

PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 46, NUMBER 4

15 JULY 1992-II

Electron mean free paths in the alkali metals

G. K. Wertheim, D. M. Riffe,* N. V. Smith, and P. H. Citrin

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 22 January 1992)

Photoemission data in which the signal from the first atomic layer is well resolved from that of the bulk are used to determine accurately the kinetic-energy dependence of the inelastic-electron mean free path in the alkali metals. At the higher kinetic energies, the data are in very good agreement with the theory of Penn. Below about 10 eV, the mean free path in the heavier alkali metals drops markedly below the theoretical values. This is attributed to electron decay processes involving the unoccupied *d* bands.

INTRODUCTION

The electron inelastic mean free path (MFP) determines the sampling depth in photoelectron spectroscopy. This is an important parameter in the interpretation of vacuum ultraviolet and soft-x-ray photoemission spectroscopy data, because in many materials the MFP drops to values close to the interatomic spacing for kinetic energies between 10 and 60 eV. In this region the photoemission signal comes from such a small number of near-surface atomic layers that the signal from the first layer alone may well dominate the response. Although a great deal of effort, both empirical and theoretical, has been devoted to establishing the general nature of the MFP, there is relatively little experimental information about the MFP in the simplest of systems, the free-electron metals (Al is a notable exception¹). Theory²⁻⁵ shows that in these metals the MFP is simply a function of the conduction electron density and that it has a similar energy dependence in all materials.

Measurement of the MFP has generally been based on the growth of overlayers of known thickness on a chemically distinct substrate.¹ The MFP in the overlayer can then be determined both from the thickness dependence of the intensity of a substrate photoemission line, as well as from the intensity of the overlayer emission. This method suffers from well-known problems. It requires a calibrated source of overlayer atoms, as well as knowledge of the coverage-dependent sticking coefficient. More serious are the limitations imposed by the nature of thin-film epitaxy itself. The method works well only when layerwise growth is assured, but this is usually the

exception rather than the rule. Pores and clusters often defeat this approach, signaling their presence by deviations either from exponential attenuation of the substrate signal or from exponential growth of the overlayer signal with coverage.

An alternative method, which has been applied to Au,⁶ makes it possible to avoid the problems of epitaxy altogether. It is applicable whenever the signals from one or more of the outermost atomic layers can be resolved from those of the deeper layers of a bulk solid. This approach is predicated on the fact that the surface layer of atoms generally has a distinct core-electron binding energy. It is feasible provided that the surface-atom core-level shift is larger than the core-electron linewidth. The fractional intensity (area) of the bulk signal then suffices to determine the MFP, which is obtained in units of the layer spacing of the solid in the direction of observation.

This alternative approach is straightforward and quantitative, provided that the areas of the bulk and surface photopeaks can be accurately determined. This requires knowing the line shapes of the individual components. Earlier studies of surface-atom photoemission from metals^{6,7} have assumed that the line shapes of bulk and surface peaks are identical, but recent work⁸⁻¹⁰ has shown that, in fact, this is not the case. In particular, the surface component has a larger Gaussian width due to enhanced vibrational broadening^{8,9} and a significantly larger singularity index than the bulk due to greater contributions of *s*-wave screening of the core hole.^{8,10} In some metals, e.g., W, it has even been shown that the Lorentzian core-hole lifetime width of the surface atoms is different.⁸ This is, however, not a significant factor in the alkali met-

als. The improved characterization of the surface and bulk photoemission line shapes now enables a more quantitative determination of the MFP.

Here we present data from epitaxial layers of alkali metals grown on Ni(001) surfaces, taken as a function of photon energy. This is an extension of work^{9,11} in which the temperature dependence of the core-electron binding energies were investigated at a single photon energy. The low-temperature data in this work, as in our earlier study,⁹ exhibit photopeaks from the first atomic layer of the (110)-oriented alkali-metal films, which are very well resolved from those of the deeper layers. Combined with our much improved characterization of the photoemission line shapes, these new data avoid the complications of overlayer growth and make it possible to determine the mean free path of photoelectrons with very high accuracy.

