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Analyses of the x-ray thresholds of Li, Na, Mg, and Al—a reply to comments by G. D. Mahan

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Criticisms of our work by Mahan are rebutted. Calculations of d- and s-wave dipole matrix elements, using *precise* Hartree-Fock core wave functions, are found to produce values of d to s intensity ratios an order of magnitude smaller than the values obtained by Mahan, who used approximate wave functions with unrealistically large core radii. Atomic calculations cited as supporting those approximate wave-function calculations refer to $2p$-to-$3d$ transitions, not to the $2p$-to-$3s$ transitions in question. Evaluation of the corrections to our $L_{2,3}$ edge analyses using Mahan's phase shifts reveals that the corrections lie well within our previously estimated uncertainties. The 2-eV energy gap (Stokes's shift) which the criticism has attributed to our phonon model is shown to occur only if lattice relaxation times ($\sim 10^{-12}$ sec) are shorter than or comparable with Auger decay times (estimated by Mahan to be $\sim 3\times 10^{-15}$ sec).

I. INTRODUCTION

In recent papers,[1,2] G. D. Mahan has criticized our analyses of x-ray edges.[3–11] Here we rebut his criticisms.[12]

The discussion of this paper centers on the Nozières–de Dominicis[13] (ND) theory for the x-ray absorption $\epsilon_2(\omega)$,

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

where we have

$$\alpha_l=2\delta_l/\pi+\alpha_\infty$$

and

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

Here A_l is proportional to a dipole matrix element between the core state and a conduction electron state with angular-momentum quantum number l. ξ is a cutoff energy, E_T is the threshold energy, $\Theta(x)$ is a unit step function, and δ_l are phase shifts for scattering of Fermi-energy electrons by the core hole.

The principal experimentally relevant prediction of the ND theory, that K edges are rounded and $L_{2,3}$ edges peaked, was based on computations (such as Mahan's[14]) of exponents for simple metals which suggested that $L_{2,3}$ edge exponents are generally large and positive,

$$\alpha_0\gtrsim 0.4\,, \tag{3a}$$

whereas K edge exponents are negative,

$$\alpha_1<0\,. \tag{3b}$$

This form of the theory is referred to as the MND theory.[15–17] Our analyses have shown that the existing experimental data cannot be consistently described using this form of the theory and have pointed out that the prediction of significantly rounded K edges for all metals is an artifact of model potentials with bound states.[7,11] (See Fig. 1.)[15–17]

Mahan's criticisms have been directed against our analyses; the present paper[18–21] is concerned with a reply to those criticisms.

In Sec. II we show that the large values Mahan obtains for the d-to-s intensity ratio are consequences of inaccuracies in the core wave functions

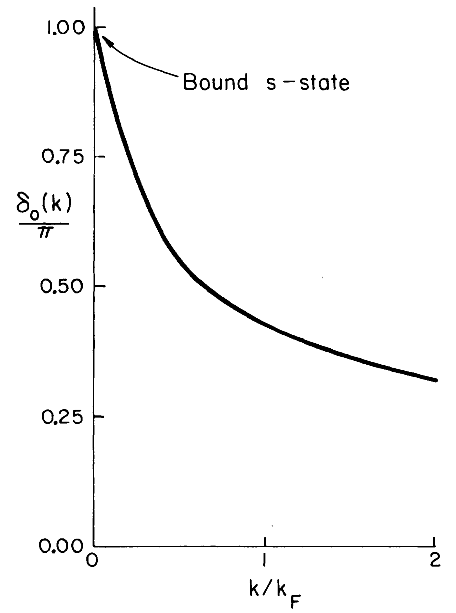

FIG. 1. Phase shift $\delta_0(k)$ for s-wave scattering against wavevector k in units of the Fermi wavevector k_F, after Mahan(Ref. 11). Note that by Levinson's (Ref. 11) theorem the number of bound s states is $\lim_{k\to 0}[\delta_0(k)/\pi - \delta_0(\infty)/\pi] = 1$.

used. In Sec. III we show that this intensity ratio is multiplied by a factor that vanishes at threshold causing the d-wave corrections to be even smaller than we have previously estimated. In Sec. IV we show that the corrections to the compatibility relations are of second order in the d-wave phase shifts. Using phase shifts from Ref. 1, we evaluate these corrections and find them smaller than our previous estimates. Section V takes up the question of a Stokes's shift, and our conclusions are summarized in Sec. VI. Section VII treats the K edge of Li. Two appendices contain details of our calculations.

