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Exchange, spin-orbit, and correlation effects in the soft-x-ray magnetic-circular-dichroism spectrum of nickel

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A tight-binding analysis of soft-x-ray-absorption and magnetic-circular-dichroism (MCD) spectra on Ni at the $2p \rightarrow 3d$ thresholds yields values for the valence spin-orbit parameter and exchange splitting which are respectively larger and smaller than the ground-state band-structure values by a factor of ~ 2. The discrepancies are attributed to core-hole correlation effects. A feature that appears 4 eV above the main white lines, but only in the MCD spectrum, is also attributed to correlation effects.

Many-body dynamical effects manifest themselves in photoabsorption measurements as edge singularities in core-level spectra[1] and in the need for valence self-energy corrections.[2] In this paper, we show that the advent of soft-x-ray magnetic-circular-dichroism (MCD) spectroscopy[3,4] offers a vantage point from which to examine such correlation phenomena. We focus on recent MCD measurements at the L_2 ($2p_{1/2} \rightarrow 3d$) and L_3 ($2p_{3/2} \rightarrow 3d$) edges in ferromagnetic Ni. We obtain, using a Slater-Koster analysis, values for the Ni $3d$ spin-orbit and exchange parameters which are at variance (by factors of about 2) with the ground-state one-electron band-structure values. The directions of the discrepancies are consistent with the expected electronic rearrangements accompanying the creation of the core hole. A discrete feature found in the MCD spectrum has no counterpart in our one-electron analysis, and can now be attributed to a many-body shake-up or shake-off process.

The salient results of Ref. 3 may be stated as follows. The $I(L_3)/I(L_2)$ intensity ratio of the L_3 white line to the L_2 white line in the absorption spectrum is not the 2:1 value based on core-level degeneracies, but is significantly larger, (2.55 ± 0.10):1. The $I(L_3)/I(L_2)$ intensity ratio in the MCD spectrum is not -1:1 as in the simple exchange model of Erskine and Stern,[5] but is $-(1.60 \pm 0.10)$:1. Initially, we assumed that these discrepancies could be explained away by incorporating spin-orbit splitting into the Ni $3d$ valence band. Indeed, such an explanation is anticipated in a 1949 paper by Mott[6] who, in the related case of Pt, argued that valence spin-orbit interaction enhances the proportion of $j = \frac{5}{2}$ character at the top of the valence band and thereby favors the L_3 ($p_{3/2}$) over the L_2 ($p_{1/2}$) edge. The original intent of our work was to test Mott's hypothesis and to extract refined experimental values for the spin-orbit parameter ξ and the exchange splitting Δ_{ex}. It was further anticipated[7,8] that such an approach might expose the need for many-body corrections.

Figure 1 compares our optimal simulation (to be defined below) with our latest experimental results.[9] Our calculations employ the Slater-Koster approach as elaborated in the recent handbook by Papaconstantopoulos,[10] which is extended to include spin-orbit splitting and relativistic dipole selection rules.[11] This method lacks the rigor of the first-principles calculations already addressed to this kind of problem,[12] but has the advantage of computational speed. We may perform numerous numerical experiments to quantify the influence of the governing parameters, notably ξ and Δ_{ex}.

Our procedure is to examine certain intensity ratios. It is useful to distinguish between *intra*spectral ratios, that is to say the $I(L_3)/I(L_2)$ intensity ratios within the individu-

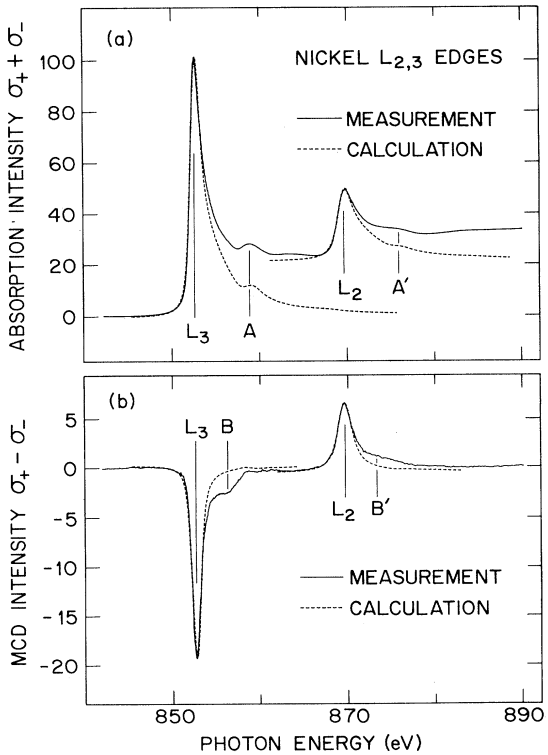

FIG. 1. Comparison between experimental soft-x-ray spectra (full curves) and an optimal tight-binding simulation (dashed curves) of the L_3 and L_2 white lines in Ni: (a) the total absorption $(\sigma_+ + \sigma_-)$; (b) the magnetic-circular-dichroism $(\sigma_+ - \sigma_-)$. The raw experimental MCD spectrum shown here has been magnified by a factor of 1.85 to account for incomplete photon polarization and sample magnetization.

