K-edge x-ray spectra of Mg and other simple metals: Absence of evidence for orthogonality catastrophes*

John D. Dow

Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

(Received 15 October 1973)

It is shown that those simple free-electron metals (e.g., Li, Na, Mg, Al), whose x-ray emission spectra do not reveal bound-exciton states, generally cannot exhibit the significantly rounded K-edge threshold anomalies associated with the "orthogonality catastrophe." Thus, the recently measured rounded K-emission spectrum of magnesium cannot be interpreted as evidence for the orthogonality-catastrophe effect.

I. INTRODUCTION

Calculated one-electron densities of states, suitably truncated by a step-function[1] Fermi factor to account for Pauli's exclusion principle, describe the gross features of x-ray absorption and emission spectra quite well, especially for simple metals such as Na, Al, Mg, and Li. However, high-resolution x-ray measurements reveal anomalous absorption and emission edge shapes which do not resemble abrupt step functions but instead are peaked or rounded—shapes thought to be inexplicable in terms of one-electron theory.[2] Mahan first demonstrated that these x-ray threshold anomalies can be understood as caused by the interactions of excited-state conduction-band electrons with localized core holes[3]; he predicted the threshold shapes for absorption $\epsilon_2(\omega)$ and emission $I(\hbar\omega)$:

$$\epsilon_2(\omega) = \sum_{l=0}^{\infty} A_l^2 \left(\frac{\hbar\omega - E_T}{\xi} \right)^{-\alpha_l} \Theta(\hbar\omega - E_T) , \tag{1}$$

$$I(\hbar\omega) \propto \epsilon_2[(2E_T/\hbar) - \omega] . \tag{2}$$

Here $2\pi\hbar$ is Planck's constant, $\hbar\omega$ is the photon energy, E_T is the threshold energy (equal to the energy of the Fermi level relative to the core level, in the one-electron approximation) and A_l^2 is proportional to the one-electron transition rate for a core electron initially localized at the origin to absorb an x ray and recoil into the lowest unoccupied conduction band state with angular momentum quantum number l. The energy ξ is a cutoff parameter thought to be ≈ 5 eV for simple metals. Electron-hole scattering enhances the absorption by the Mahan factor

$$[(\hbar\omega - E_T)/\xi]^{-\alpha_l} , \tag{3}$$

which diverges or vanishes at threshold, depending on whether the dominant Mahan exponent α_l is positive or negative. The principal exponent is normally the most-positive α_l for which A_l is nonzero; this dominance is controlled primarily by parity selection rules[4,5]: K edges involve transitions from s-like core levels, hence A_0, A_2, etc., are zero and α_1 dominantes; $L_{2,3}$ edges involve p-core levels; hence, A_0 is nonzero and α_0 is the principal exponent.[6]

The Mahan threshold law is valid only near threshold, involves the imperfectly known parameters A_l, ξ, and α_l, and must be phenomenologically broadened for comparison with data; thus the extent to which the theory accurately describes the x-ray data for light metals cannot be easily determined. To date, the principal quantitative tests of the theory have been based on Nozières's and De Dominicis's derivation of an expression for the Mahan exponent in terms of the Fermi-energy partial-wave phase shifts δ_l (Ref. 7):

$$\alpha_l = 2\delta_l/\pi - \Delta , \tag{4}$$

where we have the "orthogonality-catastrophe" contribution

$$\Delta = 2 \sum_{j=0}^{\infty} (2j+1) \left(\frac{\delta_j}{\pi} \right)^2 . \tag{5}$$

Since the electron-hole interaction is attractive, the phase shifts δ_l are normally[6] positive, helping the exponents α_l to be positive and encouraging the absorption at threshold $\epsilon_2(E_T/\hbar)$ to diverge. Competing with this divergence is the orthogonality catastrophe[8] which tends to make exponents negative, causing the threshold absorption to vanish.

