This report is to be attached to the form for **Application for beamtime at ESRF** (1st half of 2000), entitled "Impurity and conduction band states in $Eu_{1-x}Gd_xO$ films: a *spin-resolved* photoemission/resonant-Auger and *circularly-polarized* X-ray absorption study", by L.H. Tjeng *et al.*, University of Groningen, The Netherlands.

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Report

The layered perovskite Sr_2RuO_4, which has the same crystal structure as the high-T_c superconductor $La_{2-x}Sr_xCuO_4$, is metallic and becomes superconducting at temperatures below $T_c = 0.93$ K [1]. The recently synthesized Ca_2RuO_4 on the other hand, is an antiferromagnetic Mott insulator ($T_N = 110$ K), although the Ru ions have the same valence and oxygen coordination [2]. In order to understand the electronic structure of these two oxides and the relationship with their interesting but also contrasting physical properties, it is essential to study the spin and orbital polarization of the Ru 4d t_{2g} bands, especially in view of the fact that the atomic spin-orbit coupling in the Ru 4d shell is not at all negligible in comparison with the 4d t_{2g} bandwidth.

To obtain the required information, we set out to do a spin-polarized photoemission experiment on these paramagnetic (Sr_2RuO_4) and antiferromagnetic (Ca_2RuO_4) using circularly polarized light. The net spin-polarization of the photoemission spectra will then give a measure for the spin and orbital quantum numbers of the relevant Ru 4d states.

In this experiment we cannot make use of a resonant condition involving a deep spin-orbit-split core level. The use of such a condition would have been extremely effective to enhance the spin polarization of the photoemission signal, but this is good only if one is interested mainly in the *spin* character of the valence band: see for example our work on CuO, Ni and NiO where we have observed polarizations of 40% or more [3-5]. Instead, for the present experiment we have

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to be optimally sensitive to the *spin-orbit* interaction within the Ru 4d shell. We therefore have to carry out the measurements in the direct photoemission mode and consequently we have to expect that the degree of the measured spin polarization is possibly not more than several percents. This in turn put a severe constraint on the performance of the entire beamline and spin-resolved photoemission set-up: there is little tolerance for spurious asymmetries in the spin-resolved signals.

In order to determine the reliability of the recently constructed spin-resolved set-up at ID12B, we have first carried out a null check experiment on Cu metal. Here we have measured the spin-up ($e^{\uparrow}$) and spin-down ($e^{\downarrow}$) photoemission spectra with both the plus (σ^{+}) and minus (σ^{-}) helicities of the light. The photoemission spectrum with the photon and electron spin parallel is then given by ($e^{\uparrow}\sigma^{+} + e^{\downarrow}\sigma^{-}$), and that with the antiparallel alignment by ($e^{\uparrow}\sigma^{-} + e^{\downarrow}\sigma^{+}$). The difference and the sum of these two spectra (i.e. parallel vs. antiparallel) are shown in Fig.1. We can clearly observe in the difference spectrum the presence of the spin-orbit interaction in the Cu 3d shell, despite the fact that the 3d band width is much larger that the spin-orbit interaction. More important is the fact that the integration of the difference spectrum yields a value of essentially zero: the integrated difference is less than 0.2% of the integrated sum, while the statistical error is 0.3%. Indeed, a zero value is expected on the basis that the closed Cu 3d shell cannot have a spin or orbital moment. This result therefore shows that the experimental set-up is working well and can reliably detect very small spin-resolved/circularly-polarized signals.
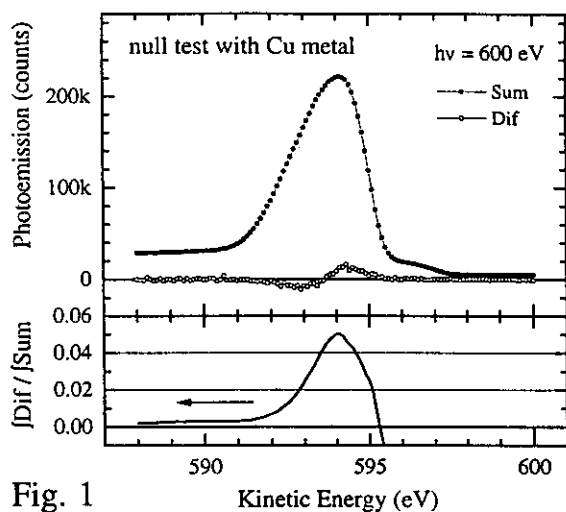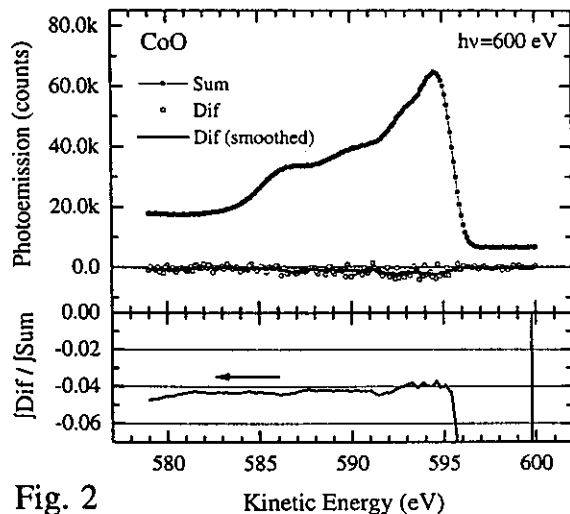