al absorption $(\sigma_+ + \sigma_-)$ and MCD $(\sigma_+ - \sigma_-)$ spectra, and *inter*spectral ratios, that is to say the between-spectra intensity ratios $(\sigma_+ - \sigma_-)/(\sigma_+ + \sigma_-)$ for the L_3, L_2 white lines. The latter are subject to more uncertainty since they depend on a calibration of the degree of circular polarization in the incident x-ray beam and on the degree of sample magnetization.

The $I(L_3)/I(L_2)$ intensity ratio in both $\sigma_+ + \sigma_-$ and $\sigma_+ - \sigma_-$ depends almost exclusively on ξ, and only weakly on Δ_{ex}. This is seen in Fig. 2 which plots the calculated $I(L_3)/I(L_2)$ ratio versus Δ_{ex} for various trial values of ξ. Agreement with experiment (indicated in Fig. 2 by the toned horizontal strips) can be achieved simultaneously for both $\sigma_+ + \sigma_-$ and $\sigma_+ - \sigma_-$. We choose as our optimal value $\xi = 0.0095 \pm 0.000$ Ry which is significantly greater than the atomic value[13] (0.0055 Ry) or one-electron band-structure value[14] (0.0067 Ry). By contrast, the intensity ratio of $(\sigma_+ - \sigma_-)/(\sigma_+ + \sigma_-)$ depends primarily on Δ_{ex}, and only slightly on ξ, as illustrated in Fig. 3. The low experimental values for the $(\sigma_+ - \sigma_-)/(\sigma_+ + \sigma_-)$ ratio ($20 \pm 4\%$ for L_3 and $12.5 \pm 2.5\%$ for L_2) imply $\Delta_{ex} = 0.025 \pm 0.010$ Ry for the exchange splitting. This value is much lower than the one-electron band-structure values[10,14] (~ 0.05 Ry), and is remarkably close to other experimental values [0.019 ± 0.004 Ry (Ref. 15), 0.023 ± 0.002 Ry (Ref. 16)] obtained from angle-resolved valence-band photoemission. This similarity is perhaps testimony to the degree of localization of a Ni $3d$ valence hole.

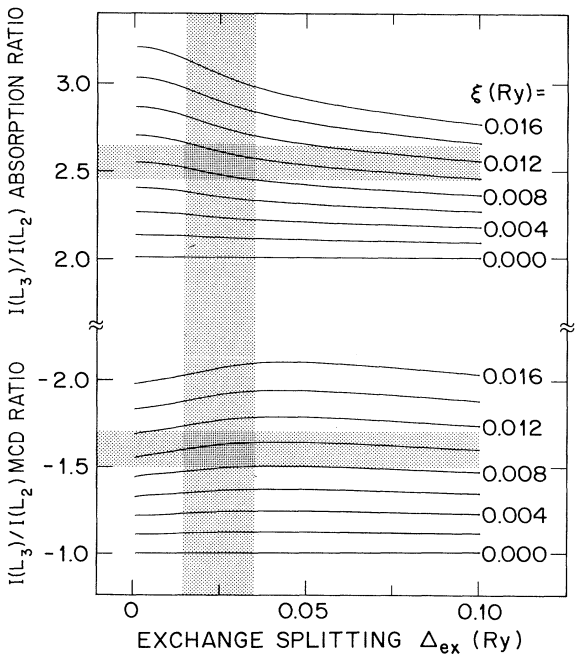

FIG. 2. Dependence of the calculated intraspectral $I(L_3)/I(L_2)$ intensity ratio on the exchange splitting Δ_{ex} for various values of the spin-orbit parameter ξ. The toned horizontal strips represent the experimentally determined values: 2.55 ± 0.10 for the total absorption $(\sigma_+ + \sigma_-)$, and -1.60 ± 0.10 for the MCD $(\sigma_+ - \sigma_-)$. The toned vertical strip represents the range of preferred values for Δ_{ex} as explained in the text. The optimal value for ξ is found to be 0.0095 Ry.

