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Study of magnetism using circularly polarized soft X-rays¹

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Abstract

It has recently been shown that spin-resolved valence band photoemission spectra can be obtained from macroscopically non-magnetic transition metal materials. This is achieved by combining circularly polarized soft X-rays, electron spin detection and $2p_{3/2}$ (L₃) resonant photoemission.

These experiments have been performed at the European Synchrotron Radiation Facility (ESRF) by combining a helical undulator, HELIOS I, a 'Dragon' spherical grating monochromator and the New York University (NYU) spin-resolved spectrometer, specifically designed for soft-X-ray photoemission experiments.

Examples will be given of applications to antiferromagnetic materials (e.g. CuO) and paramagnets (e.g. nickel metal above its Curie temperature). © 1998 Elsevier Science B.V. All rights reserved

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1. Introduction

The purpose of this paper is to show that it is possible to obtain the spin-resolved valence band of macroscopically non-magnetic transition metal materials (antiferromagnets, paramagnets and materials with disordered magnetic structure). This can be achieved by using circularly polarized radiation, electron spin detection and by doing the photoemission at a photon energy at resonance with spinorbit split core levels.

This is illustrated by two examples: nickel metal

and copper oxide (CuO). The angle resolved photoemission data on these two materials show that the valence bands are shifted compared with a one electron calculation: in addition structures appear (around 6 eV for Ni and 12 eV for CuO) that are not predicted by the one electron calculation. These structures, called 'satellites', are the result of many-body effects and are well understood. They are two hole bound states corresponding to 3d⁸ final states (singlets ¹S, ¹D, ¹G and triplets ³P, ³F). It has been shown in the past that these satellites show very strong enhancement (giant resonance) when the photon energy is tuned near the 2p levels (hv = 931.5 eVfor Cu and hv = 852.7 eV for Ni), allowing a detailed study of the various multiplets. In this paper, we present results obtained on Ni above its Curie temperature (T_c) and in the case of CuO we show that the top

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Fig. 1. The upper panel shows the experimental geometry and the insert the relevant resonant photoemission transition. The lower panel shows the absorption spectra for Ni taken with left and right circularly polarized and the corresponding dichroism spectrum, given by the difference between the spectra taken with left and right circularly polarized.

of the valence band is of pure singlet character, supporting the existence of Zhang-Rice singlets in high- T_c cuprates.

2. Experimental aspects

The experiments were performed using the helical undulator [1] Dragon beam line ID12B [2], together with the New York University's spin resolved electron spectrometer specifically designed for soft-X-ray photoemission experiments [3]. The overall monochromator and electron analyser resolution was set at 1.5 eV. The degree of the circular polarization at the Ni and Cu L_3 photoabsorption white lines was ~0.85 and the detector's spin sensitivity (Sherman

function) was 0.07. The angular acceptance of the analyser was $\pm 4.5^{\circ}$. The experimental geometry is shown in Fig. 1. The spectra were recorded with the four possible combinations of light helicity (σ^+/σ^-) and spin detector channels (e⁻¹/e⁻¹, measured simultaneously), in order to exclude any systematic errors.

3. Local electronic and magnetic structure of Ni below and above T_c

Despite a large body of experimental data, a complete description of finite temperature magnetism remains controversial, with some recent results on Ni supporting a Stoner-like behaviour [4], fluctuating



Fig. 2. Spin resolved circular polarized $2p_{3/2}$ (L₃) resonant valence band photoemission spectrum of Ni. Panel (a) shows the spin integrated spectrum (solid line) together with the break down in terms of singlets (Δ) and triplets (∇). Panel (b) depicts the spin polarization below the Curie temperature (0.49 T_c) and panel (c) above the Curie temperature (1.04 T_c). The inset shows the experimental geometry.

band theory [5], or suggesting even more complex behaviour [6], and as far as the electronic structure is concerned, most of this discussion can be reduced to the question as to whether or not the atomic Hund's rule correlations have survived the strong band formation. Such local exchange interactions, together with the suppression of charge fluctuations due to Coulomb interactions, may account for the failure of mean-field theories to calculate T_c properly and may give a plausible explanation for the retention of local moments and short range magnetic order above T_c in late transition metals [7].

To provide a better insight in these phenomena, we have investigated the local electronic structure of Ni and its temperature dependence, with special emphasis on the spin polarization of the atomic-like 3d orbitals. For this we have used the spin-resolved circularly-polarized 2p (L_3) resonant photoemission technique, a newly developed spectroscopic tool with the unique property that it is capable of measuring the local 3d spin polarization independent of the orientation of the local moment, which is a necessary condition to study local moments above T_c .

