Interplay between magnetic anisotropy and exchange interactions in rare-earth - transition-metal ferrimagnets

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Chapter 5

The magnetic anisotropy of DyCo_{10}V_{2}

The magnetic properties of the ferrimagnetic tetragonal compound DyCo_{10}V_{2} are characterized by the different temperature dependencies of the Dy- and the Co-sublattice moments. Below $T_C = 470$ K, the magnetic moments order parallel to the [001] direction. The Dy-sublattice moment grows strongly at lower temperatures, and magnetic compensation occurs at $T_{comp} = 118$ K. A spin reorientation occurs at 42 K, where the ordered moment rotates away from the [001] direction. This rotation is marked by an anomalous increase of the magnetic moment parallel to the [001] direction. Besides these effects, DyCo_{10}V_{2} shows a large and strongly temperature dependent coercivity at low temperatures. We performed magnetization and neutron-diffraction experiments on a single crystal to elucidate the magnetic properties of DyCo_{10}V_{2}. The results indicate that the coercivity is related to the occurrence of narrow Bloch walls. As the temperature approaches the compensation temperature, the coercivity diverges. An analysis of the temperature dependence of the magnetic moment around the spin-reorientation temperature was performed by means of the two-sublattice crystal-field model. This analysis indicates that higher-order crystal-field terms for the Dy moment account for both the spin-reorientation and the anomalous increase of the moment parallel to the [001] direction.
5. The magnetic anisotropy of DyCo$_{12}$V$_2$

5.1 Introduction

5.1.1 Investigations on polycrystalline YCo$_{12-x}$V$_x$ and DyCo$_{12-x}$V$_x$ compounds

Motivated by the search for new permanent-magnet materials, different researchers have focussed their attention on the compounds of composition YCo$_{12-x}$V$_x$. In reports by Jurczyk et al. [92,93], the compound YCo$_{10}$V$_2$ is reported to exhibit a Curie temperature of 611 K, a saturated magnetic moment at 77 K of 7.2 $\mu_B$/f.u., and an easy-plane type of anisotropy at room temperature. Further research by the same authors [94] made clear that there is a strong dependence of the Curie temperature and the saturation moment on the V content. With $x$ increasing from 1.6 to 3.5, the Curie temperature is reported to decrease from 710 K to below 77 K. At the same time, the saturation moment at 77 K decreases from about 9.85 $\mu_B$/f.u. to 0.29 $\mu_B$/f.u.. Easy-plane type of anisotropy was found for 1.6 $\leq x \leq$ 3.5.

In another report, by Brabers et al. [95], a Curie temperature of 428 K and a saturated moment of 6.8 $\mu_B$/f.u. at 4.2 K is found for YCo$_{10}$V$_2$. These values are considerably lower than those reported by Jurczyk et al. [92–94]. The strong composition dependence of the Curie temperature and the saturation magnetic moment was found also by Brabers et al. [95]. In this work, the Curie temperature was found to decrease from 660 K for $x = 1.7$ to 185 K for $x = 2.4$. The saturation moment at 4.2 K decreases from 8.8 $\mu_B$/f.u. for $x = 1.7$ to 3.8 $\mu_B$/f.u. for $x = 2.6$.

In a third report, by Zhang et al. [96], a Curie temperature of 657 K is reported for YCo$_{10}$V$_2$, and a spontaneous moment of 6.6 $\mu_B$/f.u. at 5 K. The easy magnetization direction at 300 K is reported to be in the basal plane.

Concerning the crystal structure, neutron-diffraction experiments have been performed on a sample of the compound YCo$_{9.6}$V$_{2.4}$ [11]. They revealed that the V atoms have a strong preference for the 8i crystallographic position in the ThMn$_{12}$-type of crystal structure.

Electronic-structure calculations have been performed on YCo$_{10}$V$_2$ [97]. These calculations yielded also magnetic moments. Two configurations for the two V atoms on the 8i crystallographic positions were considered, A ($\pm\alpha 00$) and B ($\alpha 00, 0\alpha 0$). These two configurations yield different results for the magnetic moments, 9.11 $\mu_B$/f.u. for A and 8.11 $\mu_B$/f.u. for B. We consider configuration B here, since it best reproduces the experimental results described above. Different Co moments were calculated to occur on the different crystallographic positions occupied by Co, with the 8i Co moment largest, 1.4 $\mu_B$, and 0.9 $\mu_B$ for the 8j position, and 0.8 $\mu_B$ for the 8f position. On the V and Y atoms induced moments were found, oriented antiparallel
5.1. Introduction

to the Co moments. The values are 0.3 $\mu_B$ for Y and 0.5 $\mu_B$ for V, which results in a moment of 0.9 $\mu_B$ on the 8i positions.

In a systematic study of RCo$_{12-z}$V$_z$ compounds by Brabers et al. [95], the compound DyCo$_{10}$V$_2$ was also included. For DyCo$_{10}$V$_2$, a Curie temperature of 442 K was found and magnetic compensation near 100 K. From high-field free-powder measurements, Brabers et al. deduce a intersublattice molecular-field coefficient $n_{\text{DyCo}}$ of value 5.5 T.f.u./$\mu_B$, leading to an intersublattice molecular-field coefficient of $J_{\text{DyCo}}/k_B = -8.8$ K. Furthermore, a Co-sublattice moment of 8.9 $\mu_B$/f.u. was derived for DyCo$_{10}$V$_2$, by taking the Dy-sublattice moment equal to the free-ion value of 10 $\mu_B$. This value for the Co-sublattice moment is anomalously large compared to the 6.8 $\mu_B$/f.u. found for YCo$_{10}$V$_2$.