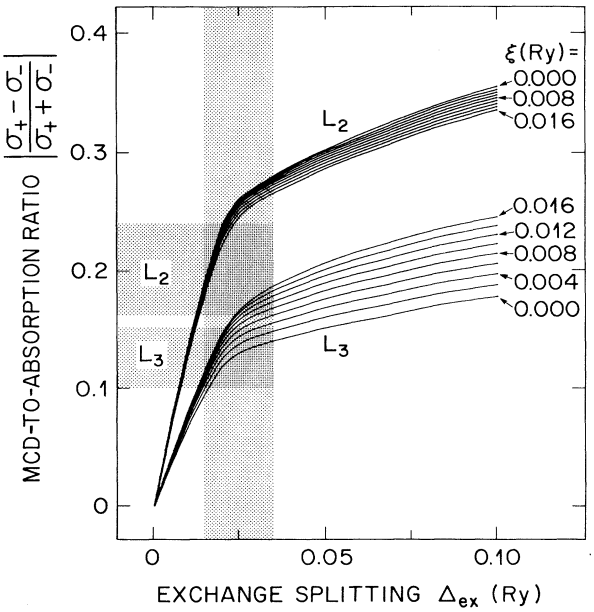

FIG. 3. Dependence on Δ_{ex} of the calculated interspectral intensity ratios $(\sigma_+ - \sigma_-)/(\sigma_+ + \sigma_-)$ for the L_3 and L_2 white lines in Ni for various values of ξ. Best estimates of the experimentally measured ratios lead, as indicated by the toned regions, to an optimal value 0.025 Ry for Δ_{ex}.

From these numerical experiments we arrive at the values $\xi = 0.0095$ Ry and $\Delta_{ex} = 0.025$ Ry which have been used to generate the optimal simulation of the experimental spectra shown in Fig. 1. The precise numbers depend to some extent on the method of line-shape analysis. These details, which will be spelled out elsewhere,[11] do not affect the conclusions of this paper. The simulation accounts nicely for the relative intensities and line shapes of the $L_{2,3}$ white lines, as well as the density-of-states feature A (A'). There is a background above the white lines which is not reproduced. Possible explanations of this background include: $2p \rightarrow 4s$ oscillator strength (neglected in these calculations); multielectron excitations; or an artifact of the detection method.[11] Neither of these would affect our main conclusions, and it is to be noted that this difficulty (i.e., a background) does not arise in the MCD spectrum. We note, incidently, that a large value of ξ implies a significant orbital contribution to the magnetic moment. Our optimal parameter set generates $0.05\mu_B$ and $0.52\mu_B$, respectively for the orbital and spin magnetic moments. These values are consistent with estimates by other methods.[17,18]

We must conclude that one-electron band theory fails—or rather that it can be rescued only by invoking effective values for $\xi(\Delta_{ex})$ much larger (smaller) than the ground-state values. Qualitatively speaking, the senses of these discrepancies are consistent with many-body dynamical expectations. On creation of the core hole, the $3d$ valence electrons will see a stronger attractive core potential, and the spatial extent of their orbitals will contract. Relativistic effects (e.g., spin-orbit splitting) will be stronger and exchange interaction among neighbors will be weaker. In the final state we have $3d^{n+1}$ rather than a

$3d^n$ configuration, and the screening of the core hole by the extra $3d$ electron will reduce, but not eliminate, this effect. In the spirit of the equivalent core approximation, we note that the $3d$ spin-orbit splitting is greater for Cu than for Ni, a trend consistent with our argument. These results are presumably susceptible to calculation by the theoretical methods[19–22] developed for the analysis of angle-resolved[15,16] and resonant[23] photoemission data on Ni.

As further evidence of correlation effects, we draw attention to the feature B (B') in the L_3 (L_2) MCD spectrum, $\sigma_+ - \sigma_-$, of Fig. 1(b). This was attributed initially,[3] in one-electron band-structure terms, to hybridization of d-like character into states above the nominal top of the Ni $3d$ band. The absence of such a feature in our present calculations indicates that one-electron interpretations should be abandoned. In contrast, feature A (A') in the absorption spectrum, $\sigma_+ + \sigma_-$, of Fig. 1(a) *is* reproduced by our one-electron calculations and those of others.[12,24] We now incline to the view that the B (B') feature represents a shake-up or shake-off phenomenon analogous to the much discussed[19–23] 6-eV hole-hole correlation satellite in photoemission. The 6-eV satellite is known both theoretically[19] and experimentally[25] to be spin polarized, and so it is provocative that the B (B') feature appears prominently in the MCD spectrum but is imperceptible in the total absorption spectrum.

In summary, we have offered an analysis of soft-x-ray absorption and MCD in Ni providing strong evidence for correlation effects in the photoexcitation event. The high precision with which the intensity ratios, particularly the intraspectral ratios, can be determined should place stringent constraints on future theoretical treatments.

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