A thick (~100 Å) Ni film was grown epitaxially in-situ on a Cu(001) surface, yielding L_{2,3} X-ray absorption and spin-unpolarized photoemission spectra identical to those measured previously (Figs 1 and 2) [8]. No Cu signal could be observed in the spectra during all measurements below and above the Curie temperature of Ni ($T_c = 627$ K) indicating good sample quality. The sample geometry is shown in Fig. 1, with $\vartheta = \Phi = 45^\circ$ and normal emission.

The measurements were first performed at room temperature, i.e. below T_c (T = 295 K = 0.47 T_c). In order to obtain an accurate comparison between the spectra taken below and above T_c , as discussed later, we purposely demagnetized the room-temperature Ni film. The demagnetized state was determined by the reduction of the dichroic effect in the L_{2,3} X-ray absorption spectrum Fig. 1) to a few percent of its fully magnetized value [9].

The thick solid line in Fig. 2a shows the valence band photoemission spectra with photon energy tuned at the Ni $2p_{3/2}$ (L₃) white line. This is the sum of the spectra taken with parallel ($\sigma^+ \varepsilon^{\uparrow} + \sigma^- \varepsilon^{\downarrow}$) and antiparallel ($\sigma^+ \varepsilon^{\downarrow} + \sigma^- \varepsilon^{\uparrow}$) alignment of the photon and electron spin. The spectrum reveals primarily the Ni 3d⁸ final states [8], and the peak at 6 eV binding energy is the much discussed satellite of atomic-like ¹G character [8,10–15].

More important is to investigate the degree of spin polarization defined as the ratio between the difference vs the sum of the spectra taken with parallel and antiparallel alignment of the photon and electron spins. The result is presented in Fig. 2b, after taking into account the spin detector sensitivity, the degree of circular polarization and the experimental geometry. We observe that this polarization is very large, up to about 40%, which is quite remarkable in view of the fact that we are studying a demagnetized Ni film.

It is evident that without the use of circularly polarized light one would not measure a net spin polarization from a non-magnetized sample since the spin resolved signals from magnetically opposite Ni sites would cancel each other. Yet, it is important to realize 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 [16]. Consequently, direct (non-resonant) photoemission on 3d transition metals would produce little spin signal, because the spin-orbit interaction (of order 0.1 eV) is negligible compared with other interactions like crystal fields and hybridization (of order 1 eV). To resolve this problem we made use of the $2p_{3/2}$ (L₃) resonance condition (Fig. 1) [8] in our photoemission work: when the photon energy is near the Ni 2p ($L_{2,3}$) absorption edges, the photoemission consists not only of the direct channel $(3d^9 + hv \rightarrow 3d^8 + e)$ but also, and in fact overwhelmingly, of the de-excitation channel in which a photoabsorption process is followed by a non-radiative Auger decay $(2p^63d^9 + hv \rightarrow 2p^53d^{10} \rightarrow$ $2p^{6}3d^{8} + e$). With the presence of the 2p core level in the intermediate state we now have the opportunity to take advantage of the large 2p spin-orbit splitting (of order 20 eV, Fig. 1) and the strong L_{2,3} magnetic circular dichroism (Fig. 1) [9]. 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). The fact that the photoelectron carries information concerning the local moment in the ground state is essential, since the probability and degree of spin-polarization with which the core-hole is created depends on the spin and multiplet character of the valence hole in the ground state, and since the core excited electron is a participator in the Auger decay process. The resulting degree of spin polarization of the photoelectron is determined by selection rules, and details are given elsewhere [17].

Analysis of the data reveals that the peak assigned as the $3d^{8}$ ¹G-like state has a degree of polarization of about + 40%. This compares very well with an analysis of the selection rules [17] for a $3d^9$ initial state configuration, in which the polarization is found to be +5/12 (+42%) for the ¹S, ¹D, ¹G and -1/3 * 5/12 (-14%) for the ³P, ³F 3d⁸ final states (neglecting the small 3d spin-orbit interaction). The data therefore show that for 6 eV and higher binding energies only singlet states are present, and that for lower binding energies both singlet and triplet states are present since the polarization is much reduced but not negative.