The physical origin[9] of the divergence is the large number of small-energy conduction-band electron-hole pairs created as the perturbed Fermi sea comes into equilibrium with the core-hole created by the x ray. The orthogonality catastrophe is caused by the imperfect overlap of the many electrons in the undistorted and hole-perturbed Fermi seas of the ground and excited states.

Within the context of the many-electron theory, a rounded x-ray edge would be associated with a negative dominant exponent, and therefore would provide evidence of an orthogonality catastrophe.

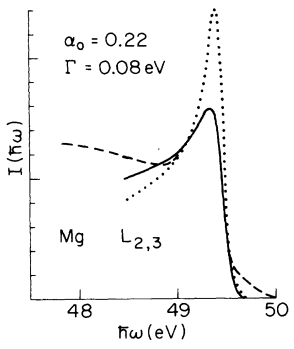

FIG. 1. Emission intensity $I(\hbar\omega)$ (in arbitrary units) vs photon energy $\hbar\omega$ (in eV) for the $L_{2,3}$ edge of Mg. The curves are normalized at the common point of coincidence. Dashed line: data of Ref. 14; solid line: theory [Eq. (2)], Gaussian broadened with $\alpha_0 = 0.22$ and $\Gamma = 0.08$ eV; dotted line: theory with $\alpha_0 = 0.453$ [computed from Eq. (9) for $\alpha_1 = -0.9$, the exponent used to fit the K edge].

Ausman and Glick[4] and Mahan[10] have computed the phase shifts δ_l and the exponents α_0 and α_1 using a Fermi-Thomas screened electron-hole interaction; they have concluded that α_0 should be positive and α_1 should be negative for all simple metals. Thus the principal experimentally relevant prediction of the theory would appear to be that electron-hole interactions cause an orthogonality catastrophe effect, rounding and suppressing K edges ($A_0 = 0$, $A_1 \neq 0$, $\alpha_1 < 0$), while enhancing L edges ($A_0 \neq 0$, $A_1 = 0$, $\alpha_0 > 0$).

The x-ray spectra of aluminum reveal threshold enhancement of the $L_{2,3}$ edge and suppression of the K edge.[11–14] Although the aluminum data have been cited as evidence for the Asuman-Glick-Mahan conclusion, they are quantitatively at odds with the theory; for, even in terms of the Ausman-Glick-Mahan calculations, the observed K edge is excessively suppressed (α_1 too negative) and the $L_{2,3}$ edge is insufficiently enhanced (α_0 too small).[15]

Recent measurements of the K and $L_{2,3}$ emission of magnesium reveal a rounded K edge and an enhanced $L_{2,3}$ edge, similar to the edge shapes of aluminum.[14] In this paper (Sec. II), the magnesium spectra will be analyzed, and it will be shown that they, also, lie outside the domain of applicability of the present version of many-electron theory. The K-emission threshold shape of magnesium cannot be interpreted as evidence for an orthogonality catastrophe. The implications of these results will be detailed in Sec. III. Appendix A contains a theoretical demonstration that the exponent α_1 is positive for simple metals.

II. ANALYSES OF DATA

In analyzing the data, we shall adopt only those premises implicit or explicit in previous work.[4,7,10] However, in contrast to previous calculations,[4,10] which have assumed the Fermi-Thomas form of the electron-hole interaction, we shall not specify the interaction other than to require that it satisfy Friedel's self-consistency criterion[16]:

$$Z = 2(\delta_0/\pi) + 6(\delta_1/\pi) + z\,, \tag{6}$$

where we have

$$Z = 1 \tag{7}$$

and

$$z = 2\sum_{l=2}^{\infty} (2l+1)\,\frac{\delta_l}{\pi}\,. \tag{8}$$

The Friedel rule, together with the Nozières–De Dominicis expression for the exponents leads to the compatibility relationship first applied to the x-ray spectra of aluminum[15]:

$$\alpha_1 = \alpha_0 - 1 \pm \tfrac{1}{3}[9 + 6(Z-z) - 3(Z-z)^2 - 24\alpha_0 - 24\chi]^{1/2}\,. \tag{9}$$

