

X-Ray Edges of Simple Metals: Dependence on Electron Density*

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Data analyses reveal that the Mahan form of the x-ray absorption threshold law, $\epsilon_2(\omega) = A[\hbar\omega - \hbar\omega_T]/\xi]^{-\alpha_0}$, can describe $L_{2,3}$ edge data of Al, Mg, and Na, with the empirical rule $\alpha_0 \approx 0.068r_s$. However, the many-electron interpretation of the Li K edge cannot be reconciled with this rule, and the exponents α_0 can be calculated from the Nozières-De Dominicis expression only if the electron-hole interaction exhibits unusual properties.

On the basis of his many-electron calculations, Mahan^{1,2} has proposed that simple metals should exhibit anomalously shaped soft-x-ray adsorption edges $\epsilon_2(\omega)$ near threshold:

$$\epsilon_2(\omega) = A_l [(\hbar\omega - \hbar\omega_T)/\xi]^{-\alpha_l} \quad (1)$$

Here A_l and ξ are constants, $2\pi\hbar$ is Planck's constant, $\hbar\omega$ and $\hbar\omega_T$ are the x ray's energy and the threshold energy, respectively, and α_l is the Mahan exponent, an expression for which has been obtained by Nozières and De Dominicis³:

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

Here δ_l is the l th partial wave phase shift of a Fermi-energy electron scattered by the electron-hole final-state interaction. For the L -edge spectra of interest here, the final-state electron is in a primarily s -like conduction-band state; hence we have $l=0$.

We have analyzed⁴ the L -edge absorption spectra⁵ of Al, Mg, and Na to obtain the exponents α_0 listed in Table I and plotted in Fig. 1 as a function of the electron-gas radius parameter⁶ r_s . The data are well described by the empirical rule

$$\alpha_0(r_s) \approx 0.068r_s \quad (3)$$

Efforts to fit α_0 by functions of the form Cr_s^β or $Dn_{\text{ion}}^{-\gamma/3}$, where n_{ion} is the ion density and C and D are constants, with $\beta=2$ or 3 , and with $\gamma=1, 2$,

TABLE I. L x-ray edge exponents α_0 extracted from data of Ref. 5, as a function of electron-gas radius parameter r_s (Ref. 6).

Metal	r_s	α_0
Na	3.93	0.26 ± 0.04
Mg	2.65	0.18 ± 0.04
Al	2.07	0.15 ± 0.04

or 3 , were deemed failures. Observe that at infinite free-electron density ($r_s \rightarrow 0$), α_0 must vanish.

Before discussing the implications of the empirical rule (3), a word of caution is in order. Although the general shape of a spectrum specifies the exponent α_0 and the broadening Γ rather precisely, and these values are not influenced by small modifications of the data, nevertheless a sizable error in the data could lead to a significantly altered exponent. Furthermore, only two independent exponents support the empirical rule; the third exponent, together with the condition $\alpha_0(0)=0$, determines the straight line in Fig. 1. Hence it is of the utmost importance that the L -edge exponent of a fourth material (say, potassium¹ with $r_s=4.86$) be measured in order to test the empirical rule.

If we assume the validity of the empirical rule (3), then two theoretical problems remain: (i) demonstration of the linear relationship between α_0 and r_s , and (ii) evaluation of the coefficient 0.068 . Both of these problems can be attacked for $r_s \rightarrow 0$ (Fermi energy E_F and wave vector $k_F \rightarrow \infty$), in which case the phase shifts are to be

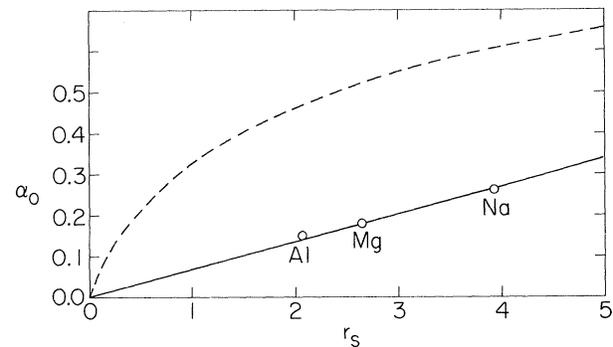


FIG. 1. L x-ray edge exponents α_0 as a function of r_s . Circles, data of Table I; solid line, empirical rule [Eq. (3)] $\alpha_0 = 0.068r_s$; dashed line, theory for the limit $r_s \rightarrow 0$ [Eq. (9)]. For $r_s \gtrsim 1$, the approximations leading to Eq. (9) cease to be valid.

