

## Two-dimensional orbital ordering in $d^1$ Mott insulator $\text{Sr}_2\text{VO}_4$

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**Abstract.** The Mott insulator  $\text{Sr}_2\text{VO}_4$  is a unique  $d^1$  two-dimensional compound exhibiting an orbital ordering transition. In addition to the orbital ordering transition at about 100 K, we discovered a ferromagnetic transition below 10 K, thus confirming the predictions of recent band structure calculations. The magnetic properties proved to be strongly sensitive to the material purity, the actual oxygen stoichiometry and the crystallographic parameters. An additional transition is observed at 125 K, which is believed to be due to structural modifications.

### 1. Introduction

Since the discovery of high  $T_c$  superconductivity in perovskite based cuprates [1], quite a vain effort has been done in searching for Cu-free materials with a similar structure that exhibit a superconducting behaviour.  $\text{Sr}_2\text{VO}_4$  is regarded as the electronic mirror of  $\text{La}_2\text{CuO}_4$ , the parent compound of high  $T_c$  superconductors. These two compounds have in common the same crystal structure and the same layered 2-dimensional spin-1/2 array. Theoretical predictions based on LDA band structure calculations suggested  $\text{Sr}_2\text{VO}_4$  to become superconducting upon opportune doping [2], but the attempts of doping bulk  $\text{Sr}_2\text{VO}_4$  and make it conduct (or even superconduct) have not been successful so far [3,4]. Only in thin films of  $\text{Sr}_{2-x}\text{La}_x\text{VO}_4$  optical studies revealed a Mott-Hubbard gap and a M-I transition was successfully induced by doping [5]. The ground state was experimentally found to be insulating antiferromagnetic [3-4,6-7] in disagreement with the metallic ferromagnetic ground state theoretically predicted [2].

Recently, first principle band structure calculations pointed out the close competition in energy between ferro- and antiferro-magnetic ground states and predicted a non-trivial orbital-stripe structure, with a  $2 \times 4$  period due to orbital degeneracy and long range exchange [8]. The temperature variation of the optical spectrum observed by Matsuno et al. can be explained within this scenario [9]. In 2007, Zhou et al. reported the experimental evidence of such an orbital ordering in  $\text{Sr}_2\text{VO}_4$  [10].

In the present work, we confirm the existence of the orbital ordering and we investigate its origin by means of transport, magnetic, thermodynamic and optical studies. We discuss the dependence of the physical properties on the sample purity. The discrepancies existing in the literature can be ascribed to the off-stoichiometry and sample degradation. In addition, we report the presence of a weak ferromagnetic transition at low temperatures ( $T \leq 10$  K). The evidence of a ferromagnetic

ground state, in agreement with the theoretical predictions, is provided here for the first time. Our experimental data also highlights an additional transition at about 125 K. After optical investigations, this is likely to have a structural origin and to be a prelude to the orbital ordering transition.

## 2. Experimental details

Sr<sub>2</sub>VO<sub>4</sub> ceramics were obtained by solid state reaction in two steps. First, we synthesised Sr<sub>4</sub>V<sub>2</sub>O<sub>9</sub> from a stoichiometric mixture of SrCO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> at 800 °C for 60 h in air. Weak reactions with the Al<sub>2</sub>O<sub>3</sub> crucibles were observed and were avoided by using BaZrO<sub>3</sub> as crucible material. This improves the purity of the precursor and of the final samples of Sr<sub>2</sub>VO<sub>4</sub> as well. In the second step, Sr<sub>4</sub>V<sub>2</sub>O<sub>9</sub> was reduced at 900 - 950 °C for 48 h in evacuated quartz tubes with Zr as reducing agent. This procedure was repeated until the X-Ray pattern shows at least 95 % of tetragonal Sr<sub>2</sub>VO<sub>4</sub>.

XRD experiments were done using Cu K<sub>α</sub> wavelength with 0.02° step. The properties of the samples are summarized in Table 1.

The measurement of the DC electrical resistivity was carried out with a homemade four-probe setup. The magnetic moment was measured between 2 and 300 K in magnetic fields between 0 and 5 T in a Quantum Design MPMS SQUID magnetometer, and the heat capacity was measured in the same temperature range in a Quantum Design PPMS by the relaxation method. The optical properties were investigated using ellipsometry in the visible range and reflectivity in the infrared range down to 20 cm<sup>-1</sup>.

## 3. Experimental results

Differential Thermal Analysis performed under either inert or reducing atmosphere shows a phase transition at 1100°C, which marks the instability of the tetragonal Sr<sub>2</sub>VO<sub>4</sub> phase in the advantage of the high-temperature orthorhombic phase. The samples treated at high temperature (>1050°C) contain amounts of the orthorhombic phase that grow with the annealing temperature, as already observed in previous reports [10].

