Environment of Iodine Ions. A spectroscopic, magnetic and structural investigation on transition - metal diiodides
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CHAPTER III
MAGNETIC STRUCTURES AND PROPERTIES OF $\text{VI}_2$
LONG- AND SHORT-RANGE ORDER AND MÖSSBAUER SPECTROSCOPY

ABSTRACT

Single-crystal measurements of the magnetic susceptibilities of $\text{VI}_2$ show an anomaly at a critical temperature of about 14 K. Neutron-diffraction data show that this anomaly can be ascribed to a magnetic phase transition from a $120^\circ$ structure to a collinear arrangement of the spins with a magnetic unit cell $a_{\text{magn}} = a\sqrt{3}$, $b_{\text{magn}} = 2a$ and $c_{\text{magn}} = 2c$. The collinear structure is compatible with low-temperature Mössbauer spectra. The $120^\circ$ structure is not a magnetic phase with long-range order but rather a paramagnetic phase with a high degree of short-range order.

* Rewritten from:


and

III.1 INTRODUCTION

$\text{VI}_2$ is a layered compound which crystallizes in the well-known $\text{Cd(OH)}_2$ structure, space group $D^{3d}_3$ [1]. The magnetic structure of $\text{VI}_2$ has not been reported previously.

According to the layer character of $\text{VI}_2$ one might suspect it to behave like a metamagnetic system. A proposition along these lines for the magnetic structure of $\text{VI}_2$ has been given by Friedt, Sanchez and Shenoy on the basis of data from $^{129}$I-Mössbauer spectroscopy [2]. These authors concluded from the transferred hyperfine field at the iodine nucleus that the spins on the three vanadium atoms coordinated to an iodine atom are parallel to one another.

Niel et al. [3,4] reported the magnetic powder susceptibilities of the dihalides of vanadium as a function of the temperature. These authors found for $\text{VI}_2$ a critical temperature of 15 K, whereas the susceptibility reaches its maximum at 25 K. The difference between both temperatures reflects the presence of short-range order.

In this chapter we report magnetic susceptibilities of single crystals of $\text{VI}_2$. Neutron diffractograms obtained at a few selected temperatures, reveal the presence of two different magnetic structures.

III.2 SYNTHESIS OF $\text{VI}_2$

Synthesis of $\text{VI}_2$ was carried out at a temperature of about 500°C in a quartz tube starting from the elements and using a small excess of the metal, in order to avoid the formation of $\text{VI}_3$. To avoid the growth of a mirror of silicates of vanadium the tube was filled with argon with a pressure of 0.1 atm.

After a few weeks the reaction was complete, as shown by the absence of free iodine in the vapour phase. No sublimation or transport of $\text{VI}_2$ took place at 500°C. Then the tube was heated to 800°C at one side and 700°C at the other side. The sublimation of $\text{VI}_2$ from the hot to the cold side of the tube is a slow process and the growth of single crystals may take several months.

III.3 MAGNETIC SUSCEPTIBILITIES OF $\text{VI}_2$

Measurements of the magnetic susceptibility and magnetization of single crystals have been performed on a Faraday-type system (Oxford Instruments) equipped with a Mettler ME 21 electronic vacuum microbalance, described pre-
The susceptibilities for two directions of the magnetic field (8.61 kOe), H//c-axis and H⊥c-axis, are shown in Figure III.1 for the temperature range from 5 K to 100 K. Both curves are corrected for diamagnetism, $\chi_{\text{dia}} = -119 \times 10^{-6}$ cm$^3$/mol [6], and a temperature-independent Van Vleck susceptibility. For the Van Vleck term $8k^2N\mu_B^2/\Delta$ a value of $210 \times 10^{-6}$ cm$^3$/mol was calculated using the crystal-field splitting $\Delta = 7870$ cm$^{-1}$ [7] and assuming an orbital reduction factor of $k' = 0.9$ [8,9].

Figure III.1: Magnetic susceptibilities of VI$_2$ as a function of the temperature in an applied field of 8.61 kOe. The broken curves have been calculated with the two-dimensional model of Niel et al. (see text).
The susceptibility data of Ni et al. [4] agree very well with ours. These authors found a Curie-Weiss type behaviour at temperatures above 150 K. A paramagnetic Curie temperature $\theta = -143$ K and $\mu_{\text{eff}} = 4.07 \mu_B$ were calculated indicating the presence of $V^{2+}(3d^3)$ ions with $S = 3/2$ and a $g$ value of 2.02. The fact that the $g$ value is larger than 2, and not smaller as in most $V^{2+}$ compounds, can be explained by the contribution of the spin-orbit coupling acting between a $t_{2g}$ and an $e_g$ orbital [10].

