Spin-polarized photoemission study of the Fe 3s multiplet

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(Received 28 October 1994)

The results of a spin-polarized photoemission study of the Fe 3s level clearly reveal the multiplet structure characterizing the final states of the excitation process. The energy separation between the high-spin and low-spin ionic states of 3.5 eV is smaller than has previously been measured, to our knowledge. The two spin components of the high-spin ionic state are clearly resolved and shown to be separated in binding energy by 0.9 eV. Line-shape fitting provides evidence that the individual peak widths reflect the total spin of the ionic final state rather than the spin of the core hole.

With the recent development of several experimental techniques reliant on the measurement of electron-spin polarization, there has been a considerable increase in research devoted to the study of surface and thin-film magnetism.[1] The interest in these problems stems in part from the potential for technological applications in both the device[2] and the magnetic recording industries.[3] In studying the properties of thin films and multilayers, it is often useful to have site-specific information on the local magnetic properties. However, many techniques provide information that is effectively averaged over a number of atomic sites. Such techniques include the spin-polarized versions of electron microscopy,[4] electron-energy-loss spectroscopy,[5] and valence-band photoemission spectroscopy.[6] Another class of experiment provides more local information through the excitation of site-specific core levels. These techniques include the spin-polarized versions of Auger electron spectroscopy,[7] core-level photoemission,[8-12] and magnetic circular[13] and linear dichroism.[14] All of the latter techniques have the potential for providing site-specific magnetic information, but in all cases we may anticipate complexity due to both initial- and final-state effects.

Core-level photoemission from magnetic systems has been extensively studied in both spin-integrated[15,16] and spin-resolved studies.[8-12] Studies of the 3s core levels of magnetic materials have revealed evidence of a satellite that is not present in the spectra from nonmagnetic materials. This satellite is interpreted as evidence of an exchange interaction between the final-state core hole and the net spin in the valence bands. A simple model due to Van Vleck suggests that the splitting between the satellite and the main peak should reflect the local moment. However, several experimental studies indicate that the splitting is much smaller than would be expected on the basis of such a theory.[16] Configuration interaction of the different multiplets in the final state has been invoked as a mechanism for explaining the observed reduction.[17] Such a mechanism requires the observation of satellites at a higher binding energy, as has indeed been observed in a number of studies of the 3s core-level photoemission from Mn.[18]

It has been suggested that because excitation of the 3s core level results in the emission from two final states with different spin polarizations, it should prove an excellent internal source of spin-polarized electrons for studies of spin-polarized photoelectron diffraction.[19] Such studies require a detailed knowledge of the spin polarization in the different peaks. However, no previous study has clearly resolved the anticipated multiplet structure within the majority-spin channel.[10,11] This absence of any well-defined structure, has led to theoretical models suggesting that the final states are influenced by effects associated with the itinerant valence bands rather than the more localized atomic effects.[20]

Here we present experimental observations relating to the photoemission from the 3s core level of ferromagnetic Fe. With higher sensitivity than has previously been obtained to our knowledge, we are able to resolve the atomic multiplets in the final state. This allows a more detailed examination of the role of final-state configuration interactions in the excitation.

Our studies were carried out on the high-flux, high-resolution soft-x-ray X1B beamline at the National Synchrotron Light Source.[21] Spin-polarized photoemission is accomplished using a hemispherical analyzer backed by a low-energy spin detector[22] of the type developed by the NIST group.[23] The analyzer collects electrons over a solid angle of $\pm 3°$. For the present study iron films were grown on a Ag(001) substrate to a thickness of the order of 20 layers and subsequently magnetized in plane with an adjacent coil. The angle of incidence of the linearly polarized light is approximately 60°, and the angle of electron collection is 15° away from the surface normal. The sample is magnetized in a direction orthogonal to the incident light polarization. Effects due to linear dichroism[14] will not be observed in the present study because there is no spin-orbit interaction for the 3s core level.

