Local Electronic and Magnetic Structure of Ni below and above T_C: A Spin-Resolved Circularly Polarized Resonant Photoemission Study

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We report the measurement of the local Ni $3d$ spin polarization, not only below but also above the Curie temperature (T_C), using the newly developed spin-resolved circularly polarized $2p$ (L_3) resonant photoemission technique. The experiment identifies the presence of $3d^8$ singlets at high energies and $3d^8$ triplets at low energies extending all the way to the Fermi energy, both below and above T_C, showing that it is the orbital degeneracy of the $3d$ band and the Hund's rule splitting which is of utmost importance to understand Ni and other $3d$ ferromagnets. [S0031-9007(97)04363-9]

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Itinerant ferromagnetism in late transition metals at finite temperatures has been for a long time a subject of scientific debate [1]. Neutron scattering experiments [2] and also photoemission measurements on Ni [3,4] at high temperatures have in particular stimulated much discussion on the validity of the simple Stoner-Wohlfarth mean-field theory [5] which predicts the collapse of exchange splitting above the Curie temperature (T_C) and the disappearance of local moments. Observations of different k dependent exchange splitting behavior with temperature gave rise not only to fluctuating band theory [6] which assumes the persistence of a certain degree of short-range magnetic order above T_C, but also to the two-pole *ansatz* plus effective medium approach for the Hubbard model [7] which predicts the retention of local moments above T_C together with a collapse of the exchange splitting. However, despite a large body of experimental data, a complete description of the finite temperature magnetism remains controversial, with some recent results on Ni supporting a Stoner-like behavior [8], fluctuating band theory [9], or suggesting even more complex behavior [10]. 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 not account only for the failure of mean-field theories to calculate T_C properly, but, more important, may also give a plausible explanation for the retention of local moments and short-range magnetic order above T_C in late transition metals [11].

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 atomiclike $3d$ 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. We have been able to observe a strong spin polarization in the valence band of Ni, not only *below* but also *above* T_C. The low and high temperature spectra provide the direct identification of the separate local singlet and triplet $3d^8$ states, both of which have a considerable amount of band character. The singlets are located at much higher energies than the triplets which extend all the way to the Fermi energy, providing strong support that the orbital degeneracy of the $3d$ band and the Hund's rule splitting play an important role in ferromagnetic exchange interactions in bandlike late transition metals, both below and above T_C.

The experiments were performed using the helical undulator [12] Dragon beam line BL26/ID12 [13] at the European Synchrotron Radiation Facility (ESRF) at Grenoble, together with the New York University's spin-resolved electron spectrometer specifically designed for soft-x-ray photoemission experiments [14]. The overall monochromator and electron analyzer resolution was set at 1.5 eV. The degree of the circular polarization at the Ni $2p_{3/2}$ (L_3) photoabsorption white line ($h\nu = 852.7$ eV) was 0.85 and the detector's spin sensitivity (Sherman function) was 0.07. The measurements were carried out with normal electron emission and circularly polarized light incident at 45° with respect to the surface normal. The spin detector was set to measure the degree of transverse electron spin polarization within the photoemission plane defined by photon incidence and electron emission direction [see inset in Fig. 1(a)]. The spectra were recorded with the four possible combinations of light

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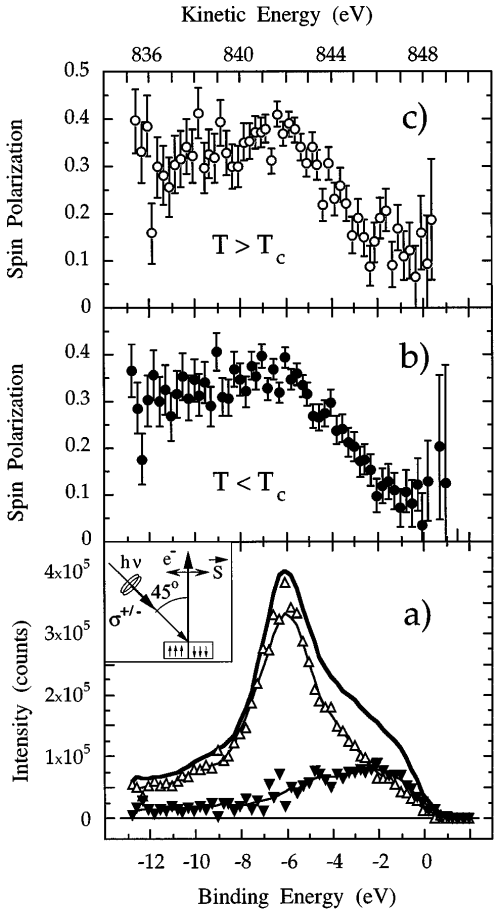

