that the frequencies, and hence the stability, of a dumbbell depend very sensitively on the presence of a nearby vacancy. Thus the instability volume[4,1] of a Frenkel pair and the correlated recovery stages[6] should be closely related to resonance modes.

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Compatibility Relationships for X-Ray Threshold Shapes

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Bounds on the exponents of the many-electron x-ray threshold anomaly are obtained, and a relationship between soft- and hard-x-ray threshold shapes is derived. The spectra of Mg_xSb_{1-x} alloys and Al metal are shown to be inconsistent with the many-electron theory of threshold exponents.

Many-electron theories of the soft-x-ray absorption spectra of simple metals predict the "anomalous" absorption-threshold shape[1]

$$\epsilon_2(\omega) \cong \sum_{l=0}^{\infty} A_l^2 \left(\frac{\hbar\omega - E_T}{\xi}\right)^{-\alpha_l} \theta(\hbar\omega - E_T). \qquad (1)$$

A similar expression describes emission spectra. Here $\epsilon_2(\omega)$ is the imaginary part of the dielectric function, $\hbar\omega$ is the photon energy, E_T is the threshold energy, ξ is a parameter with dimensions of energy, $\theta(x)$ is the unit step function, $2\pi\hbar$ is Planck's constant, and A_l is proportional to the optical transition matrix element between a core electron initially localized at the origin and a spherical-wave conduction-band electron with angular momentum quantum number l. The exponents of the threshold law, α_l, can be expressed in terms of the partial-wave phase shifts δ_l for an electron at the Fermi energy experiencing the scattering potential of the hole[2]:

$$\alpha_l = 2\frac{\delta_l}{\pi} - 2\sum_{j=0}^{\infty} (2j+1)\left(\frac{\delta_j}{\pi}\right)^2. \qquad (2)$$

[In the absence of final-state interactions, α_l is zero and Eq. (1) gives the step-function one-electron threshold law.]

Attempts to compare quantitatively the predicted threshold law with experimental data have been frustrated by the absence of accurate values of the parameters A_l and ξ, and by uncertainties about the precise values of the phase shifts and the form of the net electron-hole interaction. Nevertheless, two qualitative predictions[3] of the many-electron theory seem to have been confirmed by observations: (1) For forbidden transitions from s-like core levels to even-parity conduction bands, A_0 is zero and the p-wave exponent α_1 is often negative: The electron-hole interaction causes a suppressed, rounded threshold shape. (2) For allowed transitions, A_0 is nonzero, the s-wave exponent α_0 is normally positive, and $\epsilon_2(\omega)$ exhibits a divergent "spike anomaly."

The purposes of this paper are (1) to emphasize that the Friedel sum rule relates the exponents α_0 and α_1, (2) to derive a set of inequalities

satisfied by the exponents, and (3) to illustrate how these inequalities severely restrict the class of possible threshold shapes. Particular attention will be paid to aluminum, for which there exist measurements both of allowed transitions[4,5] from the $2p$ core level to the conduction band ($\alpha_0 > 0$, $\hbar\omega \approx 73$ eV) and of forbidden transitions[6] involving the $1s$ core ($\alpha_1 < 0$, $\hbar\omega \approx 1560$ eV). Therefore knowledge of either the 73- or the 1560-eV threshold shape determines the other. The many-electron theory of threshold exponents can be tested by comparing one of the observed spectra with a spectrum computed using exponents extracted from the other.

The primary assumptions of this work are (1) that the final-state electron-hole interaction is the same for allowed and forbidden transitions, and (2) that the d-wave and higher angular-momentum phase shifts are negligible. The former assumption is valid for the deep, narrow core levels which satisfy the infinite-hole-mass postulate of the many-electron theory.[7] The latter holds for simple metals such as Na and Al, in which the d-wave phase shift is small [$(\delta_2/\pi) \lesssim 0.02$ for a Thomas-Fermi potential][3,8]; for example, the inclusion of d waves typically introduces a negligible 5% correction to the compatibility relationship, Eq. (8) below.

The Friedel sum rule[9] relates the s- and p-wave phase shifts:

$$\delta_1/\pi = -\delta_0/3\pi + \tfrac{1}{6}. \tag{3}$$

Thus the exponents can be expressed parametrically in terms of the s-wave phase shift:

$$\alpha_0 = \tfrac{3}{3}(\delta_0/\pi) - \tfrac{3}{3}(\delta_0/\pi)^2 - \tfrac{1}{6}, \tag{4a}$$

$$\alpha_1 = \tfrac{1}{6} - \tfrac{8}{3}(\delta_0/\pi)^2. \tag{4b}$$

Of course, δ_0 can be eliminated from Eqs. (4), yielding α_0 as a function of α_1 or *vice versa*.