evaluated in the high-energy limit. Using the Nozières-De Dominicis expression (2) and the Born approximation, we find

$$\lim_{r_s \rightarrow 0} \alpha_0 = \lim_{r_s \rightarrow 0} 2\delta_0/\pi, \quad (4)$$

$$2\delta_0/\pi = - (2/k_F^2\pi)(R\alpha^2)^{-1} \times \int_0^\infty (\sin^2 x)V(x/k_F) dx. \quad (5)$$

Here R and a are the appropriate Rydberg and Bohr radius with m/m_0 the ratio of band effective mass to free electron mass (henceforth taken to be unity):

$$R = 13.605(m/m_0) \text{ eV}; \quad a = 0.53(m_0/m) \text{ \AA}. \quad (6)$$

Note that the Fermi wave vector k_F is inversely proportional to r_s :

$$k_F a = (9\pi/4)^{1/3} r_s^{-1} = 1.919 r_s^{-1}. \quad (7)$$

The electron-hole interaction has been taken to be a spherically symmetric local potential $V(r)$. If, following other authors,⁸ we take a Fermi-Thomas screened interaction

$$V(r) = (e^2/r) \exp(-k_s r), \quad (8)$$

we find

$$\alpha_0 - 2\delta_0/\pi = (k_F \pi)^{-1} a^{-1} \ln[1 + 4(k_F/k_s)^2]. \quad (9)$$

Here the Fermi-Thomas screening wave vector is inversely proportional to the square root of r_s :

$$k_s a = (144/\pi^2)^{1/6} r_s^{-1/2} = 1.563 r_s^{-1/2}. \quad (10)$$

This function α_0 [Eq. (9)] has been plotted in Fig. 1 and fails to reproduce the empirical rule (3) near $r_s = 0$ where its slope is too great; for $2 < r_s < 5$ (in which case the validity of the Born approximation is limited) the magnitude of α_0 is too great, but its slope agrees with the data. Indeed, the dependence of the screening wave vector on r_s would have to be $k_s a \approx 5.39 r_s^{-1}$ for the Born approximation to describe the empirical rule. Furthermore, almost any electron-hole interaction capable of describing the empirical rule would have to be Coulombic near $r = 0$ with a range proportional to r_s . Although screening lengths proportional to $r_s^{1/2}$ and $r_s^{3/2}$ are features of Fermi-Thomas and Debye-Hückel theory, respectively, a screening length proportional⁹ to r_s is sufficiently unusual to cast doubt on the applicability of the Nozières-De Dominicis formula (2) to the empirical rule (3).

It is noteworthy that the empirical rule predicts $\alpha_0 = 0.22$ for Li, with $r_s = 3.25$. This result, to-

gether with the compatibility relationships¹⁰ implied by the Friedel sum rule, gives a K -edge exponent for Li of $\alpha_1 = 0.08$. Such a positive exponent is at odds with the presently accepted interpretation of the data¹¹ ($\alpha_1 \approx -0.3$) and suggests that the edge anomaly in the K spectrum of lithium is not attributable to a Mahan-type many-electron effect, in accord with previous work.¹²

Also note that, even if the empirical rule were to be dismissed as quantitatively invalid, the lithium K edge would still lie outside the present many-electron theory: An exponent $\alpha_1 = -0.3$ corresponds¹⁰ to $\alpha_0 = 0.49$, causing $\alpha_0(r_s)$ to be a discontinuous function of r_s and destroying the evidence for the importance of final-state interactions.

The principal results of this paper are as follows: (i) The empirical rule (3) relating the exponents of the L x-ray absorption spectra to r_s indicates the importance of conduction electron density and final-state interactions in shaping the Mahan anomalies. (ii) The fact that the spectra can be fitted with a phenomenologically broadened form of the Mahan theory supports, but does not confirm, that theory [α_0 is essentially an inverse linewidth, and a considerable range of physical alternatives could be forced to conform to Eq. (1)]. (iii) An unusual form of the electron-hole interaction is required to fit the empirical rule if the Nozières-De Dominicis form [Eq. (2)] of the exponent is used. (iv) The K absorption edge of Li appears to lie outside the domain of the present many-electron theory.¹²

If many-electron theory is to describe the soft x-ray threshold shapes of Al, Mg, Na, and Li, then improved expressions [Eq. (2)] for the exponents α_i will have to be developed, and possibly a revised version of the theory will be necessary.