Here we have

$$\chi = 2\sum_{l=2}^{\infty} (2l+1)\left(\frac{\delta_l}{\pi}\right)^2\,, \tag{10}$$

and the sign in Eq. (9) is the sign of δ_1, normally positive.[6]

Recall that d and higher-angular-momentum waves in simple metals generally account for approximately 10% of the Friedel sum[17]; hence, we neglect z and χ, an approximation which affects the value of α_1 in Eq. (9) by a negligible amount, typically $\approx 5\%$:

$$z = 0, \quad \chi = 0. \tag{11}$$

Note that the compatibility relationship Eq. (9) is a general result, independent of details of the electron-hole interaction. In a sense, it permits the *experimental* specification of the electron-hole scattering, since the K-edge exponent α_1 is to be computed from the experimentally determined L exponent α_0. The exponents α_0 determined by fitting the broadened Mahan theory to L-edge absorption[18] and emission data (Fig. 1) agree and are listed in Table I.[11–14] Taking $\alpha_0 = 0.22 \pm 0.06$,

TABLE I. Exponents α_0 (L edge) and α_1 (K edge) and broadenings Γ_0 (L edge) and Γ_1 (K edge) for Mg x-ray spectra.

α_0	α_1	Γ_0 (eV)	Γ_1 (eV)
0.18 ± 0.04[a]	···	0.05 ± 0.03	···
0.22 ± 0.06[b]	···	0.08 ± 0.02	···
···	-0.9 ± 0.2[b]	···	0.3 ± 0.2[c]
0.45[d]	···	···	···
···	0.0841[d]	···	···

[a]Reference 11.

[b]Extracted from data of Ref. 14.

[c]This value agrees with the results of atomic calculations. See W. Bambynek *et al.*, Rev. Mod. Phys. 44, 716 (1972), Fig. 2-4.

[d]Computed using Eq. (9) from exponents of data of Ref. 14.

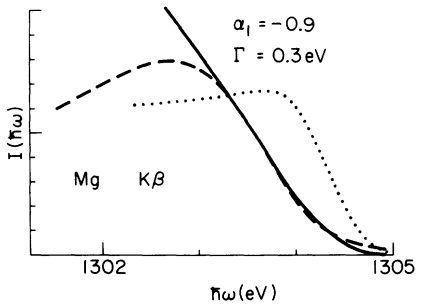

FIG. 2. Emission intensity $I(\hbar\omega)$ (in arbitrary units) as a function of photon energy $\hbar\omega$ (in eV) for the K edge of Mg. Dashed line: data of Ref. 14; solid line: theory [Eq. (2)] with $\alpha_1 = -0.9$, $\Gamma = 0.3$ eV, fit to the observed emission edge; dotted line: theory with $\alpha_1 = 0.0841$ (computed from $\alpha_0 = 0.22$ for the L edge), $\Gamma = 0.3$ eV.

the compatibility relationship yields an exponent $\alpha_1 = 0.084 \pm 0.06$, the corresponding theoretical curve is plotted with the data in Fig. 2.[19]

The basic point is that, even allowing for a wide range of error in the experimental exponent α_0, the value of α_1 computed from the compatibility relationship Eq. (9) is *positive*[20] (see Appendix A). The observed K-edge threshold, however, is rounded; to explain this rounding, the many-electron theory demands an exponent α_1 that is not only negative but *very negative* $\alpha_1 \approx -0.9$.[21] (See Figs. 2 and 3.) Indeed, experimentally α_1 must be more negative than $-\frac{1}{2}$, a situation that requires $\delta_1 < 0$ and $\delta_0 > \frac{1}{2}\pi$! But a Fermi-energy s-wave phase shift greater than $\frac{1}{2}\pi$ indicates the existence of a bound exciton state,[22-24] which should manifest itself in x-ray emission spectra. No such bound exciton states have been observed in the simple metals, although they are a general feature of screened-potential calculations.[10]

