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Bulk and Surface Singularity Indices in the Alkali Metals

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Photoemission data from (110) films of Li, Na, and Rb, in which the signal from the first atomic layer is well resolved, show that the core-hole-screening singularity index is $\sim 40\%$ larger at the surface than in the bulk for all three metals. This result, which is indicative of the more atomiclike character of metal surface atoms, in general, is particularly large for the alkali metals because their conduction-electron screening is mainly s-like. In addition to quantifying the difference in screening at the surface, the data provide bulk singularity indices of 0.22, 0.16, and 0.14 for Li, Na, and Rb, respectively. These new values are in better agreement with theory and with the threshold exponents than earlier values derived from incompletely bulklike x-ray photoemission data.

I. INTRODUCTION

The conduction-electron screening of a photoexcited core hole in a metal is effected by the creation of electron-hole (e-h) pairs near the Fermi level. The energy spectrum of these e-h pairs is of the form[1] $\sin(\pi\alpha)/[\hbar(\omega-\omega_0)/\xi]^{1-\alpha}$, where ξ is an energy of the order of the bandwidth, ω_0 is the threshold energy for photoexcitation, and α is the singularity index.[2] The e-h pair excitations are manifest in the energy spectrum of the core-electron photopeak as an asymmetric tail toward greater binding energy, making the screening process directly accessible to experimental investigation.

Early x-ray photoelectron spectroscopy (XPS) analyses of surface-atom core-level shifts in metals[3] have assumed that surface and bulk photopeak line shapes are identical, i.e., that the natural core-hole lifetime and phonon widths, as well as the conduction-electron screening responses, are the same in the bulk and surface. These assumptions were dictated by the fact that the bulk and surface lines were poorly resolved, preventing the determination of independent values for these parameters. The assumption that the surface singularity index α_S is identical to the bulk value α_B has been maintained in all (save one[4]) subsequent studies of surface core-level shifts,[5-8] even though data with higher resolution were frequently obtained. In recent work on the alkali metals[7,8] this assumption was retained because theory[9] showed that bulk and surface singularity indices in these metals are indeed very similar. There has also been experimental evidence to support this view. For example, the singularity index obtained by constraining the bulk and surface components to a common value in synchrotron data from Na (Ref. 6) was in good agreement with that obtained from corresponding XPS data in which the bulk signal is dominant.[10,11] Moreover, the singularity index for Rb (Ref. 8) determined from data taken with 40.8-eV He II resonance radiation was close to the previously determined value for Na, suggesting a common screening behavior for the alkali metals.

While it would appear that there is ample evidence to put this issue to rest, closer inspection suggests otherwise.

Recall that the original XPS work[10,11] preceded the discovery of the surface-atom core-level shift,[3] so that the early analyses were carried out with only a single bulk component. The possibility that a surface component existed in the data which could affect the overall shape of the observed spectrum was simply not considered. Furthermore, in the only study in which α_S was not set equal to α_B, that of the W(110) surface,[4] the singularity index for the surface atoms was found to be distinctly larger than that for the bulk. No satisfactory explanation for this difference in W has been offered, but the result does raise a basic question concerning the validity of the assumption that the screening of a surface core hole is the same as that of one in the bulk. Indeed, the fact that the surface electronic structure is known to be more free-atom-like than the bulk suggests that a different screening response is a general phenomenon which should be observable in metals other than tungsten.

Why, then, have there been no other reports of distinct singularity indices for bulk and surface metal atoms? The reason lies in the fact that these two parameters are ill defined unless the data satisfy three essential criteria. First, and most important, the bulk and surface components must be well resolved. This means that the instrumental energy resolution, as well as the natural width of the core level, must be smaller by at least a factor of 2 than the surface-atom core-level shift. For the alkali metals other than Li, which have shifts of ~ 0.2 eV and outer-p core-level widths of 10–50 meV, an instrumental resolution better than 0.1 eV is required. Second, the perturbation of the core-electron binding energy at the surface must be (largely) confined to the outermost atomic layer, i.e., contributions from shifted subsurface components must not interfere with either the surface or bulk core-level line shape. Third, the surface-to-bulk intensity ratio must span a wide range of values, ideally including data in which this ratio is much less than and much greater than one. This usually requires data taken at different photon energies (i.e., surface sensitivities) to ensure that reliable characterization of each of the two components is achieved.