Figure 1 shows the spin-integrated and spin-polarized photoemission spectra recorded from the Fe 3s level with incident photons of energy 250 eV. The majority-spin spectrum clearly shows a two-peaked structure rather than the single peak observed in earlier studies. This ob-

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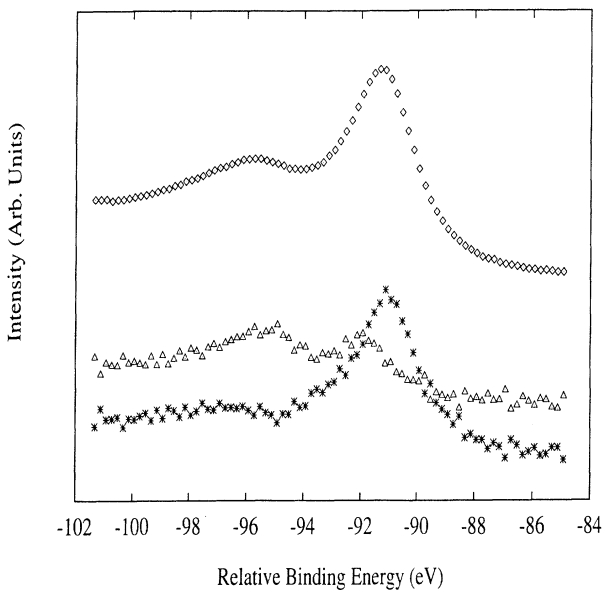

FIG. 1. Spin-resolved photoemission spectra from the Fe 3s level recorded at a photon energy of 250 eV. The solid line shows the spin-integrated spectrum, the open triangles represent the spin-resolved majority-spin spectrum, and the asterisks the minority-spin spectrum. The angle of incidence of the light is approximately 60°, and the angle of electron collection is 15° away from the surface normal.

servation is evidence that the spectra cannot simply be treated as the removal of a majority-spin or a minority-spin electron from the initial state. The photoemission process must be considered as the excitation from an initial state of total spin S with z component $S_z = S$ in the valence band to some final state, still with total spin S, but now with a photoelectron in the continuum carrying spin $\pm\frac{1}{2}$. The ion in the final state will, as we have already noted, be left either in the high-spin state $(S+\frac{1}{2})$ or in a low-spin state $(S-\frac{1}{2})$; the former being reached through the emission of a majority-spin or a minority-spin photoelectron, the latter being reached solely through the emission of a majority-spin electron. Examination of Fig. 1 shows that this is indeed the case. However, surprisingly the two spin components in the high-spin state show a separation in binding energy. We will discuss this further below.

In Fig. 2 we show the Doniach-Sunjic line-shape fits to the individual peaks in the majority- and minority-spin spectra. In such an analysis it is unclear as to how one should treat the individual backgrounds in the two spin channels. In Fig. 2(a) we have therefore subtracted a background below each component in the two spin channels. The majority-spin spectrum is fitted with two peaks and a separate background associated with each of these peaks. The minority-spin channel is fitted with a single peak and associated background. The Doniach-Sunjic line shapes are broadened with a Gaussian of full width at half maximum of 0.6 eV to simulate the overall instrumental resolution of the experiment. Our fits indicate that the two majority-spin peaks at relative binding energies of 97.6 and 101.1 eV are separated by 3.5 eV, and the two components, majority and minority spin, of the high-spin ionic state, at relative binding energies of 97.6 and 96.7 eV, are separated by 0.9 eV.