Upper bounds on the exponents α_l follow from Eq. (4):

$$\alpha_0 \leq \tfrac{1}{2}, \tag{5a}$$

and

$$\alpha_1 \leq \tfrac{1}{6}. \tag{5b}$$

One important conclusion to be drawn from the inequality (5a) is that some exponents α_0 extracted from Mg_xSb_{1-x} alloy measurements[10] are inconsistent with the present form of many-electron theory, since they exceed $\frac{1}{2}$. To be sure, the process of extracting exponents from x-ray absorption data is extremely difficult and merits careful, skeptical examination. Nevertheless the experimentally determined variation of the Mg_x-Sb_{1-x} exponents with composition x is similar to the resistivity's observed variation (suggesting a correlation of exponent with free charge density); and the parameter ξ of Eq. (1), as determined by using the experimental exponents in fitting Eq. (1) to the data, appears to be nearly independent of x.[11] Thus the extracted exponents are definitely both nonrandom and also consistent with the form of Eq. (1). If one accepts these Mg_xSb_{1-x} exponents at face value, then it follows that either (i) the Nozières–De Dominicis expression for α_l [Eq. (2)] is inaccurate (at least for those low free-electron densities corresponding to the $\alpha > \frac{1}{2}$ exponents), or (ii) bound exciton states are forming in the high-resistivity alloys, requiring some modifications[12] of the theory,[2] or (iii) the Mg_xSb_{1-x} thresholds are not examples of the many-electron threshold anomaly. If the exponent α is a continuous function of x, as suggested by Slowik and Brown,[10] then this last conclusion would imply that what currently passes as a many-electron threshold anomaly in Mg (i.e., Mg_xSb_{1-x} for $x = 1$) is not one. The deletion of Mg from the list of materials exhibiting many-electron anomalies would leave only the spectra of Li, Al, and Na as strong evidence for the effect—and it has recently been proposed that Li also be removed from the list.[13]

An even more interesting case is that of aluminum, which is thought to exhibit both many-electron threshold enhancement for the allowed transitions from the L shell ($\alpha_0 > 0$; $2p$ hole, $\hbar\omega \approx 73$ eV) and also threshold suppression for the forbidden hard-x-ray K-shell transitions ($\alpha_1 < 0$; $1s$ hole; $\hbar\omega \approx 1560$ eV). For this case, with the assumption that the phase shifts are positive for the attractive electron-hole interaction, the following inequalities are valid [see Eqs. (4)]:

$$\tfrac{1}{4} < \delta_0/\pi < \tfrac{1}{2}, \tag{6a}$$

$$0 < \delta_1/\pi < \tfrac{1}{2}, \tag{6b}$$

and

$$\tfrac{1}{3} < \alpha_0 < \tfrac{1}{2}, \tag{7a}$$

$$-\tfrac{1}{2} < \alpha_1 < 0. \tag{7b}$$

Furthermore the p-wave exponent α_1 can be expressed in terms of the s-wave exponent α_0:

$$\alpha_1 = -1 + \alpha_0 + \tfrac{2}{3}(3 - 6\alpha_0)^{1/2}. \tag{8}$$

This compatibility relationship, Eq. (8), be-

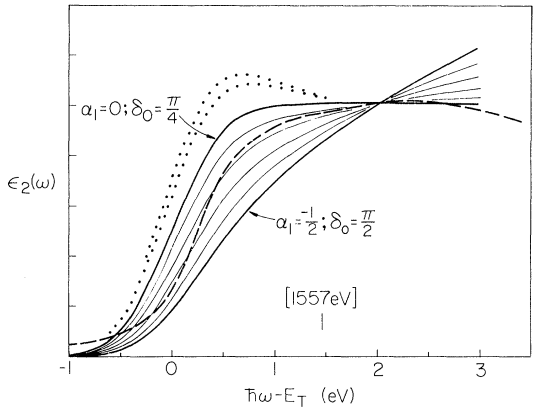

FIG. 1. Hard-x-ray absorption of Al, $\epsilon_2(\omega)$ [in arbitrary units], versus photon energy relative to the threshold energy E_T in eV ($E_T \approx 1558.5$ eV). Solid lines, Eq. (1), Gaussian broadened with $\Gamma = 0.4$ eV, with exponents ranging from $\alpha_1 = 0$ ($\delta_0 = \pi/4$) to $\alpha_1 = -\frac{1}{2}$ ($\delta_0 = \pi/2$) for equal increments of δ_0. Dashed line, *K-emission* measurements of Läuger (Ref. 6), reflected through threshold to give approximate absorption edge shape. Dotted lines, theory for $\alpha_1 = 0.14$ ($\delta_0 = 0.1\pi$) and $\alpha_1 = 0.106$ ($\delta_0 = 0.15\pi$) for values of δ_0 corresponding to dotted lines of Fig. 2. The energy $\hbar\omega = 1557$ eV for the emission data is indicated.