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¹G. D. Mahan, Phys. Rev. **163**, 612 (1967).

²For a current review, see G. D. Mahan, to be published.

³P. Nozières and C. T. De Dominicis, Phys. Rev. **178**, 1097 (1969).

⁴Although Eq. (1) should be summed over l , we consider only the term for $l=0$; near threshold the terms for $l>0$ are negligible, altering the fit by less than 10% (J. D. Dow, D. L. Smith, and B. F. Sonntag, to be published). Equation (1) is convoluted with a Gaussian broadening function $B(x) = (2\pi\Gamma^2)^{-1/2} \exp[-\frac{1}{2}(x/\Gamma)^2]$, and compared with the data to obtain optimum values of Γ and α_0 . The size of Γ is virtually determined by the abruptness of the experimental absorption edge, whereas the value of α_0 is fixed primarily by the height and high-energy slope of the threshold spike. It is noteworthy that, within appropriate limits of error, the data of Ref. 5 yield the same exponent α_0 for Al as do other absorption [C. Gähwiller and F. C. Brown, Phys. Rev. B **2**, 1918 (1970)] and emission [H. Neddermeyer and G. Wiech, Phys. Lett. **31A**, 17 (1970)] data. The only values of Γ compatible with the data are $\Gamma = 0.06 \pm 0.03$ eV, comparable with instrumental broadening. The details of the analyses will be discussed elsewhere (Dow, Smith, and Sonntag, *op. cit.*).

⁵C. Kunz, R. Haensel, G. Keitel, P. Schreiber, and B. Sonntag, in *Electronic Density of States*, edited by L. H. Bennett, U.S. National Bureau of Standards Special Publication 323 (U.S. G.P.O., Washington, D.C., 1971), p. 275.

⁶In terms of the conduction-electron density n and the Bohr radius $a = \hbar^2/me^2$, we have $\frac{4}{3}\pi(r_s a)^3 = n^{-1}$.

⁷A table of r_s for various metals is given by C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1971), 4th ed., p. 248.

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⁹The screening wave vector obtained using Eqs. (41) and (42) of K. S. Singwi, A. Sjölander, M. P. Tosi, and R. H. Land, Phys. Rev. B **1**, 1044 (1970), also produced an unsatisfactory description of the data.

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Effective-Medium Theory for the ac Behavior of a Random System*

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It is shown that the ideas of effective-medium theory can be applied to the evaluation of the ac behavior of a random system. The results for systems of which the components have no dispersion, show dispersion. In particular, it is found that the ω^8 behavior of the ac conductivity of many disordered systems is reproduced to a good approximation over a limited frequency range.

The method of approach of substituting an effective medium for the real medium in the treatment of transport problems in inhomogeneous media has been emphasized by several authors,¹⁻⁵ most recently by Cohen and Jortner.⁶ Here we shall be not so much concerned with relating the model macroscopically inhomogeneous medium to its underlying microscopic structure, as with discussing the ac behavior of the model. The motivation for this comes from experiments which closely resemble the model,^{7,8} and the fact that these experiments yield results which closely parallel those in systems such as amorphous semiconductors, transition-metal glasses, and chalcogenide glasses.

When using some measurement system to determine the real and imaginary parts of the conductivity (or alternatively the dielectric constant), one experimentally defines the real part

σ_m and imaginary part ϵ_m such that

$$\begin{aligned}\sigma_m^*(\omega) &= \sigma_m(\omega) + i\omega\epsilon_0\epsilon_m(\omega), \\ \epsilon_m^*(\omega) &= \epsilon_m(\omega) - i\sigma_m(\omega)/\epsilon_0\omega.\end{aligned}\tag{1}$$

Since these quantities are experimentally defined, there must exist an experimentally defined average field $E_m^*(\omega)$ within the sample. The problem is to relate the average or measured values of (1) to the values of σ and ϵ of the components of the medium. We choose a medium consisting of two components, one with complex dielectric constant ϵ_1^* and concentration C , the other being defined by ϵ_2^* and $1-C$. We insist that the frequency of the applied field be such that this field is the same at all points in space at any instant of time. For sample thicknesses $\sim 1 \mu\text{m}$, this limits the present model to frequencies of about 30 GHz, that is, within the frequency range of standard bridge, stand-