

Experiment Report Form

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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: On the importance of the spin-orbit interaction in V_2O_3 .	Experiment number: HE 1327
Beamline:	Date of experiment: from: 13-11-2003 to: 19-11-2003	Date of report: 25-02-2003
Shifts:	Local contact(s): Dr. N.B. Brookes*, Dr. C. De Nadai*	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Prof. Dr. L.H. Tjeng*, II. Physikalisches Institut, University of Cologne Dr. Z. Hu*, II. Physikalisches Institut, University of Cologne Dr. C. Schüßler-Langeheine*, II. Physikalisches Institut, University of Cologne Dr. G. Ghiringhelli*, Dipartimento di Fisica, Politecnico de Milano Drs. M. Haverkort, II. Physikalisches Institut, University of Cologne Dr. N.B. Brookes*, E.S.R.F. - Grenoble Dr. C. De Nadai*, E.S.R.F. – Grenoble		

Report:

The V_2O_3 system displays a very rich phase diagram which involves antiferromagnetic (AFI), paramagnetic metallic (PM) and paramagnetic insulating (PI) regimes. The metal-insulator transitions, from PM to AFI at low temperatures and from PM to PI at higher temperatures, are considered to be classical examples of Mott transitions. An extremely large amount of work, both experimentally and theoretically, have been devoted to this paradigm system in the 1940-1980 period, totalling perhaps to more than 500 papers. Excellent reviews are given in references [1,2].

After a dormant period of about two decades, recent new experimental data [3-7] have triggered a very strong renewed interest in the V_2O_3 problem. New theories with completely different approaches [8-14] are being explored now in order to understand the complex phenomena in this material. In particular, the resonant scattering data by Paolasini *et al.* [5] and the polarization dependent soft-x-ray absorption data of Park, Tjeng *et al.* [6] have established that the V ions are in the $S=1$ state, and that therefore the V_2O_3 problem cannot be mapped onto an effective $S=1/2$ Hamiltonian as previously accepted. This has caused the theorists to make a serious overhaul about their assumptions and starting points for the modelling. In fact, one key point for any kind of model dealing with V_2O_3 is the orbital occupation number, which changes in the different phases. Recent soft x-ray absorption measurements [6] have established a new reference point for the orbital occupation numbers to be reproduced by the various theoretical scenarios being developed now [9-14].

One of the most remarkable aspects of these new theories, is that none of them, with the exception of one [14], takes the spin-orbit interaction in the V $3d$ shell into account. This is surprising in view of the fact that Paolasini *et al.* [5] have determined that the orbital moment $\langle L_z \rangle$ in the AFI phase is as large as $0.5 \mu_B$, which is not at all small compared to the spin moment $2 \langle S_z \rangle$ which amounts to $1.7 \mu_B$. Indeed, such a large number for the orbital moment is not unusual if one considers that one is dealing with a partially

unfilled t_{2g} shell system (other examples include CoO, FeO, YVO₃ [15], Ca₂RuO₄ [16]). The only theoretical work so far, that includes the spin-orbit interaction explicitly, is the one by Tanaka [14]. He proposes a model that can explain most of the new experimental data on V₂O₃, including the changes in the orbital occupation numbers across the various phase transitions. Crucial in his approach is the inclusion of the spin-orbit interaction, otherwise those experimental occupation numbers cannot be reproduced.

We have carried out spin-resolved circularly-polarized bulk-sensitive photoemission spectroscopy on the valence band of 1.2% Cr-doped V₂O₃ in order to determine the spin-orbit signal in this material in the AFI, PM and PI phases. The principle of this technique is based on the Fano effect, i.e. the creation of spin-polarized electrons when circularly polarized light is used, as a consequence of the spin-orbit interaction and the dipole selection rules. Crucial for our measurements is the use of the sum-rule derived by van der Laan and Thole [17], in which the spin polarization of the integrated valence band photoemission spectrum can be related to the expectation value of a spin-orbit operator of the system in the initial state:

$$\frac{\rho^{11}}{\rho^{00}} = \frac{2A_1 \langle \sum_i l_z(i) s_{z'}(i) \rangle}{A_0 \langle n \rangle}$$

where ρ^{00} is the integrated isotropic photoemission intensity and ρ^{11} is the so-called integrated spin-orbit intensity, defined as the difference between the integrated intensities taken with parallel and anti-parallel alignment of the photon angular momentum and electron spin. $\langle n \rangle$ is the number of electrons with index i , and the constants A_0 and A_1 depend on the transitions considered ($A_0 = 1/5$ and $A_1 = -1/15$ for $d \rightarrow f$). z gives the direction of the Poynting vector of the light and the quantization axis of the angular components, and z' indicates the spin quantization axis. ρ^{11} depends on the relative orientation of z , z' , and of the sample magnetization axis, but a net macroscopic or long range magnetic order is not necessary for ρ^{11} to be non-zero. For an isotropic (e.g. paramagnetic) system and $z = z'$, $\langle \sum_i l_z(i) s_z(i) \rangle$ becomes $\langle \sum_i l_i s_i \rangle / 3$ [17].

