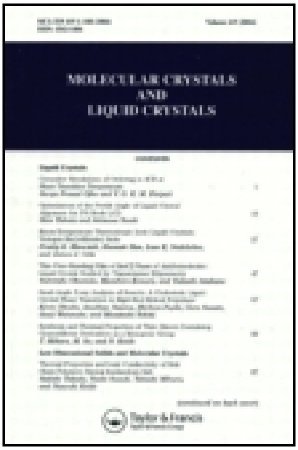

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

# Magnetic Properties of Monohydrate and Anhydrous Vanadyl Sulfates

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To cite this article: Gerard Villeneuve , Luis Lezama & Teofilo Rojo (1989): Magnetic Properties of Monohydrate and Anhydrous Vanadyl Sulfates, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 176:1, 495-505

To link to this article: http://dx.doi.org/10.1080/00268948908037506

*Mol. Cryst. Liq. Cryst.*, Vol. 176, pp. 495–506
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Printed in the United States of America

# MAGNETIC PROPERTIES OF MONOHYDRATE AND ANHYDROUS VANADYL SULFATES

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Abstract - Three different compounds, $VOSO_4.H_2O$, $\alpha$-$VOSO_4$ and $\beta$-$VOSO_4$ have been prepared under argon atmosphere by dehydration of the pentahydrate $VOSO_4.5H_2O$. They were characterized by their X-ray powder diffraction patterns, thermogravimetric analysis and ESR spectra. From a structural point of view, the monohydrate clearly exhibits a layered structure, when $\alpha$ - and $\beta$-$VOSO_4$ may be described either as $|VO_6||SO_4|$ layers or $|VO_6|$ chains. In every case the magnetic susceptibility analysis shows that the main magnetic interactions occur within the layers through $|SO_4|$ entities. Nevertheless, three different magnetic behaviors are observed : (i) weak antiferromagnetic coupling ($J/k = -0.9$ K) in the monohydrate, (ii) weak ferromagnetic coupling ($J/k=+1.5$ K) in $\alpha$-$VOSO_4$ and (iii) short range ferrimagnetic behavior in $\beta$-$VOSO_4$. A tentative of magnetostructural correlation involving V-O-S-O-V bond angles is proposed.

## INTRODUCTION

A systematic investigation of low dimensional magnetic interactions involving vanadyl ions has been achieved during the last few years[1-4]. The materials concerned were mostly vanadyl phosphates belonging to the families of monohydrogenphosphates $VO(HPO_4).nH_2O$ (n = 0.5, 1, 2, 3 or 4), dihydrogenphosphate $VO(H_2PO_4)_2$ or arseniate $VO(H_2AsO_4)_2$, metaphosphate $VO(PO_3)_2$ and pyrophosphate $(VO_2)P_2O_7$. So far the general explanation of sign and strength of the exchange interaction laid to a direct $d_{xy}$-$d_{xy}$ overlapping. Nevertheless, strong discrepancies from such a model have been recently observed[4]. The analysis of magnetic behavior is inconsistent with a direct exchange coupling. Furthermore $^{31}P$ NMR study clearly shows a direct dependence of the lineshift on the exchange interaction[4]. Thus some correlation must exist between the geometry of the $|VO_6|$-$|PO_4|$-$|VO_6|$ connection and the exchange coupling.

Another way for trying to understand the mechanism was to change the nature of the $|XO_4|$ anion.Hence we have carried out the study of the magnetic properties of the vanadyl sulfates $VOSO_4.H_2O$, $\alpha$-$VOSO_4$

and ß-$VOSO_4$, which are isostructural with the homologous phosphates despite modification of the oxidation state of vanadium.

The monohydrate $VOSO_4.H_2O$ has a layered structure formed by $|VO_6|$ octahedra linked by corner sharing with sulfate tetrahedra. The water molecules are inserted between the layers of $VOSO_4$ [5].