II. *d-TO-s* INTENSITY RATIO

Mahan states that "the $L_{2,3}$ edge is predominatly d-wave," that the d-to-s intensity ratio $\mathfrak{F} \equiv A_2^2/A_0^2$ is very large and is "the most important parameter for calculating the theoretical spectra."[1] He terms our approximation of neglecting the d-wave intensity a "serious blunder which negates [our] analyses."[1]

These claims are invalid because they are based on calculations of dipole matrix elements A_l using approximate $2p$ core wave functions which are known to be inaccurate[22,23] (see Fig. 2). We have repeated the calculations of $\mathfrak{F}$ using accurate Hartree-Fock core orbitals,[24] and established expressions for that ratio,[13,25] and we have found considerably smaller values of $\mathfrak{F}$, in agreement with our previously estimated upper bound.[8] (See Table I.) Calculations by Gupta and Freeman,[19] Smrcka,[26] Longe,[17] and Almbladh and von Barth[27] also produce values of the d-to-s ratio at the $L_{2,3}$ edge below our previous estimate.

It is easy to see physically why the d-to-s ratios of Na, Mg, and Al computed in Ref. 1 are excessively large: the $2p$ core wavefunctions employed are hydrogenic orbitals with effective charges Z^* determined by equating the effective Rydberg to the energy gap between the core level and the bottom of the conduction band. The resulting charges Z^* are even smaller (and the corresponding core radii even larger) than those determined from the core-level ionization potentials—which have long been understood to yield effective charges substantially smaller than those which best describe core wave functions.[22,23] Therefore the $2p$ wavefunctions of Ref. 1 extend well beyond the d-wave centrifugal barrier and significantly overlap the conduction band d wave, making A_2 and $\mathfrak{F}$ large.

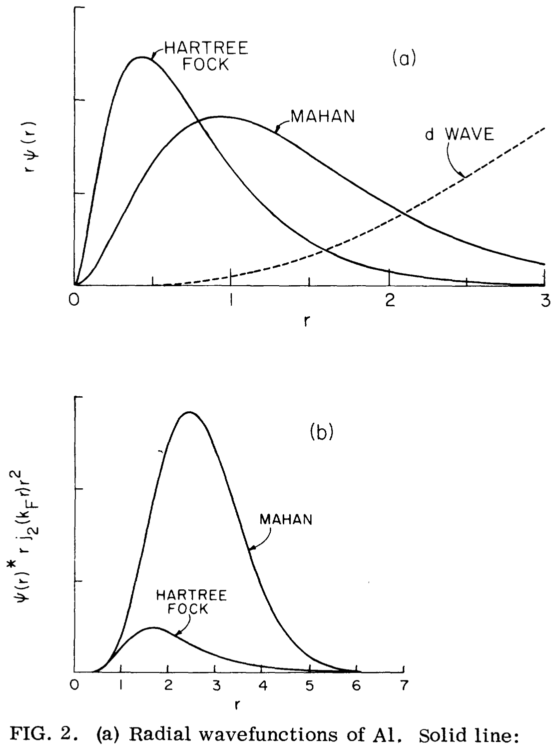

FIG. 2. (a) Radial wavefunctions of Al. Solid line: precise Hartree-Fock $2p$ wave function; dashed line: Mahan's hydrogenic representation of the same $2p$ wave function; alternating dashed-dotted line, a d-wave function $j_2(k_F r)$; (b) the corresponding integrands, $\Psi(r)^* r j_2(k_F r) r^2$, which when integrated and squared are proportional to the intensity A_2^2. Note that Mahan's wave function is responsible for an inflated core-d-overlap and integrand.

TABLE I. d-to-s intensity ratios $|A_2/A_0|^2$ computed (i) by Mahan using approximate core orbitals, (ii) by us using precise Hartree-Fock atomic orbitals, and (iii) by other authors. Note the overestimate obtained in Ref. 1.

