

Study of Magnetic Materials Using Spin-Resolved Circularly-Polarized Resonant Photoemission

L. H. TJENG¹, N. B. BROOKES², J. B. GOEDKOOP^{2,*}, B. SINKOVIC^{3,**}, F. M. F. DE GROOT¹, R. HESPER¹, S. ALTIERI¹, E. PELLEGRIN^{1,***}, Arata TANAKA⁴, S. L. HULBERT⁵, E. SHEKEL^{3,****}, N. T. HIEN⁶, A. A. MENOVSKY⁶ and G. A. SAWATZKY¹

¹*Solid State Physics Laboratory, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

²*European Synchrotron Radiation Facility, B.P. 220, 38043 Grenoble Cedex, France*

³*Physics Department, New York University, 2 Washington Place, New York, NY 10003, U.S.A.*

⁴*Department of Materials Science, Faculty of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*

⁵*National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973, U.S.A.*

⁶*Van der Waals-Zeeman Laboratory, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands*

(Received October 31, 1998; accepted for publication November 26, 1998)

We have recently demonstrated that it is possible to obtain spin-resolved valence band spectra with a very high degree of spin polarization from macroscopically non-magnetic transition metal materials if the excitation light is circularly polarized and has an energy close to the cation $2p_{3/2}$ (L_3) white line. Using the layered compound $Sr_2CuO_2Cl_2$ as a test system, we report in this paper that the degree of spin polarization is strongly dependent on the transition metal 3d orbital orientation relative to the Poynting vector of the light.

KEYWORDS: spin-resolved photoemission, soft-x-ray magnetic circular dichroism, strongly correlated solids

1. Introduction

To determine the nature and behaviour of quasi-particles in strongly correlated magnetic transition metal materials, including oxides and high- T_c superconductors, it is highly desirable to have experimental information about the energies and band widths of the different spin and multiplet states in the single-particle excitation spectrum. Identification of these states, which have their meaning within the Anderson impurity model, could facilitate the modelling of the low-energy excitations of the lattice in terms of those of the impurity. Knowledge of the character of the first ionization states is important for a better understanding of, for example, the stability of the magnetic state and the behavior of the charge carriers in doped materials.

Making use of the on-going advancements in synchrotron radiation technology, we have recently been able to obtain spin-resolved valence band spectra with a very high degree of spin polarization from antiferromagnetic and paramagnetic transition metal materials if the excitation light is circularly polarized and has an energy close to the cation $2p_{3/2}$ (L_3) white line.¹⁻³ We were able, for instance, to unravel the different spin states in the single particle excitation spectrum of CuO and show that the top of the valence band is of pure singlet character,¹ which provides strong support for the existence and stability of Zhang-Rice singlets in high- T_c superconducting cuprates.⁴⁻⁸ We have

also measured the Ni 3d spin polarization below and above the Curie temperature, and have found that the $3d^8$ triplets in the valence band spectrum are extending all the way to the Fermi energy.² This means that the atomic Hund's rule correlations survive the strong band formation, and that these correlations together with the orbital degeneracy of the 3d band are of utmost importance to understand Ni and other 3d ferromagnets.

In this paper we investigate more in detail the selection rules that are involved in the spin-resolved circularly-polarized resonant photoemission process. In particular, we carry out a study on the influence that the transition metal 3d orbital orientation might have on the degree of the spin polarization of the outgoing photoelectrons. For this we have used the layered compound $Sr_2CuO_2Cl_2$ as a test system: the material contains two-dimensional CuO_2 planes which have a quite similar electronic structure as CuO, but with the advantage that high quality single crystal surfaces can be obtained with a well defined orientation, namely parallel to the CuO_2 planes. We find that the degree of spin polarization is strongly dependent on the transition metal 3d orbital orientation relative to the Poynting vector of the light. For the Cu $3d^8$ (1G) final state, we find that the polarization can vary between 0% and the extremely high value of 83%.

2. Experimental

The experiments were performed using the helical undulator⁹ Dragon beam line BL26/ID12¹⁰ at the European Synchrotron Radiation Facility (ESRF) at Grenoble, together with the New York University (NYU) spin-resolved spectrometer specifically designed for soft-x-ray photoemission experiments.¹¹ The overall monochromator and electron analyzer resolution was set at 1.5 eV. The degree of the circular polarization at the Cu $2p_{3/2}$ (L_3) photoabsorption white line ($h\nu = 931.5$ eV) was 0.85 and

* Present address: Van der Waals-Zeeman Laboratory, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands.