In the region of the critical temperature (14 K) and of the temperatures where the susceptibilities are maximal, the susceptibilities show a very anisotropic behaviour. Whereas the curve for $H \perp c$ shows a broad maximum (25 K), the maximum for the $H//c$ curve is quite sharp (14.4 K).

From 14.4 K to 12.5 K both susceptibilities sharply decrease and only the $H//c$ susceptibility increases again between 12.5 and 5 K. This increase of the susceptibility for $H//c$ cannot be attributed simply to a paramagnetic impurity (d$^3$) as only the $H//c$ curve shows the increment. Furthermore, the magnetization versus applied field at 5.1 K for the two directions of the field shows straight lines up to 40 kOe and a saturation as expected (only in case of a rather large concentration) for paramagnetic moments is not observed. The presence of a small amount of paramagnetic $V^{3+}(d^2)$ ions in VI$_2$ may account for the anisotropic behaviour of the susceptibility at low temperatures. The ground state of $V^{3+}(d^2)$ in a cubic ligand field is $^3T_{1g}(t_{2g})$. If a trigonal field and a relatively small spin-orbit interaction are included in the Hamiltonian, this leads to very anisotropic $g$ values ($g_{//} \approx 2, g_\perp \approx 1.6$ [11]).

The anisotropy of the magnetic susceptibility of VI$_2$ at high temperatures is not large (smaller than 10%), and might be due to weighing errors. Our samples weighted only about 6 mg.

III.4 MAGNETIC STRUCTURES

Neutron-diffraction data were obtained from a powder of VI$_2$ at the high-flux reactor of the ECN at Petten at temperatures of 300, 16.5, 14.4, 12.5, 7 and 5.5 K, using neutrons with a wavelength of $\lambda = 2.5858 \ \text{Å}$.

At 300 K the neutron diffractogram can be described with the simple Cd(OH)$_2$ structure, space group D$_3^3$ [1]. The hexagonal cell dimensions are: $a = 4.057 \ \text{Å}$ and $c = 6.760 \ \text{Å}$. The relative $z$-coordinates of the iodine ions have been refined to $z = 0.240$. In the 16.5 K diffractogram a broad maximum is observed in the region where a magnetic reflection peak is observed in the 14.4 K diffractogram, at about $2\theta = 700$ DMC (10$^4$ DMC = 360°) (Figure III.2).
Figure III.2: A: Neutron diffractogram of \( \text{VI}_2 \) at 14.4 K. The dots indicate the measured counts. The full line is calculated with the 120° structure (spins in ac-plane). \( M \) and \( N \) denote magnetic and nuclear reflections.

B: Neutron diffractogram of \( \text{VI}_2 \) at 5.5 K. The full line is calculated with the structure shown in Figure III.4.

By lowering the temperature to 12.5 K the above-mentioned magnetic reflection disappeared and two new reflections are clearly observed at about 590 and 830 DMC. In Figure III.2 the 5.5 K diffractogram is shown. The intensities of the magnetic reflections at 5.5 K have increased as compared to those at 7 and
TABLE III.1: Observed and calculated intensities of the magnetic reflections of the 14.4 K diffractogram for two planes in which the spins possibly rotate ($\lambda = 2.5858 \text{Å}$).

<table>
<thead>
<tr>
<th>$2\theta$</th>
<th>hkl</th>
<th>$I_{\text{obs}}$</th>
<th>$I_{\text{calc}}^{ab}$</th>
<th>$R_M^{ab}$ (%)*</th>
<th>$I_{\text{calc}}^{ac}$</th>
<th>$R_M^{ac}$ (%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>748</td>
<td>101</td>
<td>10200</td>
<td>9100</td>
<td></td>
<td>10000</td>
<td></td>
</tr>
<tr>
<td>1165</td>
<td>103</td>
<td>2900</td>
<td>3300</td>
<td>20.0</td>
<td>2200</td>
<td>6.2</td>
</tr>
<tr>
<td>1438</td>
<td>201</td>
<td>2600</td>
<td>1600</td>
<td></td>
<td>2100</td>
<td></td>
</tr>
</tbody>
</table>

* $R_M = 100 \times \frac{\sum |J_i^2(\text{obs}) - J_i^2(\text{calc})|}{\sum J_i^2(\text{obs})}$, where $J_i$ is the magnetic coherent scattering cross section.