Author	Na	Mg	Al	Comment
Mahan	0.48	1.64	2.68	Ref. 1, approximate core orbitals
This work	0.047	0.16	0.39	Precise Hartree-Fock core orbitals of Ref. 24.
Almbladh and von Barth	0.11	...	0.52	Ref. 27.
Smrcka	...	...	0.66	Ref. 26, estimated from figure.
Longe	0.011	0.038	0.072	Ref. 17.
Gupta and Freeman	0.08	0.45	...	Ref. 19, estimate from figure.

In contrast, a realistic $2p$ core orbital has a small radius and the centrifugal barrier prevents the d wave from significantly overlapping the $2p$ core—making A_2 and $\mathfrak{F}$ small (see Fig. 2).

Citations[2] of atomic structure calculations[28] in support of the large d-to-s ratio at the $L_{2,3}$ edge are, in our opinion, irrelevant because those atomic calculations do not refer to the $L_{2,3}$ edge ($2p$-to-conduction band) transitions, but to higher energy ($2p$-to-$3d$) transitions which are spectroscopically distinct in both the atom and the solid.

III. EVALUATION OF d-WAVE CORRECTIONS

The statement by Mahan,[1] that we assume $\mathfrak{F}=0$, is incorrect. The fractional correction to our analyses associated with neglecting d waves [the $l=2$ term in Eq. (1)] is

$$\mathfrak{F}((\hbar\omega - E_T)/\xi)^{2(\delta_0-\delta_2)/\pi}\,, \tag{4}$$

and is negligible near threshold, as shown previously.[8] The many-body factor vanishes at threshold even if $\mathfrak{F}\equiv(A_2/A_0)^2$ is large. Indeed, we show in Appendix A that these corrections, evaluated using phase shifts of Ref. 1, are considerably smaller than our previously estimated uncertainties[8] and nowhere near as large as suggested in Ref. 1.

IV. COMPATIBILITY RELATIONS

Criticism[1] has also been directed at our use of the compatibility relation[6,7]

$$\alpha_0=\alpha_1-\tfrac{1}{3}+\tfrac{2}{3}(1-6\alpha_1)^{1/2}(1-H)^{1/2} \tag{5}$$

to argue the invalidity of the interpretation of K edges as significantly rounded by a very negative exponent α_1. Here we have

$$H\equiv\left[\frac{3}{4}\left(\sum_{j=2}^{\infty}2(2j+1)(\delta_j/\pi)\right)^2 + 6\sum_{j=2}^{\infty}2(2j+1)(\delta_j/\pi)^2\right]\Big/(1-6\alpha_1)\,. \tag{6}$$

The criticism is leveled at our approximation of setting $H=0$, an approximation stated as responsible for "a significant error for aluminum where the d waves contribute over 20% to the Friedel sum rule and change the value of α_2 by a factor of 2."[1] The large corrections implied do not occur—because the corrections are of *second order* in the d-wave phase shifts. Since the value of α_2 for Al in Ref. 1 is nearly zero, the factor of 2 change is presumably a negligible change of 0.02 (our quoted uncertainty is ±0.04). Moreover, we use the compatibility relation only to relate α_0 and α_1; α_2 does not enter our analyses of edges, because the d-wave contribution can be neglected near thresh-

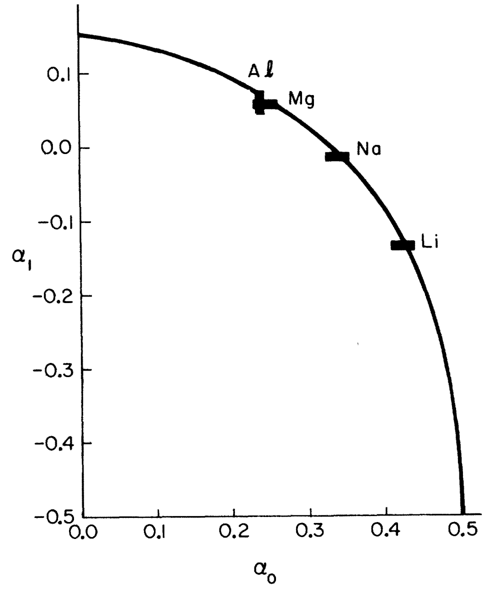

FIG. 3. Compatibility relation $\alpha_0(\alpha_1)=\alpha_1-\frac{1}{3}+\frac{2}{3}(1-6\alpha_1)^{1/2}$, neglecting scattering by d and higher angular momentum partial waves. Mahan's exponents for Li, Na, Mg, and Al are denoted by rectangles. Note that Mahan's exponents do satisfy the compatibility relation, contrary to the impression conveyed in Ref. 1.