The data presented here have been designed to meet

these criteria. We show that using these guidelines, independent bulk and surface singularity indices can be reliably determined for Li, Rb, and, with somewhat less certainty, Na. Because of their inherently simple electronic structure, these systems elucidate the origin of the difference between the metal bulk and surface screening response in general.

II. EXPERIMENTAL DETAILS

The data were taken on the AT&T Bell Laboratories—University of Oregon beamline U4A at the National Synchrotron Light Source at Brookhaven National Laboratory, which provides resolution better than 100 meV up to 140 eV photon energy. Samples of Li, Rb, and Na were prepared *in situ* by deposition of alkali vapor from commercial SAES Getters sources onto a Ni(100) substrate cooled to liquid-nitrogen temperature, resulting in alkali-metal layers with a (110) surface orientation.[6] None of the alkali-metal surfaces is known to reconstruct.

The data were analyzed[12] by fitting them with line shapes generated by convolving the Doniach-Šunjić (DŠ) function[1] with a Gaussian to represent the combined phonon and instrumental broadening. The essential shape of the DŠ function is determined by two parameters, the Lorentzian lifetime width γ and the singularity index α. Three additional parameters, the Gaussian width, position, and amplitude, are required to define an individual photoemission line. The background was represented by a combination of a linear and a power-law term. In the least-squares-fitting procedure the background and line-shape parameters were adjusted simultaneously to optimize the fit to the raw data. As mentioned below, certain constraints could be imposed. For example, the α's or γ's of two or more lines could be made equal, with the joint value still freely adjustable.

III. RESULTS

As an initial step, the data were analyzed with common lifetime width and singularity for the bulk and surface components. The resulting values of α varied with photon energy for all the alkali metals, becoming smaller at the larger excitation energies. Since the data are taken far from threshold, where the sudden approximation is valid, the change in singularity index cannot be due to a fundamental physical effect on α itself.[13] A more likely possibility is that the increasing photon energy, which increases the bulk-to-surface intensity ratio, also changes the average α because α_B is smaller than α_S. Results obtained by allowing the α's to be freely adjustable tend to confirm this suggestion, but the numerical values gave satisfactory results only for Li. For the other alkali metals, the α's varied significantly from spectrum to spectrum. The difficulty of determining independent α's arises from the fact that the quality of the fit, measured by χ^2, improves very little when the bulk and surface α's are allowed to assume independent values, even when the final values for bulk and surface differ by factors as large as 1.5. The least-squares routine gives adequate warning

that the α's are not well determined, in that they are typically coupled to each other and to other parameters by correlation coefficients greater in magnitude than 0.9. Under these conditions the true minimum in χ^2 is often not reached in the least-squares adjustment. Other approaches are therefore required.