The intensities in the different peaks provide a test of any theory of the excitation process. The peak areas that come out of the fit will of course depend on the form of

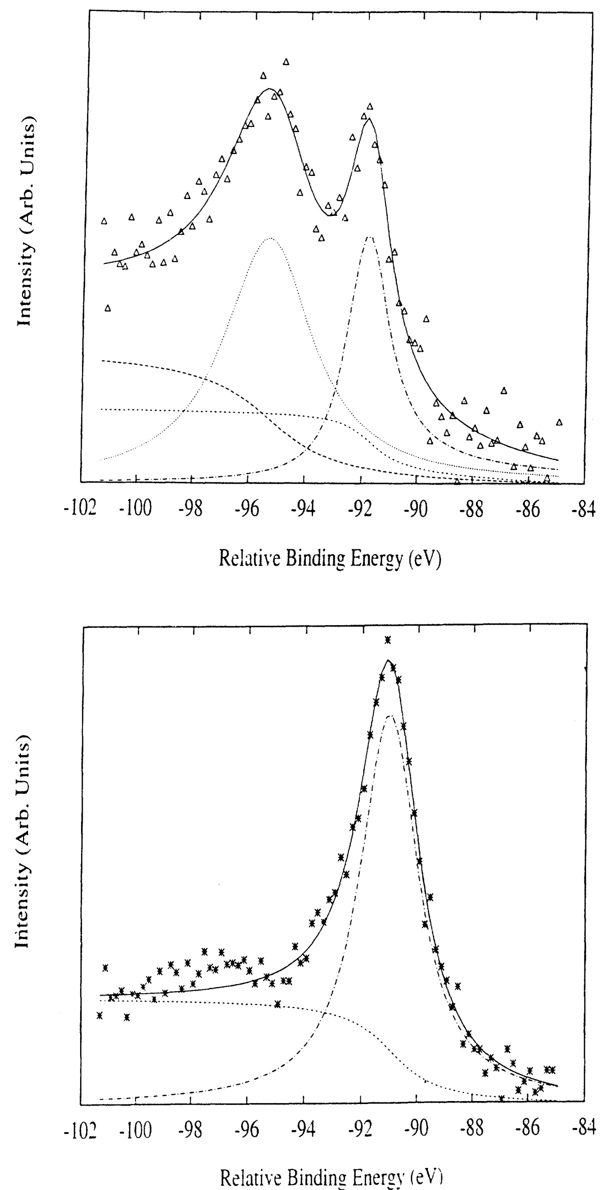

FIG. 2. (a) Line-shape fitting for the majority-spin channel of the spectra shown in Fig. 1. Each peak is fitted with a Doniach-Sunjic line shape and individual backgrounds. The solid line through the experimental points indicates the integrated fit. (b) As in (a) but now for the minority-spin channel. The sum of the solid lines in (a) and (b) reproduces the spin integrated spectrum in Fig. 1.

the background that is chosen. The intensities in the different peaks may also show a photon energy dependence reflecting spin-dependent scattering of the type discussed elsewhere.[19] However, our fits indicate that the two components in the majority-spin channel have an intensity ratio of 1.72:1. The two components, minority spin and majority spin, of the high-spin state have an intensity ratio of 3.4:1. The ratio of the total majority-spin emission in the two peaks to the emission in the minority-spin peak is 0.8.

We may compare these experimental observations with the predictions of calculations. In the absence of configuration interaction, the use of Clebsch-Gordon coefficients allows the determination of the relative intensities of the majority- and minority-spin components in the ionic high-spin state.[19,24–26] This simple model yields a ratio for the two components of the high-spin state, minority spin to majority spin, of $(2S+1)$:1, resulting in a polarization of $-S/(S+1)$. In the present case the two spin components of the high-spin state are separated in binding energy, and it is therefore of less relevance to discuss the net spin polarization. However, if we assume for metallic Fe a value of $S=1$ corresponding to a moment of $2\mu_B$, we obtain a value of 3:1 for the ratio of the two spin components which is close to our experimental observation.

The relative intensities in the ionic low-spin state and the ionic high-spin state reflect the isotropic intensities. Thus in the single configuration the ratio of the two peaks in the majority-spin channel will be $S:(S+1)/(2S+2)$, which reduces to $2S$:1. With $S=1$ again, we obtain a ratio of 2:1 which is higher than the experimental observation.