TABLE II. Exponents α_0 computed using the compatibility relation Eq. (5) and Mahan's phase shifts (Table III), including d-phase shifts [α_0 (exact)] and omitting them [α_0 (neglect δ_2)]. Note that in all cases the error is less than ±0.040, the value quoted in previous work (Ref. 5).

	α_0 (exact)	α_0 (neglect δ_2)	Error
Li	0.427	0.429	−0.002
Na	0.341	0.349	−0.008
Mg	0.247	0.265	−0.018
Al	0.242	0.271	−0.030

old[8] (see Appendix A). In Appendix B we use the phase shifts of Ref. 1 to show that the corrections to the compatibility relations are negligible (see Fig. 3), lie well within the previously estimated uncertainty of 0.04 (see Table II), and are generally smaller than the round-off errors associated with those phase shifts (see Table III).

V. STOKES'S SHIFT

A Stokes's shift (gap) between emission and absorption edges occurs when the excited state lifetime is long enough ($T \gtrsim 10^{-13}$ sec) to permit lattice relaxation around the excitation before emission. The statement of Ref. 1 that our theory should exhibit a Stokes's shift assumes that the Li K-edge lifetime is longer than ~10^{-13} sec (see Fig. 4). In the same paper[29] the Auger lifetime for the 1s hole is estimated to be $\tau \approx 3\times10^{-15}$ sec ($\approx \hbar/0.2$ eV), about two orders of magnitude shorter than characteristic lattice relaxation times. If all the 1s holes decay without radiating before the lattice relaxes, there can be no electron-hole recombination after lattice relaxation and hence no Stokes's-shifted emission.

TABLE III. Values of Mahan's phase shifts δ_j, and the Friedel sum (which should equal π). The round-off errors in the values quoted by Mahan were sufficiently large that we renormalized his phase shifts so that the Friedel sum rule is satisfied (values in parentheses).

Metal	δ_0	δ_1	δ_2	$\sum_{j=0} 2(2j+1)\delta_j$
Li	1.02	0.14	0.025	3.13
	(1.024)	(0.1405)	(0.02509)	(π)
Na	0.76	0.20	0.042	3.14
	(0.7604)	(0.2001)	(0.04202)	(π)
Mg	0.55	0.25	0.056	3.16
	(0.5468)	(0.2485)	(0.05567)	(π)
Al	0.53	0.23	0.073	3.17
	(0.5253)	(0.2279)	(0.07235)	(π)

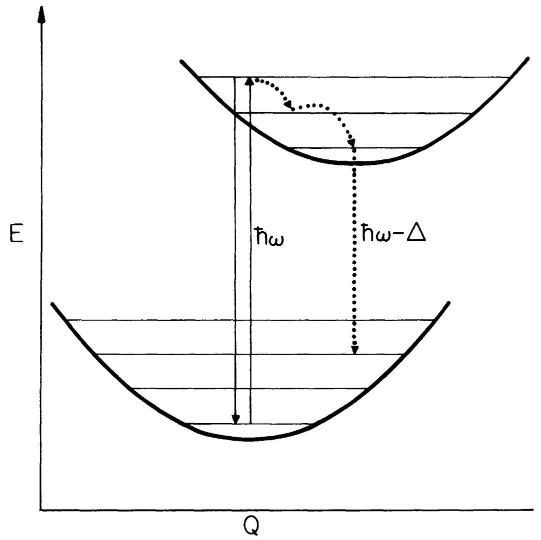

FIG. 4. Energy vs configuration coordinate Q illustrating the fact that a Stokes's shift of Δ between absorption and emission edges is observed only if lattice relaxation occurs before (dotted lines) emission. No Stokes's shift occurs if the observed radiation is emitted before lattice relaxation.

At time T, after lattice relaxation, only a small fraction of the 1s holes, $e^{-T/\tau}$, would not have been annihilated by radiationless transitions. Using the value 0.2-eV Auger width[29] and $T \sim 10^{-13}$ sec, we find the fraction of holes remaining, and hence the quantum yield for x-ray emission occurring after lattice relaxation to be unobservably low ($< 5\times10^{-15}$); this is to be compared with the total fluorescence yield of[30] $\approx 10^{-4}$. No Stokes's shift should be observed for such a short Auger lifetime. Hence any Stokes's shift would be indicative of a long Auger lifetime.

