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Influence of many-body effects and intra-atomic exchange interactions on the shape of x-ray emission and photoemission lines of 3d metals

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The asymmetry and width of the x-ray emission and x-ray photoemission lines of iron transition metals are discussed in terms of many-body final-state effects and of the exchange interaction between a core hole and unpaired 3d electrons.

It has been suggested that many-body effects[1,2] give rise to the observed asymmetry and broadening of the characteristic x-ray emission lines[1] (XES) and x-ray photoemission lines[1-8] (XPS) of metals.

(i) Doniach and Sunjic,[1] following the theory of Mahan[9] and Nozières and de Dominicis,[10] have considered many-electron interactions of the conduction electrons with a suddenly created core hole. They showed that the readjustment of the Fermi gas to the hole potential will manifest itself directly as a line asymmetry of the core-level photoemission spectra. In the x-ray emission process, in turn, the transfer of a hole from an inner level to an outer level causes a change in the effective screened potential acting on the conduction electrons. Similarly to the case of XPS spectra, the relaxation of the Fermi gas leads to a skew line shape in x-ray emission.

(ii) According to the model of Kotani and Toyozawa[2] a core hole pulls down the empty d states of transition metals close to or below the Fermi level E_F. During the screening process this localized d hole scatters the conduction electrons via an s-d hybridization at E_F.

Both approaches (i) and (ii) lead exactly to the same analytical form of the singularity. Since the core-hole spectra are influenced by the many-body final-state effect it has been argued by several authors[3-7] that photoemission of the valence band of metals may not reflect properties of the single-particle electron density of states $N(E)$ of metals.

Kemeny and Shevchik[5] have reported on great similarities between the shapes of the XPS valence-band spectrum and the XPS core-level spectrum of nickel. They suggested that these spectra are strongly distorted by the many-body effect and that the banding effect itself is small in the former spectrum. Recently, Hüfner *et al.*[6,7] have proposed that the many-electron interaction is mainly responsible for the asymmetry of the XPS lines of d-group transition metals.

Narrowing and shifting of the Ni valence band when Cd or Zn were diluted in Ni were observed in the XPS spectra of Ni-Cd,[3] and Ni-Zn[5] binary alloys. The asymmetry and width of the Ni $2p_{3/2}$ XPS line were found to correlate with $N(E_F)$ of Ni atoms, and this correlation was taken as a decisive experimental evidence for the importance of the many-body effect. Richardson and Hisscott[8] studied Ni-Fe alloys and observed that the Fe $2p$ XPS lines of the Ni_3Fe lattice were notably broadened when compared with the $2p$ line of pure Fe, while no essential difference could be found for the Ni $2p$ line widths in pure Ni and Ni_3Fe. They interpreted this effect as due to the many-body interaction.

Concerning x-ray emission spectra, Doniach and Sunjic[1] pointed out that even the large asymmetry of 1.6 of the Fe $K\alpha_1$ line, observed by Bearden and Shaw,[11] can be explained as due to the mechanism (i).

While there is hardly any doubt that the core-hole screening makes some contribution to the XPS and XES line shapes, conclusions drawn in the case of 3d metals seem to be oversimplified.[3-8] The analysis of the line shape in terms of the above theories completely disregards the multiplet splitting of core levels. It is well known that the core-hole–unpaired-3d-electron exchange interaction in ionic compounds of iron transition atoms with a large total spin causes a strong multiplet splitting of the core-hole state.[12-17] Unresolved splitting would also contribute to the asymmetry of the XES and XPS lines, and this may well be the case for metals having a small number of unpaired spins.

The present work stems from our studies of the shapes of the $K\alpha$ lines of iron transition metals and their binary alloys. We have used the double-crystal x-ray emission technique.[18] This method yields almost the natural linewidth of emission and is rather insensitive to spurious surface effects of a sample. In these studies[19] we have found that alloying changes the $K\alpha_1$ line shape in a manner which can be associated with the local atomic spin moment μ (the number of unpaired 3d electrons) at a lattice site. We will bring up here several ob-

servations which seem to favor the core-hole–3d interaction, rather than the many-body effect, as the dominant factor in shaping core-level lines, at least for ferromagnetic nickel, cobalt, and iron.

The many-body theory postulates that the line asymmetry increases with $N(E_F)$ of a metal. In order to study the adequacy of the theory in this respect we have given in Table I theoretical[20-29] and experimental[30-33] $N(E_F)$ for Ni, Co, and Fe. The experimental $N(E_F)$'s are calculated from electronic specific heat coefficients. The natural $K\alpha_1$ linewidths[34] Γ_0, asymmetry indices[35] α, and atomic spin moments μ are also given for these elements and manganese.

The $N(E_F)$ data appear to be too much at variance to allow for a definite conclusion. In addition, no estimates are made for core–hole–conduction-electron matrix elements which may be different for these metals. We can see, however, that the tendency of both theoretical and experimental $N(E_F)$ is to *decrease* when going from Ni to Fe; i.e., α should also decrease on the assumption that the matrix elements do not vary remarkably for the metals. However, just the opposite is observed; α and Γ_0 *increase* and reach a maximum at Fe (α is known to have the largest value for Fe among all elements). On the other hand, the line shape (α and Γ_0) neatly follows the trend of μ throughout the range from Ni to Mn implying that α and Γ_0 are related to μ.

TABLE I. Density of states $N(E_F)$ at E_F for ferromagnetic Ni, Co, and Fe. The magnetic moment μ for Ni through Mn and the natural linewidth Γ_0 and asymmetry index α of $K\alpha_1$ are also given.