TABLE III.2: Observed and calculated intensities of the magnetic reflections of the 5.5 K diffractogram ($R_M = 7.8\%$).

<table>
<thead>
<tr>
<th>$2\theta$</th>
<th>hkl</th>
<th>$I_{\text{obs}}$</th>
<th>$I_{\text{calc}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>595</td>
<td>011</td>
<td>15500</td>
<td>15100</td>
</tr>
<tr>
<td>784</td>
<td>111</td>
<td>15150</td>
<td>15100</td>
</tr>
<tr>
<td>1067</td>
<td>013</td>
<td>1500</td>
<td>2000</td>
</tr>
<tr>
<td>1232</td>
<td>113</td>
<td>2500</td>
<td>2700</td>
</tr>
<tr>
<td>1359</td>
<td>211</td>
<td>4600</td>
<td>4600</td>
</tr>
</tbody>
</table>

12.5 K. The observed magnetic reflections for the two structures are listed in Table III.1 and Table III.2.

The magnetic reflections at 14.4 K can be indexed on the basis of a hexagonal unit cell with $a_{\text{magn}} = a\sqrt{3}$ and $c_{\text{magn}} = 2c$. The magnetic contributions have been calculated with the form factor for $V^{2+}$ ions given by Watson and Freeman [12]. The observed intensities are explained by the well-known $120^\circ$ structure with an antitranslation of $1/2 c_{\text{magn}}$ (Figure III.3). It is possible to determine the orientation of the spins in the magnetic structures from the observed intensities. In Table III.1 a comparison is made with calculated intensities of two structures with the magnetic moments in the ab-plane and the ac-plane, respectively. The arrangement with the spins in the ab-plane has been found, for instance, in LiCrS$_2$ [13], the arrangement with the spins in the ac-plane has been found for RbNiCl$_3$ and CsNiCl$_3$ [14]. The agreement be-
Figure III.3: Arrangement of the spins of $V^{2+}$ in the 120° structure. The spins lie in a plane perpendicular to the ab-plane. The orientation of the spin in the origin of the cell is arbitrary.

The arrangement of the magnetic moments of $V^{2+}$ is shown in Figure III.4. The orientation of the magnetic moments is not along one of the orthorhombic axes. The intensities of the observed reflections are best fitted with magnetic moments in the ac-plane and making an angle of 61 degrees with the a-axis. The observed and calculated intensities are listed in Table III.2.
Figure III.4: Arrangement of the spins of $\nu^{2+}$ at 5.5 K. The spins lie in the $ac$-plane. The angle between the magnetic moment and the $a_m$ axis decreases slightly from 5.5 to 12.5 K (see Table III.3).

The refined magnetic parameters at various temperatures are listed in Table III.3.

<table>
<thead>
<tr>
<th>$T$(K)</th>
<th>Structure</th>
<th>$M_x(\mu_B)$</th>
<th>$M_z(\mu_B)$</th>
<th>$M(\mu_B)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.5</td>
<td>short range</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.4</td>
<td>120° (Fig. III.3)</td>
<td>1.05</td>
<td>1.91</td>
<td>2.18</td>
</tr>
<tr>
<td>12.5</td>
<td>collinear</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>structure</td>
<td>1.14</td>
<td>2.03</td>
<td>2.33</td>
</tr>
<tr>
<td>5.5</td>
<td>(Fig. III.4)</td>
<td>1.08</td>
<td>2.37</td>
<td>2.60</td>
</tr>
</tbody>
</table>

III.5 DISCUSSION

The magnetic susceptibilities of VI$_2$ at high temperatures are well described by a two-dimensional model, as shown by Niel et al. [3,4]. These au-
thors obtained from a series expansion of the magnetic susceptibility of a two-dimensional Heisenberg antiferromagnet a value of $|J| = 6 \, K$ for the exchange interaction in the layers. With the same series expansion we obtain from our data slightly different values of $|J| = 7.8 \, K$ for the susceptibility for $H \perp c$, and $|J| = 6.6 \, K$ for $H//c$. This series expansion of the susceptibility fails completely at temperatures near that where the maximum of the susceptibility is reached. From the value of $|J|$ one calculates a value of $\approx 45 \, K$ for the Stanley-Kaplan transition temperature $T_{SK} = \frac{1}{5}(z-1)[2S(S+1) - 1]|J|/k$, with $z = 6$ and $S = 3/2$ [4,18]. Thus, the observed critical temperature $T_c$ is much lower than expected on the basis of calculations which take into account only exchange interactions between nearest neighbour magnetic ions (Section III.6). This low value of $T_c$ is due to the presence in $\text{VI}_2$ of competing antiferromagnetic interactions $J_1$ between nearest neighbours and ferromagnetic interactions $J_2$ between next nearest neighbours in the ab-plane.