VI. LITHIUM

Arguments[1,2] that our model predicts an edge breadth for solid Li that scales as $T^{1/2}$ at large temperature overlook the fact that the high-temperature regime is inaccessible in solid Li because the melting temperature (443 K) is nearly equal to the Debye temperature (400 K).[31] (If the lattice vibrations are treated in an Einstein model, the edge breadth is approximately proportional to $\coth(T_0/2T)^{1/2}$ where $k_B T_0$ is the Einstein energy.) The statement[2] that the Li edge width shows no temperature dependence is at odds with published observations.[31,32]

VII. SUMMARY

In analyzing data, we have assumed the accepted interpretations of the x-ray edge anomalies and have shown that these interpretations lead to inconsistencies. There are, to be sure, corrections to our analyses, corrections associated with energy-dependent matrix elements, band structure, spin-dependent scattering, or as yet unexamined physical mechanisms. We have defined our approximations[8] so that our analyses can be repeated, and our results have been confirmed by others. For example, the importance of core broadening processes at the K edge of Li appears to have been documented experimentally[31,32] and theoretically[3,33,34]: phonon and Auger effects of the predicted order of magnitude[3,35,36] have been reported.[31,32] At the $L_{2,3}$ edges, Slusky *et al.*[38,39] find $L_{2,3}$ exponents $\alpha_0 = 0.23 \pm 0.03$ and[40] 0.18 ± 0.01 for Na and Mg; these values compare favorably with ours: $\alpha_0 = 0.26 \pm 0.04$ and 0.18 ± 0.04.[41] (They also confirm for Mg that the analyses are insensitive to d-wave exponent α_2.)[40]

In summary, we have examined the conclusions of Mahan[1,2] and have found that they cannot be justified.

ACKNOWLEDGMENTS

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APPENDIX A: ANALYSES OF $L_{2,3}$ EDGES: CENTRAL ISSUES

The analyses of $L_{2,3}$ edges were based on Eq. (1) which we rewrite as

$$\epsilon_2(\omega) = |A_0|^2 \xi^{\alpha_0} (\hbar\omega - E_T)^{-\alpha_0} \times \left[1 + \left|\frac{A_2}{A_0}\right|^2 \left(\frac{\hbar\omega - E_T}{\xi}\right)^{\alpha_0 - \alpha_2}\right] \Theta(\hbar\omega - E_T).$$

To account for instrumental and lifetime broadening, this equation is Gaussian broadened, by convolution with the function $(2\pi\Gamma^2)^{-1/2} e^{-(1/2)(x/\Gamma)^2}$ before comparison with L_3 edge data. The L_2 edges have similar shapes to the L_3 edges, but lie at higher energy by virtue of the spin-orbit splitting.

The comments by Mahan[1,2] on the $L_{2,3}$ edge analyses are based on our approximation that, near threshold, the d-wave contribution can be neglected,

$$D \equiv \left|\frac{A_2}{A_0}\right|^2 \left(\frac{\hbar\omega - E_T}{\xi}\right)^{\alpha_0 - \alpha_2} \ll 1. \tag{A1}$$

In our letter,[5] we estimated corrections of less than 10% due to the omission of D. (Mahan incorrectly states that we assume $|A_2/A_0|^2 = 0$; both factors in D are important.)

By neglecting D, we were able to analyze the data without knowing A_2, A_0, ξ, and α_2 separately. If D is neglibible, as we suggested, then the *only* parameters of the fitting procedure are (i) E_T, which is precisely specified by the position of the edge; (ii) the broadening Γ, which is accurately determined by the small breadth of the edge; (iii) the intensity parameter $A_0\xi^{\alpha_0}$, which is fixed by normalizing the spectrum as far away from threshold as is practical but close enough to minimize energy-dependent one-electron corrections (e.g., almost the spin-orbit splitting above threshold—immediately before the onset of the L_2 edge); and (iv) the exponent α_0 which then determines both the height and the high-energy slope of the threshold spike—and therefore can be determined with accuracy (estimated uncertainty ± 0.04).