The crystal structure of α-$VOSO_4$ may be described as formed by infinite chains of corner sharing $|VO_6|$ octahedra running parallely to the c axis [6]. Each chain is connected to four other ones via sulfate tetrahedra as shown in Fig. 1. This structure is able to give rise

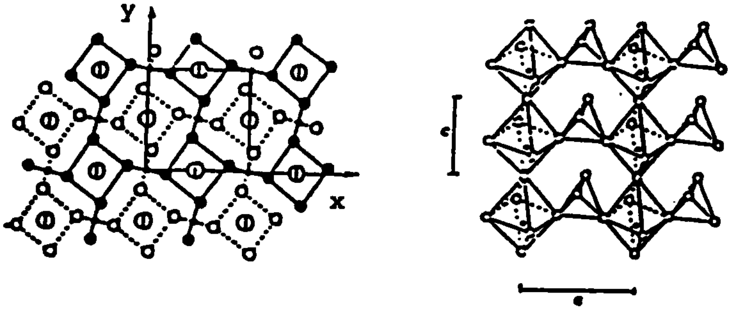

FIGURE 1. Crystal structure of α-$VOSO_4$ projected on the a-b plane (a) and on the a-c plane (b).

either to monodimensional interactions along the c-axis by direct V-V coupling or to bidimensional couplings within the basal a-b plane by superexchange mechanism.

The crystal structure of ß-$VOSO_4$ consists of infinite chains parallel to the a-axis and formed by distorded $|VO_6|$ octahedra linked together by sharing opposite corners. The octahedra of the chains are also pairwise connected by a sulfate group via corner sharing [7]. The two remaining oxygen atoms of each $SO_4$ tetrahedra partake in linking with two further chains of $|VO_6|$ octahedra yielding a three dimensional framework as shown in Fig.2.

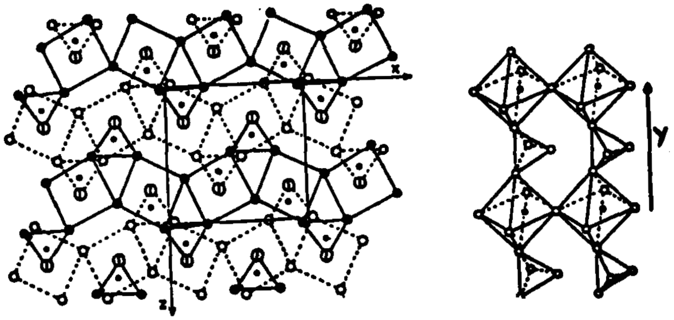

FIGURE 2. Schematic structure of ß-$VOSO_4$
(a) : view along the direction |010|
(b) : linking in the b direction.

In this case the structure is not layered because of the sulfate groups.

In this paper we describe the magnetic properties of the three phases. Section II is devoted to the experimental techniques and characterization of materials. Their magnetic properties are described in Section III and are discussed with respect to bidimensional magnetic models.

## EXPERIMENTAL

### Preparation

The starting material, a commercial "Prolabo" vanadyl sulfate pentahydrate $VOSO_4.5H_2O$ was placed in an alumina crucible and heated under argon atmosphere in a thermogravimetric balance at different temperatures and times of heating.The vanadyl sulfate monohydrate $VOSO_4.H_2O$ was obtained after heating the pentahydrate up to 130°C. α-$VOSO_4$ was prepared at 260°C ; its crystallinity was improved by heating the sample at 330°C during 4 hours, making it less susceptible to rehydration. Finally, heating the sample for two days at 380°C, ß-$VOSO_4$ was obtained. The latter was also prepared from the reaction of $H_2SO_4$ and $V_2O_5$ following ref.[8].

## Characterization

The water loss was controlled by thermogravimetric analysis using a Setaram microbalance at a heating rate of 10°C/hour. The temperature was monitored by an Eurotherm temperature programmer. The observed weight loss was 28.6% for the monohydrate and 35.8% for the anhydrous forms (theoretical loss 28.5 and 35.7% respectively).

The products were characterized by their X-ray diffraction powder pattern with a Philips diffractometer using Cu Kα radiation. Table I gives the obtained cell parameters, in excellent agreement with those previously proposed by other authors [5,8,9].