Fig. 2a shows a break down of the experimental 3d⁸ final states in terms of singlets and triplets, using the above mentioned selection rules and the facts that the measured total intensity is the sum of the two contributions $(I_{tot} = I_s + I_t)$ and that the measured total polarization is a weighted sum of the singlet and triplet polarization ($P_{tot} = (P_s * I_s + P_t * I_t)/I_{tot}$). The results demonstrate clearly that this type of experiment can unravel the different multiplet or spin states of the valence band of transition metal materials. For Ni we can establish that the singlets are located at much higher binding energies than the triplets and that the triplets extend all the way to the Fermi energy, providing support to the suggestions presented in early spin unpolarized Auger studies [18,19]. Our data indicate that the on-site Coulomb and exchange matrix elements, and in particular, the Hund's rule still play an important role in determining the energetics of the valence band states of Ni despite the strong band formation. Moreover, our data suggest strongly that the ground state has a considerable triplet 3d⁸ character since these extend to the Fermi energy.

The study has also extended the measurements above T_c ($T = 653 \text{ K} = 1.04 T_c$). The sum of the high temperature spectra taken with parallel and anti-parallel alignment of the photon spin and electron spin is identical to that of the room temperature spectra shown in Fig. 2a. More informative is to look at the spin polarization of the high temperature spectra, which is depicted in Fig. 2c. It is quite striking that the line shape of the polarization function is very similar to that at low temperatures as shown before in Fig. 2b. This is also true for the magnitude of the polarization function, with values up to 40%. These high temperature results, maybe more so than the room temperature results on the demagnetized sample, clearly demonstrate that this technique is a powerful tool to obtain strong spin-polarized signals from the valence band of transition metal materials which are magnetically disordered and have no net macroscopic magnetization. Moreover, these results show that the observed polarization in this experiment does not depend on the orientation of the local moment, but only on the magnitude of the local moment, making it an ideal tool for studying local moments in itinerant ferromagnets above T_c .

The lack of change in the local 3d polarization in going through $T_{\rm c}$ indicates also that at high temperatures the singlets are located at much higher energies than the triplets and that these triplets extend all the way to the Fermi energy. The latter implies that the ground state has a considerable high spin 3d⁸ character, or in other words, that local moments of 3d character are still present above T_c . This result shows clearly one of the shortcomings of mean-field theory [20], which predicts the disappearance of local moments above T_c . More interestingly, our data may provide an insight as to why such theories fail to calculate $T_{\rm c}$ properly [7]. A consequence of the oneelectron approximation is that charge fluctuations are purely statistically distributed since they do not cost extra energy. They are also independent of spin for a non-magnetic system. Our spectra indicate, however, that such a condition is met only for the (low lying) triplets and that charge fluctuations involving singlets are quite energetic, up to 6–9 eV for the ¹G, ¹S-like states. It is this neglect of the Hund's first rule (triplets lower in energy than singlets) and Coulomb correlations (high energy singlet 3d⁸ satellites) that causes mean-field theories to underestimate the gain in potential energy by keeping the 3d electrons localized relative to the gain in kinetic energy by allowing those electrons to form a band. This underestimation is much more serious in the non-magnetic than in the ferromagnetic case, since in the latter a strong reduction of charge fluctuations can be achieved due to the fact that electrons can move primarily in one of the two spin bands and not in both. Consequently, the energy difference between a non-magnetic and magnetic state is overestimated in mean-field theories, resulting in a too high prediction of $T_{\rm c}$.

4. Direct observation of Zhang-Rice singlets in CuO

CuO is often seen as a model compound for high- T_c cuprates, since in comparing it with the insulating



parent compounds of the superconductors, the magnitude of the insulating gap, the antiferromagnetic superexchange interactions, the basic structural unit (CuO₄), the Cu–O distances, as well as the Cu valence appear to be quite similar. Therefore the characteristics of the first ionization states in CuO (two hole final state in photoemission) may be representative for the behaviour of the doped holes in cuprates (ground state) [23].

The angle between the electron emission direction and the light beam was set at 90° ($\vartheta = 90^{\circ}$) 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 CuO sample was prepared in-situ by high-pressure (2–10 mbar O₂) and high-temperature (400 °C)



oxidation of polycrystalline Cu as described in earlier studies [20–22], yielding unpolarized spectra identical to those measured previously. The measurements were carried out at room temperature.