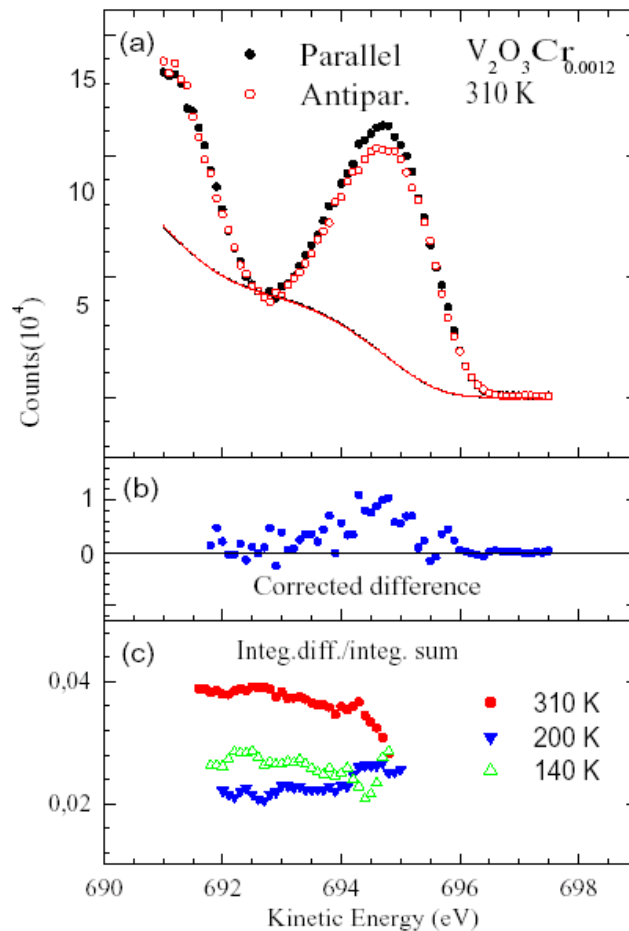


Fig. 1. Spin-resolved circularly-polarized valence band photoemission spectra of 1.2% Cr-doped V₂O₃ taken at 140 K, 200 K and 310 K.

The results are shown in Fig. 1. We found that the integrated intensity of the difference spectrum divided by the integrated intensity of the sum spectrum is 0.03 for the AFI phase, 0.02 for the PM phase, and 0.04 for the PI phase. With the integrated intensity of the sum spectrum being equal to $2/3\rho^{00}$ and estimating that $\langle n \rangle$ is roughly 2.8 [see ref. 18], we arrive at the result that $\langle \Sigma_i \mathbf{l}_i \mathbf{s}_i \rangle$ is about -0.25 for the AFI, -0.17 for the PM and -0.34 for the PI phase. These numbers are not small if one considers the fact that $\langle \Sigma_i \mathbf{l}_i \mathbf{s}_i \rangle$ is about -0.7 for a free ionic $3d^2-t_{2g}^2$ configuration in O_h point group. Our data are therefore not inconsistent with the finding of Paolasini *et al.* [5] in that the orbital moment $\langle L_z \rangle$ in the AFI phase is as large as $0.5 \mu_B$. Moreover, the $\langle \Sigma_i \mathbf{l}_i \mathbf{s}_i \rangle$ numbers change significantly across the metal-insulator transitions, which immediately draws our attention since also the orbital occupations changes dramatically as observed in the recent XAS measurements by Park, Tjeng *et al.* [6]. Combining these two sets of data brings us to the suggestion that the spin-orbit interaction play an active role in determining which orbitals are occupied in the different phases, a scenario that indeed has been proposed by Tanaka [14].

We now have to do a more detailed analysis of the data. In particular, we have to do cluster calculations involving low-symmetry crystal-field energy splittings in order to determine the delicate energy level diagram for the vanadium ion in the different phases, as to reproduce both the measured $\langle \Sigma_i \mathbf{l}_i \mathbf{s}_i \rangle$ numbers and the XAS spectra. In doing so we hope that we can obtain a better understanding about the mechanism that is behind the very rich and complex phase diagram of the V_2O_3 system.

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