TABLE I

| Compounds | Parameters (Å) |
|---|---|
| $VOSO_4.H_2O$ | a = 6.260 (2)<br>c = 6.096 (3) |
| $\alpha$-$VOSO_4$ | a = 6.2596 (6)<br>c = 4.099 (2) |
| $\beta$-$VOSO_4$ | a = 7.365 (2)<br>b = 6.272 (3)<br>c = 7.083 (1) |

X-band ESR spectra were recorded on a Bruker ER 200 tt spectrometer. The temperature was stabilized by an Oxford-Instrument regulation. The frequency inside the cavity was measured with a Hewlett-Packard 5342 A counter. The magnetic field, calibrated by the ESR signal of DPPH was measured by a Bruker BNM20 NMR gaussmeter. No appreciable modifications were observed either in the position or in the shape of the line in the range 4.2-290 K. Due to the linewidth rather large, a poor resolution only causes strong dissymetry (Fig.3). Simulations of the spectra were performed in good agreement with the position and the singularities of the lines, yielding the following values for the parallel and perpendicular components of the g tensors:

$VOSO_4.H_2O$ : $g_{//} = 1.932$ $g_{\perp} = 1.978$

$\alpha$-$VOSO_4$ : $g_{//} = 1.913$ $g_{\perp} = 1.984$

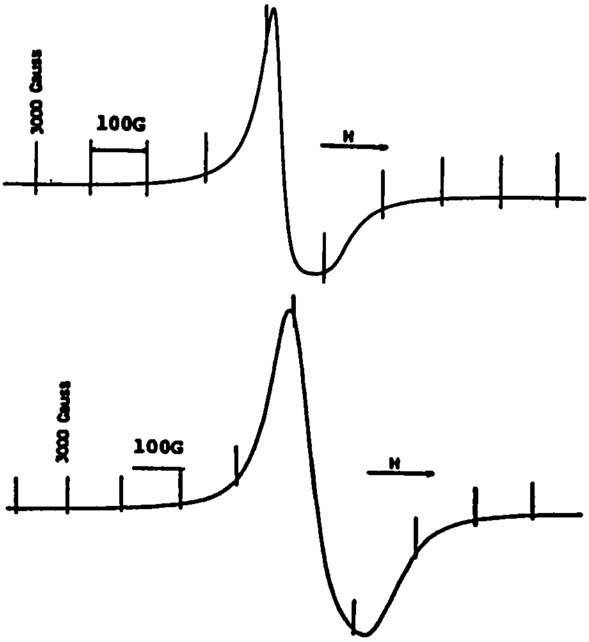

FIGURE 3. X-band ESR spectra of $VOSO_4.H_2O$ (a) and $\alpha$-$VOSO_4$ (b).

### Magnetic measurements

Magnetic measurements were carried out between 2 and 100 K with a SQUID-SHE magnetometer using a magnetic field of 0.1 T, value at which the magnetization vs magnetic field curve is still linear even at 2 K for the three compounds.

## RESULTS AND DISCUSSION

### $VOSO_4.H_2O$

The thermal evolution of the reciprocal susceptibility is shown in Fig. 4. Above 20 K, the data are well described by a Curie-Weiss law (solid line):

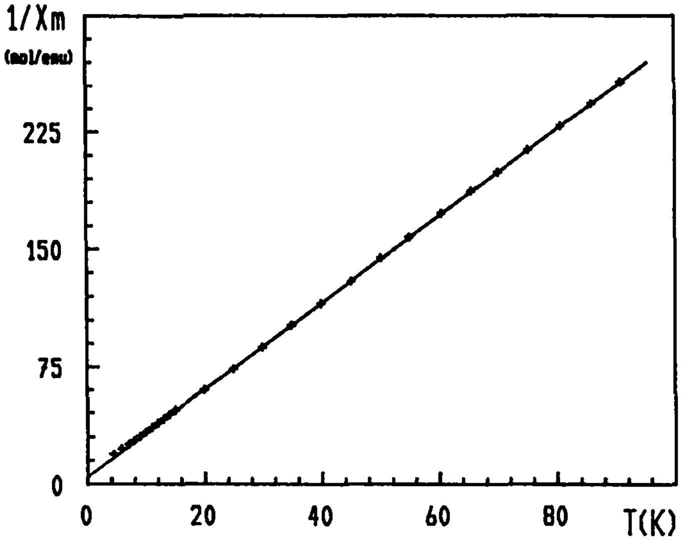

FIGURE 4. Reciprocal molar magnetic susceptibility vs temperature for $VOSO_4.H_2O$.