Observe that in general the condition for the orthogonality catastrophe's suppression of K edges, $\alpha_1 < 0$, implies a large s-wave exponent $\alpha_0 > \frac{1}{3}$ and phase-shift $\delta_0 > \frac{1}{4}\pi$. But calculations of Fermi-energy phase shifts indicate that δ_0 generally exceeds $\frac{1}{4}\pi$ only if the electron-hole interaction produces a bound state.[21,22] In practice, for the suppression to be both significant and observable, the K exponent must be considerably more negative: $\alpha_1 \lesssim -0.3$; the compatibility relationships then demand an L exponent, $\alpha_0 \approx 0.5$, larger than any observed in free-electron metals,[18] and large enough that strongly bound excitons should have been observed in the L emission spectra of those simple metals with rounded K edges.[24]

Two conclusions are inescapable: (i) the observed K and L threshold shapes of magnesium are inconsistent with the expression [Eq. (4)] for the exponents as functions of the Fermi-energy phase shifts; and (ii) the primary prediction of the many-electron theory, that electron-hole interactions cause $L_{2,3}$ edges to be rounded and K edges to be spiked, does not apply to those simple metals which fail to exhibit bound exciton states[22-24] below their main x-ray emission bands (e.g., Li, Na, Mg, and Al). The rounded K edges of the simple metals are not manifestations of the orthogonality catastrophe.

III. IMPLICATIONS

The rejection of the expression [Eq. (4)] for the threshold behavior of magnesium follows a similar result for aluminum. The x-ray absorption and emission spectra of lithium also exhibit features incompatible with the presently accepted many-electron interpretation.[2] Thus, of the simple metals cited as exhibiting x-ray edge anomalies, all but sodium exhibit data at least partially inconsistent with the present form of the many-electron theory. Moreover, K-emission data for sodium are not presently available; in the likely case that sodium's K edge is rounded (as are the K edges of Li, Mg, and Al), then all the data presently cited as evidence for the many-electron theory actually serve to contradict that theory in some manner.

It should be emphasized that we have raised no objections to the many-electron theory *per se*. Indeed, we have demonstrated only that the interpretation of the Mg data in terms of the many-electron theory with $\alpha_0 > 0$ and $\alpha_1 < 0$ is inconsistent.

It is conceivable that the basic many-electron theory could be reconciled with the Mg data, provided (i) the K exponent α_1 is positive, (ii) the K-edge rounding is attributed to some broadening mechanism[25] other than the orthogonality catastrophe effect, and (iii) the K-emission data are altered to account for significant reabsorption. Although one can only speculate about the likelihood that these conditions will be met for Mg, it is noteworthy that Neddermeyer has recently demonstrated the importance of reabsorption

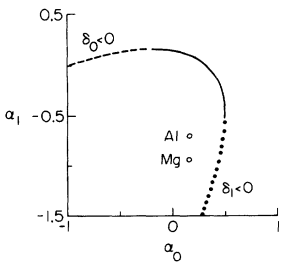

FIG. 3. Exponent α_1 as a function of α_0 [Eqs. (9)–(11)]. The phase shifts δ_0 and δ_1 are both positive for the solid segment of the curve, whereas δ_0 and δ_1 are negative for dashed and dotted segments, respectively. Note that the exponents extracted from Al and Mg data (open circles) do not intersect the theoretical curve and hence are incompatible with Eq. (9).

corrections to the K edge of Al.[26] Even if the K-edge data remain unaltered, it may be possible to preserve the many-electron interpretation by arguing that the electron-hole interaction is state dependent and nonlocal, thereby invalidating the compatibility relationships. However, crude estimates[27] of such effects indicate that they are unlikely to account for the discrepancy found here. Moreover, if nonlocal electron-hole interactions are indeed important, then the principal experimentally relevant prediction of the theory—the dependence [Eq. (4)] of the exponents on l—is vacuous.[28–30] The precise range of applicability of the many-electron theory will have to be determined by comparing observed x-ray anomalies with the theory—a task that will be difficult until the parameters ξ and α_l are more thoroughly understood.

