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X-RAY EDGES OF FREE-ELECTRON METALS: COMPARISON OF THEORY WITH DATA[§]

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Because one-electron theory had predicted that simple metals should exhibit soft x-ray absorption and emission edges abruptly truncated by Fermi factors, the occurrence of peaked $L_{2,3}$ thresholds in spectra of free-electron metals posed a special challenge to theorists. The earliest explanations, several decades ago, had attributed the peaks to rapid variations in the conduction band densities-of-states, but more recent theories have assigned the spikes to many-electron final-state interactions. The purpose of this paper is to critically review existing data in the light of the Mahan-Nozieres-de Dominicis theory (MND theory) of many-body effects and x-ray threshold shapes(1,2).

The spiked edges cited as evidence for the MND theory are the $L_{2,3}$ thresholds of Na, Mg, Al, and Mg_xSb_{1-x} alloys. In addition, the rounded K edges of Li, Mg, and Al have also been explained in terms of the many-body mechanism(3). The theory states that, near threshold; the imaginary part of the dielectric function has the form:

$$\varepsilon_2(\omega) = \left[M_0^2 \left(\frac{\hbar\omega - E_T}{\xi} \right)^{-\alpha_0} + M_1^2 \left(\frac{\hbar\omega - E_T}{\xi} \right)^{-\alpha_1} + \cdots \right] \times \theta(\hbar\omega - E_T) \qquad (1)$$

Here E_T is the threshold energy; the step function $\theta(x)$ accounts for the sharp Fermi surface; M_ℓ are single-particle transtion matrix elements between core states and conduction wave functions with angular momentum quantum number ℓ; ξ is a cutoff energy thought to be a Fermi energy or a band-width; and the threshold exponents α_ℓ are given in terms of the phase shifts δ_ℓ of a Fermi-energy electron scattered by the hole:

$$\alpha_\ell = (2\delta_\ell/\pi) - \sum_{j=0}^{\infty} 2(2j+1)(\delta_j/\pi)^2 \quad . \tag{2}$$

Implicit in the theory are predictions concerning the dependence of threshold anomalies on (i) conduction electron density, $n=(3/4\pi)(r_s a)^{-3}$; (ii) the cutoff energy ξ; and (iii) the angular momentum quantum number ℓ (through the exponents α_ℓ and the matrix elements M_ℓ).

Studies of the $L_{2,3}$ edge of Mg in Mg_xSb_{1-x} alloys produce an approximate value of the cutoff energy ξ (4). Fitting the edge shape with

$$\varepsilon_2(\omega,x) = M_0^2\,(x)\left(\frac{\hbar\omega - E_T}{\xi}\right)^{-\alpha_0(x)}\theta(\hbar\omega - E_T), \tag{3}$$

and assuming that variation in the factor M_0 (which depends on dipole matrix elements and the Fermi energy density of states) is sufficiently small to be neglected, we find

$$\ln \varepsilon_2(\omega) = \ln M_0^2 + \alpha_0(x)\ln(\xi/\hbar\omega - E_T) \tag{4}$$

Thus a plot of $\ln \varepsilon_2$, for $\hbar\omega - E_T$ fixed, as a function of α_0 produces a value for ξ (Fig. 1). We find that ξ is approximately constant with the value 0.24 ± 0.1 eV. Since the MND theory is only valid for $|\hbar\omega - E_T| \ll \xi$, and it is generally believed that ξ must be either a band-width

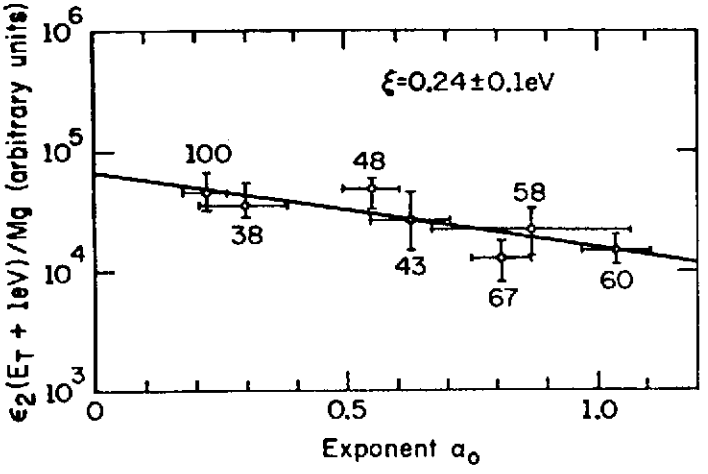

Fig. 1. ln ϵ_2 vs. α_0 for Mg_xSb_{1-x}. The values of x are denoted on the figure. A negative slope indicates ξ < 1eV. (Ref.4).