$$\chi_m = C_m/(T-\theta)$$

where $C_m = 0.36$ is the molar Curie constant and $\theta = -1.8$ K is the Weiss temperature. The experimental $C_m$ value agrees very well with that calculated taking the g-values from the ESR spectrum :

$$C_m = \frac{N\beta^2}{3k} < g >^2 S(S+1)$$

The thermal variation of the $\chi_m/T$ product decreases with decreasing temperature below 20 K (Fig. 5) as a consequence of antiferromagnetic interactions. Considering the structure proposed by Ladwig [5] for this compound, only bidimensional couplings within the a-b plane, by superexchange mechanism via sulfate tetrahedra could be expected. Therefore the experimental data were fitted under this hypothesis.

The expression of the magnetic susceptibility can be determined from a high temperature expansion series for the quadratic layer Heisenberg antiferromagnetic studied by Rushbrooke and Wood [10]. The terms of the series were taken from Lines [11], with an exchange hamiltonian

$\mathcal{H} = -2J \sum S_i S_j$, yielding the following susceptibility expression:

$$\chi = \frac{N < g >^2 \beta^2}{4kT} \left(1 + \frac{2}{x} + \frac{2}{x^2} + \frac{1.333}{x^3} + \frac{0.25}{x^4} + \frac{0.4833}{x^5} + \frac{0.003797}{x^6}\right)^{-1}$$

with $x = kT/J$.

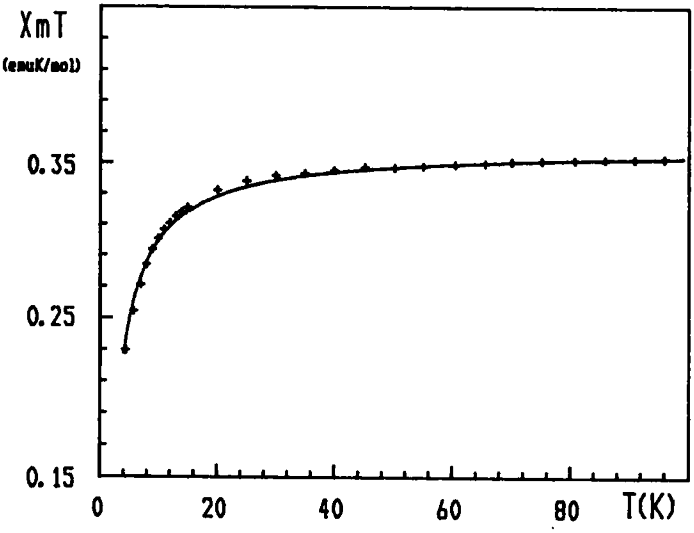

FIGURE 5. $\chi_m T$ vs T for $VOSO_4.H_2O$.

Due to the knowledge of only a small number of terms in the infinite series, the above expression becomes not quantitative as the ratio kT/J nears unity. Solid line in Fig. 5 shows the least square fit of the susceptibility data for $VOSO_4.H_2O$ using the above equation. The parameters obtained are $J/k = -0.9$ K and $< g > = 1.96$. The obtained J-value is in good agreement with the observed $\theta = -1.8$ K value which represents theoretically twice the J/k value for such a system. Therefore, as expected, the 2-D Heisenberg model gives a good representation for the magnetic behavior of this compound.

$\alpha$-$VOSO_4$

The variation of the reciprocal molar magnetic susceptibility vs temperature is plotted in Fig. 6. Above 10 K, the magnetic susceptibility follows a Curie-Weiss law with $C_m$ = 0.35 and $\theta$ = +2.9 K. The positive temperature intercept indicates that the main interactions are ferromagnetic. The data are also plotted in Fig. 7 as $_m$T vs T. The strong increase of $\chi_m T$ below 20 K clearly confirms the ferromagnetic nature of the interactions, in contradiction with the behavior observed by previous authors [6].