A. Lithium

Lithium, which has the largest surface-atom core-level shift of the alkali metals and offers a well-resolved two-line 1s spectrum, is the most favorable case for more detailed investigation. Data for a Li layer taken with 90-eV radiation are shown in Fig. 1(a). The two lines can be well defined with common singularity index and lifetime width, yielding $\alpha = 0.28 \pm 0.01$. The resulting fit, with $\chi^2 = 1.013$ (compared with a value of 1.00 for a perfect fit), is well represented by the line drawn through the data points. The value of α is, however, much larger than the one obtained when XPS data were fitted with a single bulk line, giving $\alpha = 0.23 \pm 0.02$.[10,11] The discrepancy between these two α values is too large to attribute to experimental uncertainties. Since the 90-eV spectrum is dominated by the surface signal while the XPS data are dominated by the bulk, the discrepancy might simply be explained if α_S is significantly larger than α_B. To test this possibility, a fit was made in which the two lines were given independent α's. This gave two well separated α's, namely $\alpha_B = 0.22$ and $\alpha_S = 0.30$, but produced only a small decrease of χ^2 to 0.925. The fitted line and components shown in Fig. 1(a) are the result of this analysis. A comparison of the residuals from the two fits shows that small (2σ) systematic fluctuations are re-
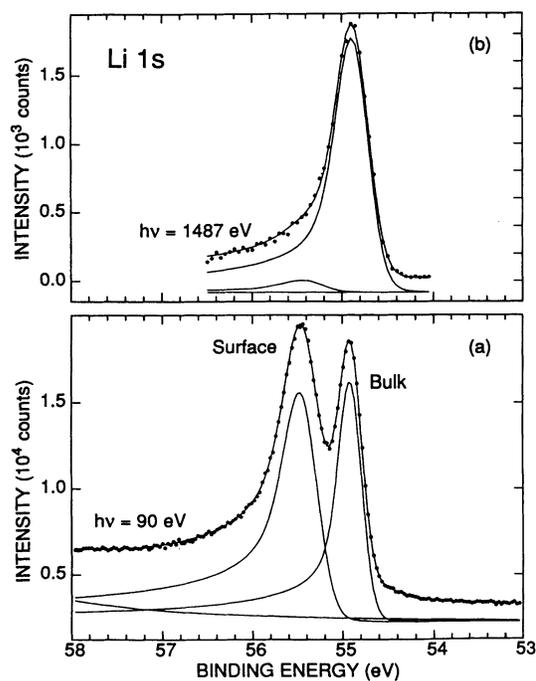

FIG. 1. (a) Fit to 90-eV Li 1s spectrum with independent bulk and surface singularity indices. (b) Fit to 1487-eV Li 1s spectrum (from Ref. 11) with bulk and surface components.

moved by allowing bulk and surface to have individual α's. Note that α_B is now in good agreement with the XPS value.

Since the original analysis of the XPS data[10,11] was done prior to the discovery of the surface-atom core-level shift,[3] it is necessary to see whether the surface contribution was indeed small enough to neglect in that analysis. A look at the fit to the data in Ref. 10 shows a small positive deviation from the fitted single DŠ line in the data for all three temperatures at an energy now known to correspond to the surface component. In Fig. 1(b) we show the result of refitting the lowest-temperature data (90 K) with a bulk and a surface line, separated by the known surface shift. The analysis yields a well-defined surface contribution and a value of $\alpha_B = 0.21$, smaller than the original value but still in good agreement with the result obtained here in the more surface-sensitive data. From the intensity of the surface component we obtain an escape depth of 45 Å at a kinetic energy of 1432 eV. This result is in very good agreement with the mean-free-path calculations of Penn[14] (see Fig. 2), providing support for the (albeit small) contribution of the surface component in the XPS data. The theoretical curve shown does not include the effects of core excitations, which are estimated to reduce the mean free path by 10%, so that the good agreement is even better than indicated.

The values most consistent with all the data are $\alpha_B = 0.22 \pm 0.01$ and $\alpha_S = 0.30 \pm 0.02$. The ratio of α_S/α_B is 1.36. The surface-atom core-level shift of 524 meV, determined here with independent α_B and α_S values, is slightly smaller than the 543-meV shift[7] obtained from the same data analyzed assuming $\alpha_S = \alpha_B$. The difference is due to the fact that the asymptote of the many-body singularity lies below the peak of the Gaussian- and Lorentzian-broadened line by an amount that depends on α.

B. Rubidium

For Rb we do not have XPS data, and so we must rely on the range of photon energies available on our beamline. Data taken near the minimum of the escape depth curve and at a larger photon energy are shown in Fig. 3. In the 22-eV data the surface signal is significantly enhanced by an additional scattering mechanism,[7] making the data particularly well suited for the determination of α_S. The highest photon energy at which satisfactory data could be obtained is determined by the size of the photoelectric cross section, which decreases by 2 orders of magnitude from threshold to 100 eV photon energy.[15]