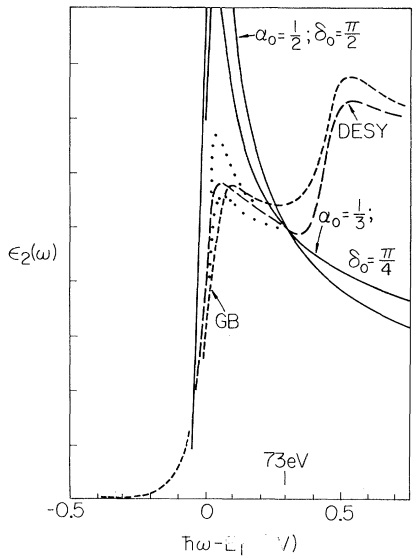

FIG. 2. Soft-x-ray absorption of Al, $\epsilon_2(\omega)$ [in arbitrary units], versus photon energy relative to the threshold E_T in eV ($E_T \approx 72.7$ eV). Note that the second experimental peak is due to spin-orbit interaction neglected in the theoretical curves. Solid lines, Eq. (1), Gaussian broadened with $\Gamma = 0.03$ eV, for $\alpha_0 = \frac{1}{2}$ ($\delta_0 = \pi/2$), and for $\alpha_0 = \frac{1}{3}$ ($\delta_0 = \pi/3$). Dashed curves, absorption measurements from DESY (Ref. 4) and Gähwiller and Brown (GB) (Ref. 5). The experimental energy $\hbar\omega = 73$ eV is indicated. Dotted lines, Eq. (1), with $\Gamma = 0.03$ eV, for $\alpha_0 = 0.0733$ ($\delta_0 = 0.1\pi$) and $\alpha_0 = 0.1733$ ($\delta_0 = 0.15\pi$). Observe that the data do not lie between the $\alpha_0 = \frac{1}{2}$ and $\alpha_0 = \frac{1}{3}$ curves.

tween α_0 and α_1 (and the inverse relationship) can be tested for Al by comparing soft- and hard-x-ray spectra.

Läuger's K-emission spectrum[6] of Al, converted to $\epsilon_2(\omega)$ by reflection of the data in E_T, is depicted as a dashed line in Fig. 1. Theoretical spectra for $l = 1$ [Eq. (1)], Gaussian broadened[14] with $\Gamma = 0.4$ eV (the atomic Auger width of the 1*s* level[15]), are plotted as solid lines for $-\frac{1}{2} \leq \alpha_1 \leq 0$, corresponding to the permitted range of exponents for suppressed spectra. Depending on the choice of E_T, the agreement between theory and experiment can be made acceptable, especially for $-0.2 < \alpha_1 < 0$. It follows from Eq. (7) that the exponent for the L edge should lie in the range $\frac{1}{3} < \alpha_0 < \frac{1}{2}$.

The soft-x-ray L-threshold spectrum of Al, as observed both by the DESY group[4] and by Gähwiller and Brown,[5] is plotted in Fig. 2. Theoretical curves for $l = 0$, broadened[14] with $\Gamma = 0.03$ eV to account for imperfect instrumental resolution, are plotted as solid lines for the limiting values $\alpha_0 = \frac{1}{3}$ and $\alpha_0 = \frac{1}{2}$. The observed spectra should lie between those theoretical curves if the inequality (7a) is valid. Instead the data are compatible with $0.0733 < \alpha_0 < 0.1733$ (dotted lines in Fig. 2); however such small values of α_0 imply positive values for α_1 and a peaked hard-x-ray spectrum (dotted lines in Fig. 1), in qualitative disagreement with the data.

The K and L edge spectra of Al and the Nozières–De Dominicis expression [Eq. (2)] for the threshold exponent are incompatible; no single self-consistent choice of phase shifts can produce both soft- and hard-x-ray spectra in agreement with the data.

The analyses for Al illustrate how severely the compatibility relationships [Eqs. (7), (8)] restrict the class of permitted exponents. Indeed, those relationships largely contradict the many-electron theory in its two principal predictions: (i) Allowed transitions are enhanced ($\alpha_0 > 0$), and (ii) forbidden transitions are suppressed ($\alpha_1 < 0$). The combination $\alpha_0 > 0$ and $\alpha_1 < 0$ is possible only for $\alpha_0 > \frac{1}{3}$, a condition usually met by the calculations,[3,8] but rarely satisfied by the x-ray data for simple metals.[16]

These results demand either a more sophisticated many-electron theory or a new interpreta-

tion of the spectra. Perhaps the threshold law itself, Eq. (1), will eventually be abandoned and a completely new model of final-state interactions created. But less drastic alterations or refinements[17] of the simple Mahan–Nozières–De Dominicis model could conceivably modify the predicted threshold law, Eq. (1), or correct the exponent formula, Eq. (2), thereby remedying the theory's ills.

Observe that, in order to obtain a tractable model capable of producing the expression Eq. (2) for the exponents, Nozières and De Dominicis were forced to approximate the net final-state electron-hole interaction with an unrealistic separable potential. A more realistic model interaction could possibly lead both to a somewhat different expression for the exponents α_l and to quantitative agreement between many-electron theory and experiment for the x-ray spectra of Al, Mg, and Mg_xSb_{1-x}.

In the absence of such a refined theory, experimenters should study x-ray threshold anomalies in pure metals and alloys comparing K and L thresholds, in order to determine the dependences of final-state interaction effects on Fermi energy, electron angular momentum, and electron-hole coupling strength.

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