** Present address: Department of Physics, University of Connecticut, 2152 Hillside Road, U-46, Storrs, CT 06269-3046, U.S.A.

*** Present address: Forschungszentrum Karlsruhe, ANKA Project Group (PEA), P.O. Box 3640, D-76021 Karlsruhe, Germany.

**** Present address: El-Op, Tel Aviv, Israel.

the detector's spin sensitivity (Sherman function) was 0.07. The angle between the electron emission direction and the light beam was set at 90° and the spin detector was set to measure the degree of the electron spin polarization in the direction along the light beam in order to obtain complete parallel and anti-parallel alignment of the photon spin and electron spin. The spectra were recorded with the four possible combinations of light helicity (σ^+/σ^-) and spin detector channels (e^\uparrow/e^\downarrow , measured simultaneously), in order to exclude any systematic errors. The $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ sample was grown by means of the floating zone technique, using an elliptical furnace.¹²⁾ The sample was cleaved *in situ* and measured at room temperature, which is above the Neel temperature of $\sim 225\text{K}$.

3. Results and Discussion

The top panel of figure 1 shows the valence band photoemission spectrum of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ with the photon energy tuned at the Cu $2p_{3/2}$ (L_3) white line, taken at a $\Theta=45^\circ$ angle between the Poynting vector of the light and the *c*-axis (surface normal) of the crystal. The spectrum is the sum of two spectra, one collected with parallel ($\uparrow\uparrow = \sigma^+e^\uparrow + \sigma^-e^\downarrow$) and the other with anti-parallel ($\uparrow\downarrow = \sigma^+e^\downarrow + \sigma^-e^\uparrow$) alignment of the photon spin and electron spin. Aside from a slightly poorer energy resolution, it is quite similar to the unpolarized $2p$ resonant photoemission spectrum of CuO and the high- T_c superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ from earlier works.^{13,14)} The spectrum reveals primarily the Cu $3d^8$ final states, and the peaks at 16.2 and 12.5 eV binding energy are states derived from the typical atomic-like 1S and 1G states, respectively, as explained before.¹³⁻¹⁷⁾

The middle panel of figure 1 displays the degree of spin polarization, defined as the ratio between the difference spectrum relative to the sum spectrum of the parallel and anti-parallel spectra. A correction for the spin detector sensitivity and the incomplete polarization of the light has been included. We observe that this spin polarization is extremely large, up to roughly 60% for the states assigned as 1S and 1G like. This is significantly higher than the 42% maximum value found for polycrystalline CuO.¹⁾

From the sum spectrum (top panel) and the polarization spectrum (middle panel) we can also calculate the true individual parallel and anti-parallel spectra, and the results are shown in the bottom panel of figure 1. The large difference between these two spectra is another manifestation for the high degree of spin polarization that can be obtained from this type of resonant photoemission spectroscopy.

In this photoemission work on $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ we make use of the Cu $2p_{3/2}$ (L_3) resonance condition: when the photon energy is near the Cu $2p_{3/2}$ (L_3) absorption edge, the photoemission consists not only of the direct channel ($3d^9 + h\nu \rightarrow 3d^8 + e$) but also, and in fact overwhelmingly, of the deexcitation channel in which a photoabsorption process is followed by a non-radiative Auger decay ($2p^63d^9 + h\nu \rightarrow 2p^53d^{10} \rightarrow 2p^63d^8 + e$). In principle, to observe spin signal one needs only the use of a spin detector and circularly