Completely different properties of DyCo$_{10}$V$_2$ were reported by Jurczyk et al. [98]. They find a Curie temperature of 840 K and a saturation moment at 77 K of 7.9 $\mu_B$/f.u.. Furthermore, two spin-reorientations were found. At high temperatures, the magnetic moments were found parallel to the [001] direction. Near room temperature, a conical moment arrangement is found, and below 10 K the easy magnetization direction is in the crystallographic plane.

In a follow-up to the work of Brabers et al., Zhang et al. [99] made a more detailed investigation of the magnetic properties of DyCo$_{10}$V$_2$. They find that the easy magnetization direction of DyCo$_{10}$V$_2$ is parallel to the [001] direction at room temperature and report magnetic compensation near 120 K. Furthermore, a spin-reorientation transition is observed near 41 K, presumably to an easy-cone configuration. The authors conclude from this behavior that the anisotropy of DyCo$_{10}$V$_2$ is dominated by the Dy-sublattice anisotropy. Higher-order crystal-field terms are supposed to be responsible for the spin-reorientation near 41 K. From the shape of hysteresis loops measured on a field-aligned-powder sample, it is concluded that a large and strongly temperature dependent coercivity exists in DyCo$_{10}$V$_2$. In a later publication, Zhang et al. [100] describe the magnetization at low temperatures in terms of the occurrence of different types of particles in the samples.

Finally, Kuz'min et al. [15] performed density-functional electronic-structure calculations for ThMn$_{12}$-type compounds. They obtained values for the crystal field coefficients describing the anisotropy of the Dy sublattice in DyCo$_{10}$V$_2$. 
5.2 Experimental results

5.2.1 Sample preparation and characterization

A single-crystalline rod of DyCo$_{10}$V$_2$ of nominal composition was grown from the melt in the modified Czochralsky equipment at the FOM-ALMOS centre at the Van der Waals-Zeeman Instituut of the Universiteit van Amsterdam [53]. Samples cut from this rod were shown by x-ray diffraction to have the tetragonal ThMn$_{12}$-type of structure. Electron microscopy and electronprobe micro-analysis (EPMA) have shown that tiny parts on the periphery of the cut sample have a deviating, Co-rich, composition. For the present investigation, we will assume that the influence of these impurities is of minor importance. The composition of the main phase was found to be DyCo$_{10.12}$V$_{1.88}$, which is in good agreement with the nominal composition. For our measurements, several different samples were used. In view of the strong composition dependence of the magnetic properties, see above, they were characterized magnetically below room temperature and found to have the same properties.

5.2.2 High-temperature magnetic properties

In order to determine the Curie temperature of DyCo$_{10}$V$_2$ a measurement in the Faraday balance was performed. For this measurement a small piece from the single-crystalline rod was used. The measuring field was 0.1 T. The results are shown in Figure 5.1. The Curie temperature is taken as the temperature where the derivative of the magnetization as a function of temperature is minimal, shown in the inset. This leads to a Curie temperature of 470 (5) K, which is near the 442 K reported by Brabers et al. [95].

5.2.3 Neutron diffraction in zero field

For the neutron-diffraction experiment a small spherical sample of diameter 1.3 mm (mass ~ 9 mg) was cut. The crystal was characterized using the instrument E1 at the HMI, Berlin, configured as a two-axis diffractometer. The neutron wavelength was 2.42 Å. The sample was mounted with the [001] direction parallel to the measurement axis. We collected 11 independent (h00) reflections at 5, 50, 115, 300, and 500 K. Refinements based on the measured squares of the structure factors were performed by the program MAGLSQ of the Cambridge Crystallography Subroutine Library (CCSL) [67]. For the neutron-scattering lengths, the values $b_{\text{Dy}} = 1690$ fm, $b_{\text{Co}} = 249.0$ fm and $b_{\text{V}} = -38.2$ fm were used [65]. For the magnetic calculations,
5.2. Experimental results

Figure 5.1: High-temperature magnetization of DyCo$_{10}$V$_2$ as a function of temperature. The inset shows the derivative $\frac{dM}{dT}$, from which $T_C$ is determined as 470(5) K. The line is a guide to the eye.

analytical dipole approximations of the radial integrals, $<j_0>$ and $<j_2>$ for the Dy$^{3+}$ ion and $<j_0>$ for the Co$^{3+}$ ion, were used [66].

We observed that the sample consists of a few equally sized grains with orientations that are a few degrees apart. The reflections contained overlapping Gaussian curves. It was difficult to determine the intensities of the reflections by means of $\omega$-$2\theta$ scans, because there is always a varying amount of intensity from secondary grains. Therefore, the integrated intensities were determined by means of $\omega$-scans.

Since the number of independent reflections is small, the number of parameters to be refined was kept as small as possible, to obtain statistically relevant refinements. As a guide to determining the relevance of the refined models, we used the goodness-of-fit-parameter $G$ [101]. If $G$ approaches 1, the model is consistent with the correctly weighted data.