Fig. 1

Fig. 2

We have also carried out another test experiment: in order to verify the concept that the integration of the difference spectrum obtained from these type of experiments yields <L•S> like expectation values [6], which in turn is related to the spin and orbital contributions to the local magnetic moments, we have measured a well known antiferromagnetic material, namely CoO. The Co^{2+} ($3d^{7}$) ion is in the high spin state (S=3/2) and the orbital contribution to the magnetic moment can be as large as 1 μ_{B}. The experimental results are shown in Fig.2. The integration of the small difference spectrum yield a net value of -4.5%± 0.5% (relative to the integration of the sum spectrum). Configuration-interaction cluster calculations by Tanaka [Hiroshima University] predict a value of 5%. The good agreement between experiment and theory shows that this type of experiments can indeed provide quantitative information about L and S in macroscopically non-magnetic materials.

Returning now to our main subject: Sr_2RuO_4 and Ca_2RuO_4 have four electrons in three nearly degenerate Ru 4d t_{2g} orbitals. The relative strength of the Hund's coupling J_H to the crystal field splitting 10 Dt between the (xy) orbital on one hand and the (yz) and (zx) orbitals on the

other hand, determines their local electronic configurations. There are three possibilities:

(1) $(yz)^2(zx)^2$ with S=0 for 10Dt > J_H,
(2) $(xy)(yz)^2(zx)$ and $(xy)(yz)(zx)^2$ with S=1 for J_H > 10Dt > 0, and
(3) $(xy)^2(yz)(zx)$ with S=1 for 10Dt < 0.