The anisotropic behaviour of the susceptibilities at high temperatures could be due to anisotropic g factors and trigonal field effects, but these effects are small for $\text{V}^{2+}(3d^3)$ ions in a slightly distorted octahedral coordination [10].

The maxima in the susceptibility curves for $H//c$ and $H \perp c$ have a completely different character. Whereas the maximum for $H \perp c$ is very broad, the maximum for $H//c$ is very sharp. This is probably a consequence of the different dimensionality of the short-range ordering in the two directions. The deviations due to neglecting short-range order are more severe in a low-dimensional system [19]. Thus, the $H \perp c$ susceptibility reflects an appreciable short-range order in the hexagonal plane above the critical temperature.

Table III.3 shows that the z-component of the magnetic moment increases about 24% from 12.5 to 5.5 K, while the x-component remains approximately constant.

Recently, Güntherodt et al. [20] recorded Raman spectra of $\text{VI}_2$. They observed three new Raman lines at 66, 195 and 220 cm$^{-1}$ at temperatures below 15 K. These lines are attributed to zone-boundary-phonon Raman scattering. Only those phonons are observed which modulate the exchange interaction. On the basis of the collinear structure of Figure III.4 two Raman lines can be explained, corresponding to the $A_u$ modes (65 and 220 cm$^{-1}$) at the point M in the Brillouin Zone. The remaining frequency of 195 cm$^{-1}$ could not be explained within our structure model. Therefore Güntherodt et al. suggest a different arrangement of the spins in the c-direction, the ordering of spins in the $a_b_m$-plane is maintained. In stead of our translation of $\frac{1}{2}b_m + \frac{1}{2}c_m$, which leads to
a systematic extinction of \( k + 1 \neq 2n \) reflections, a translation of \( \frac{1}{2}a_m - \frac{1}{2}b_m + \frac{1}{2}c_m \) was suggested. With this spin arrangement we calculate a large intensity for the 110 reflection at 780 DMC (Figure III.2B). Therefore the structure proposed by Günterodt is not compatible with our neutron data, since no intensity is observed for the 110 reflection.

**III.6 SHORT- AND LONG-RANGE ORDER IN VI₂**

Usually, the short-range order above the critical temperature \( T_c \) of a second-order phase transition is of the same nature as the long-range order below \( T_c \). However, a number of observations suggest that in VI₂ the short-range order above 14.4 K has a different character than the long-range order at low temperatures. First, the magnetic reflections of the 120° structure are broader (by a factor 1.5 at 14.4 K) than the reflections of the collinear structure; at 16.5 K the magnetic reflections are strongly broadened. Secondly, neither the magnetic susceptibility, nor the neutron data show indications of a phase transition to a paramagnetic phase. Finally, magneto-optical spectra of VI₂ [21] show at 4.2 K considerable fine structure, which disappears at 14.7 K; above 14.7 K (up to 30 K) a new absorption band appears, which broadens severely with increasing temperature, while the magnetic circular dichroism (mcd) intensities diminish rapidly. The temperature of 30 K is in better agreement with the calculated Stanley-Kaplan temperature (Section III.5) than the critical temperature.

We discuss the stability of the magnetic structures. First, only exchange interactions between nearest neighbours (\( J_1 \)) and next-nearest neighbours (\( J_2 \)) in a layer are considered. Figure III.5 shows the stability of several structures as a function of the exchange constants \( J_1 \) and \( J_2 \), obtained with a simple molecular field model [8]. The 120° structure is stable for \( J_1 < 0 \) and \( J_2 > 0 \), and if the anisotropy is small. These signs of \( J_1 \) and \( J_2 \) agree with the Goodenough-Kanamori rules [22,23]. In the case of a large magnetic anisotropy, favouring one particular orientation of the spins, and with \( J_1 < 0 \) and \( J_2 > 0 \), the collinear structure observed in VI₂ is stable.

Because the single-ion anisotropy of \( V^{2+} (^{4}A_{2g} \text{ ground state in } O_h) \) is small, the orientation of the spins will be determined by the dipolar energy. With the aid of a computer program called "DIPSUM" [8], we calculated the lattice sums needed for the calculation of the dipolar energy of the 120° structure and the collinear structure of Figure III.4. The magnetic dipolar energies for the 120° structure with the magnetic moments in the ab-plane and
Figure III.5: Stability diagrams for two-dimensional structures in hexagonal layers of magnetic ions with nearest ($J_1$) and next-nearest ($J_2$) neighbour interactions, left without anisotropy, right with strong anisotropy.