All measured reflections could be indexed according to the $I4/mmm$ space group of the ThMn$_{12}$-type of crystal structure. We assumed that the V ion has a complete preference for the 8i crystallographic site, as was previously
5. The magnetic anisotropy of DyCo₁₀V₂

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>$B_{iso}$ (Å²)</th>
<th>occ.</th>
</tr>
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<tr>
<td>Dy (2a)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6.0(3)</td>
<td>1</td>
</tr>
<tr>
<td>Co1 (8f)</td>
<td>1/4</td>
<td>1/4</td>
<td>1/4</td>
<td>6.0(3)</td>
<td>1</td>
</tr>
<tr>
<td>Co2 (8j)</td>
<td>0.277(5)</td>
<td>1/2</td>
<td>0</td>
<td>6.0(3)</td>
<td>1</td>
</tr>
<tr>
<td>Co3 (8i)</td>
<td>0.368(12)</td>
<td>0</td>
<td>0</td>
<td>6.0(3)</td>
<td>0.52(7)</td>
</tr>
<tr>
<td>V (8i)</td>
<td>0.368(12)</td>
<td>0</td>
<td>0</td>
<td>6.0(3)</td>
<td>0.48(7)</td>
</tr>
</tbody>
</table>

Measured reflections: 42
Independent reflections: 11

<table>
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<th>λ</th>
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</thead>
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</tr>
<tr>
<td>$R$</td>
<td>5.6</td>
</tr>
<tr>
<td>$G_{of}$</td>
<td>1.12</td>
</tr>
</tbody>
</table>

Table 5.1: Crystallographic parameters determined by neutron diffraction at 500 K (paramagnetic). The refinement factor $R = \sum |F_{obs}^2 - F_{calc}^2| / \sum F_{obs}^2$, and the goodness-of-fit parameter $G_{of} = (\sum w|F_{obs}^2 - F_{calc}^2|^2/(N_{obs} - N_{var}))^{1/2}$ characterize the quality of the refinement.

found for the isostructural compound YCo₁₀V₂ [11]. The 500 K (above $T_C$) set of reflections was first refined allowing variation of the positional parameters for the $8i$ and $8j$ crystallographic sites, the occupancy of the $8i$ site and an overall isotropic thermal factor. Extinction was not included, which is reasonable, since the crystal is very small and not of a very good quality.

The results for the refinement of the 500 K data are summarized in Table 5.1. The positional parameters for the $8i$ and $8j$ sites agree with those found in literature for similar compounds [8], and for YCo₁₀Ti₂ [11]. The $8i$ site was found to be occupied for 52 (7)% by Co and for 48 (7)% by V ions. Note that this occupancy of the $8i$ site leads to a composition DyCo₁₀.₁V₁.₉, which is in excellent agreement with the EPMA results and the nominal composition. Concerning the refined overall thermal factor, a value of 6.0(3) Å² is unphysically large. However, the effect of absorption as a function of the scattering angle on the integrated intensities has a similar shape as the effect of thermal vibrations [64]. Especially Dy, but also Co, are well known neutron absorbers [65,102].

For the lower temperature sets, the positional parameters and the occupancy of the $8i$ site were fixed. The Co moment (the same for all Co-containing sites), the Dy moment and an overall thermal factor were left free to vary. The magnetic moments were constrained along the [001] direction. At 115 K and lower, the Co moment was found not to vary significantly
5.2. Experimental results

<table>
<thead>
<tr>
<th>Temperature</th>
<th>300 K</th>
<th>115 K</th>
<th>50 K</th>
<th>5 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_{\text{Dy}}(\mu_B/\text{Dy})$</td>
<td>-2.56 (11)</td>
<td>-6.69 (10)</td>
<td>-8.07 (16)</td>
<td>-8.42 (19)</td>
</tr>
<tr>
<td>$M_{\text{Co}}(\mu_B/\text{Co})$</td>
<td>0.79 (4)</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>$B_{\text{iso}}(\text{Å}^2)$</td>
<td>6.55 (8)</td>
<td>5.96 (13)</td>
<td>5.87 (21)</td>
<td>5.71 (27)</td>
</tr>
<tr>
<td>$R$</td>
<td>1.1%</td>
<td>1.6%</td>
<td>2.2%</td>
<td>2.6%</td>
</tr>
<tr>
<td>$G_{\text{of}}$</td>
<td>0.28</td>
<td>0.67</td>
<td>1.03</td>
<td>1.50</td>
</tr>
</tbody>
</table>

Table 5.2: Magnetic moments parallel to the [001] direction determined by neutron diffraction at 300, 115, 50 and 5 K. The refinement factor $R = \sum |F_{\text{obs}}^2 - F_{\text{calc}}^2|/\sum F_{\text{obs}}^2$, and the goodness-of-fit parameter $G_{\text{of}} = [\sum w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2/(N_{\text{obs}} - N_{\text{var}})]^{1/2}$ characterize the quality of the refinements.

...more text...

5.2.4 High-field magnetization measurements

For the high-field measurements\(^1\), we used a single crystalline sphere with a diameter of 2 mm. The experiments were performed at 4.2 K, in applied fields up to 38 T.

\(^1\)In this chapter demagnetizing-field effects are not taken into account, because they are small. The demagnetizing field is estimated to amount to about 30 mT/($\mu_B$/f.u.) for this sample.
5. The magnetic anisotropy of DyCo$_{10}$V$_2$

![Diagram](image_url)

**Figure 5.2:** High-field magnetization of DyCo$_{10}$V$_2$ measured at 4.2 K for the field applied parallel to the [001] direction, measured with decreasing semicontinuous field. The solid lines were measured with continuously increasing and decreasing fields.

In Figure 5.2, the magnetization for $B \parallel [001]$ is shown, measured both with increasing and decreasing field strengths. Starting at zero fields, with increasing field strength the magnetization initially has a very low value, and then, near 2 T the sample suddenly becomes magnetized, and remains magnetized, even after the field has been removed. This effect will be discussed in detail below. Up to about 10 T, the magnetization increases linearly with increasing field strength. In fields higher than 10 T, the increase becomes larger. The magnetization amounts to about 6 $\mu_B$/f.u. at 38 T. The magnetization extrapolated to zero field amounts to about 1.7 $\mu_B$/f.u..

