involved in the exchange interactions. In order to verify our assumptions, a microscopic technique is necessary such as X-ray magnetic circular dichroism.

A similar behavior is encountered in the $R\text{Co}_2$ compounds with $R = \text{Dy}$, Ho and Er that display a first-order ferrimagnetic-paramagnetic transition [18]. In the absence of the magnetic rare-earth component, no magnetic order exists within the Co sublattice as found, e.g., for YCo_2 [36]. The Co magnetic moment is induced by the exchange field coming from the magnetic R sublattice. The higher the rare-earth spin, the higher is the Co magnetic moment and the higher is the magnetic ordering temperature [18]. The polarized Co sublattice maintains the exchange interactions among the R atoms, and the disappearance of the Co magnetic moment destroys the long-range magnetic order in $R\text{Co}_2$.

4 Conclusions

Thermal expansion measurements and low temperature X-ray diffraction have been performed across the first-order paramagnetic-antiferromagnetic transition of the $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ compound. No indication of a structural phase transformation has been found, although the hexagonal crystal structure undergoes a small orthorhombic distortion of the order of 2×10^{-5} at the Néel temperature. The distortion is seen from an anisotropic step-wise lattice contraction with the overall volume effect of about 6×10^{-5} . Consequently, the distance between the nearest Dy atoms reaches an absolute minimum around the Néel temperature. As the magnitude of the structural changes at the phase transition might not account for its first order-type, we suggest that the phase transformation is driven primarily by exchange interactions sustained by the Ru $4d$ electronic band which is polarized by the Dy $4f$ moments.

Acknowledgements

The work was performed in MLTL (<http://mltl.eu/>), which is supported within the program of Czech Research Infrastructures (Project No. LM2011025). D.K. acknowledges the support of the Austrian Science Fund (FWF): J3523-N27 and Z.M. is grateful to the Czech Science Foundation (project 14-08124S).

References

- [1]. Ramirez, AP. Handbook of Magnetic Materials. Buschow, KHJ., editor. Vol. 13. Elsevier; Amsterdam: 2001. p. 423
- [2]. Greedan JE. J Alloys Comp. 2006; 408–412:444.
- [3]. Petrenko OA, Ritter C, Yethiraj M, McK Paul D. Phys Rev Lett. 1998; 80:4570.
- [4]. Ramirez AP, Espinosa GP, Cooper AS. Phys Rev Lett. 1990; 64:2070. [PubMed: 10041569]
- [5]. Keren A, Le LP, Luke GM, Wu WD, Uemura YJ, Ajiro Y, Asano T, Kuriyama H, Mekata M, Kikuchi H. Hyperfine Inter. 1994; 85:181.
- [6]. Gingras MJP, Stager CV, Raju NP, Gaulin BD, Greedan JE. Phys Rev Lett. 1997; 78:947.
- [7]. Dunsiger SR, Kiefl RF, Chow KH, Gaulin BD, Gingras MJP, Greedan JE, Keren A, Kojima K, Luke GM, MacFarlane WA, Raju NP, et al. Hyperfine Inter. 1997; 104:275.
- [8]. Zhou HD, Wiebe CR, Harter A, Dalal NS, Gardner JS. J Phys: Cond Matter. 2008; 20:325201.
- [9]. Gladyshevskii RE, Strusievicz OR, Cenxual K, Parthe E. Acta Cryst B. 1993; 49:474.
- [10]. Niermann J, Jeitschko W. Z Anorg Allg Chem. 2002; 628:2549.