Note that sufficiently close to the thresholds (where we fit the spectra), the values of D are unquestionably negligible, since $\hbar\omega - E_T$ is small and $\alpha_0 - \alpha_2$ is positive. In practice, finite broadening limits the smallness of $\hbar\omega - E_T$ to a value $\approx \Gamma$.

The fitting procedure determines α_0 primarily by fixing the height of the threshold spike (at $\hbar\omega - E_T \approx \Gamma$) relative to the height of the spectrum at the spin-orbit energy W above threshold; that is, by fixing the ratio

$$\frac{(\Gamma/\xi)^{-\alpha_0} + |A_2/A_0|^2 (\Gamma/\xi)^{-\alpha_2}}{(W/\xi)^{-\alpha_0} + |A_2/A_0|^2 (W/\xi)^{-\alpha_2}} = \left(\frac{\Gamma}{W}\right)^{-\alpha_0} \left(\frac{1 + (A_2/A_0)^2 (\Gamma/\xi)^{\alpha_0 - \alpha_2}}{1 + (A_2/A_0)^2 (W/\xi)^{\alpha_0 - \alpha_2}}\right). \tag{A2}$$

Thus we find the fractional error C associated with neglecting the terms proportional to A_2^2:

$$C \equiv \frac{1 + (A_2/A_0)^2 (\Gamma/\xi)^{\alpha_0 - \alpha_2}}{1 + (A_2/A_0)^2 (W/\xi)^{\alpha_0 - \alpha_2}} - 1 \simeq \left|\frac{A_2}{A_0}\right|^2 \left[\left(\frac{\Gamma}{\xi}\right)^{\alpha_0 - \alpha_2} - \left(\frac{W}{\xi}\right)^{\alpha_0 - \alpha_2}\right]. \tag{A3}$$

In our letter,[5] we estimated $|C| \lesssim 0.1$. By neglecting D, we introduce an uncertainty $\Delta\alpha$ into the extracted exponents α_0:

$$1 + C \simeq (\Gamma/W)^{-\Delta\alpha},$$

or

$$\Delta\alpha \simeq \frac{\ln(1 + C)}{\ln(W/\Gamma)} \simeq \frac{C}{\ln(W/\Gamma)}. \tag{A4}$$

We shall now evaluate $|C|$ and $\Delta\alpha$, and we shall show that our original estimates $|C| \lesssim 0.1$ and

TABLE IV. Parameters used in evaluation of the importance of *d* waves.

	Na	Mg	Al	Comment
r_s	3.93	2.65	2.07	
α_0 (Dow-Sonntag)	0.26	0.18	0.15	Extracted from data, Ref. 5, ±0.04.
α_0 (Mahan)	0.34	0.25	0.24	Computed, Ref. 1.
δ_2/π (Dow, Robinson, Slowik, Sonntag)	0.02	0.02	0.02	Self-consistent calculations, Ref. 29, of $\delta_2(r_s)$, together with $\alpha_0(r_s)$ Ref. 5) produce $\delta_2(\alpha_0)$.
δ_2/π (Mahan)	0.013	0.018	0.023	Computed, Ref. 1.
α_0-α_2 (Dow-Sonntag)	0.29	0.19	0.15	Ref. 5.
α_0-α_2 (Mahan)	0.46	0.32	0.29	Ref. 1.
Γ (eV)	0.06	0.06	0.06	Ref. 5, ±0.03 eV.
ξ	3.24	7.14	11.7	$\xi = E_F \equiv 13.6\ (\frac{1}{4}9\pi)^{2/3} r_s^{-2}$ eV.

$|\Delta\alpha| \lesssim 0.04$ are valid, and *even somewhat conservative.*

We take values[5] of $\Gamma = 0.06$ eV; Mahan suggests[1] $\xi = E_F$ or $\xi = \frac{3}{2}E_F$, where E_F is the Fermi energy; we shall use the value favorable to his viewpoint, $\xi = E_F$. The exponents α_0 are given in our letter[5] and in Table IV. The spin-orbit energies are also given in Ref. 41.

To estimate the corrections C and $\Delta\alpha$, we must have the values of the exponents α_2 and the intensity ratios $|A_2/A_0|^2$. To obtain the former, we must estimate the d-wave phase shift δ_2. We take values of δ_2 which are even somewhat larger than Mahan's values (and therefore should produce even larger errors in our analyses); we use the intensity ratios $|A_2/A_0|^2$ of Table I.