Figure 5.3 shows the high-field magnetization for fields applied parallel to the [100] and the [110] directions. Hardly any difference is observed for these two isotherms. For both directions, the magnetization increases linearly with increasing field strengths, reaching about 6.5 $\mu_B$/f.u. at 38 T. Extrapolated to zero fields, The magnetization for both planar directions amounts to about 0.6 $\mu_B$/f.u..
5.2. Experimental results

Figure 5.3: High-field magnetization of DyCo_{10}V_{2} measured at 4.2 K both for the field applied parallel to the [100] and the [110] direction. The symbols represent semicontinuous-field measurements, the lines continuously-decreasing field measurements.

From the high-field magnetization results for the main crystallographic directions, we can conclude that the easy magnetization direction of DyCo_{10}V_{2} at 4.2 K is a cone around the [001] direction. The angle of the moment with the [001] direction, \( \theta_{[001]} \), can be estimated using the values for the moment parallel to the main directions in zero field. It is given by \( \tan \theta_{[001]} = 0.6/1.7 \), which leads to \( \theta_{[001]} = 19^\circ \).

Figure 5.4 shows the high-field magnetization at 4.2 K, in which the sample was free to rotate in the applied field. The dashed line shows the magnetization isotherm of the sphere, cooled in zero field, measured with decreasing fields from 38 T. In this measurement, the magnetization increases almost linearly up to 38 T. In zero field, the magnetic moment amounts to about 0.7 \( \mu_{B} \) f.u., and reaches about 6.4 \( \mu_{B} \) f.u. in 38 T. Note that this isotherm is very similar to the isotherms obtained for the [100] and the [110] directions.

A completely different magnetization isotherm was measured for the sam-
Figure 5.4: High-field free-crystal magnetization of DyCo$_{10}$V$_2$ measured at 4.2 K both for the zero-field cooled sample (dashed line) and the sample cooled in a field of approximately 0.3 T (full line). The zero-field cooled sample was multi-domain throughout the measurement, with an equal distribution of domains parallel and antiparallel to the [001] direction. The field-cooled sample was single domain with respect to the [001] direction.

This measurement can be divided in two parts. Starting from the lowest applied fields, the magnetization starts at about 1.8 $\mu_B$/f.u. in zero field, and slightly increases almost linearly with the applied field up to about 10 T. There, in a small field interval, the isotherm seems to coincide with the isotherm measured on the zero-field cooled sample. Above about 12 T, the magnetization increases linearly with increasing field up to 38 T, reaching about 7.3 $\mu_B$/f.u. at 38 T. The magnetization of the field-cooled sample exceeds that of the zero-field cooled sample in the whole applied-field range. Note that up to about 11 T, this isotherm is very similar to the isotherm obtained for the [001] direction.

From these high-field free-crystal measurements, it may be concluded that the zero-field cooled measurement is in fact measured with the field applied
parallel to the crystallographic plane. Apparently the sample fails to become single domain even in fields as high as 38 T, retaining a 50/50 distribution of domains parallel and antiparallel to the [001] direction. The similarity between the low-field parts of the field-cooled free-crystal isotherm and the isotherm measured with $B // [001]$ may be interpreted as follows. None of the directions in the cone around the [001] direction is most favored. Therefore, the sample orients itself with the [001] direction parallel to the applied field.

The field dependence of the magnetization below 11 T, for the field-cooled free-crystal (and for $B // [001]$) may be interpreted as due to a reduction of the cone angle with increasing field. Then, assuming that near 11 T the cone is closed and that the Dy-sublattice moment equals the free-ion moment of 10 $\mu_B$/Dy, we can estimate the Co-sublattice moment as $M_{Co} = 10 - 2.2 = 7.8 \mu_B$/Co ($M_{Dy}$ is larger than $M_{Co}$).

The intersublattice molecular-field coefficient $n_{DyCo}$ is obtained from the linearly increasing part of the field-cooled high-field free-crystal isotherm between 12 T and 38 T. We find a value of $n_{DyCo} = 5.6$ T.f.u./$\mu_B$, which is near the previously reported value of 5.5 T.f.u./$\mu_B$ [95]. With a Co-sublattice moment of 7.8 $\mu_B$/Co the intersublattice-molecular field amounts to 43 T.

5.2.5 Magnetization isotherms at elevated temperatures

For the experiments described below, a bar-shaped sample with dimensions 1x1x2 mm$^3$ was used. The [001] direction was parallel to one of the short sides, the other short side, and the long side were parallel to the [100] and [010] directions, respectively. The magnetic isotherms measured at 300, 200, and 100 K in directions parallel to the [001] direction and parallel to the [100] direction are shown in Figs. 5.5a-c. All these measurements were made with increasing field strength. At these temperatures, the coercivity, to be described below, is very small and does not interfere with the initial shape of these isotherms. It can be derived from the results shown in Figs. 5.5a-c that the easy direction is along the [001] direction at all three temperatures. The mutually antiparallel Dy- and Co-sublattice moments will bend towards each other in the applied field if the field is perpendicular to the [001] direction. For this reason, the net moment may become higher in comparatively high fields than when measurements are made with the field applied parallel to the [001] direction. This may explain the crossing of the isotherms in Figs. 5.5a and c.
5. The magnetic anisotropy of DyCo$_{10}$V$_2$

Figure 5.5: Magnetic isotherms measured of DyCo$_{10}$V$_2$ at 300 K (a), 200 K (b) and 100 K (c) with the field parallel to the [001] direction and parallel to the [100] direction. All these measurements were made with increasing field.
5.2.6 Results for B // [001]: coercive properties