EXPERIMENTAL DETAILS

The data were taken on the AT&T Bell Laboratories-University of Oregon beam line U4A at the National Synchrotron Light Source at Brookhaven National Laboratory, which provides resolution better than 100 meV up to 140 eV photon energy. The samples were prepared *in situ* by deposition of alkali vapor from SAES Getters sources onto a Ni(100) substrate cooled to 78 K, resulting in flat alkali-metal layers with (110) surface orientation.^{9,11} The data generally cover a range of kinetic energy, measured from the Fermi level, from about 5–100 eV and were taken in normal emission with the sample at 80 K.

RESULTS AND ANALYSIS

Selected data from the Li, Na, K, and Rb runs are shown in Figs. 1–4. In the Li data in Fig. 1 the bulk signal is normalized to constant peak height, so that changes in escape depth are mirrored in the strength of the surface signal, which has a shift of 0.55 eV.¹¹ The surface signal reaches its maximum amplitude in the spectrum taken with 75 eV photons, corresponding to a kinetic energy of 20 eV. At this point the escape depth is near its minimum value of 3 Å (see below). The Na data in Fig. 2 are more complicated because the 0.16-eV $2p$ spin-orbit splitting is comparable to the 0.19-eV surface-atom core-level shift.⁹ As a result, the bulk $2p_{1/2}$ component overlaps the surface $2p_{3/2}$ photopeak, so that the intensity of the surface signal is best judged by the $2p_{1/2}$ line at 30.9 eV. The relative strength of the surface signal is largest between 45 and 65 eV. Bearing in mind that the spin-orbit ratio is $\frac{1}{2}$, it is clear that the MFP is so small in this range of kinetic energy that the surface signal again exceeds the bulk signal. The K data in Fig. 3 are in many respects similar to the Na data because the $3p$ spin-orbit splitting of 0.255 eV is only slightly larger than the surface-atom core-level shift of 0.20 eV.¹¹ The data are unusual in showing a very sharp maximum in the surface-to-bulk intensity ratio at 25 eV photon energy. In Rb the $4p$ spin-orbit splitting of 0.85 eV is very much larger than the surface-atom core-level shift of 0.19 eV,¹²

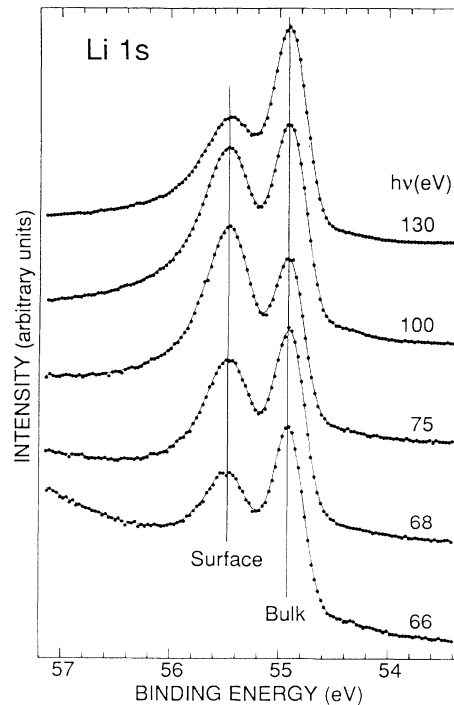


FIG. 1. Li 1s photoemission spectra from as-deposited Li surfaces at 80 K, taken with a range of photon energies.

removing the $4p_{1/2}$ components from the region of interest (see Fig. 4). In that figure, the $4p_{3/2}$ part of the surface spectrum has been normalized to fixed peak heights. The bulk component shows an unexpected be-