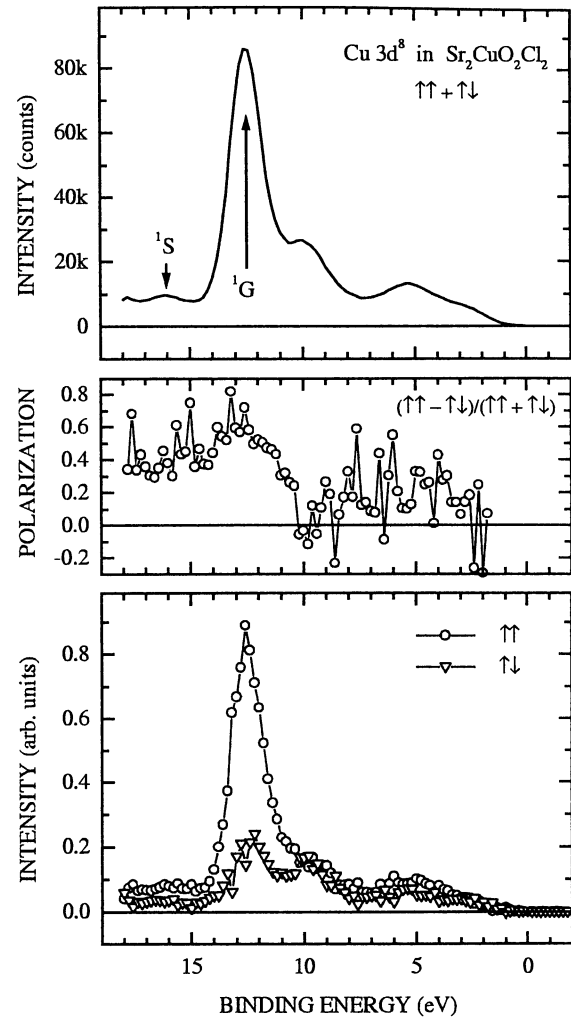


Fig. 1. Spin-resolved circularly polarized $2p_{3/2}$ (L_3) resonant valence band photoemission spectrum of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ taken at a $\Theta=45^\circ$ angle between the Poynting vector of the light and the *c*-axis of the crystal. The top panel shows the sum of two spectra, one taken with parallel and the other with anti-parallel alignment of the photon spin and electron spin. The middle panel shows the degree of spin polarization, calculated as the ratio between the difference and sum spectrum, corrected for the efficiency of the spin detector and the incomplete polarization of the light. The bottom panel depicts the individual parallel and anti-parallel spectra.

polarized light. It is important to realize, however, that circularly polarized light can only be very effective if a strong spin-orbit splitting is present in the atomic subshell under study, because then angular momenta will govern the selection rules.¹⁸⁾ Consequently, direct (non-resonant) photoemission on $3d$ transition metal materials would produce little spin signal, because the spin-orbit interaction (of order 0.1 eV) is negligible compared to other interactions like crystal fields and hybridizations (of order 1 eV). By making use of the $2p$ core level as an intermediate state in the deexcitation channel of the $2p$ resonant photoemission process, we now can take advantage of the large $2p$ spin-orbit splitting (of order 20 eV) and the

well known strong $L_{2,3}$ magnetic circular dichroism.¹⁹⁾ This forms the main principle of our technique: tuning into one of the two well separated spin-orbit split 2p white lines, circular polarized light produces a spin polarized 2p core hole, allowing the subsequent Auger decay to produce photoelectrons which are also spin polarized (with a polarization depending on the final state).

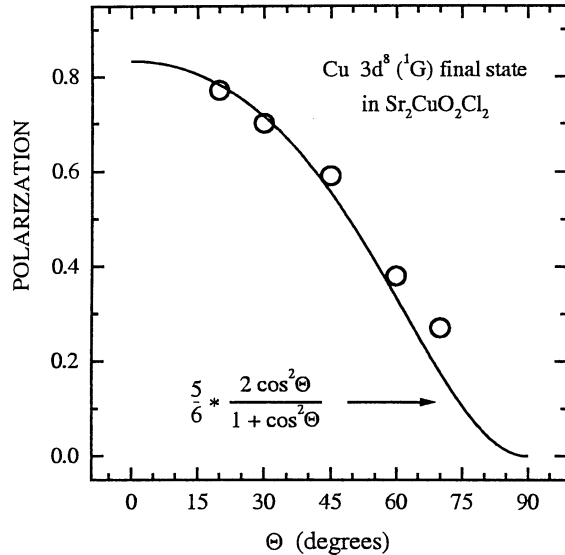


Fig. 2. Degree of spin-polarization of the Cu $3d^8$ (1G) peak in $Sr_2CuO_2Cl_2$ as a function of the angle between the Poynting vector of the light and the c-axis of the crystal.