The hysteretic behaviour of DyCo$_{10}$V$_2$ at 5 K is shown in Fig. 5.6. These results were obtained by cooling the aligned single crystal to 5 K in zero field and measuring first the virgin magnetization curve. The presence of high coercivity in conjunction with the small slope of the virgin curve can be taken as a signature of the presence of narrow domain walls [103–106]. These narrow walls are strongly pinned to magnetic obstacles of atomic dimensions. The strong increase of the magnetization on the virgin curve at $B_P = 2$ T marks the propagation field $B_P$ at which the external field is able to detach the narrow walls from the pinning sites. At higher fields, the walls are removed from the crystal. Upon decreasing the field from 5 T into the region of negative fields, reversed domains and domain walls can be nucleated but the movement of the domain walls is impeded by the pinning sites, so that the reversed domains cannot grow. This becomes possible again only for negative fields equal in magnitude to the propagation field, meaning that the
The magnetic anisotropy of DyCo$_{10}$V$_2$

Figure 5.7: Field dependence of the magnetization of DyCo$_{10}$V$_2$ measured after cooling the aligned single crystal in zero field. The lines serve as guides to the eye. The compensation temperature is indicated by an arrow.

The absolute value of the coercive field is equal to the propagation field, $B_c = B_p$. Measurements made at several other temperatures reveal essentially the same behaviour. Results are displayed in Fig. 5.7 where it can be seen that the propagation fields are strongly dependent on temperature. The temperature dependence of $B_p$ (or $B_c$) of the single crystal is shown in Fig. 5.8. Starting at 2 K, the intrinsic coercivity first decreases with increasing temperature. It seems to diverge around 120 K and at still higher temperatures it continues to decrease. Before discussing this unusual temperature dependence of the coercivity we will first discuss the temperature dependence of the magnetization because both temperature dependences are strongly correlated.

Results of measurements of the temperature dependence of the magnetization made at various fields applied along the [001] direction are shown in Fig. 5.9. Curve A was obtained after cooling the crystal to 5 K in zero field and measuring in a relatively small field of only 0.05 T. Under these conditions, the magnetization at 5 K can be represented as a point on the virgin curve. The sample is practically in the demagnetized state and the
magnetization remains low up to about 180 K. At this temperature, the coercivity has apparently dropped below the value of the measuring field and at temperatures above 180 K the sample becomes magnetized in the measuring field. This is revealed by the strong increase of the magnetization with increasing temperature. This magnetized sample was subsequently cooled again to 5 K and measurements were repeated in higher field strengths. Under these conditions, the magnetization at 5 K can be represented as a point on the upper branch of the hysteresis loop, and the temperature dependence of the magnetization of curves B and C in Fig. 5.9 can be taken as a measurement of the homogeneously magnetized sample, not affected by domain walls. As done previously [99], we attribute the discontinuity at $T_{sr} = 42$ K to the occurrence of a spin reorientation and the sharp minimum at $T_{comp} = 120$ K to mutual cancellation of the Dy- and Co-sublattice magnetizations at this temperature.

Curve A in Fig. 5.10 was obtained with the same small measuring field
5. The magnetic anisotropy of DyCo$_{10}$V$_2$

Figure 5.9: Temperature dependence of the magnetization of DyCo$_{10}$V$_2$ made with fields of various strengths applied along the [001] direction. The thermal histories of the measurements are described in the text. The spin-reorientation temperature and the compensation temperature are indicated by arrows.

(0.05 T) as curve A in Fig. 5.9, the only difference being that the sample was magnetized in 5 T before the measurements. At 5 K, the magnetization corresponds to a point on the upper branch of the hysteresis loop and, in the lower temperature range, curve A in Fig. 5.10 shows the same features as curves B and C in Fig. 5.9. However, because the measuring field is still below the coercive field at $T_{\text{comp}}$, the total magnetization is not able to re-adjust itself according to the applied field when it has reversed its direction for $T > T_{\text{comp}}$. The measured magnetization remains therefore negative until the measuring field becomes stronger than the coercivity at about 180 K. Curve B in Fig. 5.10 shows the result obtained in a field of 1 T, similar to curve B in Fig 5.9. The difference with the latter curve is that curve B in Fig. 5.10 was obtained by starting from the demagnetized state at 5 K. Inspection of the data in Fig. 5.6 shows that the magnetization in 1 T at this temperature still corresponds to a point on the virgin curve. This situation persists up to about 35 K. As can be seen in Figs. 5.7 and 5.8, the value of $B_c$ has dropped
5.2. Experimental results

Figure 5.10: Temperature dependence of the magnetization of DyCo$_{10}$V$_2$ in fields of various strengths applied along the [001] direction. The thermal history of these measurements are described in the text.

to below the measuring field at this temperature. This means that increasing temperature leads to a strong jump in the magnetization and, above 35 K, curve B in Fig. 5.10 can be regarded as representing points lying on the upper branch of the hysteresis loop. From there on, curve B in Fig. 5.10 is no longer different from curve B in Fig. 5.9. It follows from these results that a reliable shape for a curve representative for the temperature dependence of the spontaneous magnetization can only be derived from magnetization values corresponding to the upper branch of the hysteresis loop, like curves B and C in Fig. 5.9. These curves show that $M_s(T)$ initially decreases with increasing temperature. After vanishing at $T_{\text{comp}}$ it increases again.

We will now return to the temperature dependence of the coercivity shown in Fig. 5.8.