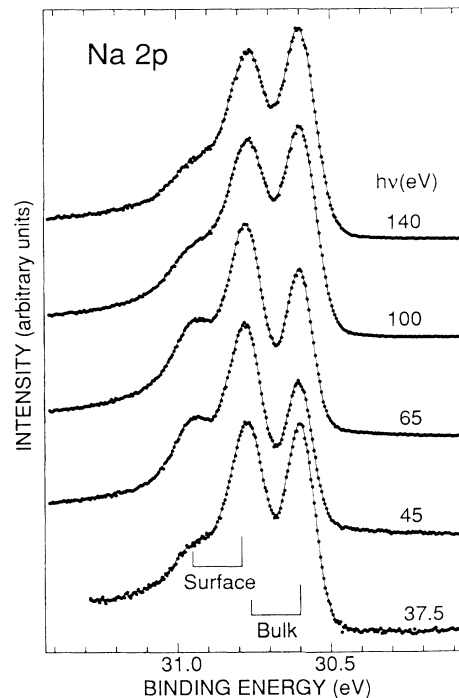


FIG. 2. Na 2p photoemission spectra from an annealed Na surface at 80 K, taken with a range of photon energies.

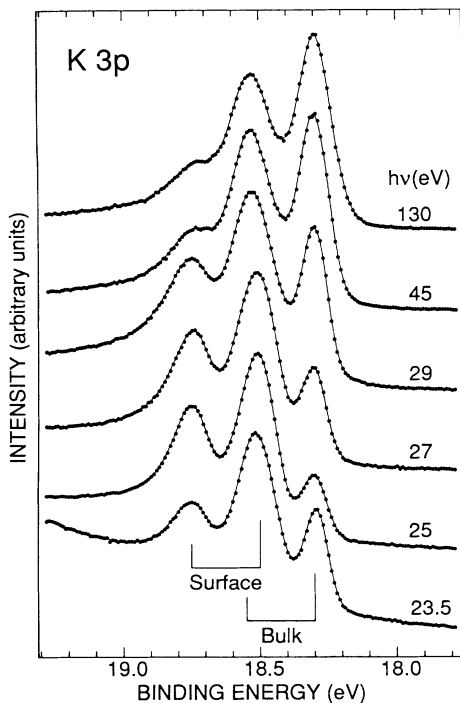


FIG. 3. K $3p$ photoemission spectra from an annealed K surface at 80 K, taken with a range of photon energies.

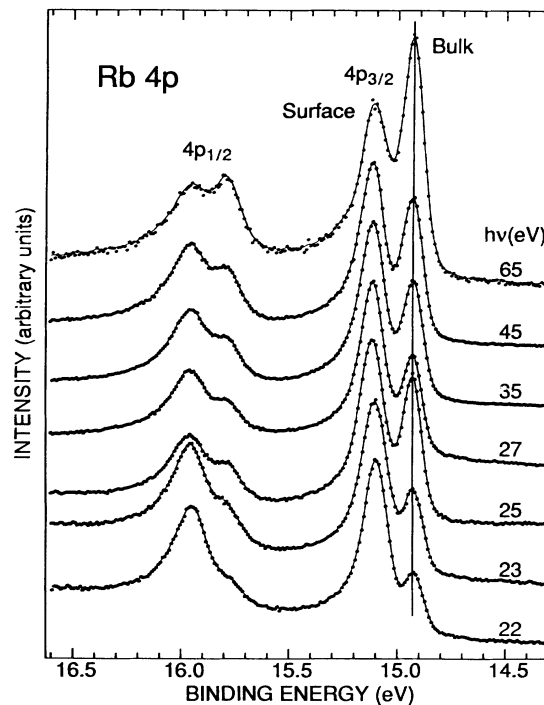


FIG. 4. Rb $4p$ photoemission spectrum from as-deposited Rb surfaces at 80 K, taken with a range of photon energies.

havior, increasing in amplitude from 22 to 25 eV photon energy, then briefly decreasing, and finally increasing from 20 up to 65 eV.

In order to obtain quantitative information about the

escape depths, the data were analyzed by least-squares fitting with a common lifetime width but distinct bulk and surface singularity indices¹⁰ in the Doniach-Šunjić (DS) line shape.¹³ The data for Na and K were fitted with