Note added in proof. Ritsko, Gibbons, and Schnatterly [Bull. Amer. Phys. Soc. 19, 275 (1974); and private communication] have recently reported measurements of electron energy-loss spectra of Li at the K edge. Their measurements are inconsistent with a negative exponent $\alpha_1 < 0$, lend strong support to the conclusions obtained here, and all but exclude the many-electron interpretation of the Li K edge by requiring both α_1 and α_0 to either vanish (the one-electron result) or be small and positive.

It is a pleasure to thank L. M. Watson and D. J. Fabian for bringing H. Neddermeyer's recent data to the author's attention; stimulating conversations with C. P. Flynn, J. E. Robinson, and B. F. Sonntag, and D. L. Smith are gratefully acknowledged.

APPENDIX A: DEMONSTRATION THAT α_1 IS POSITIVE

Taking z and χ to be zero [Eq. (11)], we find that the condition

$$\alpha_1 > 0 \tag{A1}$$

is equivalent to

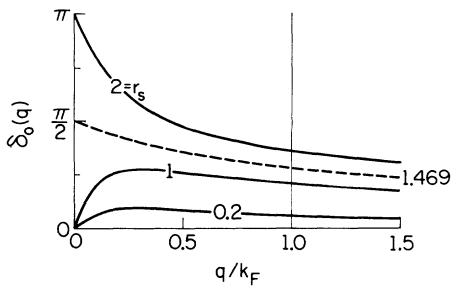

FIG. 4. Phase shift $\delta_0(q)$ vs reduced wave vector q/k_F for the potential of Eq. (A5). The values of r_s label each curve; k_F is the Fermi wave vector; and the dashed line corresponds to the s-wave phase shift for a potential which produces a zero-energy bound state.

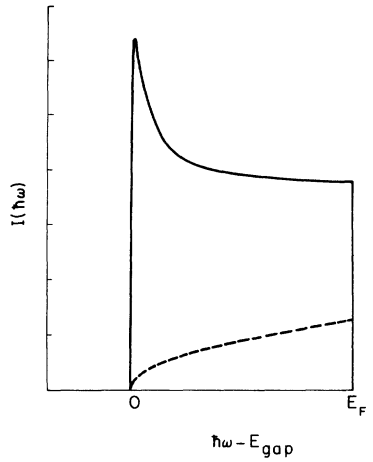

FIG. 5. Sketch of the allowed theoretical emission spectrum $I(\hbar\omega)$ (in arbitrary units) vs photon energy $\hbar\omega$ relative to E_{gap}, the gap between the core level and the bottom of the conduction band. E_F is the Fermi energy. Solid line: computed with electron-hole interaction, Eq. (A5), using the one-electron-like approximation $I(\hbar\omega) \propto \sum_\nu |\psi_\nu(0)|^2 \delta(\hbar\omega - E_{gap} - E_\nu)$. Dashed line: one-electron result.

$$\delta_1 > \delta_0 + \tfrac{1}{2}\pi \tag{A2}$$

or

$$\delta_0 > \tfrac{1}{4}\pi\,. \tag{A3}$$

The former condition [Eq. (A2)] is excluded by Newton's inequality[31–32]

$$\delta_1 < \delta_0 + \tfrac{1}{2}\pi. \tag{A4}$$

The condition that $\delta_0(k_F)$ exceeds $\frac{1}{4}\pi$ is incompatible with the notion that the emission spectra of simple metals and alloys are one-electron-like. To illustrate this point, in Fig. 4 we plot $\delta_0(q)$ as a function of the reduced wave vector q/k_F for the Hulthèn potential

$$V(r) = -\frac{e^2 k_s \pi^2/6\epsilon_0}{\exp(\frac{1}{6}k_s\pi^2 r) - 1}\,. \tag{A5}$$

