parable to what is observed experimentally.[15] With a decrease in temperature $\langle \Delta_{ij}^2 \rangle$ will tend to decrease; if, applying Mott's variable-range hopping argument,[1] one takes $\langle \Delta_{ij}^2 \rangle$ proportional to $T^{3/2}$, then S will tend to zero as $T^{1/2}$. Thus the occurrence of a nonzero thermoelectric power does not necessarily imply an asymmetric distribution of hopping states about the Fermi level.

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Many-Electron Effects in Core-Level X-Ray and Electron Spectroscopies from Na, Mg, and Al

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X-ray photoemission line shapes of 2s and 2p electrons from Al, Mg, and Na have been analyzed in terms of the theory of Mahan and of Nozières and De Dominicis. The resultant singularity indices, 0.115, 0.13, and 0.19, respectively, require that all x-ray threshold exponents, save that for the Na K edge, be positive.

The line shapes in x-ray absorption and emission spectra of simple metals have historically been the testing ground for the many-electron theory of Mahan and Nozières and De Dominicis (MND).[1,2] Its prediction of peaked $L_{2,3}$ and rounded K edges in these metals[3,4] has been the subject of debate[5,6] that has yet to reach a clear-cut resolution. Doniach and Šunjić (DS)[7] have applied the MND theory to x-ray photoemission spectroscopy (XPS) of core electrons, deriving a line shape with a tail on the low-kinetic-energy side that is independent of core-hole symmetry. Such line shapes were observed in XPS of Na metal[8] and identified as manifestations of the MND theory. Subsequent measurements in noble, transition,[9] and other simple metals[10] have quantified the phenomenon. It remains to be shown, however, whether the MND theory is quantitatively or, some argue,[5,6] even qualitatively predictive in electron *and* x-ray spectroscopies. In this Letter we present data which demonstrate for the first time that *the MND theory accurately and unambiguously predicts both XPS core and x-ray $L_{2,3}$ line shapes in Na, Mg, and Al.* However, we also show that *unless physically unrealistic d phase shifts are invoked, the many-electron phenomenon is not responsible for the rounded K x-ray edges observed in Al and Mg.*

The DS line shape for XPS core lines is specified by two parameters, the lifetime width γ and the Anderson singularity index α.[11] The latter is defined by

$$\alpha = 2\sum_{l=0}^{\infty}(2l+1)\left(\frac{\delta_l}{\pi}\right)^2 \qquad (1)$$

in terms of the partial phase shifts, which are constrained by the Friedel sum rule. The physical significance of α is clear—it accounts for the final-state readjustment (polarization) of the conduction electrons to the core hole. The phase shifts and α, in turn, are related[2] to the x-ray threshold exponent α_l by

$$\alpha_l = 2\delta_l/\pi - \alpha. \qquad (2)$$

Just as great care should be exercised in extracting x-ray exponents, e.g., accounting for self-absorption in x-ray emission,[12] so too must one be cautious in determining singularity exponents from photoemission data. During the course of our work we have found it essential to use the shape of the entire line rather than just the asymmetry at half-height[7] to determine α. This is accomplished by comparing the experimental curve—extending as much as 7 eV from the peak—with a DS line shape broadened by convolution with the instrumental response function. For each metal we have measured both the 2*s* and 2*p* core levels, the lifetime widths of which differ by about an order of magnitude. For Al and Na, two spectrometers with resolutions differing by a factor of 2.5 were used. *In all cases* the values of α determined by our method were consistent within experimental error.

Pure metal (99.99%) was repeatedly evaporated onto smooth substrates in the sample-preparation chamber of a Hewlett-Packard (HP) 5950A ESCA spectrometer[8] at a base pressure of $\sim 10^{-8}$ Torr, and *in situ* in a modified AEI ES100 instrument[13]