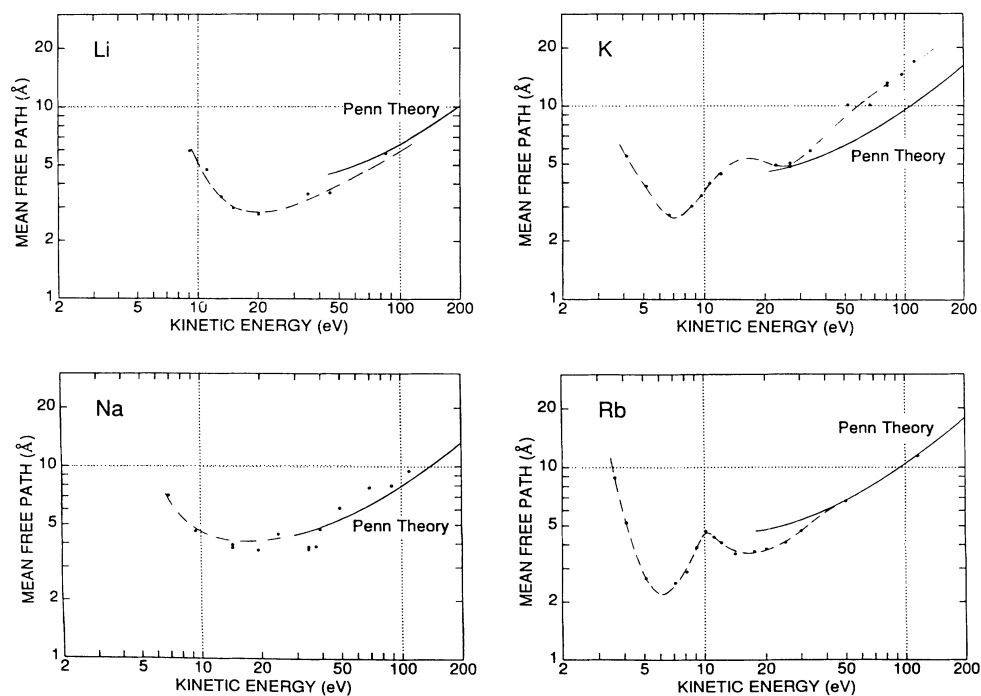


FIG. 5. Escape depth in Li, Na, K, and Rb, compared with the theory of Ref. 5 (solid line). The dashed line is a guide to the eye.

bulk and surface spin-orbit doublets of identical spin-orbit splitting. Values close to the free-ion spin-orbit splitting of the p^5s^2 configuration, appropriate for the fully screened final hole state, were obtained. For Na, the natural widths of the $2p_{3/2}$ and $2p_{1/2}$ components were taken to be the same (this has been justified in Ref. 9 on the basis of successful spin-orbit stripping); for K, independent values were required. The range of the fit was limited to an interval sufficiently small to minimize contributions from the surface plasmon at 4.2, 3.8, 2.7, and 2.5 eV in Li, Na, K, and Rb, respectively. The intensities associated with the bulk and surface components were determined from the areas under the Gaussian-broadened DS lines, with a cutoff imposed by the range of the fit. (Note that a cutoff is required since the DS lines are not integrable to increasing binding energy.)

In order to interpret the resulting intensities, we consider a (110) surface of a bcc single crystal viewed at a normal takeoff angle. We denote the (110) layer spacing by d . If the signal from the outermost layer is considered unattenuated, then the signal from the n th layer is given by $e^{-(n-1)d/\lambda}$. Summing the contributions from all layers, we find that the fractional signal from the second and deeper layers, f_B , is

$$f_B = e^{-d/\lambda}. \quad (1)$$

This corresponds to the intensity of the signal identified as "Bulk" in Figs. 1–4. In Fig. 5 we have plotted λ , calculated from this equation, for the fractional bulk intensities obtained from the analysis of the Li, Na, K, and Rb spectra.

The Li and Na data conform to the general expectations regarding the kinetic-energy dependence of escape depths in solids,¹ having a shallow minimum between 15 and 50 eV, rising rapidly at low kinetic energy, and more gradually at high kinetic energy. Plotted as a solid line is the theoretical MFP for the appropriate r_s , obtained by interpolation in Fig. 4 of Ref. 5. The agreement is generally very good.