To study in more detail the possible differences in the degree of spin polarization between the layered $Sr_2CuO_2Cl_2$ and the polycrystalline CuO, we vary the angle Θ . The results for the spin polarization of the 1G peak are shown in figure 2. A very strong variation of the spin polarization with Θ can clearly be observed. At $\Theta=20^\circ$ the polarization is about 78% and an extrapolation to $\Theta=0^\circ$ yields a value of roughly 83%. Going to higher Θ values on the other hand, the polarization quickly decreases and is expected to even vanish for $\Theta=90^\circ$.

To explain this Θ dependence of the spin polarization, we need to consider the selection rules that govern the deexcitation process. Starting from a $3d^9$ initial state with a valence shell hole which is spin-up or spin-down, the photoabsorption process will produce a 2p core hole which is spin-up and spin-down. This process is therefore determined by four different cross-sections: A^+, A^- for creating core holes with the same spin as the valence shell hole, and B^+, B^- with opposite spin, where the +/- signs refer to an antiparallel/parallel alignment, respectively, of the valence shell hole and photon spin. It is now not difficult to deduce¹⁾ that a measurement of the intensity difference ($\sigma^+e^\uparrow - \sigma^+e^\downarrow$) for singlet Auger final states, will be proportional to $(A^+-B^+)-(A^-B^-)$ for an antiferromagnet containing equal numbers of spin-up and spin-down ions (with analogous expressions for σ^- light). Consequently, the polarization,

defined as the intensity difference divided by the sum, is given by $[(A^+-B^+)-(A^-B^-)]/[(A^++B^+)+(A^-+B^-)]$. Realizing that the Cu 3d hole in the CuO_2 planes resides in the b_{1g} type of orbital of the local square planar D_{4h} point group, one finds for an (x^2-y^2) hole with the Poynting vector of the light along z (i.e. the c-axis is parallel to the Poynting vector) that the $2p_{3/2} \rightarrow 3d$ dipole transition matrix elements are $A^+=9$, $A^-=1$, $B^+=0$, and $B^-=2$, yielding a spin polarization of $5/6$. For an (x^2-z^2) or (y^2-z^2) hole on the other hand (i.e. the c-axis is along the y or x-axis and is perpendicular to the Poynting vector along z), the matrix elements are $A^+=5/2$, $A^-=5/2$, $B^+=1/2$, and $B^-=1/2$, yielding zero polarization. Rotating now the c-axis continuously away from the z-axis with an angle Θ , the polarization is theoretically given by $5/6 * 2\cos^2\Theta/(1+\cos^2\Theta)$. Here the $\cos^2\Theta$ term in the nominator simply reflects the extent in which circularly polarized light can produce a spin polarized $2p_{3/2}$ core hole: if Θ approaches 90° then the out-of-plane component of the circularly polarized light can not be absorbed any more by the (x^2-z^2) or (y^2-z^2) hole so that the absorption process is equivalent to that of linearly polarized light,²⁰⁾ yielding no net spin polarization. The $(1+\cos^2\Theta)$ denominator gives the total absorption cross section. From figure 2 we can now clearly see that this simple theoretical behavior reproduces very well the experimental data points. It is interesting to note that at the magic angle ($3\cos^2\Theta=1$) the polarization is $5/12$, which is indeed in very good agreement with the experimentally observed value of 42% for an isotropic material like CuO.¹⁾

4. Conclusion

In summary, we demonstrate the feasibility of spin-resolved valence band photoemission on macroscopically non-magnetic transition metal materials, i.e. antiferromagnets, paramagnets and materials with disordered magnetic structure, and show that a very high degree of spin polarization can be obtained. The combined use of circularly polarized light, electron spin detection and $2p_{3/2}$ (L_3) resonance condition is essential. Using the layered compound $Sr_2CuO_2Cl_2$ as a test system, we find that the degree of spin polarization is strongly dependent on the transition metal 3d orbital orientation relative to the Poynting vector of the light. For the Cu $3d^8$ (1G) final state, we find that the polarization can vary between 0% and the extremely high value of 83%. This last aspect may in turn make $Sr_2CuO_2Cl_2$ very suitable to be used as a standard material to calibrate the efficiency of spin detectors.