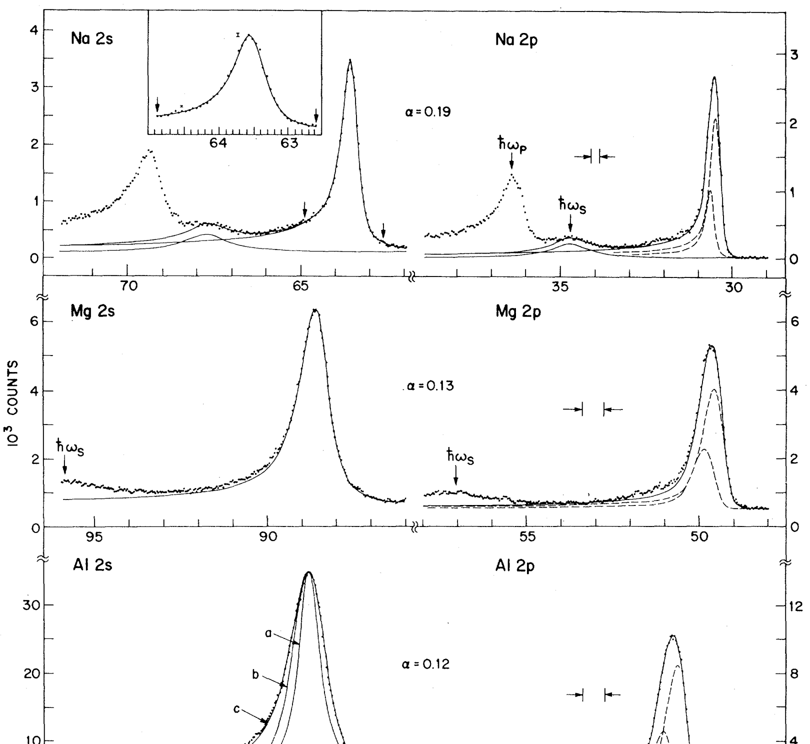

FIG. 1. Al, Mg, and Na x-ray photoemission data for 2*s* and 2*p* levels. Al 2*s*: curve *a*, pure Lorentzian ($\alpha = 0$); curve *b*, pure Lorentzian convoluted with skewed-Gaussian instrumental function; curve *c*, same as curve *b* but with $\alpha = 0.12$. The 2*p* spectra show the $2p_{3/2}$ and $2p_{1/2}$ spin-orbit components and the instrumental resolution used to analyze the respective metals. Na 2*s*: expanded energy scale illustrating detailed fit.

at $\sim 10^{-10}$ Torr. In the HP spectrometer, samples were transferred in vacuo to the measurement region. The base pressures were $\sim 10^{-9}$ and $\sim 10^{-11}$ Torr, respectively. Monochromatized Al $K\alpha$ radiation was used. Analysis of core-level and Fermi-edge shapes in a variety of metals showed the instrumental resolution functions to be a slightly skewed Gaussian, full width at half-maximum (FWHM) equal to 0.63 ± 0.03 eV, in the HP spectrometer[14] and an approximately symmetric Gaussian, FWHM $= 0.25 \pm 0.02$ eV, in the modified instrument.[14]

A spectrum of Al $2s$ electrons taken with the lower-resolution spectrometer is shown in Fig. 1. Curve *a* is a symmetric ($\alpha = 0$) Lorentzian of FWHM $= 0.78$ eV. This lifetime width was determined to ± 0.04 eV by successive comparisons of the data on the *low*-binding-energy side with a DS peak convoluted with the resolution function. The result of similarly broadening curve *a* is shown as curve *b*. The best value for α was determined through detailed comparison of the data on the *high*-binding-energy side of the peak with curves like *b*, but containing varying degrees of asymmetry (varying α's); such a curve for $\alpha = 0.12$ is shown and labeled *c*. Comparison of the data with curve *c* gives a clear indication of a small amount (< 0.3 monolayers) of surface impurity, in this case Al_2O_3, occurring at ~ 2.7 eV higher binding energy than Al. This is clearly the limiting factor in the determination of α from such a spectrum.

To illustrate the experimental uncertainty in determining α for an atomically clean surface, we consider the high-resolution Al $2p$ data shown in Fig. 2. The expanded scale shows that, after constraining the $2p_{3/2}/2p_{1/2}$ intensity ratio to the theoretical value of 2 and letting the splitting be 0.40 eV, an α of 0.115 gives an excellent fit to the data, and that its uncertainty (determined by statistics) is clearly $\pm < 0.02$. A similar limit applies to the lower-resolution data as well. As a further consistency check we have analyzed the lower-resolution Al $2p$ data, shown in Fig. 1, using the same spin-orbit splitting. The value of $\alpha = 0.12$ provides a good fit, comparable to that of the $2s$ data. A value as high as 0.161 ± 0.008 reported in Ref. 10 is not compatible with our experimental results.

The low-resolution magnesium data shown in Fig. 1 are well fitted for $\alpha = 0.13$, in agreement with Ley *et al.*[10] The different shapes of the lifetime-limited $2s$ and resolution-limited $2p$ levels serve to constrain α and establish its assignment with limits of ± 0.015. (The free-ion spin-orbit splitting of 0.28 eV was used for Mg $2p$.) Note that the presence of the 7.3-eV surface plasmon (denoted by $\hbar\omega_s$) in Mg and possible contributions of (extrinsic) inelastic energy losses in these metals do not significantly influence the shape of the tail of the DS function. This tail may be mistaken for "background." Subtraction of this background and subsequent determination of an asymmetry parameter based on half width at half-maximum values should yield erroneously small values. Surface contamination will tend to yield erroneously high values.

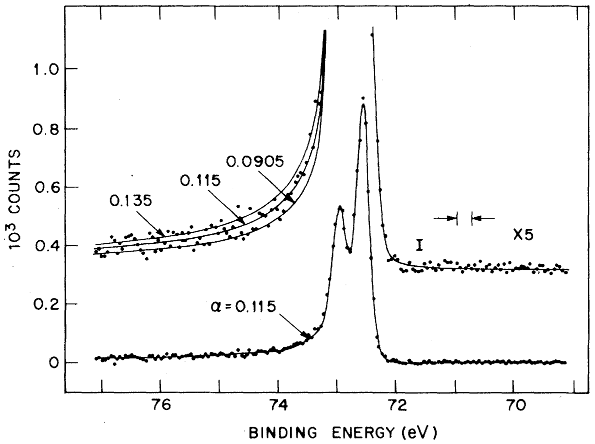

FIG. 2. Al $2p$ data compared with fits for three different values of α. Statistical error bar and instrumental resolution are indicated.