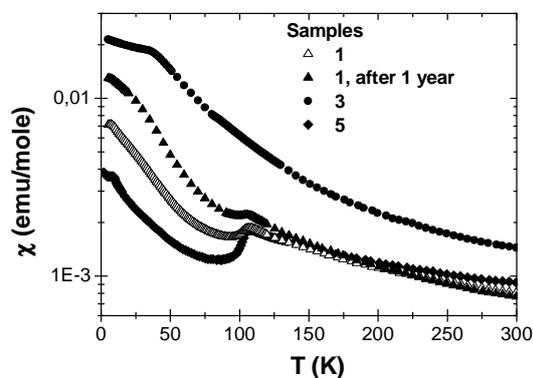
The stability of the tetragonal Sr<sub>2</sub>VO<sub>4</sub> phase in air at room temperature was also found to be a critical aspect to be checked before carrying out the various physical experiments. As a matter of fact, the material is moisture sensitive and suffers degradation in air, during which the tetragonal Sr<sub>2</sub>VO<sub>4</sub> phase partially decomposes, as confirmed by XRD. This strongly affects the magnetic properties, as shown in Fig. 1. A comparison between two m(T) curves measured at intervals of one year is shown for the sample #4. An additional magnetic contribution superposes on that of the pristine tetragonal Sr<sub>2</sub>VO<sub>4</sub> phase and the orbital ordering transition is partially hidden in the magnetic response.

**Table 1.** Thermal treatment, lattice parameters, and ordering temperatures of various samples in this study, deduced from magnetic experiments. Only the 4 and 5 samples are made using Sr<sub>4</sub>V<sub>2</sub>O<sub>9</sub> precursor synthesized in BaZrO<sub>3</sub> crucibles.

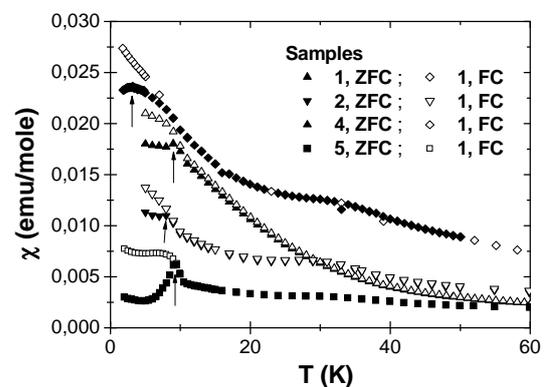
Samples	Thermal treatment	a (Å)	c (Å)	T <sub>LT</sub> <sup>max</sup> (K)	T <sub>HT</sub> <sup>min</sup> (K)	T <sub>HT</sub> <sup>max</sup> (K)	Tχ <sup>max</sup> (K)
1	4x48 h, 950°C	3.8377	12.543	9	93	107	101
2	3x48 h, 950°C	3.8337	12.587	8	84	100	93
3	1 month, 950°C	3.8416	12.654				
4	1x48 h, 900°C	3.8300	12.618	3			
5	3x48 h, 900°C	3.8373	12.549	9.5	87	107	103

There is not a general agreement in the literature on the magnetic behaviour shown in Fig.1. The reasons of such discrepancies are related either to the presence of secondary phases [3,6], or, and mainly, to the oxygen off-stoichiometry in Sr<sub>2</sub>VO<sub>4</sub>. Suzuki et al. [7] carefully studied and reported the dependence of the lattice parameters on the oxygen content. The c-axis was found to increase with increasing the oxygen deficiency in Sr<sub>2</sub>VO<sub>4-x</sub>, and ranges from 12.5602 Å to 12.5985 Å, for x ranging

from 0.18 to 0.38. Sharp orbital ordering transitions are only observed in samples with short  $c$ -axis parameter, corresponding to high oxygen content (see Table 1 and Fig.1). Our best samples, from the point of view of the orbital ordering, have a  $c$ -axis value of  $\sim 2.54$  Å. A similar value,  $c = 2.5309$  Å, and therefore a similar oxygen content, was reported by Zhou et al. [10]. On the contrary, no transition at 100 K was observed in samples with  $c = 2.57$  Å, corresponding to a lower oxygen content [6]. Our sample #3, which was subjected to 1-month long thermal treatment, exhibits no transition either (Fig. 1) and has a large  $c$ -axis (Table 1), and therefore is supposed to have lost a larger amount of oxygen. A recent study of Kini and Geibel also confirms the same behaviour upon increasing the oxygen vacancies [11]. The direct measurement of the actual oxygen content is in progress, but suffers the uncertainty due to stoichiometry distribution in polycrystalline samples. These observations prove that the orbital ordering transition occurs only in samples close to the nominal  $\text{Sr}_2\text{VO}_4$  stoichiometry.