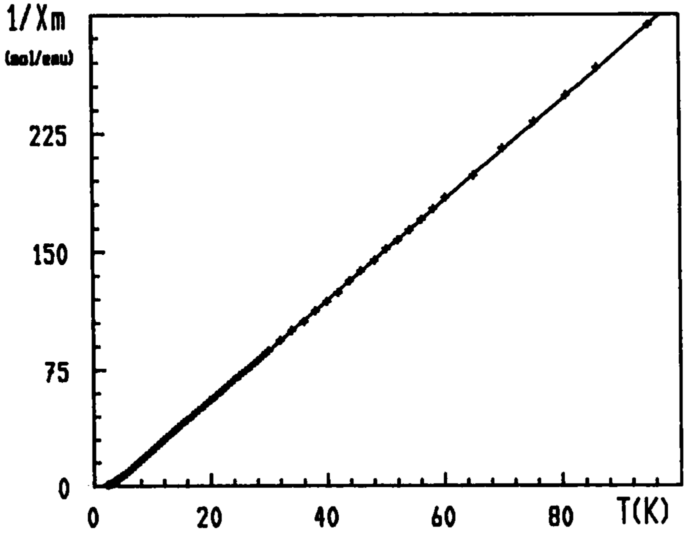

FIGURE 6. Reciprocal molar magnetic susceptibility vs temperature for α-$VOSO_4$.

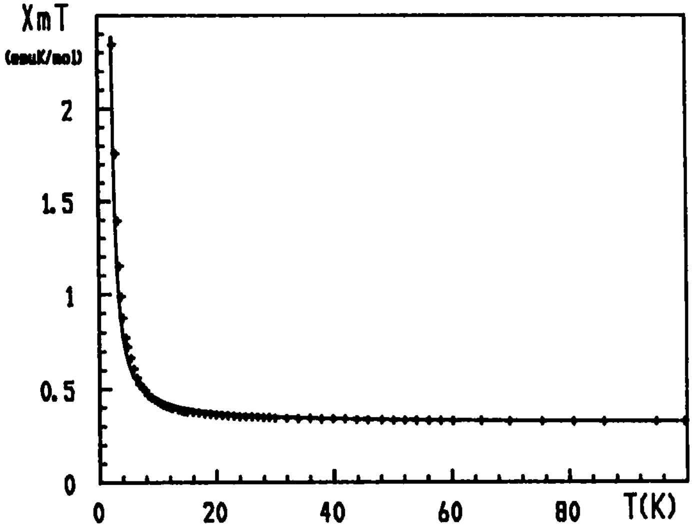

FIGURE 7. $\chi_m$ vs T for α-$VOSO_4$.

As shown above, the crystal structure of this compound (Fig.1) is able to give rise either to 1-D or 2-D interactions. The increase of $\chi_m T$ with decreasing temperature is much stronger than that expected for 1-D ferromagnetic interactions and it was impossible to obtain a satisfactory fit using the analytic expression of the magnetic susceptibility given by Baker et al[12] for a ferromagnetic chain. On the contrary a rather good agreement is obtained under the 2-D ferromagnetic hypothesis.

The magnetic susceptibility is calculated from the same way than that used for $VOSO_4.H_2O$. The corresponding series for the ferromagnetic problem can be simply obtained by introducing a $(-1)^n$ factor in each $C_n$ coefficient. The resultant expression for the magnetic susceptibility is the following:

$$\chi = \frac{N g^2 \beta^2}{4kT} \left(1 - \frac{2}{x} + \frac{2}{x^2} - \frac{1.333}{x^3} + \frac{0.25}{x^4} + \frac{0.4833}{x^5} + \frac{0.003797}{x^6}\right)^{-1}$$

with $x = kT/J$.

Full line in Fig. 7 represents the best fit obtained using J as the unique adjustable parameter. The $<g>$ value was held fixed at 1.96 as determined by ESR experiments. The calculated value $J/k = +1.5$ K agrees very well with the observed =+2.9 K (twice the J/k value in a 2-D Heisenberg model). In this calculation we did not consider the couplings between the planes. Measurements at lower temperature ($T < 1$ K) should give information on the relative importance of the intra- and interplane couplings.