The high-resolution sodium data shown in Fig. 1 were each accumulated over a 20-h period. In spite of the ultrahigh-vacuum conditions, a very small (< 0.2 monolayer) surface impurity is observable. Here, as in the case of Mg, the surface plasmon at 4.1 eV does not significantly affect the determination of α. We have illustrated this by adding a Lorentzian plasmon component to the tail. The small spin-orbit splitting in Na (using the free-ion value of 0.17 eV) is unresolved but the consistency with $\alpha = 0.19$ determined from the $2s$ data is apparent. The detailed agreement in the peak itself between the $2s$ data and our simulated curves is demonstrated in the inset (the arrows denote the expanded energy region).

The monotonically increasing values of α from Al to Mg to Na and the large rise between Mg and Na strongly suggest the influence of increasing s-wave scattering by the core hole. If we assume for the moment that *d* and higher phase shifts can be neglected in these simple metals,

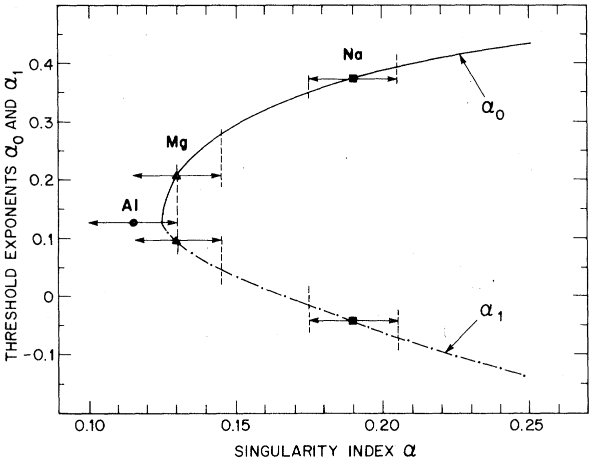

FIG. 3. Threshold exponents α_0 (solid curve) and α_1 (dot-dashed curve) versus singularity index α *assuming only s and p phase shifts.* Error bars for our measured α determine uncertainties in α_0 and α_1.

then Eq. (2) and a measurement of α uniquely determine the $L_{2,3}$- and K-absorption-edge exponents α_0 and α_1. In Fig. 3 we have plotted α_0 (solid curve) and α_1 (dot-dashed curve) versus α for this condition. The measured α's and their error bars define the corresponding ranges of the threshold exponents. Precise assignment of α_l's for Mg and Al is difficult since a small uncertainty in α corresponds to sizable uncertainties in α_0 and α_1. Furthermore, the shortcoming of the two-phase-shift analysis becomes apparent for Al since it sets a lower limit of $\alpha = 0.125$. Nevertheless, the various α_0 and α_1 literature values[6,12] of Al and Mg all fall within our limits of uncertainty. For Na, however, our value for α_0 of 0.37 ± 0.02 is well outside that of 0.26 ± 0.04 quoted by Dow and Sonntag.[6] While the trend of α_0 with r_s is, as those authors point out,[6] monotonic for Al, Mg, and Na (2.07, 2.65, and 3.99, respectively), the relationship is *not* linear because it is only an indirect manifestation of the real parameter of importance—the s-scattering phase shift δ_0.

While the magnitudes of the threshold exponents are not well determined *for Al and Mg, it remains clear that their α_1 exponents are positive and therefore are not responsible for the rounded K edges observed in the x-ray data.* This statement remains valid even with inclusion of modest amounts of d phase shifts, comparable to those in theoretical calculations.[3,15,16] For example, Ausman and Glick[3] have calculated (α_0, α_1, α_2; δ_0, δ_1, δ_2) for Na to be (0.398, −0.085, −0.173; 0.921, 0.163, 0.0244), yielding $\alpha = 0.188$, in excellent agreement with the present measurement. The same agreement applies to the calculations of Longe.[15] Very recent calculations by Mahan[16] for Na give (0.34, −0.02, −0.12; 0.76, 0.20, 0.042), yielding $\alpha = 0.14$. His phase shifts for Mg and Al yield α' s of 0.10 and 0.09. All three of his α values, being somewhat lower than our measurement, indicate an underestimate of the s phase shift. However, even with these values, α_1 remains positive for Al and Mg. *The rounded K edges in these metals, therefore, arise simply from lifetime broadening.* Interestingly, our measurements and all three calculations[3,15,16] indicate a negative α_1 for Na, putting into question the claims that the signs of α_1 in simple metals are either all negative[3,4] or all positive.[5,6]

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