Element	$N(E_F)$ $\left(\frac{\text{electron}}{\text{atom Ry}}\right)$		μ (Bohr magneton)	$K\alpha_1$ Γ_0 (eV)	α
	Theory	Expt.			
Ni	27.1 [a]	~40 [k]			
	23.56 [b]	~38 [l]	0.6	2.18	1.11
Co	23.2 [c]	~25 [k]	1.56	2.38	1.30
	16 [d]	~27 [m]			
	24.2 [e]	~32 [n]			
	15.61 [f]				
	22.3 [g]				
Fe	13.8 [h]	~27 [k]	2.2	2.48	1.37
	12.3 [i]	~29 [m]			
	13.3 [j]	~28 [n]			
Mn	•••	•••	0.9–1.5	2.36	1.32

[a] Reference 20
[b] Reference 21.
[c] Reference 22.
[d] Reference 23.
[e] Reference 24.
[f] Reference 25.
[g] Reference 26.
[h] Reference 27.
[i] Reference 28.
[j] Reference 29.
[k] Reference 30.
[l] Reference 31.
[m] Reference 32.
[n] Reference 33.

If the 2p-3d interaction is significant, it should manifest itself as a change in α and Γ upon alloying because of a change in μ. In the following we will briefly mention two findings that indicate a close relationship between α, Γ, and μ.

The first evidence for a dependence of Γ on μ when the concentration is changed comes from the $K\alpha_1$ measurements of the Cu-Ni system.[19] The width (and asymmetry) of Cu $K\alpha_1$ remains constant throughout the entire composition range ($\mu = 0$ for Cu); the width of Ni $K\alpha_1$ closely correlates with the Pauling saturation magnetization curve (α had a tendency to decrease for Cu-rich alloys, but its variations were small and remained everywhere within the experimental error limits of ±0.05). Recent studies of the 2p XPS lines of Fe and Ni in the Ni-Fe system[8] are also interesting because μ of the components are known in literature for different concentrations. In Ni_3Fe, the magnetic moment at a Fe lattice site ($\cong\mu$) is between 2.91 and 3.13 μ_B (the value depends slightly on whether the Ni_3Fe structure is ordered or disordered).[36,37] For Ni in Ni_3Fe, the magnetic moment is 0.60–0.68 μ_B (Refs. 36 and 37); i.e., almost the same as μ of pure Ni, see Table I. The observed broadening[8] of the Fe 2p line and a constant Ni 2p linewidth are exactly what one should expect on the basis of the magnetic moments.

It is quite possible that the observed behavior of the Ni $2p_{3/2}$ line shape of Ni-Cd,[3] and Ni-Zn,[5] simply reflects a change in μ of Ni through the 2p3d interaction.

In order to estimate the strength of the 2p3d coupling in Fe we have calculated the 2p hole splitting within the framework of an approximate model of Nefedow.[12] In this model only the exchange energy associated with the spin of 3d electrons is taken into account. By using $\mu = 2\ \mu_B$, the splitting of 2.3 eV between the extreme components of the Fe $K\alpha_1$ composite line was obtained. By superimposing the Lorentzian-like components with equal half-widths (1.5 eV) and with relative intensities $I(^{2S+1}P_J)$ for transitions from the $^{2S+1}P_J$ states, the resulting asymmetry of $K\alpha_1$ was about 1.4. Although this numerical coincidence with the experimental α value (1.37) is probably fortuitous the calculation predicts an appreciable 2p3d interaction which can fully explain the origin of $\alpha > 1$.

The core-hole–3d interaction depends on the orbital symmetry and shell of the ionized electron. Unfortunately, the $K\beta_{1,3}$ or $3p_{3/2,1/2}$ lines cannot

be used to check this effect because of a strong overlapping of the two spectral components with a poorly known intensity ratio. For the Ni 3*s* and 2*p* lines Hüfner *et al.*[7] have obtained nearly equal α.

Finally, we refer to our high-resolution ultraviolet photoelectron spectra (UPS) of the valence band of Fe,[38] Co,[26] and Ni,[39] irradiated by low-energy photons ($\hbar\omega \leq 21.22$ eV). The characteristic features of these spectra, including pure polycrystalline samples and single crystal faces, can be interpreted almost to perfection in terms of the one-electron band theory (in case of Ni, an additional contribution of surface effects may be present). In particular, we have not seen any indication that the *d* hole left behind in photoemission has a localized character. A weak structure appearing around −5.4 eV in UPS and XPS spectra of Ni,[5,8] Co,[8,26] and Fe,[38] may not originate from the satellite of the Kotani-Toyozawa mechanism, since no core hole is created in the uv excitation. Instead, it is possible that the observed satellite is mainly due to a double ionization of the *d* band by photon absorption. This suggestion is supported by the fact that $L_3M_{4,5}M_{4,5}$ Auger transitions show a double *d* hole to be placed at −6.1, −6.1, and −6.7 eV ± 1.0 eV relative to E_F for Fe, Co, and Ni, respectively.[40] The corresponding satellites in the UPS and XPS spectra appear at −5.4, −5.5, and −5.3 eV.

The conclusion is that no clear evidence of the importance of many-body interactions in XES and XPS spectra of iron transition metals has yet been put forward. We believe that the core-hole–unpaired-3*d*-electron interaction is the dominant factor which shapes the core lines for atoms in pure metals and alloys in the same way as it does for metal ions in chemical compounds.

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