With realistic values of the intensity ratio $|A_2/A_0|^2$, the correction term C [Eq. (A3)] can be evaluated (Table V). In all cases, it is smaller than our earlier estimate of an upper bound,[5] $|C| < 0.1$, and should produce a change in extracted exponent that lies within our quoted uncertainty. Note that although Mahan focuses attention on his intensity ratio of 2.68, implying a 268% correction to our analysis of Al, *only a 22% correction results from his large value* of $|A_2/A_0|^2$. The realistic orthogonalized-plane-wave (OPW) intensity ratio gives a 5% correction (as an approximate upper bound)—a factor of 2 smaller than our original estimate.

The corrections $\Delta\alpha$ to the exponents are given in Table VI; they too lie well within our quoted uncertainty of ±0.04.

APPENDIX B: EXPONENTS

1. Explicit corrections

The exponents α_l are given by the Nozières-deDominicis formulas, Eq. (2) where the δ_l are Fermi energy phase shifts for an electron in the scattering potential of the hole. Thus we have

$$\alpha_0 - \alpha_2 = 2\delta_0/\pi - 2\delta_2/\pi > 0\,. \qquad \text{(B1)}$$

Observe that the d waves contribute explicitly to the exponents α_0 and α_1 only through the term α_∞, in which the d-phase shift is *squared*. Since δ_2 is normally small (the Friedel rule for positive phase shifts $\delta_0 > \delta_1 > \delta_2$ requires $\delta_{2/\pi} < \frac{1}{18}$) we have

$$(\delta_2/\pi)^2 < \tfrac{1}{324} = 0.003\,, \qquad \text{(B2)}$$

TABLE V. Correction factor C, Eq. (9), computed using Mahan's parameters and ours. Note that even with Mahan's considerable overestimate of $|A_2/A_0|^2$, the largest correction would be 22%. Correction factors obtained using reasonable values of A_2/A_0 lie well within the previously estimated bounds $|C| < 0.1$.

	Na	Mg	Al	Comment
C (Mahan)	−0.04	−0.14	−0.22	Overestimate of $\vert C\vert$ due to large values of A_2/A_0.
C (this work)	−0.005	0.02	−0.05	$\vert C\vert$ is factor of 2 smaller than previous bound $\vert C\vert < 0.1$.

TABLE VI. Calculated error $\Delta\alpha$ [Eq. (10)] in the extracted value of α_0 (Ref. 6) attributable to neglect of d waves. Note that the Dow-Sonntag values lie within the quoted uncertainty of ±0.04 and that the Mahan values are large because of his too-large values of the intensity ratio $|A_2/A_0|^2$.

	Na	Mg	Al	Comment
$\Delta\alpha$ (Mahan)	-0.04	-0.09	-0.12	Overestimates of $|\Delta\alpha|$ due to large values of $|A_2/A_0|^2$.
$\Delta\alpha$ (this work)	-0.005	-0.01	-0.03	$|\Delta\alpha| < 0.04$.

and a negligible upper bound to the $j = 2$ contribution to α_∞:

$$2(2j+1)(\delta_j/\pi)^2 < \tfrac{10}{324} = 0.03\,. \tag{B3}$$

In practice, of course, the d-wave effects are considerably smaller than indicated by these rigorous bounds.

The explicit correction for $j = 2$ is, taking Mahan's value of δ_2 for Li (Table III),

$$2(2j+1)(\delta_j/\pi)^2 \simeq 6\times10^{-4}\,. \tag{B4}$$

Even in Al, taking Mahan's largest value, $\delta_2 = 0.073$, we have

$$2(2j+1)(\delta_j/\pi)^2 \approx 5\times10^{-3}\,, \tag{B5}$$

almost two orders of magnitude smaller than the 20% corrections implied in Refs. 1 and 2, and clearly negligible in an analysis with a quoted uncertainty almost ten times as large.

Mahan's "change in the value of α_2 by a factor of 2" for Al is presumably a negligibly small change of $2\delta_2/\pi = 0.05$. The exponent α_2 does not appear in any of the analyses to which he refers, because the d-wave contribution can be neglected (see Appendix A and Ref. 8). (The demonstration that d waves can be neglected is unaffected by such small uncertainties in α_2.)