It is interesting to note that the Ru-O distances in the local RuO_6 clusters are different for the two compounds. The Ru-O(in_plane) and Ru-O(apical) distances are, respectively, 1.94 Å and 2.06 Å in Sr_2RuO_4, 1.99 Å and 1.99 Å in Ca_2RuO_4 at 295 K (i.e. above T_N), and 2.02 Å and 1.98 Å at 11 K (i.e. below T_N). With the apex ratio of the RuO_6 cluster being very close to 1.00 in Ca_2RuO_4, one may expect that 10Dt is smaller than J_H ≈ 0.5 eV, so that the S=1 configurations (2) or (3) are realized in Ca_2RuO_4. For Sr_2RuO_4 on the other hand, the apex ratio is so large, that one can even envision that 10Dt is larger than J_H, so that the S=0 configuration (1) is realized. The presence of the strong spin-orbit interaction ξ ≈ 0.3 eV in the 4d shell however, causes a mixing of all these configurations. Yet, as a first order approximation, one can say that if 10Dt is much smaller than J_H and ξ, configurations (2) and (3) mixes strongly with each other thereby giving rise to an appreciable presence of orbital angular momentum in the ground state, and that if 10Dt is larger than J_H and ξ, configuration (1) is relatively unaffected giving a ground state with negligible orbital angular momentum.
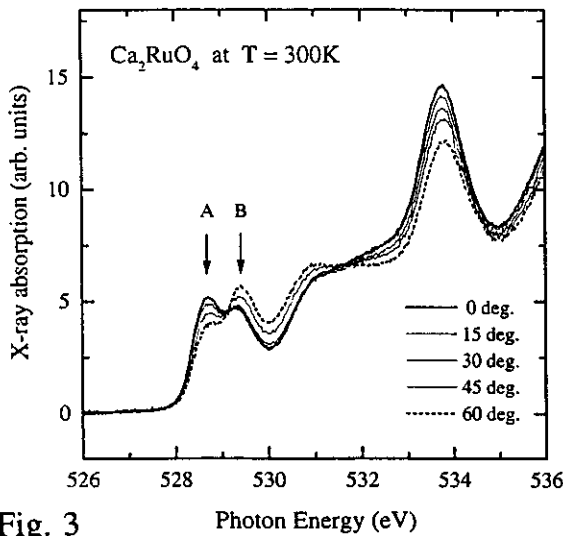
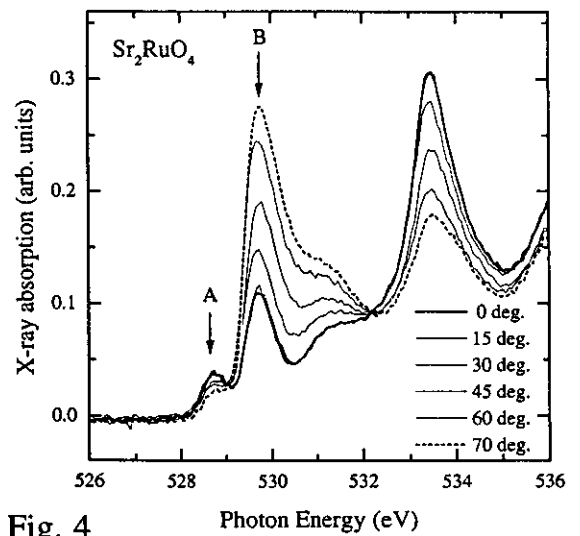

Fig. 3   Photon Energy (eV)

Fig. 4   Photon Energy (eV)

The samples were cleaved in the vacuum chamber. The cleaved surface is parallel to the RuO_2 plane. We fisrt have collected polarization dependent O K-edge X-ray absorption spectra to elucidate which of the Ru t_{2g} orbitals are possibly occupied. The results are shown in Figs. 3 and 4, where Θ denotes the angle between the surface normal and the Poynting vector of the circularly polarized light (Θ=0 means normal light incidence, i.e. the E-vector of the light within the RuO_2 plane). Here we attribute structures A and B in the spectra to absorption processes into empty states of the apical and in-plane oxygens, respectively, as a result of the hybridization with the empty Ru 4d t_{2g} orbitals. This apical (A) vs. in-plane (B) assignment is analogous to that in the $La_{2-x}Sr_xCuO_4$ case [7], and is further supported by the observation that the ratio between peak A and peak B is larger in Ca_2RuO_4 than in Sr_2RuO_4, consistent with the fact that the apex ratio in the Ca_2RuO_4 case is smaller, so that relatively more holes resides at the apical oxygens due to the larger hybridization with empty Ru 4d t_{2g} states. More support for this assignment comes from the observation (not shown here) that the A-to-B ratio in Ca_2RuO_4 increases if the sample is