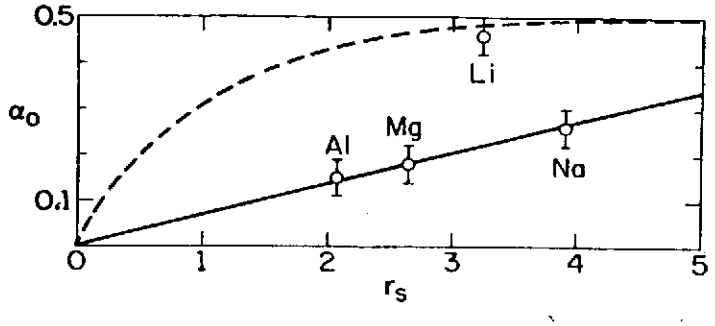

Fig. 2. Exponents α_0 vs. r_s. Solid line:data; dashed line: theory. The exponent for Li is obtained from K edge data. (Ref.4,10).

or a Fermi-energy ($\xi \gtrsim 5$eV), one must judge the theory's prediction to be unsatisfied.(Note that for $\xi=E_F$ the slope of the curve in Fig. 1 would have been large and positive for small values of α_0.)

The present MND theory forbids exponents $\alpha_0 > 0.5$; some of the Mg_xSb_{1-x} exponents exceed one-half. Furthermore, the exponents appear to define a continuous function of composition x, suggesting that both the alloy data and the Mg edge itself may lie outside the domain of applicability of the present many-body theory(5).

If the x-ray edge anomalies of Na, Mg, and Al are caused by final-state interactions, then the peak shapes should be continuous functions of conduction-electron density or the reduced radius r_s. By fitting experimental absorption lineshapes with the form

$$\epsilon_2(\omega) = M_0^2 \, \xi^{\alpha_0} (\hbar\omega - E_T)^{-\alpha_0} \, \theta(\hbar\omega - E_T) \, ,$$

suitably broadened, it is possible to extract the values of the exponents given in Fig.2 (4,5). This represents the first and, I believe, only firm evidence that the threshold anomalies of Na, Mg, and Al are related to conduction electron density and final-state interactions. In the limit of small r_s, exponents computed from screened potential phase shifts should describe the observations for $\alpha_0(r_s)$. They do not. Thus final-state interactions appear to be present, but not in the form predicted by the MND theory with screened-potential phase shifts. It is, of course, possible that the exponents α_0 are sensitive to details of the atomic charge distributions; realistic calculations of such effects are in progress. However, if the exponents should prove to be more sensitive to atomic charge distributions

than to the electron gas density, the only potentially-firm evidence for final-state interactions causing the $L_{2,3}$ edge anomalies will be placed in jeopardy. Also note that α_0^{-1} is little more than as asymmetric broadening parameter in the fitting procedure; thus the fact that α_0 is a smooth function of r_s is not, by itself, firm evidence that the threshold form, Eq.(1), is valid.

The principal experimentally-relevant prediction of the many-body theorists has dealt with the angular momentum dependence (6,7):

$$\alpha_0 > 0 \quad \text{and} \quad \alpha_1 < 0.$$

This, when taken with the selection rule $M_0=0$ for parity-"forbidden" K-edge transitions from s-cores, implies that $L_{2,3}$ edges (involving transitions from p-core levels) are peaked by the final-state interactions ($\alpha_0 > 0$), whereas K edges are rounded ($\alpha_1 < 0$). This prediction is now known to apply only to solids which exhibit bound excitons in emission; and not to free-electron metals (for which both α_0 and α_1 must be positive) (8,9). The Friedel sum rule relates the exponents α_0 and α_1, provided one is willing to either neglect phase shifts δ_ℓ for $\ell \geq 2$ or to compute them using a model potential (4,10). For free-electron metals with no bound exciton states, the resulting exponents generally lie in the ranges $0 \leq \alpha_0 < 0.3$, $0 \leq \alpha_1 < 0.1$. Thus both K and $L_{2,3}$ edges should be enhanced by final-state interactions. The observed rounded thresholds at the K edges of Li, Mg, and Al cannot be caused by the MND effect as once thought; and therefore the prediction of an angular momentum dependence is largely vacuous for absorption and emission spectra.