The Hulthèn potential is virtually indistinguishable from the Fermi-Thomas screened-point-charge potential. Here the linear-response screening wave vector k_s is

$$k_s = 1.473\, r_s^{-1/2} a^{-1}; \tag{A6}$$

$a \equiv \hbar\epsilon_0/me^2$ is the Bohr radius and $r_s \equiv (3/4\pi n a^3)^{1/3}$ is the radius parameter for an electron gas of density n. The electron-gas radius parameter r_s determines the efficiency of the screening: with increasing r_s the potential strengthens until it binds a state $[\delta_0(0) = \pi]$. If the bound state is at zero energy (the dashed line in Fig. 4), then we have $\delta_0(0) = \frac{1}{2}\pi$ and $\delta_0(k_F)$ near $\frac{1}{4}\pi$. The basic point to be deduced from Fig. 4 is that all potentials strong

enough to produce $\delta_0(k_F) \geq \frac{1}{4}\pi$ are also strong enough either to bind a state $[\delta_0(0) = \pi]$ or to produce rapid variation in the time delay [which is proportional to $d\delta_0(q)/dq$]. Either of these consequences would lead to a structured allowed emission spectrum with non-free-electron-like peaks on the low-energy side.[23,33] (See Fig. 5.)

Note that these results are independent of the details of the electron-hole interaction and depend only on the notion that the phase shifts for the interaction exhibit the same general dependences on momentum transfer $\hbar q$ as those in Fig. 4.

Finally, we note that if α_1 is positive, and if the Fermi-energy phase shifts δ_l are monotonically decreasing as a function of l:

$$\delta_0 > \delta_1 > 0$$

then Eqs. (6–10) imply that α_0 is approximately $+0.2$ and α_1 is roughly $+0.1$. Furthermore $\alpha_1 \approx 0.1$ implies an enhanced K edge, and the observed K rounding would have to be attributed to broadening processes. With such large broadening and such a small difference between α_0 and α_1, the usual symmetry-breaking experiments[29–30] proposed as tests of the Mahan, Nozières, and De Dominicis (MND) theory are unlikely to produce the dramatic and conclusive results anticipated: the changes in observed line shapes due to many-electron effects are likely to be small and comparable in size with the band-structure-related changes omitted from the MND theory.

---

*Research supported by the National Science Foundation under Grant Nos. NSF-GH-33634 and NSF-GH-39132.

[1]The Fermi energies of typical metals are so large in comparison with thermal energies that the theory here assumes zero temperature.

[2]For a current review, see G. D. Mahan, Solid State Phys. (to be published).

[3]G. D. Mahan, Phys. Rev. 163, 612 (1967).

[4]G. A. Ausman and A. J. Glick, Phys. Rev. 183, 687 (1969).

[5]J. D. Dow and D. L. Smith, J. Phys. F. 3, L170 (1973); S. Doniach, P. M. Platzman, and J. T. Yue, Phys. Rev. B 4, 3345 (1971).

[6]Normally we have $\delta_{l+2} \ll \delta_l$ and $\alpha_{l+2} \ll \alpha_l$ for an attractive potential which is monotonic in r. However, the potential of a screened point charge generally exhibits Friedel oscillations, in which case the relative signs and sizes of the phase shifts are difficult to guess. The conclusions of this paper are unaffected by negative phase shifts. The only results that change are (i) the sign of the square root in Eq. (9) is negative if the p-wave phase shift is negative, and (ii) the exponent α_1 can be considerably more negative than $-\frac{1}{2}$ for negative s- or p-phase shifts. But even if negative phase shifts are permitted, the theory and the data are incompatible.