cooled below T_N, in which case the apex ratio becomes even smaller. Interesting is now to follow the Θ dependence of peaks A and B: in both Ca_2RuO_4 and Sr_2RuO_4, peak A decreases and peak B increases if Θ is changed from $0°$ to $60°$ or $75°$. This suggests that both oxides are in a $(xy)^2(yz)(zx)$ like configuration. While this may look reasonable for the Ca_2RuO_4 system where the apex ratio is close to 1.00, it is a little bit of a surprise for the Sr_2RuO_4 system, where the large apex ratio could have led to a $(yz)^2(zx)^2$ state.

To investigate further the electronic structure of these ruthenates, we now look at the important spin and orbital quantum numbers of the Ru 4d ions using spin-resolved/circularly-polarized photoemission. The results are shown in Figs. 5 and 6. It is clear that the photoemission spectrum of the metallic Sr_2RuO_4 is quite different from that of the insulating Ca_2RuO_4. The integrated values of the "spin/circular" difference spectrum however, is quite similar for the two ruthenates: -4% ± 1%. This suggests that the expectation value for L•S in Sr_2RuO_4 is as large as in Ca_2RuO_4. This in turn implies that the ground state carries a substantial orbital angular momentum, not only in the insulating system but also in the metallic one. Whether or not such a large orbital angular momentum is of importance for the unusual superconductivity in Sr_2RuO_4 is subject of further study.
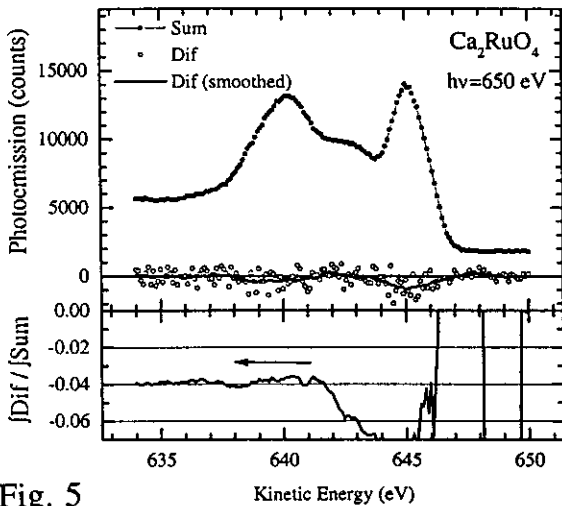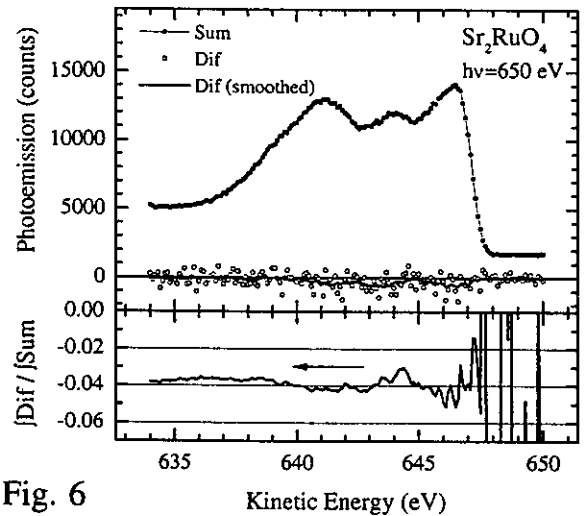

Fig. 5

Fig. 6

At the moment we are carrying out further analysis of the data: we are going to perform detailed model calculations in order to determine quantitatively the relevant spin and orbital occupation numbers of the ground state of these ruthenates. We thereby hope to get a better microscopic understanding of the rather contrasting physical properties of these two systems. We also hope to work out some kind of a sum rule for "spin/circular" difference spectra, so that perhaps a <L•S> like evaluation of 3d and 4d transition metal compounds (mostly antiferromagnets or paramagnets) can be made easily.

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