The dipolar energy of the collinear structure of Figure III.4 is $E_{\text{dip}} = -5.74 \times 10^6$ erg/mol at 12.5 K, if the magnetic moments lie in the ac-plane of the orthorhombic cell and make an angle of 60 degrees with the a-axis, as found experimentally. The dipolar energies for the same structure with the spins directed along the principal axes are for the a, b and c axes $-7.22 \times 10^6$, $+12.39 \times 10^6$ and $-5.18 \times 10^6$ erg/mol, respectively. It is clear from these values that the magnetic moments preferentially lie in the ac-plane.

The magnetic dipolar energy stabilizes the collinear structure with respect to the 120° structure. Moreover, if the 120° structure has only short-range order, one expects that dipolar interactions (which are long-range) will be strongly diminished. Another possibility is that interlayer exchange interactions stabilize the collinear structure.

These considerations explain that the magnetic structures above and below the critical temperature are different. The intralayer exchange energies of the two structures are very similar, but slightly favour the 120° structure. At higher temperatures the exchange interactions lead to appreciable short-range order of the 120° type. At the critical temperature long-range order (also along the c-axis) sets in, and the type of order switches to a collinear structure stabilized by dipolar interactions and interlayer exchange interactions.
III.7 Mössbauer Spectra of VI

129I-Mössbauer spectra of VI₂ at temperatures below 14 K could be interpreted in terms of a single magnetic iodine site, and a transferred hyperfine field $H_{hf} = 54$ kOe, making an angle $\theta = 54^\circ$ with the crystallographic c-axis [2]. These observations are compatible with the low-temperature magnetic structure.

The hyperfine field at the iodine is $H_{hf} = H_{FC} + H_{SD} + H_d$, where $H_{FC}$ is the isotropic contact field provided by the core polarization and by the finite spin density ($f_S$) in the 5s valence orbital. $H_{SD}$ is the spin dipolar term arising from an unpaired spin density ($f_\sigma, f_\pi$) transferred into the 5p$_\sigma, 5p_\pi$ valence orbitals of iodine. $H_d$ is the dipolar field induced by the magnetic moments of the metal atoms at the iodine site.

Considering only the three nearest neighbour V$^{2+}$ ions of an iodine atom, the hyperfine field components along the three equivalent and independent bonds are

$$
H_a = -(H_{iso} + H_{an}) \frac{<S_a^2>} {S} \\
H_B = -(H_{iso} + H_{an}) \frac{<S_B^2>} {S} \\
H_Y = -(H_{iso} - 2H_{an}) \frac{<S_Y^2>} {S}
$$

where

$$
H_{iso} = \frac{8\pi}{3} f_S \rho(0) \mu_B - K(f_\sigma + 2f_\pi) \langle r^{-3} \rangle \mu_B \\
H_{an} = \frac{4}{5} \mu_B \langle r^{-3} \rangle (f_\sigma - f_\pi) + 2gS\mu_B R^{-3}
$$

The 5s electron density at the iodine nucleus, taken from free-ion calculations, is $\rho(0) = 150 \times 10^{-24}$ cm$^{-3}$. The radial average over the 5p electronic charge distribution is $\langle r^{-3} \rangle = 121.5 \times 10^{-24}$ cm$^{-3}$. The core polarization field per unpaired p electron $Ku_B \langle r^{-3} \rangle$ is small and negative ($<-80$ kOe) and is neglected. R is the V-I distance (2.87 Å) and $gS\mu_B$ is the magnetic moment of V$^{2+}$ (2.60 $\mu_B$) obtained from neutron data.

The spin polarization mechanism requires that $f_S$ and $f_\sigma - f_\pi$, and also $H_{iso}$ and $H_{an}$, are negative. A combination of the experimental data with equation (1) gives two sets of solutions:
\[ f_s = -0.4\% , \quad f_\sigma - f_\pi = -3.3\% \quad \text{and} \]
\[ f_s = -0.2\% , \quad f_\sigma - f_\pi = -3.7\% \]

A comparison with the results for other transition metal halides [24] indicates that the second solution is the favoured one. The large value of \( f_s \) in V\(_I\) as compared with the value for CrI\(_3\), \( f_s = -0.146\% \) [25], is probably due to the increased 3d-4s splitting for Cr\(^{3+}\).

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III.8 REFERENCES