As mentioned above, the analysis of the Rb data with common α for bulk and surface components yields values that vary systematically with surface-to-bulk intensity ratio. Since a strong dependence of α on photon energy well above threshold is unphysical, we first investigate whether the observed variation is compatible with distinct bulk and surface singularity indices. The relationship between the average α's and the actual bulk and surface α's was established using a simple simulation. Artificial spectra containing two components with dis-
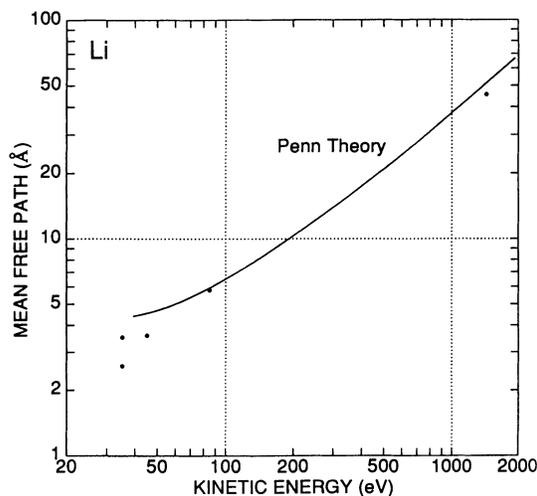

FIG. 2. Mean free path in Li compared with the theory of Ref. 14.

tinct DŠ line shapes were generated by counting random ones and zeros. The line separation was set equal to the surface-atom core-level shift of Rb, and the lifetime width and bulk and surface Gaussian widths were similarly constrained. A set of such spectra, covering the full range of surface-to-bulk intensity ratios, was generated for assumed bulk and surface α's. These spectra were then analyzed by least squares, constraining the bulk and surface α's to be the same. This yields a set of effective average α's which, plotted against the effective fractional area assigned to the bulk components in the fit, gives the smooth curve shown in Fig. 4. The α's obtained from the
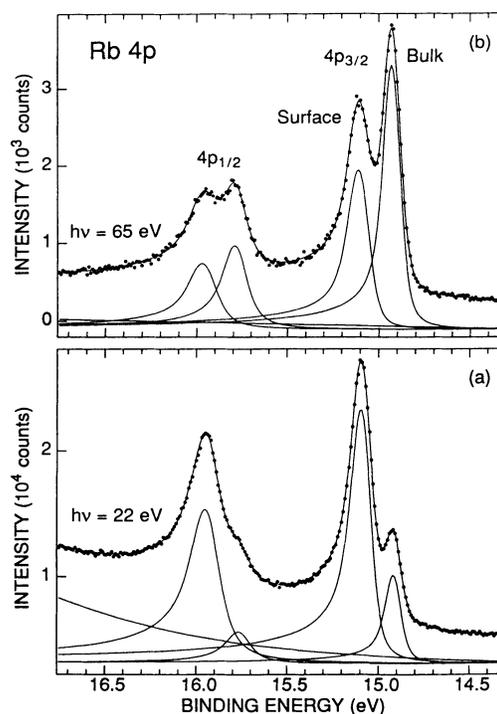

FIG. 3. Rubidium $4p$ photoemission spectra taken with (a) 22-eV and (b) 65-eV radiation.
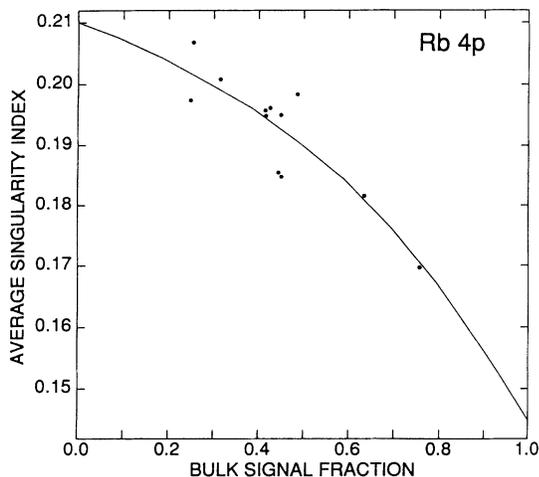
FIG. 4. Average singularity index from constrained analysis of Rb data plotted against the fractional area associated with the bulk signal. The solid line is the results of the simulation described in the text.

analysis of real data are shown by dots superposed on this plot. By varying the assumed bulk and surface α's, a curve is obtained which most closely fits the properties of the real data. The values obtained by this method are $\alpha_B = 0.145$ and $\alpha_S = 0.21$.

