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Publication Date

1979-07-01

Lawrence Berkeley Laboratory

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Materials & Molecular Research Division

Submitted to Physical Review Letters

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July 1979

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Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48 and the National Science
Foundation under Contract DMR78-03408

LBL-9422 c.2

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CORE-LEVEL SATELLITE STRUCTURE IN
PHOTOEMISSION SPECTRA OF TRANSITION METALS

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Abstract

A theory of the satellite structure of the core-level photoemission spectrum of transition metals is presented. It is applied to the $2p_{3/2}$ level of metallic nickel. The calculation is carried out for both the paramagnetic and ferromagnetic states and is based on two scattering parameters, one intraband and one interband. Agreement with experiment is very good.

X-ray photoemission spectroscopy has become an invaluable tool to study electron-electron interactions in transition metals. This has been caused by the richness of structure found in the spectra, which differ considerably from the naive picture to be expected from simple one-electron theory. Nickel in particular has been the subject of several recent studies, both experimental¹⁻⁶ and theoretical^{4,7}; these studies have been correlated to others involving Auger electron spectroscopy^{4,8-10}. The general characteristic of the experimental data is the existence of satellite lines, attached to the main core and conduction band peaks, which in general are located approximately 3-6eV below the corresponding main feature. These satellites have been unequivocally assigned to a localized many-electron excitation of the transition metal^{4,7}.

General phenomenological theories of satellites have been formulated¹¹. There are also general formulations which take account of many-body effects on the photoemission spectra of core levels¹²⁻¹⁵. These form the basis of our calculation, which is the first of its kind and aims at determining an actual experimental feature. The physical mechanism responsible for the existence of the satellites is the excitation of electron-hole pairs in the conduction d-bands of the transition metal in the presence of a photoelectron produced hole. In general these electron-hole pair excitations produce a continuum which broadens the original photoelectron line in an asymmetric fashion. However, if

the interaction between the core-level hole and the d-band hole is strong enough, it is possible that the d-band hole will become localized on the site of the core hole, producing a discrete state above the continuum of conduction-band hole states. At intermediate values of the interaction, a resonant state could exist. In either case, the broadened main line develops a characteristic structure with an additional peak. This satellite peak corresponds to events in which, in addition to the excitation of a deep hole, the discrete or resonant state -- which only exist in the presence of the deep hole -- is occupied by a d-band carrier. This effect is substantially different from the screening mechanism proposed by Kotani and Toyozawa¹¹.

A t-matrix formulation^{7,16} is eminently suitable to treat this many-body effect by which a conduction band hole is repeatedly and coherently scattered by the photoelectron hole. The t-matrix approach is particularly successful for almost full or almost empty d-bands, and consequently nickel metal is the ideal material to which we could apply it. We have calculated the satellite structure for the $2p_{3/2}$ core spectrum of nickel in this model. Our calculation is based on the following premises:

- 1) The observed spectrum $I(\omega)$ can be obtained by convolution of the intrinsic loss spectrum $B(\omega)$ with the natural shape $I_0(\omega)$ of the core line

$$I(\omega) = \int_0^{\infty} B(\omega') I_0(\omega+\omega') d\omega' ; \quad (1)$$

the function $I_0(\omega)$ is assumed to be a lorentzian whose width is determined from the experimental spectrum.

2) The loss spectrum is calculated by means of the integral equation $\sqrt{15}$.

$$\omega B(\omega) = \int_0^{\omega} B(\omega') \rho(\omega-\omega') d\omega' , \quad (2)$$

where the kernel $\rho(\omega)$ is the excitation spectrum of the system.

3) The excitation spectrum of interacting pairs in the conduction d-band of a transition metal is given by $\sqrt{13}$

$$\rho(\epsilon) = \epsilon^{-1} \sum_{vv'} \int d\epsilon_1 \int d\epsilon_2 f(\epsilon_1) [1-f(\epsilon_2)] D_v(\epsilon_1) D_{v'}(\epsilon_2) \delta(\epsilon+\epsilon_1-\epsilon_2) |T_{vv'}(\epsilon_1)|^2 . \quad (3)$$

In this equation $f(\epsilon)$ is the Fermi-Dirac distribution function, v and v' are spin-d-band indices ($v=1,2\dots 10$), $D_v(\epsilon)$ is a density of states for the v spin-band and $T_{vv'}(\epsilon)$ is the t-matrix for scattering of a hole of energy ϵ and band v into band v' because of the core-hole potential. We have assumed that the scattering potential (and hence the t-matrix) depends on the band indices but is independent of k-vector.

4) The t-matrix is calculated by standard procedures

$$\hat{T}(\epsilon) = \hat{V} [\hat{V} - \hat{V}\hat{G}(\epsilon)\hat{V}]^{-1}\hat{V} ; \quad (4)$$

here $\hat{V}$, $\hat{T}$ and $\hat{G}$ are (10x10) matrices, and

$$G_{vv'}(\epsilon) = \sum_{\vec{k}} G_v(\vec{k}, \epsilon) \delta_{vv'} \quad (5)$$

where $G_v(\vec{k}, \epsilon)$ is the unperturbed Green's function.