According to the model proposed by Barbara and Uehara [106], the temperature dependence of the coercivity can be described by the expression

$$\frac{1}{B_c(T)} = \frac{1}{B_c(0)} + \alpha T,$$  \hspace{1cm} (5.1)
where $\alpha$ is proportional to the spontaneous magnetization over the wall energy squared, $\alpha \propto M_s/\gamma^2$. $\gamma^2$ is proportional to the product of the average exchange energy and the average anisotropy energy. The average exchange energy is composed of the Dy and Co intrasublattice contributions and the Dy-Co intersublattice contribution. In the lowest temperature region, only the Dy intrasublattice exchange energy is expected to be temperature dependent and to lead to some decrease of the average exchange energy with increasing temperature. Also the average anisotropy energy is composed of Dy- and Co-sublattice contributions. In the lowest temperature range, the latter can be regarded as temperature independent whereas the Dy-sublattice contribution is expected to fall off with increasing temperature. Qualitatively, one may expect therefore that $\gamma^2$ decreases with increasing temperature in the lowest-temperature range. From the temperature dependences of curves B and C in Fig. 5.9, one may furthermore derive that also $M_s$ decreases with increasing temperature in the lowest-temperature range. Because in this range both $M_s$ and $\gamma^2$ decrease with increasing temperature, the overall result may be that $\alpha \propto M_s/\gamma^2$ is hardly temperature dependent in the lowest-temperature range. It means that one may expect $1/B_c$ to vary linearly with temperature, a behaviour that, in Fig. 5.8 (inset), is seen to be fairly well obeyed up to about 65 K.

It is relatively unimportant whether $\gamma^2$ becomes less or more temperature dependent above 65 K. Because of the presence of the compensation temperature where $M_S = 0$, one derives from Eq. 5.1 that $B_c$ is expected to diverge at this temperature. This fact is clearly revealed in the experimental data shown in Fig. 5.8.

5.2.7 Temperature dependence of the cone angle

In order to obtain accurate values for the angle of the spontaneous moment with the [001] direction as a function of temperature, we measured both the parallel and perpendicular components of the magnetization\(^2\) with respect to the applied field. For this experiment, we used the spherical sample also used in the high-field experiments. We oriented the crystal such that the field was applied in the (100) plane, making an angle of 60° with the [001] direction. It should be noted here, that experiments with the field applied in the (110) plane yielded results that were not significantly different from the results presented here.

\(^2\)In these experiments, we observed that the moment does not rotate out of the (100) plane. Therefore, the magnetization process is two-dimensional, and it suffices to mention only the parallel and perpendicular components.
5.2. Experimental results

We measured in fields decreasing from 5 to 0.5 T at temperatures between 5 and 65 K. It was observed that a field of 5 T is sufficient to make the sample single domain with this orientation.

In Figure 5.11, the parallel ($M_{\text{par}}$) and perpendicular ($M_{\text{perp}}$) components of the magnetization, as well as the vector sum ($M_{\text{tot}}$), measured at 50 K, above the spin-reorientation temperature, are shown. With increasing field, $M_{\text{par}}$ increases linearly, while $M_{\text{perp}}$ decreases linearly. This indicates a rotation of the magnetic moment towards the applied field direction. Extrapolated to zero fields, $M_{\text{tot}}$ has a value of about 1.1 $\mu_B$/f.u., which is very near the value obtained previously for $B // [001]$. This indicates that the magnetic moment is saturated throughout this measurement. With increasing field strength, a slight increase of $M_{\text{tot}}$ is observed. This increase may be related to a bending towards each other of the mutually antiparallel Co- and Dy-sublattice moments, causing them to compensate each other to a lesser extent. On the other hand, it may be related to a high-field susceptibility of the compound.

By simple geometry, the angle of the magnetic moment with the applied field direction $\theta_B$ can be obtained. The inset in Figure 5.11 shows $\theta_B$ as a function of applied field. Extrapolated to zero field, $\theta_B$ is slightly below 60°, as expected from the alignment of the crystal.

The results obtained at 5 K, below the spin-reorientation temperature, are displayed in Figure 5.12. As above, both $M_{\text{par}}$ and $M_{\text{tot}}$ increase nearly linearly with increasing field, while $M_{\text{perp}}$ decreases. The inset shows $\theta_B$ as a function of applied field. Extrapolated to zero field, $\theta_B$ is slightly below 45°. This indicates, that the easy magnetization direction has changed from parallel to [001] at 50 K, to a direction that is canted by about 14° with respect to the [001] direction at 5 K.

Values for $\theta_B$ in zero field and the spontaneous moment $M_s$ at various temperatures between 5 K and 65 K were obtained by extrapolation. We obtained the angle of the spontaneous moment with the [001] direction, $\theta_{[001]}$, by subtracting $\theta_B$ at zero field from 60°. The results are displayed in Fig. 5.13. With decreasing temperature, the angle $\theta_{[001]}$ increases from 0° above the spin-reorientation temperature of 42 K to about 14° at 5 K. This increase is rapid just below 42 K and saturates upon approaching the lowest temperatures. The spontaneous moment $M_s$ increases with decreasing temperature, apparently approaching saturation slightly above 42 K. Just below 42 K, however, it shows an anomalous rapid increase with decreasing temperature that saturates upon approaching the lowest temperatures, similar to the temperature dependence of $\theta_{[001]}$. Note that results agree fairly well with the high-field measurements.
5. The magnetic anisotropy of DyCo$_{10}$V$_2$

Figure 5.11: Parallel ($M_{\text{par}}$) and perpendicular ($M_{\text{perp}}$) components and the vector sum ($M_{\text{tot}}$) of the magnetization of DyCo$_{10}$V$_2$ measured at 50 K with decreasing field. The lines are guides to the eye. The field was applied in the (100) plane, making an angle of 60° with the [001] direction. The inset shows the angle $\theta_B$ of $M_{\text{tot}}$ with the applied field direction as a function of applied field.