Rather than using the single configuration, Bagus and Mallow recently examined the role of configuration interaction via the use of multiplet hole theory (MHT).[27] Considering an Fe $3d^7$ ion as a reasonable approximation of the Fe atom in the metallic state, they predict that the two spin components of the high-spin state will have an intensity ratio of 4:1, giving a spin polarization in this peak of 60%. A ratio of 4:1 is precisely what would be expected for the atomic d^7 configuration, where Hund's rule will predict that the lowest-energy state corresponds to $S=1.5$. Thus the high-spin state is relatively unaffected by the configuration interaction. Bagus and Mallow further predict that the two peaks in the majority-spin channel will have a ratio of 2.25. This ratio, which is reduced from that obtained in the simple model with $S=1.5$, reflects the observation that the excitation of satellites takes intensity out of the low-spin state. This is consistent with results of the present study, where, as noted above, the ratio of the two peaks in the majority-spin channel is smaller than that predicted by the single configuration approach. Interestingly the intensities calculated by Bagus and Mallow lead to a ratio of the total spin in the majority-spin channel to that in the minority channel for the main components shown in Fig. 1 of 0.8, which is identical to the experimental observation. The remaining majority-spin intensity is lost to the satellites at higher binding energy. Finally the MHT theory predicts a binding-energy separation between the high- and low-spin states of 2.9 eV which is to be compared with our measured value of 3.4 eV. The close agreement between the calculation and our experimental observation lends strong support to the idea that configuration interaction plays an important role in the excitation process. However, we should note that any agreement between the calculated intensities and the experiment may be fortuitous in that the latter will reflect the choice of background subtraction.

The Doniach-Sunjic line-shape fits allow us to comment on the widths of the individual spin components. In a number of earlier studies, the observation of only a single peak in the majority-spin channel has led to the suggestion that the marked asymmetry in the widths of the majority- and minority-spin peaks resulted from spin-dependent lifetime effects reflecting the local spin density in the valence bands, i.e., a majority-spin core hole is filled by majority-spin valence electrons. It is now clear that, in those earlier studies, the much broader peak in the majority-spin channel resulted from the presence of the two predicted peaks rather than a single peak. However, the present study reveals additional information about the different line shapes. It is noticeable that the low-spin majority-spin peak at the higher binding energy is considerably broader, approximately 2.5 times, than the majority-spin peak at lower binding energy, even though the core hole in the two states has the same spin polarization. Our fitting also indicates that in the high-spin state the minority-spin component is broader than the majority-spin component. One possible explanation of these observations would be that the lifetime of the final state reflects the total spin of the ion rather than the spin polarization of the individual core hole. However, it is also possible that the widths may reflect the coupling of the different atomic states to the conduction bands, i.e., a solid-state effect. Thus the low-spin state would be broader because it is derived from more atomic configurations.

To summarize, therefore, the present study clearly resolves the different spin-dependent components of the 3*s* multiplet, and confirms a picture where the excitation process is dominated by configuration interactions. The observed binding-energy separation between the high- and low-spin ionic states of 3.4 eV is smaller than previously measured but in closer agreement with calculation. The 0.9-eV splitting of the two components of the high-spin state is not predicted in calculations of the 3*s* multiplet, and suggests that it may be necessary to include other electronic arrangements in the calculation. One possibility is the inclusion of the valence 4*s* electron in the electronic configuration. Such a calculation has previously been carried out in a study of the multiplet structure of the Co and Ni 3*s* levels.[28] Another possibility is that the observed splitting is an indication of a binding-energy separation of the two spin components in the initial state. Indeed first-principles fully linearized augmented-plane-wave (FLAPW) calculations predict a splitting of the order of 2–3 eV for the Fe 3*s* level.[29] However, these calculations are essentially a mean-field approach, and the core levels tend to follow the mean separation of the valence bands. Indeed the same calculation predicts a separation of the same order for the Fe 3p level which has not been identified.

The authors would like to acknowledge useful discussions with M. Weinert, P. Bagus, and G. van der Laan. The help of S. Hulbert with the fitting procedure is also gratefully acknowledged. This work is supported in part by the Department of Energy under Contract No. DE-AC02-76CH00016.

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