**Figure 1** Temperature dependence of the magnetic susceptibility of different samples (see text) at 2 T

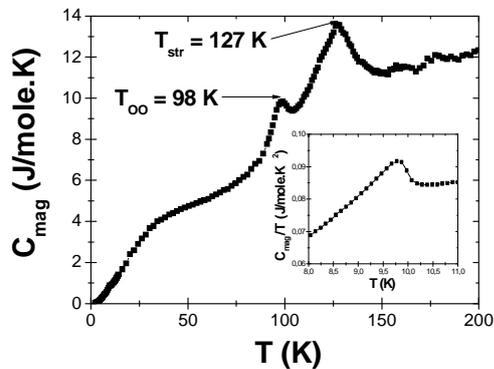


**Figure 2** Temperature dependence of the magnetic susceptibility of different samples (see text) at 0.2 T which evidence of the weak ferromagnetic transition below 10 K

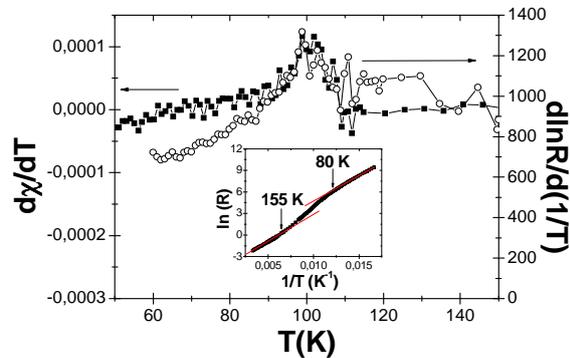
In Fig. 1, we can see that the samples exhibiting the orbital ordering transition also exhibit a magnetic irreversibility at low temperature, marked by a separation between zero field-cooled (ZFC) and field cooled (FC) susceptibility curves below 10 K. This can be the signature of either a weak ferromagnetism or a canted antiferromagnetism. It is worth noticing that the ordering temperature of this transition roughly scales with the orbital ordering transition temperature and both are sharper in samples with higher oxygen contents. These considerations indicate the intrinsic nature of the low temperature ferromagnetic transition and exclude the possibility of a spin glass behavior at low temperature. The weak lambda peak in the specific heat at 9.5 K (inset of Fig. 3) provides a direct experimental confirmation of this scenario.

The orbital ordering transition temperature  $T_{\text{OO}}$  measured by the peak in the specific heat coincides with the maximum of the derivative of the magnetic susceptibility. An additional peak is measured at  $T = 127$  K in the  $C_p(T)$  curve (Fig. 2). The splitting of some diffraction peaks observed by Zhou et al [10] between  $T_{\text{OO}}$  and 122 K was interpreted as being due to the coexistence of two tetragonal phases with different lattice parameters. Our observation of a single phase transition at 127 K in  $C_p(T)$  rather suggests that a lowering of the symmetry of the crystal structure occurs in this temperature range, and is the prelude of the orbital stripe state. Further low-X-ray diffraction experiments as a function of temperature are needed to elucidate the nature of such a transition. However, optical ellipsometry and reflectivity point up a structural effect to be associated to the transition at 127 K [12].

In Fig. 4 we show the effect of the orbital ordering transition on the electrical resistivity. The O-O transition does not change appreciably the value of the energy gap deduced from the activation energy determined from the Arrhenius plot. We find  $E_g = 128 \text{ meV} = 2 E_{\text{act}}$ , which is in good agreement with the transport and optical experiments on thin films of  $\text{Sr}_2\text{VO}_4$  done by Matsuno et al [5,9].



**Figure 3.** Temperature dependence of the magnetic contribution of the heat capacity. Inset : Evidence of the weak ferromagnetic transition at 10 K from  $C_{\text{mag}}/T$ .



**Figure 4.** Temperature dependence of  $d\chi/dT$  and  $d(\ln R)/d(1/T)$ . Inset; Arrhenius plot of the electrical resistance  $R$  of  $\text{Sr}_2\text{VO}_4$ .

#### 4. Conclusion

We have investigated the magnetic properties of tetragonal  $\text{Sr}_2\text{VO}_4$  and confirmed the existence of an orbital ordering transition at 100 K by various experimental techniques. We have investigated the effect of the oxygen stoichiometry and sample purity on the magnetic properties and found that sharp orbital ordering transitions take place in samples close to the nominal  $\text{Sr}_2\text{VO}_4$  composition. In these samples, we also discovered a low temperature ( $< 10 \text{ K}$ ) magnetic transition, which is due to either a weak ferromagnetic or a canted antiferromagnetic ground state. This is consistent with the predictions of band structure calculations that tetragonal  $\text{Sr}_2\text{VO}_4$  is close to ferromagnetic instability. Finally, we observed a structural transition occurring in tetragonal  $\text{Sr}_2\text{VO}_4$  at about 125 K.

#### References

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