[7]P. Nozières and C. T. De Dominicis, Phys. Rev. 178, 1097 (1969).

[8]P. W. Anderson, Phys. Rev. Lett. 18, 1049 (1967).

[9]J. J. Hopfield, Comments Solid State Phys. 2, 40 (1969).

[10]G. D. Mahan, J. Res. Natl. Bur. Stds. 74A, 267 (1970). See also P. Longe [Phys. Rev. B 8, 2572 (1973)] whose computations of exponents α_l lead to similar but somewhat different conclusions.

[11]C. Kunz, R. Haensel, G. Keitel, P. Schreiber, and B. Sonntag, in *Electric Density of States*, edited by L. H. Bennett, Natl. Bur. Stds. Spec. Publ. No. 323 (U.S. GPO, Washington, D.C., 1971), p. 275.

[12]K. Läuger (unpublished). See G. Wiech, in *Soft X-ray Band Spectra*, edited by D. J. Fabian (Academic, London, 1968), p. 62.

[13]H. Neddermeyer and G. Wiech, Phys. Lett. A 31, 17 (1970).

[14]H. Neddermeyer, in *Band Structure Spectroscopy of Metals and Alloys*, edited by D. J. Fabian and L. M. Watson (Academic, London, 1973), p. 153.

[15]J. D. Dow, Phys. Rev. Lett. 31, 1132 (1973). See also N. H. March, in *Band Structure Spectroscopy of Metals and Alloys*, edited by D. J. Fabian and L. M. Watson (Academic, London, 1973), p. 297.

[16]See e.g., C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963), p. 343.

[17]For example, Ausman and Glick's calculations for Li (Ref. 4) satisfy the compatibility relationship with $z = 0.11$. Setting $z = 0$ introduces an error of 5% into Eq. (9).

[18]J. D. Dow and B. F. Sonntag, Phys. Rev. Lett. 31, 1461 (1973).

[19]The L exponents α_0 extracted from absorption data (Ref. 11) are probably the most reliable, since they involve absorption data both taken and processed by B. F. Sonntag. In fitting the data, the values A_j for all $j \neq l$ were assumed zero; then $A_l^2 \xi^{\alpha_l}$ was treated as an adjustable parameter. The theory was Gaussian broadened $\{B(x) = (2\pi\Gamma^2)^{-1/2} \exp[-\frac{1}{2}(x/\Gamma)^2]\}$ and compared with the data. To estimate the size of the error introduced by taking only one term of Eq. (1), one must know A_j and ξ. For example, a crude estimate of the relative correction associated with $L_{2,3}$ transitions to d waves in the conduction band is $(A_2/A_0)^2(\Gamma/\xi)^{\alpha_0-\alpha_2}$, normally a negligible 10% effect or less. Indeed, for exponents satisfying the compatibility relationships with $\alpha_0 > 0$ and $\alpha_1 < 0$, the correction is typically 1%. A complete discussion of these effects is given by J. D. Dow, D. L. Smith, and B. F. Sonntag, Phys. Rev. B (to be published).

[20]No reasonably sized d-wave phase shift alters this conclusion.

[21]For a rounded edge, it is difficult to extract a unique value of an exponent from a spectrum, since both the broadening Γ and the negative exponent α cooperate to round the edge. (No such problem arises for peaked edges, from which accurate values of α can be extracted.) Nevertheless the Mg K edge is rounded over ≈ 2 eV, whereas the atomic Auger width is ≈ 0.3 eV. If this difference is to be attributed to an orthogonality catastrophe, then α_1 must be quite negative: $\alpha_1 \ll -0.5$. A complete discussion of the fitting procedures is given in J. D. Dow, D. L. Smith, and B. F. Sonntag, Phys. Rev. B (to be published).

[22]P. M. Morse, Rev. Mod. Phys. 4, 577 (1932); J. D. Dow, J. E. Robinson, J. H. Slowik, and B. F. Sonntag, Phys. Rev. B (to be published).