However, the angular momentum dependence of the theory can be checked using electron energy loss spectros-

copy, which measures the electron dynamic structure factor $S(\vec{q},\omega)$. The Doniach, Platzman, Yue theory (11) of the structure factor (neglecting interference terms) is:

$$S(\vec{q},\omega) \propto \left[M_0^2(\vec{q}) \left(\frac{\hbar\omega - E_T}{\xi}\right)^{-\alpha_0} + M_1^2(\vec{q}) \left(\frac{\hbar\omega - E_T}{\xi}\right)^{-\alpha_1}\right] \theta(\hbar\omega - E_T).$$

In contrast to optical experiments, in which transitions are induced by the dipole operator, the energy loss experiment measures transitions induced by the (Fourier transformed) charge density operator:

$$\langle i|\exp i\vec{q}.\vec{r}|f\rangle = i\vec{q}.\langle i|\vec{r}|f\rangle + \text{terms of order } q^2.$$

In the forward-scattering limit ($q \to 0$), the charge density operator obeys dipole selection rules and produces an energy loss spectrum with the same shape as the optical absorption spectrum. For general wavevector $\vec{q}$, it does not. Thus, according to Doniach, Platzman, and Yue, for the K edge of Li we have

$$\lim_{q \to 0} M_0(\vec{q}) = 0,$$

whereas for the $L_{2,3}$ edge of, say, Na we have

$$\lim_{q \to 0} M_1(\vec{q}) = 0.$$

For larger q, all matrix elements are generally finite. Concentrating on the fact that the energy-loss measurements produce <u>shapes</u> of the edges, not absolute values, and recognizing that the shapes are sensitive only to the ratio $M_0^2(\vec{q})/M_1^2(\vec{q})$, we see that for $\alpha_0 > \alpha_1$, the K edges should become dramatically peaked as q increases, whereas the $L_{2,3}$ edges should become flatter.

Ritsko, Gibbons, and Schnatterly (12) have measured the structure factor $S(\vec{q},\omega)$ of Li for q=0 Å^{-1}, q=0.9 Å^{-1}, and q=1.2Å^{-1}. Within an experimental uncertainty of 2%, they see no change in edge shape. Thus it is possible to conclude that none of the edge rounding in Li is caused by the MND effect, that the MND effect (if operative at all) either is approximately two-orders of magnitude weaker than once thought or enhances the edge so slightly ($\alpha_0 < 0.12$) that the most-plausible explanation of the data completely rules out the many-body mechanism in Li. Therefore, one of the following appears to be invalid for Li: (i) the MND theory; (ii) the Doniach, Platzman, Yue theory of $S(\vec{q},\omega)$; or (iii) the Ritsko, Gibbons, Schnatterly data. Since earlier absorption measurements on $Li_{1-x}Cu_x$ alloys had led to the same conclusion (13,14) as subsequently drawn by Ritsko, Gibbons, and Schnatterly, it would appear that a new theory of edge anomalies is called for.

In summary, the many-body theory makes predictions about the dependence of the x-ray threshold anomalies on (i) cutoff energy ξ; (ii) the size of the exponents α_0; (iii) the variation of the exponents with r_s; and (iv) the angular momentum dependence of the threshold shapes -- none of which are verified experimentally. On both theoretical and experimental grounds the K edges of Li, Mg, and Al can be excluded as evidence for the theory. Of the remaining data cited as supporting the theory, the $L_{2,3}$ edge-shapes of Na, Mg, and Al do not exhibit the expected dependence on r_s; and the $L_{2,3}$ edge of Mg in Mg_xSb_{1-x} yields excessively large exponents and a small value of the cutoff energy ξ.

The case against the present theory of electron-hole interactions in metals is strong now. If the predicted

dependences (15) of the energy-loss spectra on q are not verified experimentally for the $L_{2,3}$ edges of Na, Mg, and Al, then it will be necessary to develop a new theory of final-state interactions and their effects on the optical properties of metals.

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