2. Implicit corrections

In addition to the explicit dependence of the exponents on d-wave phase shifts, there is an implicit dependence which comes from the fact that s and p phase shifts depend on δ_2 through Friedel's sum rule

$$1 = \sum_{j=0}^{\infty} 2(2j+1)\frac{\delta_j}{\pi}\,. \tag{B6}$$

We have used this sum rule to obtain compatibility relations between α_0 and α_1, determining α_0 for Li from an empirical value of α_1,[4] and similarly finding α_1 and α_0 for Na, Mg, and Al.[6-8] The *exact* link between α_0 and α_1, supplied by the compatibility relation[6-7]

$$\alpha_0 = \alpha_1 - \tfrac{1}{3} + \tfrac{2}{3}(1-6\alpha_1)^{1/2}(1-H)^{1/2}\,, \tag{B7}$$

where H is given by Eq. (6).

(Note that the sums range from $j = 2$ to $j = \infty$.) In our analyses of Li, we have neglected H, *which is of second order in the d and higher angular-momentum phase shifts.* Thus, if d waves account for 20% of the Friedel sum, we expect only insignificant 4% corrections to the analyses. Omission of d wave from Eq. (B7) produces a negligible error of approximately

$$-45(\delta_2/\pi)^2(1-6\alpha_1)^{-1/2}\,.$$

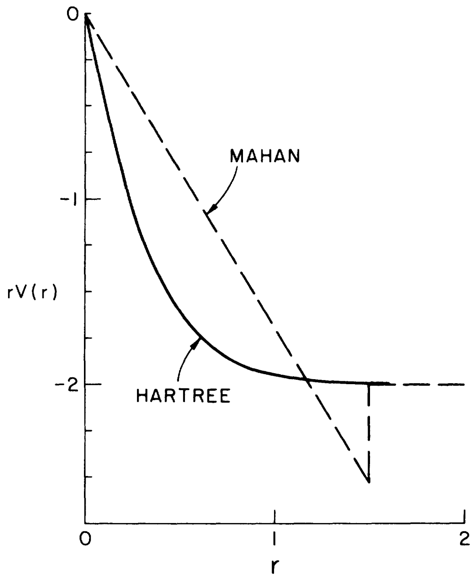

FIG. 5. Unscreened electron-hole interactions $rV(r)$ vs r for *ionic* Li$^+$ calculated according to Mahan's general procedure (difference between $1s^2$ and $1s$ configurations). Solid line: Hartree-approximation $rV = -e^2 + 2e^2(1+r/a)\times\exp(-2r/a) - e^2(1+r/b)\exp(-2r/b)$, with $a \equiv a_0/2.69$, $b \equiv a_0/2.99$, and $a_0 = 0.53$ Å. [See D. R. Franceschetti and J. D. Dow, J. Phys. F 4, L151 (1974), for a discussion of the Li wavefunctions.] Dashed line: Mahan's most recent s-wave pseudopotential approximation for Li (Ref. 1). Note that Mahan's approximate potential disagrees markedly with the Hartree potential, having an exceedingly large core radius and insufficient depth in the core (units: Ryd, Bohr radius).

[Note that α_1 was thought to be generally negative until over work, and that for $\delta_0 > \delta_1 > \delta_2 \cdots$ we have the bound $(1 - 6\alpha_1)^{-1/2} < 2$.] To illustrate the insignificance of *d* waves, we have taken phase shifts computed by Mahan for Li, Na, Mg, and Al (Table II) and his values of α_1, and we have computed α_0, first including his *d*-phase shifts ($H \neq 0$) and then omitting them ($H = 0$). The differences in the two values are so small that they are comparable with Mahan's round-off errors (see Tables II and III).

Although we have used the same phase shifts here as were used by Mahan, we note that they were obtained from pseudopotentials with Pauling's atomic radii rather than the usual Heine-Abarenkov radii. Thus the pseudopotentials used have unrealistically large cores: the core radius for Li is 0.8 Å as opposed to a 1*s* radius only $\frac{1}{4}$ as large, 0.2 Å. (See Fig. 5.) We also note that the impurity resistivities computed from these pseudopotentials do not generally agree with the data; for example, in the cases of Li and Na, these pseudopotentials produce resistivities too large by factors of 3 or more.[39]

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‡Summer visitor.

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