The singularity indices can also be obtained by least-squares fitting the data directly, as in the case of Li, provided both α's are not simultaneously adjusted. The surface singularity index is determined by fitting the data in Fig. 3(a) with α_B constrained to a wide range of values. This analysis yields $\alpha_S = 0.20$, a value which is quite insensitive to the assigned α_B. In fact, for values in the range $0.08 \leq \alpha_B \leq 0.18$, which includes a weak minimum in χ^2, α_S is equal to 0.202 ± 0.003 for this particular data set. This value is in good agreement with that of 0.205 obtained from the surface-dominated data in Ref. 8. No conclusion can be drawn at this point about α_B because the fit to the 22-eV data is so insensitive to this parameter. An estimate of the bulk singularity index can, however, be obtained from the data in Fig. 3(b), in which the bulk signal dominates. By varying α_S we find a minimum in χ^2 for $\alpha_S = 0.195$, very close to the value found above from the 22-eV data. At the minimum, α_B is equal to 0.136.

From the two different methods of analysis we find that the best values are $\alpha_S = 0.20 \pm 0.01$ and $\alpha_B = 0.14 \pm 0.01$. The ratio α_S / α_B is 1.43, which is comparable to that in Li. The spin-orbit splitting of 856 meV is close to the free-ion splitting of 845 meV in the $4p^5 5s^2$ configuration.[16] The surface-atom core-level shift of 175 meV is, as in the case of Li, somewhat smaller than that obtained with the α's constrained to be the same, which gave 190 meV.[7,8]

C. Sodium

The analysis of the Na data is complicated by the fact that the surface-atom core-level shift is comparable in

magnitude to the spin-orbit splitting. As a result, the $2p_{3/2}$ surface line overlaps the $2p_{1/2}$ bulk line, so that neither the surface-atom shift nor the spin-orbit splitting can be determined by inspection. Spin-orbit stripping has been used to obtain estimates of these parameters,[6] yielding a spin-orbit splitting of 160 meV and a surface-atom shift of 190 meV. The determination of bulk and surface singularity indices requires least-squares analysis.

In general, analysis of data with overlapping, unresolved lines can lead to unphysical results unless constraints are imposed. For the Na $2p$ spectrum it is most reasonable to constrain the bulk and surface spin-orbit splittings to be the same, and to fix the bulk and surface spin-orbit ratios at the statistical value of 0.5. In addition, the lifetime width of all components was constrained to a common value of 12 meV. This is slightly larger than the value of 10.5 meV reported for the $2p_{3/2}$ line,[17] but it gave slightly better results.[18] Proceeding as in the case of Rb, we first fit the data in which the surface component is strongest [see Fig. 5(a)], fixing α_B at various values. We find that α_S falls in the range 0.222 ± 0.008 for $0.14 \leq \alpha_B \leq 0.20$. Since χ^2 does not have a well-defined minimum in this range, α_B cannot be established by these fits. Next, we consider data taken at high photon energy [Fig. 5(b)] in which the bulk component is dominant. Fixing α_S at 0.22, we obtain $\alpha_B = 0.158$. For values of α_S ranging from 0.20 to 0.24, α_B ranges from 0.14 to 0.17.

From the above analysis, we quote values of $\alpha_S = 0.22 \pm 0.02$ and $\alpha_B = 0.16 \pm 0.02$. While the determinations are less well defined than those for Rb and Li, the
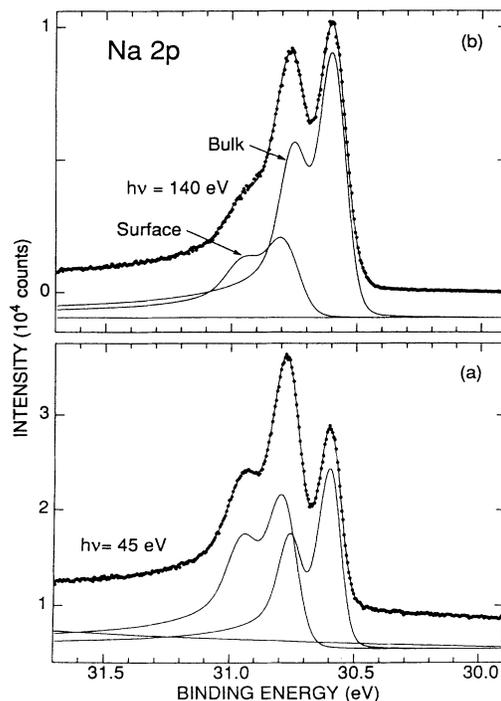