5.3 Analysis

5.3.1 The spin-reorientation: higher-order CF effects

The following is an attempt to describe the phenomenology of the spin re-orientation at 42 K. Below the spin-reorientation temperature, the magnetic moment rotates away from the [001] direction, which is the easy direction above 42 K. At the same time, the projection of the magnetic moment on the [001] direction increases sharply, resulting in an anomalous temperature dependence of the magnetic moment when measured parallel to [001]. The same increase below $T_{\text{SR}}$ was found for an aligned polycrystalline powder sample [99], where it was noted to be probably due to the distribution of the alignment of the grain particles and the easy-cone configuration of the magnetic moments within the grains. Our investigations point at another
5.3. Analysis

Figure 5.12: Parallel ($M_{\text{par}}$) and perpendicular ($M_{\text{perp}}$) components and the vector sum ($M_{\text{tot}}$) of the magnetization of DyCo$_{10}$V$_2$ measured at 5 K with decreasing field. The lines are guides to the eye. The field was applied in the (100) plane, making an angle of $60^\circ$ with the [001] direction. The inset shows the angle $\theta_B$ of $M_{\text{tot}}$ with the applied field direction as a function of applied field.

mechanism, since we found the same effect for the single crystal.

It was also noted [99], that the spin reorientation from easy-axis to easy-cone is probably due to higher-order crystal-field effects. To verify this, we analyzed the magnetic moment as a function of temperature in zero applied field. We used a computer program that calculates the spontaneous magnetic moment and its angle with the [001] direction by minimizing the free energy in the two-sublattice crystal-field model (Section 2.5).

Our analysis is based upon a few assumptions. We assume that the Co-sublattice anisotropy constant is temperature independent and equal to $K_{1, \text{Co}} = -10 \text{ K/f.u.}$ (This leads to an easy-plane preference with an anisotropy field of about 4 T for the Co sublattice). It should be noted that we also tried other, reasonable, values for the Co-sublattice-anisotropy constant. The influence of the Co-sublattice anisotropy on the spin-reorientation transition and on its mechanism was found to be small. We further assumed that the
Figure 5.13: The spontaneous moment ($M_s$) of $\text{DyCo}_{10}V_2$ and the angle of the spontaneous moment with the [001] direction ($\theta_{[001]}$), obtained from vector measurements as a function of temperature. The lines are guides to the eye.

The Co moment is constant, at least up to about 150 K. To account for a Dy moment that is possibly smaller than the free-ion moment of 10 $\mu_B$, the value of the Co moment is derived from the experimental magnetization for every set of crystal-field coefficients. The strength of the molecular field on the Dy moment was also taken to be constant. The value of the molecular-field strength was, for this analysis, determined from the temperature dependence of the magnetic moment between 100 and 150 K. This temperature dependence is, in this simple approach, completely determined by the temperature dependence of the Dy moment. We found that, as the values of the crystal-field coefficients are changed (within the limits of our analysis), at a given temperature, the Dy moment changes significantly. However, the change in absolute value of the Dy moment between about 100 and 150 K does not depend very much on the values of these coefficients. Therefore, the calculations for different sets of crystal-field coefficients result in parallel curves of the magnetic moment as a function of temperature between 100 and 150 K. These curves can be shifted to match the experimental data, by changing the Co-sublattice...
moment. In this way, we find for the molecular field a value of 49 T, which is comparable to the value of 43 T from the free-sphere-magnetization experiment (Section 5.2.4). Finally, we have assumed the crystal-field coefficients $A_4^4$ and $A_6^6$ to be equal to zero. In our experiments, we find no clear difference between the magnetization isotherms measured with the field applied parallel to the (110) and parallel to the (100) plane. This means that the coefficients $A_4^4$ and $A_6^6$ do not play a crucial role in the mechanism of the spin reorientation. There are three coefficients to be determined, $A_0^0$, $A_4^0$, and $A_6^0$. A large number of sets can be found that produce a spin reorientation near 42 K. For a given value for $A_0^0$, values for $A_4^0$ and $A_6^0$ can be found that produce a spin reorientation at 42 K. For our purpose here, finding a phenomenological description of the spin-reorientation transition, it is sufficient if $A_0^0$ is positive and large enough, because the moments stay parallel to [001] up to high temperatures. We took a value for $A_0^0$ of 80 K $a_0^{-2}$, which may be justified because it was also found for the related compound GdCo$_{11}$Ti by means of Mössbauer spectroscopy [91].

For comparison, in Figure 5.14, we show the results of three such calculations. In this figure, the spontaneous moment as a function of temperature, and, in the inset, its angle with the [001] direction, are shown. The dots are the experimental results, and the lines are the results of calculations.

The full line, I, is calculated with crystal-field coefficients $A_0^0 = 80$ K $a_0^{-2}$, $A_4^0 = -10$ K $a_0^{-4}$, and $A_6^0 = 0$ K $a_0^{-6}$. The value of $M_{\text{Co}}$ obtained in this calculation is 7.7 $\mu_B$/f.u.. For this set of coefficients, the value of $M$ as a function of temperature shows hardly any discontinuity at the spin-reorientation temperature, whereas it is observed in the temperature dependence of $\theta_{[001]}$, that the spin-reorientation occurs near 41 K. The angle $\theta_{[001]}$ reaches about 20° at the lowest temperature. The value of $M_{\text{Dy}}$ at 5 K is calculated to be equal to the free-ion value of 10 $\mu_B$.