[23]Even for an electron gas somewhat more dense than one that supports a bound excitonlike state, the remnant of

the bound state would appear as a peak at the low-energy edge of the x-ray emission spectrum. (See Ref. 22.) Such peaks are absent from the emission spectra of Mg and other simple metals. The argument that a large Fermi energy phase shift $\delta_0 \gtrsim \frac{1}{4}\pi$ implies such a bound-state or continuum peak is based on calculations (Ref. 22) of s-wave phase shifts for Thomas-Fermi-type potentials. Although the actual effective electron-hole interaction undoubtedly exhibits Friedel oscillations, orthogonalization repulsion, and other features missing from a screened point-charge's potential, the s-wave phase shift for the case of a zero-energy bound state should decrease, as a function of momentum transfer $\hbar\vec{q}$, from $\frac{1}{2}\pi$ at $q=0$ to $\delta_0 \approx \frac{1}{4}\pi$ at the Fermi energy, much the same as the computed screened-potential phase shift does. Hence the qualitative conclusion that δ_0 is less than $\frac{1}{4}\pi$ for simple metals, while not rigorously derived for all possible forms of the electron-hole interaction, is amply justified by the screened-potential calculations. For a more detailed discussion of these ideas as they relate to K edge spectra, see J. D. Dow, L. N. Watson, and D. J. Fabian, J. Phys. F (to be published).

[24]No such bound excitons have been observed at the bottom of emission bands. There are differing opinions about whether emission spectra should exhibit such bound states, as discussed by J. Friedel, Comments Solid State Phys. 2, 21 (1969). For an opposing viewpoint, see M. Combescot and P. Nozières, J. Phys. Paris 32, 913 (1971).

[25]J. D. Dow, J. E. Robinson, and T. R. Carver [Phys. Rev. Lett. 31, 729 (1973)] R. A. Ferrell [Phys. Rev. 186, 399 (1969)], and C. Wood and W. E. Parry [J. Phys. C 4, 1387 (1971)] discuss phonon effects, thermal broadening, and lifetime broadening, respectively.

[26]H. Neddermeyer, Phys. Lett. A 44, 181 (1973).

[27]J. D. Dow (unpublished).

[28]Numerous experimental questions about the threshold anomalies of simple metals remain unanswered: (i) Why do the absorption and emission K edges of Li and perhaps Al overlap? [J. D. Dow, J. E. Robinson, and T. R. Carver, Phys. Rev. Lett. 31, 759 (1973).] (ii) Why is the energy ξ so small (≈ 0.24 eV) and independent of composition x for amorphous Mg_xSb_{1-x} alloys? [J. D. Dow, J. E. Robinson, J. H. Slowik, and B. F. Sonntag, Phys. Rev. B (to be published).] (iii) Why is the density dependence of the exponents of Na, Mg, and Al inexplicable in terms of simple models of the electron-hole interaction? [J. D. Dow and B. F. Sonntag, Phys. Rev. Letters 31, 1461 (1973).] (iv) Why does not the K absorption edge of Li become peaked when inversion symmetry is broken? (Refs. 29, 30). See *Note added in proof*.

[29]S. Doniach, P. Platzman, and J. T. Yue, Phys. Rev. B 4, 3345 (1971).

[30]J. D. Dow and D. L. Smith, Brit. J. Phys. F 3, L170 (1973); and unpublished ; B. F. Sonntag, J. Phys. F 3, L255 (1974).

[31]R. Newton, *Complex j-Plane* (Benjamin, New York, 1964), Appendix B.

[32]Corrections to Newton's inequality for realistically nonlocal interactions are unlikely to alter our conclusions.

[33]Even the "forbidden" emission bands should exhibit such peaks if inversion symmetry is adequately destroyed by impurities or phonons. [See Ref. 30, D. L. Smith and J. D. Dow, Phys. Rev. B (to be published).]