- [11]. Bukhan'ko NG, Tursina AI, Malyshev SV, Gribov AV, Seropegin Yu D, Bodak OI. *J Alloys Comp.* 2004; 367:149.
- [12]. Ge W, Ohta H, Michioka Ch, Yoshimura K. *J Phys: Conf Ser.* 2012; 344:012023.
- [13]. Gorbunov DI, Henriques S, Andreev AV, Skourski Y, Dušek M. *J Alloys Compd.* 2015; 634:115.
- [14]. Gorbunov DI, Henriques MS, Andreev AV, Gukasov A, Petříček V, Baranov NV, Skourski Y, Eigner V, Paukov M, Prokleška J, Gonçalves AP. *Phys Rev B.* 2014; 90:094405.
- [15]. Nakamura S, Toyoshima S, Kabeya N, Katoh K, Nojima T, Ochiai A. *JPS Conf Proc.* 2014; 3:014004.
- [16]. Pasturel M, Tougait O, Potel M, Roisnel T, Wochowski K, Noel H, Tro R. *J Phys: Condens Matter.* 2009; 21:125401. [PubMed: 21817462]
- [17]. Tro R, Pasturel M, Tougait O, Sazonov AP, Gukasov A, Sulkowski C, Noel H. *Phys Rev B.* 2012; 85:064412.
- [18]. Duc NH, Hien TD, Brommer PE, Franse JJM. *J Phys F: Met Phys.* 1988; 18:275.
- [19]. Fujita A, Fujieda S, Fukamichi K, Mitamura H, Goto T. *Phys Rev B.* 2001; 65:014410.
- [20]. Pecharsky VK, Holm AP, Gschneidner KA Jr, Rink R. *Phys Rev Lett.* 2003; 91:197204. [PubMed: 14611610]
- [21]. Haskel D, Lee YB, Harmon BN, Islam Z, Lang JC, Srajer G, Mudryk Y, Gschneidner KA Jr, Pecharsky VK. *Phys Rev Lett.* 2007; 98:247205. [PubMed: 17677990]
- [22]. Mori A, Miura Y, Tsutsumi H, Mitamura K, Hagiwara M, Sugiyama K, Hirose Y, Honda F, Takeuchi T, Nakamura A, Hiranaka Y, et al. *J Phys Soc Japan.* 2014; 83:024008.
- [23]. Kriegner D, Matěj Z, Kužel R, Holý V. *J Appl Cryst.* 2015; 48:613. [PubMed: 25844084]
- [24]. Petříček V, Dušek M, Palatinus L. *Z Kristallogr.* 2014; 229:345.
- [25]. Rotter M, Müller H, Gratz E, Doerr M, Loewenhaupt M. *Rev Sci Instr.* 1998; 69:2742.
- [26]. Cohen RL, Hüfner S, West KW. *Phys Rev.* 1969; 184:263.
- [27]. Ito T, Ito K, Oka M. *Jpn J Appl Phys.* 1978; 17:371.
- [28]. Baranov NV, Inoue K, Michor H, Hilscher G, Yermakov AA. *J Phys: Cond Matter.* 2003; 15:531.
- [29]. Baranov NV, Michor H, Hilscher G, Proshkin A, Podlesnyak A. *J Phys: Cond Matter.* 2008; 20:325233.
- [30]. Abrahams SC, Bernstein JL, Sherwood RC, Wernick JH, Williams HJ. *J Phys Chem Solids.* 1964; 25:1069.
- [31]. Cyrot M, Lavagna M. *J Phys France.* 1979; 40:763.
- [32]. Talik E, Neumann M, Lebarski A, Winiarski A. *Physica B.* 1995; 212:25.
- [33]. Yano K, Umehara I, Sato K, Yaresko A. *Solid State Commun.* 2005; 136:67.
- [34]. Mizumaki M, Yano K, Umehara I, Ishikawa F, Sato K, Koizumi A, Sakai N, Muro T. *Phys Rev B.* 2003; 67:132404.
- [35]. Yano K, Tanaka Y, Matsumoto I, Umehara I, Sato K, Adachi H, Kawata H. *J Phys: Condens Matter.* 2006; 18:6891.
- [36]. Bleaney R. *Cobalt.* 1966; 33:201.

Fig. 1. Crystal structure of $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ (upper panel) and its projection onto the (ab) plane (lower panel). The larger atoms are the Dy atoms (orange), whereas Ru (light green) and Al (dark blue) are smaller.

Fig. 2.
Low-temperature specific heat of $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$. The inset shows the C_p/T vs. T^2 data for $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ and $\text{Y}_3\text{Ru}_4\text{Al}_{12}$.

Fig. 3. X-ray diffraction patterns of $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ at 300 K (upper panel) and 3 K (lower panel). The experimental patterns (red open symbols) are shown with the Rietveld calculated pattern (black line) and the difference profile (bottom blue line). The calculated Bragg positions for $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ are marked by the green vertical bars. The inset shows the diffraction pattern at 300 K in the angular range between 20 and 60 degrees.

Fig. 4. Projections of the peak positions as a function of temperature for the diffraction patterns of $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$ collected upon heating.

Fig. 5.

Temperature dependence of the lattice parameters, a and c , and the lattice volume, V , in the temperature intervals between 2.5 and 300 K (a and b) and between 2.5 and 12 K (c and d). The inset shows the temperature dependence of the nearest Dy-Dy distances.

Fig. 6. Temperature dependence of the linear thermal expansion along the [100], [120] and [001] directions (upper panel) and of the coefficient of linear thermal expansion along the [100] direction (lower panel) of $\text{Dy}_3\text{Ru}_4\text{Al}_{12}$.