The top panel of Fig. 3 shows the valence band photoemission spectra of CuO with photon energy tuned at the Cu $2p_{3/2}$ (L₃) white line (hv = 931.5 eV). The thick solid line is the sum of the spectra taken with parallel $(\sigma^+ \varepsilon^{\uparrow} + \sigma^- \varepsilon^{\downarrow})$ and anti-parallel $(\sigma^+ \varepsilon^+ + \sigma^- \varepsilon^+)$ alignment of the photon spin and electron spin. Aside from a slightly poorer energy resolution, it is identical to the unpolarized 2p resonant photoemission spectrum in an earlier work [20]. The spectrum reveals primarily the Cu 3d⁸ 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 [3,21,22]. The thin line with open circles is the difference between the spectra taken with parallel and antiparallel alignment of the photon and electron spins. After taking into account the spin detector sensitivity and the degree of circular polarization, we observe that this difference is very large, up to 41% of the sum spectrum, which is quite remarkable since we are studying a system with randomly oriented local moments. To verify that this observation is not flawed by instrumental errors, we have performed a zero check experiment. We repeated the measurements under identical conditions with the carbon target replacing in-situ the gold target of the spin detector. Since the carbon target is not sensitive to the spin of the electron being analysed, any difference signal detected can be ascribed to instrumental asymmetries. As shown in Fig. 3, we measured a difference spectrum which is zero, proving that the experiment has been set up correctly and that the above mentioned spin-resolved signals are real.

Fig. 3 also shows that the difference spectrum has a different lineshape from the sum spectrum. For further analysis, we represent in the bottom panel of Fig. 3 the data in terms of the degree of spin polarization defined as the ratio between the difference and the sum spectrum. The states assigned as ¹S and ¹G-like have a polarization of about +35% and +41%, respectively, and this compares very well with an analysis of the selection rules in which the polarization for a $3d^9$ ion, neglecting the small 3d spin-orbit interaction, is found to be +5/12 (+42%) for the singlet and -1/3 * 5/12

(-14%) for the triplet final states. While for 12 eV and higher binding energies only singlet states are present, between 1 and 12 eV the polarization is much reduced but not negative, indicating the presence of both singlet and triplet states as proposed in earlier studies [3,19,20]. Quite remarkable is that the polarization is high again for states located at the top of the valence band, suggesting strongly that they are singlets, i.e. the Zhang-Rice singlets in cuprates. With a value of +35%, one is tempted to make a comparison with the polarization of the high energy ¹S state (also +35%) and suggest a common origin. In fact, model calculations [22,23] showed that both the first ionization state and the high energy ${}^{1}S$ state belong to the ${}^{1}A_{1}$ irreducible representation of the D_{4h} point group, and that the first ionization state, which is mainly 3d⁹L like, acquires some (\sim 7%) 3d⁸ character which is now being probed in this resonant photoemission experiment (L denotes an oxygen ligand hole). The calculations [22,23] also showed that it is the strongly noncubic environment, present in all cuprates, that makes the first ionization state a singlet. In CuO, the stability of this singlet with respect to other states can be estimated from the width of the high polarization region, which is about 1 eV.

Fig. 4 shows a breakdown of the 3d⁸ final states in



Fig. 4. A breakdown of the spin-resolved circularly polarized $2p_{3/2}$ (L₃) resonant valence band photoemission spectrum of CuO in terms of singlets and triplets. The inset shows that the top of the valence band consists of singlets only.

terms of singlets and triplets, using the above mentioned selection rules. The results demonstrate clearly that this type of experiment can unravel the different spin states of the valence band of transition metal materials. A quantitative analysis that includes Auger matrix elements could provide a much more accurate modelling of the complicated electronic structure of such strongly correlated systems. In our case, a qualitative analysis is more than sufficient to establish that the first 1 eV of the valence band consists of singlets only, as can be seen from the inset of Fig. 4. While much theoretical work has been carried out in the past [23–25], our study provides the direct experimental support for a meaningful identification of Zhang–Rice singlets in cuprates.

In summary, we demonstrate the feasibility of spinresolved 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 $2p_{3/2}$ (L₃) resonance condition is essential. We have been able to observe a strong spin polarization in the valence band of Ni [26], not only below but also above $T_{\rm c}$. Identification of the separate local singlet and triplet 3d⁸ states provide support for the relevance of Hund's rule in the formation of the magnetic state in band-like late transition metals. Upon crossing T_c , the high spin $3d^8$ states continue to dominate at very low energies, indicating that local moments and short-range magnetic order persist above $T_{\rm c}$. We have also been able to unravel the different spin states in the single particle excitation spectrum of CuO [17] and show that the top of the valence band is of pure singlet character, which provides strong support for the existence and stability of Zhang–Rice singlets in high- T_c cuprates.