FIG. 5. Sodium $2p$ photoemission spectra taken with (a) 45-eV and (b) 140-eV radiation. The bulk and surface spin-orbit doublets are shown, together with the fitted background.

ratio α_S/α_B of 1.38 for Na is, nevertheless, comparable to the corresponding ratio of the other alkali metals. The spin-orbit splitting of 159±2 meV is close to the values obtained in the analysis of Na L-edge data,[17,19] but smaller than the free-ion value of 169 meV.[16] The surface-atom core-level shift is 184 meV in the 45-eV data and 195 meV in the 140-eV data, compared to 190 meV obtained earlier with common α in 45-eV data.[6,7] The increased shift in the bulk-dominated data may be indicative of a small (20 meV) subsurface shift.

The analysis of Na XPS data gave α of 0.20 ±0.015,[10,11] about 25% larger than the bulk value obtained here. Since the surface-atom core-level shift had not yet been discovered at the time of that work (and is smaller than the resolution available in XPS), only a single bulk component was used in the analysis. This undoubtedly increased α, just as in the case of Li. However, unlike the Li XPS data, the Na XPS data are not suitable for more detailed analysis because the spacing of the data points is ten times larger than that in Fig. 5, so large in fact that the spin-orbit splitting and surface-atom core-level shift span less than four data points. The presence of a weak surface oxide (see Figs. 10 and 11 of Ref. 11) also argues against reanalysis of those XPS data.

Another XPS study[20] gave $\alpha=0.19$, again without considering the surface signal. Using an escape depth of 70 Å (Ref. 14) and a take-off angle of 52° appropriate for the Hewlett-Packard spectrometer, the unresolved surface signal would have contained 6.8% of the total intensity. Using the same simulation procedure as in the case of Rb, we find that such a small, unresolved surface contribution in the XPS data of Na would increase the bulk singularity index from 0.16 to 0.17 in a fit with only a bulk component. In view of the ±0.02 uncertainty in the bulk value of 0.16 determined here, that is sufficient to reconcile these measurements within their stated uncertainties. Data at higher photon energy could be of considerable help in obtaining a more precise value for the bulk singularity index of Na.

IV. DISCUSSION

In the present investigation, the question whether or not the screening response at the surface is different than in the bulk for metals other than W has been answered in the affirmative. We find that for Li, Rb, and Na the surface singularity indices are all generally larger than the corresponding bulk value by ~40%. We now address the issue of why this is so and what implications follow from these results.

Recall that the singularity index is given by[21]

$$\alpha = \sum_l 2(2l+1)(\delta_l/\pi)^2 , \tag{1}$$

where δ_l are the partial scattering phase shifts. For the sceening of a charge Z, these phase shifts are constrained by the Friedel sum rule[22]

$$Z = \sum_l 2(2l+1)\delta_l/\pi . \tag{2}$$

Equations (1) and (2) provide information about the na-

ture of the charge that screens the core hole ($Z=1$). For example, if the screening charge is strictly s-like ($l=0$), then $\alpha=0.5$, the maximum value it can assume. With increasing p- or d-wave scattering, the value of α decreases. The smallest value is obtained when all the phase shifts are equal, in which case

$$\alpha_{min} = 1/2(l_{max}+1)^2 . \tag{3}$$

Thus, $\alpha_{min}=\frac{1}{8}$ for s- and p-wave scattering and $\frac{1}{18}$ for screening electrons with s, p, and d symmetry. From this we see that the larger α is, the greater is the fractional contribution of s-like screening of the core hole.