The dashed line, II, is calculated with crystal-field coefficients $A_0^0 = 80$ K $a_0^{-2}$, $A_4^0 = 0$ K $a_0^{-4}$, and $A_6^0 = 2.2$ K $a_0^{-6}$. The value of $M_{\text{Co}}$ obtained in this calculation is 7.8 $\mu_B$/f.u.. For this set of coefficients, a slight discontinuity for $M_s$ as a function of temperature is observed at the spin-reorientation temperature. The angle $\theta_{[001]}$ reaches about 19° at the lowest temperature. The value of $M_{\text{Dy}}$ at 5 K is 9.9 $\mu_B$, which is slightly below the free-ion value of 10 $\mu_B$.

Finally, the dotted line, III, is calculated with crystal-field coefficients $A_0^0 = 80$ K $a_0^{-2}$, $A_4^0 = 40$ K $a_0^{-4}$, and $A_6^0 = 10$ K $a_0^{-6}$. The value of $M_{\text{Co}}$ obtained in this calculation is 7.9 $\mu_B$/f.u.. For this set of coefficients, the temperature dependence of $M_s$, including the discontinuity at the spin-reorientation temperature, nearly reproduces the experimental values. Also the temperature dependence of $\theta_{[001]}$ is nearly the same as the experimental value, reaching a
The magnetic anisotropy of DyCo$_{10}$V$_2$

5. The magnetic anisotropy of DyCo$_{10}$V$_2$

Figure 5.14: The spontaneous moment ($M_s$) of DyCo$_{10}$V$_2$ and the angle of the spontaneous moment with the [001] direction (inset) ($\theta_{[001]}$) as a function of temperature. The lines I, II, and III, are the results of crystal-field two-sublattice calculations, see text. The symbols are experimental results.

value of about 15° at the lowest temperature. For this calculation, the value of $M_{\text{DY}}$ is equal to 9.6 $\mu_B$ at 5 K.

Although the final values of the crystal-field coefficients, the intersublattice-exchange energy and the Co-anisotropy constant were not sufficient to reproduce the results of the high-field magnetization measurements, the phenomenology of the spin reorientation in DyCo$_{10}$V$_2$ is described very well. With these parameters, the near saturation of the spontaneous moment above the spin-reorientation temperature is related to a mixed state of the Dy (2$J+1$) 4f levels with a moment of about 9.1 $\mu_B$ at 42 K. A calculation with a molecular field of 49 T that is fixed parallel to the [001] direction, shows that the Dy moment would become smaller below about 42 K, reaching, at 0 K, a value of 8.66 $\mu_B$ (which is equal to $g_J(J - 1) = 4 \frac{13}{2}$). This would imply a reduction of the intersublattice-exchange energy with decreasing temperature. By rotating the molecular field slightly away from the [001] direction, the intersublattice-exchange energy can become slightly larger, instead of
smaller, with decreasing temperature. However, the Dy moment does not reach the value of the free-ion moment of 10 $\mu_B$ at the lowest temperature.

The value of the intersublattice-molecular field obtained from the high-field free-crystal measurement amounts to 43 T (Section 5.2.4), with a Co-sublattice moment of 7.8 $\mu_B$ and an intersublattice molecular-field coefficient $n_{DyCo} = 5.6$ T.f.u./$\mu_B$. This agrees fairly well with the 49 T obtained here and indicates that the bending process above 12 T involves the full free-ion Dy moment. Furthermore, the increase of the magnetization of about 0.5 $\mu_B$ from zero field up to about 11 T could, besides the previously mentioned closing of the cone, be due to an increase of the Dy-sublattice magnetization, reaching the free-ion value of 10 $\mu_B$ near 11 T.

5.4 Concluding remarks

We have investigated the magnetic properties of a single crystal of the compound DyCo$_{10}$V$_2$. The easy magnetization direction is parallel to the [001] direction at high temperatures. The magnetization tilts away from the [001] direction below the spin-reorientation temperature ($T_{sr} = 42$ K), reaching an angle of $\theta_{[001]} = 14^\circ$ at 5 K. We found that the temperature dependence of the magnetization shows several unusual features.

The occurrence of an easy cone at low temperatures is related to higher-order crystal-field terms describing the Dy-sublattice anisotropy. The rotation of the moment away from the [001] direction and the anomalous increase of the magnetization parallel to the [001] direction below $T_{sr}$, can be calculated with a set of crystal-field coefficients that includes a sizable value of $A_8^0$. These crystal-field coefficients imply that the Dy moment has a value lower than the free-ion value of 10 $\mu_B$, even at the lowest temperature. This is corroborated by the neutron diffraction experiment, that, with rather poor statistics, resulted in a Dy moment lower than the free-ion value of 10 $\mu_B$.

A further anomaly in the $M(T)$ curves in the form of a sharp minimum at $T_{comp} = 118$ K, is due to the magnetic compensation of the Co- and Dy-sublattice magnetizations. The shape of the $M(T)$ curves is not only strongly field dependent but depends also considerably on the thermal history of the sample. This behaviour is attributed to the development of a rather strong intrinsic coercivity at low temperatures originating from the presence of narrow Bloch walls. The present results, obtained on fairly large single crystals, refute previous explanations of the high coercivity at 5 K in terms of small single domain particles [100]. The most prominent result obtained in the course of the present investigation is the unusual temperature dependence of the coercivity. The results presented here demonstrate quite clearly that
the presence of narrow Bloch walls leads to a divergence of the coercivity at the compensation temperature.