5) For the scattering potential due to the core hole we do not perform a complete self-consistent calculation. Instead we choose a phenomenological two-parameter scattering potential matrix such that $V_{vv} = V_1$; $V_{vv'} = V_2$ if v and v' correspond to the same spin; and $V_{vv'} = 0$ for two bands of opposite spin. This corresponds to approximating the interaction by a purely intra-atomic one, with momentum-independent band mixing.

6) The band-by-band density of state functions $D_v(\epsilon)$ have been calculated¹⁷ for the "canonical" d-band structure¹⁸ of the face-centered cubic metals and are available to us.

7) The calculation was performed for both ferromagnetic and paramagnetic nickel. In the first case the two spins were displaced by an exchange constant and the Fermi level was set so as to have 5 electrons in the majority spins (5 full bands) and 4.4 electrons in the minority spins. For the paramagnetic case the number of electrons was equal to 4.7 in each (degenerate) spin.

The main results of our calculations are shown in Figures 1 and 2. In these the intrinsic linewidth of the

$2p_{3/2}$ level was taken to be 0.68eV and the values of V_1 and V_2 were varied.

Figure 1 shows the experimental spectrum⁶ and the calculated one for the ferromagnetic state, with $V_1=10\text{eV}$ and $V_2=1\text{eV}$. The relatively high values of the experimental curve at high "binding energies" is due to a sizeable background over which the satellite is clearly seen. This background arises from $2p_{3/2}$ level photoelectrons which have lost energy by other processes. If this background is subtracted, agreement between theory and experiment can be considered very good.

In Figure 2 we show three calculated spectra: two for the ferromagnetic state, $V_1=10\text{eV}$ and $V_2=1\text{eV}$ and 0.8eV ; and one for a paramagnetic state, $V_1=10\text{eV}$ and $V_2=1\text{eV}$. It can be seen that the satellite structure -- position, strength and width -- is quite sensitive to the interband matrix elements and to the spin polarization of the conduction band. This can be easily understood if we realize that: (a) the excited electron in the satellite process can only go to a single spin-band in the ferromagnetic case and to two opposite-spin bands in the paramagnetic state; (b) the interband matrix elements V_2 mix the five one-spin bands in a way proportional to their strength, and the smaller V_2 , the weaker the contribution from "other" bands to the formation of the quasi-bound state, and therefore the sharper the structure of the satellite. The paramagnetic state exhibits a

substantial change in the satellite structure with respect to the ferromagnetic state with identical values of V_1 and V_2 ; as can be seen in Figure 2 the peak is reduced in size and shifted to higher loss energy.

It may seem counter-intuitive that a matrix element of 10eV gives an excitation energy of 5.1eV. Consider, however, the limiting case $V_2=0$. Then only the unfilled spin-bands contribute, and the condition for a discrete state of energy ϵ becomes

$$1 - \frac{V_1}{\epsilon + \bar{\epsilon}_v} \sum_q f(\epsilon_{vq}) = 0 \quad ,$$

where v refers to one unfilled spin-band and $\bar{\epsilon}_v$ is an average energy of the filled states in this band, roughly (-0.3) eV. The factor corresponding to the number of occupied states in the band equals about 0.4 for the ferromagnetic state, and 0.7 for the paramagnetic one, giving excitation energies of about 5 and 8eV respectively, in qualitative agreement with the detailed calculation. Clearly the result of higher excitation energy for the paramagnetic state is very general, for almost full-band metals, depending only on the larger number of filled states in the top band for the paramagnetic case.

For the case shown in Figure 1 we calculated the width of the hole-hole resonance to be less than 0.2eV, i.e. several times narrower than the intrinsic width of the $2p_{3/2}$ level. The lifetime of this correlated state is therefore dominated by the lifetime of the core hole, and for all

practical purposes the valence hole-core hole resonance can be regarded as a discrete state.

Our theory can be easily applied to the study of other core-level photoemission spectra (e.g. other levels of Ni as well as Fe and Co) and the addition of s-p conduction band states, which will only contribute to lifetime effects, can be easily accomplished.

Acknowledgments

One of us (J.T.) would like to acknowledge the support of the National Science Foundation through its Graduate Fellowship Program. This work was supported by the Division of Material Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract number W-7405-Eng.-48 and by the National Science Foundation through grant DMR78-03408.

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Figure Captions

Figure 1 Solid line, experimental photoemission spectrum, Ni $2p_{3/2}$ level. Dashed line, calculated spectrum for ferromagnetic Ni, $V_1=10\text{eV}$, $V_2=1\text{eV}$. The difference is mainly background of secondary $2p_{3/2}$ photoelectrons.

Figure 2 Solid line, calculated spectrum for ferromagnetic Ni, $V_1=10\text{eV}$, $V_2=1\text{eV}$ (as in Figure 1). Dotted line, same except $V_2=0.8\text{eV}$. Dashed line, calculated spectrum for paramagnetic Ni, $V_1=10\text{eV}$, $V_2=1\text{eV}$.

FIGURE 1

FIGURE 2

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