$\beta$-$VOSO_4$

Above 20 K the susceptibility follows a Curie-Weiss law with $C_m = 0.35$ and $\theta = -4.7$ K (Fig. 8). The thermal variation of the $\chi_m T$ product appears to decrease with decreasing temperature down to 15 K, then below this temperature an increase is observed (Fig. 9). The negative temperature intercept and the characteristics of the $\chi_m$ T vs T curve are in agreement with a ferrimagnetic behavior for $\beta$-$VOSO_4$.

The difference of behaviors of "in-plane" magnetic interactions can be ascribed to the topology of the V-O-S-O-V sequency. The magnetic orbital is mainly the non bonding $d_{xy}$ orbital with certainly a small admixture of $d_{x^2-y^2}$ and also $d_{z^2}$. The complexity of the problem

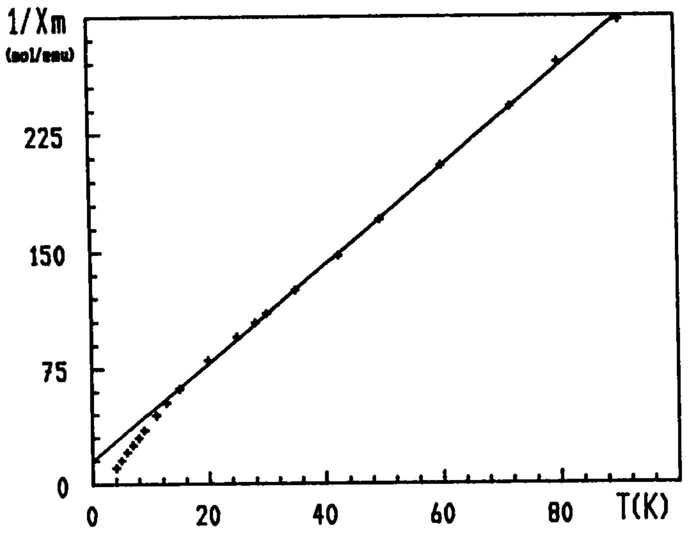

FIGURE 8. Reciprocal molar magnetic susceptibility vs temperature for ß-$VOSO_4$.

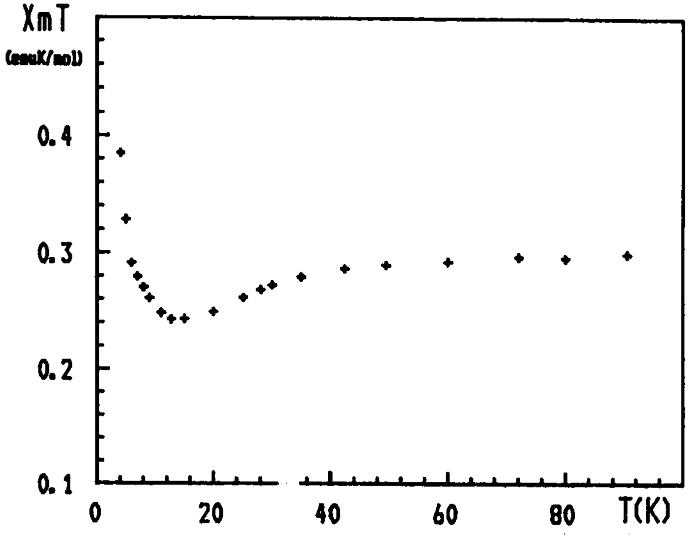

FIGURE 9. $\chi_m T$ vs T ß-$VOSO_4$.

results from the fact that the ferromagnetic and the antiferromagnetic components of the exchange interaction are both rather small and in fact of the same order of magnitude. A small variation of the bond angles may obviously favorize either ferromagnetic (in $\alpha$-$VOSO_4$) or antiferromagnetic interactions (in $VOSO_4.H_2O$). The weak ferrimagnetism observed in ß-$VOSO_4$ may be ascribed to the tilt of the connexion of $|VO_6|$ octahedra associated with the anisotropy of the g-factor.

As this stage of the investigation, it appears that a quantitative study using Extended Huckel and X$\alpha$ calculations should be carried out in order to try to understand the different behaviors of these similar compounds.

Acknowledgments - This work has been supported by the EEC (grant ST2J-0164-4). L.L. wishes to thank the Basque Government/Euzko Jaularitza for a doctoral fellowship.

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