Acknowledgements

It is a pleasure to acknowledge technical assistance of J.C. Kappenburg, L. Huisman, J.F.M. Wieland. We are grateful to the ESRF staff for their support, in particular R. Mason and J. Klora. We thank C.T. Chen, J.-H. Park and V. Chakarian for making testing facilities available at the AT&T Bell Laboratories Dragon beamline. This investigation was supported by the Netherlands Foundation for Chemical Research (SON), the Netherlands Foundation

for Fundamental Research on Matter (FOM) with financial support from the Netherlands Organization for the Advancement of Pure Research (NWO), the New York University Research Challenge Grant 5-201-396, and the National Science Foundation Grant DMR-9625340. The research of LHT and FMFdG has been made possible by fellowships of the Royal Netherlands Academy of Arts and Sciences.

References

- 1) L.H. Tjeng, B. Sinkovic, N.B. Brookes, J.B. Goedkoop, R. Hesper, E. Pellegrin, F.M.F. de Groot, S. Altieri, S.L. Hulbert, E. Shekel, and G.A. Sawatzky, *Phys. Rev. Lett.* **78** (1997) 1126.
- 2) B. Sinkovic, L.H. Tjeng, N.B. Brookes, J.B. Goedkoop, R. Hesper, E. Pellegrin, F.M.F. de Groot, S. Altieri, S.L. Hulbert, E. Shekel, and G.A. Sawatzky, *Phys. Rev. Lett.* **79** (1997) 3510.
- 3) N.B. Brookes, B. Sinkovic, L.H. Tjeng, J.B. Goedkoop, R. Hesper, E. Pellegrin, F.M.F. de Groot, S. Altieri, S.L. Hulbert, E. Shekel, and G.A. Sawatzky, *J. Electron Spectrosc. Relat. Phenom.* **92** (1998) 11.
- 4) P.W. Anderson, *Science* **235** (1987) 1196.
- 5) F.C. Zhang and T.M. Rice, *Phys. Rev. B* **37** (1988) 3759.
- 6) H. Eskes and G.A. Sawatzky, *Phys. Rev. Lett.* **61** (1988) 1415.
- 7) A.K. McMahan, R.M. Martin, and S. Satpathy, *Phys. Rev. B* **38**, (1988) 6650.
- 8) E. Dagotto, *Rev. Mod. Phys.* **66** (1994) 763.
- 9) P. Elleaume, *J. Synchr. Rad.* **1** (1994) 19.
- 10) J. Goulon, N.B. Brookes, C. Gauthier, J.B. Goedkoop, C. Goulon-Ginet, and M. Rogalev, *Physica B* **208** (1995) 199.
- 11) B. Sinkovic, F. Shekel, S.L. Hulbert, *Phys. Rev. B* **52** (1995) R15703.
- 12) N.T. Hien, J.J.M. Franse, J.J.M. Poethuizen, T.W. Li, A.A. Menovsky, *J. Cryst. Growth* **171** (1997) 102.
- 13) L.H. Tjeng, C.T. Chen, J. Ghijsen, P. Rudolf, and F. Sette, *Phys. Rev. Lett.* **67** (1991) 501.
- 14) L.H. Tjeng, C.T. Chen, and S.-W. Cheong, *Phys. Rev. B* **45** (1992) 8205.
- 15) J. Ghijsen, L.H. Tjeng, J. van Elp, H. Eskes, J. Westerink, G.A. Sawatzky, M.T. Czyzyk, *Phys. Rev. B* **38** (1988) 11322.
- 16) J. Ghijsen, L.H. Tjeng, H. Eskes, and G.A. Sawatzky, *Phys. Rev. B* **42** (1990) 2268.
- 17) H. Eskes, L.H. Tjeng, and G.A. Sawatzky, *Phys. Rev. B* **41** (1990) 288.
- 18) B.T. Thole, G. van der Laan, and G.A. Sawatzky, *Phys. Rev. Lett.* **55** (1985) 2086.
- 19) C.T. Chen, F. Sette, Y. Ma, and S. Modesti, *Phys. Rev. B* **42** (1990) 7262.
- 20) C.T. Chen, L.H. Tjeng, J. Kwo, H.L. Kao, P. Rudolf, F. Sette, and R.M. Fleming, *Phys. Rev. Lett.* **68** (1992) 2543.