The larger values of the singularity index at the surface of the alkali metals clearly indicates a greater degree of s-wave scattering there. Upon reflection, this is just what would be expected because the surface layer, being more atomiclike, has weaker s-p hybridization, i.e., the s^1 electronic configuration of the atom is approached. The similar ratios of α_S/α_B for the three different alkali metals reflect the similarity of their metallic and atomic electronic structures. This simple interpretation in the alkali metals can be applied to other systems as well. The singularity index of the W(110) surface is 0.063, compared to a bulk value of 0.035.[4] Both indices are smaller than those of the alkali metals because higher angular momentum orbitals are involved in the screening. However, the fact that α_S is larger than α_B indicates again that s- and p-wave scattering is increased at the surface. This is in accord with a change of electronic configuration at the W surface from $5d^56s$, characteristic of the metal, toward the $5d^46s^2$ configuration of the free atom.

The above results imply that the singularity indices at the surface are almost always larger than in the bulk because, with very few exceptions, such as Pd and Pt, the free-atom configuration exhibits a greater degree of s character than in the metal. The simple electronic structure of the alkali metals, and in particular their relatively large degree of s character at the Fermi surface, makes these metals especially favorable for the study of the surface screening response. That distinct bulk and surface α's were first observed in W, however, indicates that even the strong d character which reduces the line asymmetry of transition metals is no obstacle to further experimental investigations. On the theoretical side, it remains to be explained why the calculation of Ref. 9 did not find significantly different values for α_S.

The new, smaller values for the bulk singularity indices obtained here call for another look at the theoretical work summarized in Table V of Ref. 19. For Li, with $\alpha_B=0.21$, the closest results are those of Mahan,[23] who obtained 0.22, and Ohmura and Sano,[24] who obtained 0.20. For Na, with $\alpha_B=0.16$, the closest theoretical results are again those of Mahan[23] and of Ohmura and Sano[24] who both report 0.14. We are not aware of calculations for Rb.

The effect of these bulk α's on the compatibility with the absorption edge threshold singularity is not large, at least within the original formulation of Mahan[25] and Nozières and De Dominicis.[26] For Li, the new value of

$\alpha = 0.21 \pm 0.01$ corresponds to $\alpha_1 = -0.08 \pm 0.02$, while the earlier value of $\alpha = 0.23$ corresponds to $\alpha_1 = -0.11$. The analysis of Li K edges from various sources all gave $\alpha_1 \sim 0$.[19] Thus, while the new α_B helps to account for the lack of many-body rounding in the Li K edge, it still does not eliminate the disagreement with experiment. For Na, the new α of 0.16 leads to somewhat better agreement with the $L_{2,3}$-edge exponent of $\alpha_0 = 0.37$ determined in Ref. 9. Note that both Refs. 23 and 24, which report $\alpha = 0.14$ for Na, calculate $\alpha_0 = 0.34$; Ausman and Glick,[27] with $\alpha = 0.19$ (closer to the original[11] value of 0.20), calculate $\alpha_0 = 0.40$. The new experimental α_B lies midway between these different calculations, as does α_0. For Rb, the new bulk α value of 0.14 ± 0.01 greatly reduces the disagreement with the $N_{2,3}$ absorption edge exponent $\alpha_0 = 0.19$,[28] resulting from the larger α obtained from a surface-dominated He II spectrum.[8] Neglecting $l = 2$ phase shifts, this α_B value corresponds to $\alpha_0 = 0.26$, with lower and upper limits of 0.21 and 0.29.

Finally, we note that the original theoretical description of absorption edge singularities[25,26] may need to be modified in view of recent work[29] which obtains peaked $M_{2,3}$ edges for K without explicitly considering conduction-electron screening. Final judgment about the agreement between theory and experiment for x-ray edges, therefore, must wait until the impact of this formulation is evaluated.

V. CONCLUSIONS

We have shown that the surface singularity index in the alkali metals is $\sim 40\%$ larger than that of the bulk, indicating that the core-hole scattering phase shifts at the surface of these metals are increasingly s-like in character. This result is argued to be generally true in most metals. The new, smaller values for α_B are in good agreement with the theoretical values of Mahan and of Ohmura and Sano for Li and Na. The larger values obtained in the early XPS work were largely the result of unresolved surface contributions. The present bulk values improved the agreement with x-ray-absorption edge threshold exponents previously obtained for Li and Na, and reduce the discrepancy in the case of Rb.

ACKNOWLEDGMENTS

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