FIG. 1. Spin-resolved circularly polarized $2p_{3/2}$ (L_3) resonant valence band photoemission spectrum of Ni. (a) shows the spin integrated spectrum (solid line) together with the breakdown in terms of singlets (△) and triplets (▼). (b) depicts the spin polarization below the Curie temperature ($T = 0.47T_C$) and (c) above the Curie temperature ($T = 1.04T_C$). The inset shows the experimental geometry.

helicity (σ^+/σ^-) and spin detector channels ($e^\uparrow/e^\downarrow$, measured simultaneously), in order to exclude any systematic errors. The Ni sample was a thick (≈100 Å) film grown *in situ* and epitaxially on a Cu(001) surface, yielding $L_{2,3}$ x-ray absorption and spin-unpolarized photoemission spectra identical to those measured previously [15]. 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 measurements were first performed at room temperature, i.e., below T_C ($T = 295$ K $= 0.47T_C$). 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 to a few percent of its fully magnetized value [16]. The thick solid line in Fig. 1(a) shows the valence band photoemission spectra with photon energy tuned at the Ni $2p_{3/2}$ (L_3) white line. This is the sum of the spectra taken with parallel ($\sigma^+e^\uparrow + \sigma^-e^\downarrow$) and antiparallel ($\sigma^+e^\downarrow + \sigma^-e^\uparrow$) alignment of the photon and electron spin. The spectrum reveals primarily the Ni $3d^8$ final states as explained before [15], and the peak at 6 eV binding energy is the much discussed satellite of atomiclike ^1G character [15,17–22].

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. 1(b), after taking into account the spin detector sensitivity, the degree of circular polarization, and the 45° angle between the photon spin and electron spin as given by 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. We have verified that this observation is not flawed by instrumental errors: the measurements were repeated under identical conditions with the carbon target replacing *in situ* the gold target of the spin detector; no difference signal could be detected, and since the carbon target is not sensitive to the spin of the electron being analyzed, this confirms the absence of instrumental asymmetries.

It is evident that without the use of circularly polarized light one would not measure a net spin polarization from a nonmagnetized 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 be very effective only if a strong spin-orbit splitting is present in the atomic subshell under study, because then angular momenta will govern the selection rules [23]. Consequently, direct (nonresonant) photoemission on $3d$ transition metals 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). To resolve this problem we made use of the $2p_{3/2}$ (L_3) resonance condition [15] 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 ($3d^9 + h\nu \rightarrow 3d^8 + e$) but also, and in fact overwhelmingly, of the deexcitation channel in which a photoabsorption process is followed by a nonradiative Auger decay ($2p^63d^9 + h\nu \rightarrow 2p^53d^{10} \rightarrow 2p^63d^8 + e$). 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) and the well known strong $L_{2,3}$ magnetic circular dichroism [16]. This forms the main principle of our technique: tuning into one of the two well separated spin-orbit split $2p$ white lines, circularly 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). Essential is the fact that the photoelectron carries information concerning the local moment in the ground state, 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 [24].

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 [24] for a $3d^9$ initial state configuration, in which the polarization is found to be $+\frac{5}{12}$ $(+42\%)$ for the $^1S, ^1D, ^1G$ and $-\frac{1}{3} \times \frac{5}{12}$ (-14%) for the $^3P, ^3F$ $3d^8$ 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. We note that we now can assign firmly the shoulder at about 9 eV binding energy to a ^1S-like state.