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References

- [1] P. Elleaume, J. Synchr. Rad. 1 (1994) 19.
- [2] J. Goulon, N.B. Brookes, C. Gauthier, J.B. Goedkoop, C. Goulon-Ginet, M. Rogalev, Physica B 208/209 (1995) 199.
- [3] B. Sinkovic, F. Shekel, S.L. Hulbert, Phys. Rev. B 52 (1995) R15703.
- [4] W. von der Linden, M. Donath, V. Dose, Phys. Rev. Lett. 71 (1993) 899.
- [5] K.-O. Kamper, W. Schmitt, G. Guntherodt, Phys. Rev. B 42 (1990) 10696.
- [6] P. Aebi, T.J. Kreutz, J. Osterwalder, R. Fasel, P. Schwaller, L. Schlapbach, Phys. Rev. Lett. 76 (1996) 1150.
- [7] P. Fulde, Electron Correlations in Molecules and Solids, chap. 11, Springer Series in Solid-State Sciences 100, Springer, Berlin, 1991, p. 241.
- [8] L.H. Tjeng, C.T. Chen, P. Rudolf, G. Meigs, G. van der Laan, B.T. Thole, Phys. Rev. B 48 (1993) 13378.
- [9] C.T. Chen, F. Sette, Y. Ma, S. Modesti, Phys. Rev. B 42 (1990) 7262.
- [10] C. Guillot, Y. Ballu, J. Paigné, J. Lecante, K.P. Jain, P. Thiry, R. Pinchaux, Y. Pétroff, L.M. Falicov, Phys. Rev. Lett. 39 (1977) 1632.
- [11] L.C. Davis, L.A. Feldkamp, Phys. Rev. B 23 (1981) 6239.
- [12] R. Clauberg, W. Gudat, E. Kisker, E. Kuhlmann, G.M. Rothberg, Phys. Rev. Lett. 47 (1981) 1314.
- [13] Y. Sakisaka, T. Komeda, M. Onchi, H. Kato, S. Masuda, K. Yagi, Phys. Rev. Lett. 58 (1987) 733.
- [14] T. Kinoshita, T. Ikoma, A. Kakizaki, T. Ishii, J. Fujii, H. Fukutari, K. Shimada, A. Fujimori, T. Okane, S. Sato, Phys. Rev. B 47 (1993) R6787.
- [15] A. Kakizaki, F. Fujii, K. Shimada, A. Kamata, K. Ono, K.-H. Park, T. Kinoshita, T. Ishii, H. Fukutani, Phys. Rev. Lett. 72 (1994) 2781.
- [16] B.T. Thole, G. van der Laan, G.A. Sawatzky, Phys. Rev. Lett. 55 (1985) 2086.
- [17] 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, G.A. Sawatzky, Phys. Rev. Lett. 78 (1997) 1126.

- [18] J.C. Fuggle, P. Bennett, F.U. Hillebrecht, A. Lenselink, G.A. Sawatzky, Phys. Rev. Lett. 49 (1982) 1787.
- [19] G.A. Sawatzky, in: C.L. Briant, R.P. Messmer (Eds.), Auger Electron Spectroscopy, Treatise on Materials Science and Technology, vol. 30, Academic Press, New York, 1988, p. 167.
- [20] H. Eskes, L.H. Tjeng, G.A. Sawatzky, Phys. Rev. B 41 (1990) 288.
- [21] E.P. Wohlfarth, Rev. Mod. Phys. 25 (1953) 211.

- [22] J. Ghijsen, L.H. Tjeng, J. van Elp, H. Eskes, J. Westerink, G.A. Sawatzky, M.T. Czyzyk, Phys. Rev. B 38 (1988) 11322; J. Ghijsen, L.H. Tjeng, H. Eskes, G.A. Sawatzky, R.L. Johnson, Phys. Rev. B 42 (1990) 2268.
- [23] H. Eskes, G.A. Sawatzky, Phys. Rev. Lett. 61 (1988) 1415.
- [24] F.C. Zhang, T.M. Rice, Phys. Rev. B 37 (1988) 3759.
- [25] A.K. McMahan, R.M. Martin, S. Satpathy, Phys. Rev. B 38 (1988) 6650.
- [26] 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, G.A. Sawatzky, Phys. Rev. Lett. 79 (1997) 3510.