Figure 1(a) shows a breakdown of the experimental $3d^8$ final states in terms of singlets and triplets, using the above mentioned selection rules ($P_s = \frac{5}{12}, P_t = -\frac{1}{3} \times \frac{5}{12}$), and the facts that the measured total intensity is the sum of the two contributions ($I_{\text{tot}} = I_s + I_t$) and that the measured total polarization is a weighted sum of the singlet and triplet polarizations [$P_{\text{tot}} = (P_s \times I_s + P_t \times I_t)/I_{\text{tot}}$]. 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 [25,26]. 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 $3d^8$ character since these extend to the Fermi energy. These results provide the necessary ingredients for several theoretical models concerning the ferromagnetic coupling between adjacent Ni atoms. In a double exchange model [27], for example, involving localized $3d^9$ and $3d^8$ configurations, the presence of a strong local ferromagnetic exchange is required (i.e., a local $3d^8$ triplet lower in energy than a singlet) in order to lower the total energy by forming a parallel spin alignment of neighboring sites, since this facilitates the delocalization or band formation process. In a superexchange model [28,29], as another example, involving a $3d^9$ configuration for each site and charge fluctuations of the type $(3d^9)_A(3d^9)_B \rightarrow (3d^{10})_A(3d^8)_B$ with A, B labeling nearest neighbor Ni atoms, the ferromagnetic (i.e., with parallel spin alignment of the two neighbors) contribution to the exchange will win from the antiferromagnetic one, since the triplet $3d^8$ is sufficiently lower in energy than the singlet. We note here that a perturbative solution of the models may not be adequate, because the $3d^8$ states of especially triplet character are present at very low energies degenerate with the $3d^9$ band states.

We now present spin-resolved circularly polarized resonant photoemission measurements above T_C ($T = 653\ \text{K} = 1.04T_C$). The sum of the high temperature spectra taken with parallel and antiparallel alignment of the photon spin and electron spin is identical to that of the room temperature spectra shown in Fig. 1(a). It is more informative to look at the spin polarization of the high temperature spectra, which is depicted in Fig. 1(c). 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. 1(b). 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. This can be understood as follows. First of all, for a local moment oriented along the Poynting vector of the light, the polarization for a parallel or antiparallel alignment is identical, simply by symmetry: the polarization is calculated using all four possible alignments between photon spin and electron spin. Next, for a local moment oriented perpendicular to the Poynting vector, each $3d(m_l)$ state can be expressed as a linear combination of $3d(m_l, \uparrow)$ and $3d(m_l, \downarrow)$ states with the spins $(\uparrow, \downarrow)$ along the Poynting vector. And because photoabsorption matrix elements do not couple a core level state $2p(j, m_j)$ with the $3d(m_l, \uparrow)$ and $3d(m_l, \downarrow)$ states simultaneously, these spins become effectively indistinguishable from real independent spins along the Poynting vector, with the result that each local moment yields the same polarization. This type of experiment is therefore sensitive only to 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_C indicates that also 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* $3d^8$ 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 theories [5] which predict 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_C properly [11]. A consequence of the one-electron approximation is that charge fluctuations are purely statistically distributed since they do not cost extra energy. They are also independent of spin for a nonmagnetic 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 $3d^8$ 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 nonmagnetic 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 nonmagnetic and magnetic state is overestimated in mean-field theories, resulting in a too high prediction of T_C.

Our results may provide complementary information to that obtained from angle-resolved (inverse) photoemission [8–10] studies which report a partial or complete collapse of the exchange splitting above T_C for certain spectral features. Detailed as they are, these angle-resolved data show that they cannot be fully explained by existing theories: a collapse of the exchange splitting would fit Stoner theories [5] and the two-pole *ansatz* plus effective medium approach for the Hubbard model [7], and yet, a retention of the splitting would agree more with fluctuating band models [6]. It is crucial to recognize here that the existing models have in common that the energetics involved with the Hund's rule have not been taken into account properly, and it is exactly this weakness which has been revealed by our experiments.

In summary, we have been able to observe a strong spin polarization in the valence band of Ni, not only below but also above T_C. Identification of the separate local singlet and triplet $3d^8$ states, both below and above T_C, provide support for the relevance of the orbital degeneracy of the $3d$ band and the Hund's rule splitting for the understanding of Ni and other $3d$ ferromagnets. The newly developed spin-resolved circularly polarized $2p$ (L_3) resonant photoemission technique is a local spin probe, and is therefore a promising tool for the study of not only ferromagnets, but also paramagnets and antiferromagnets.

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