DISCUSSION

The most striking features in Fig. 5 are the oscillations in the data for K and Rb. A possible explanation is strong modulation by photoelectron diffraction, an effect ignored in our analysis. The minimum in the MFP's do occur close to the kinetic energies for electron wavelengths equal to the nearest-neighbor distances. The weakness of this hypothesis, however, is that it fails to account for the absence of similar oscillations in Li and Na. Also, if electrons in this energy range are strongly diffracted by the crystal potential, there should be repercussions in the band structure. This is what we now discuss.

The heavier alkali metals K, Rb, and Cs have unoccupied d bands, and may be regarded as the leading elements of the $3d$, $4d$, and $5d$ transition-metal series. Band-structure calculations display prominent peaks in

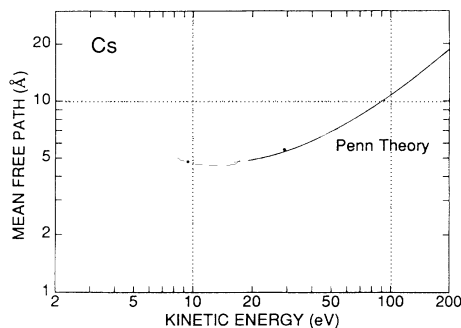


FIG. 6. Escape depth in Cs, from Ref. 10, compared with the theory of Ref. 5 (solid line). The dashed line is a guide to the eye.

the density of states just above the Fermi level.¹⁴ We therefore have a decay channel in which an electron can emit a plasmon and drop into the d band. The maximum energy for this is $E_t + \hbar\omega_p$, where E_t is the upper edge of the d band and ω_p is the bulk plasma frequency. We may reasonably equate E_t with the energies of the upper P_4 levels in the calculated band structures, and these occur at 6.8, 6.5, and 5.5 eV for K, Rb, and Cs, respectively. Adding $\hbar\omega_p$, we obtain for the respective maximum energies 11.2, 10.5, and 9.1 eV. It is seen in Fig. 5 that for K and Rb these agree well with the energies below which the MFP's deviate strongly from the Penn theory. Another strength of this hypothesis is that it accounts naturally for the absence of similar deviations in Li and Na.

If our hypothesis involving unoccupied d bands is correct, the effect should be even more pronounced in Cs. Unfortunately, the available data for Cs are sparse. We plot in Fig. 6 two values for the MFP in Cs obtained by the analysis methods of this paper from data obtained recently using He resonance radiation and polycrystalline samples.¹⁵ Agreement with theory is excellent. Below 10 eV, some early estimates of the MFP in Cs have been reported using an entirely different analysis method based on absolute quantum yields.¹⁶ These estimates lie between 1 and 2 Å, indicative of a major departure from an extrapolation of Penn's theory to low energies. It would be desirable to obtain more complete data on Cs using synchrotron radiation and to apply the analysis methods of this paper.

CONCLUSIONS

We have obtained electron mean free paths in the alkali metals from clean, (110)-oriented single-crystal surfaces. Our method, which relies not on overlayer growth but on the resolved signal from the surface layer, provides highly reliable results. The data typically cover the

range from 5 to 100-eV kinetic energy, including the minimum of the escape-depth curve. This minimum is generally near 4 Å, a value so small that the signal from the first atomic layer dominates the photoemission spectrum. Our results are relevant to the interpretation of angle-integrated as well as angle-resolved vacuum-ultraviolet and soft-x-ray photoemission studies.

ACKNOWLEDGMENTS

The photoemission research was carried out at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the Department of Energy, Division of Materials Sciences and Division of Chemical Sciences.

*Present address: Department of Physics, University of Texas, Austin, TX 78712.

¹C. J. Powell, *Surf. Sci.* **44**, 29 (1974); *Scanning Electron Microsc.* **IV**, 1649 (1984).

²J. J. Quinn, *Phys. Rev.* **126**, 1453 (1962).

³B. I. Lundqvist, *Phys. Status Solidi* **32**, 273 (1969).

⁴J. C. Shelton, *Surf. Sci.* **44**, 305 (1974).

⁵D. R. Penn, *Phys. Rev. B* **13**, 5248 (1976).

⁶P. H. Citrin, G. K. Wertheim, and Y. Baer, *Phys. Rev. Lett.* **41**, 1425 (1978); *Phys. Rev. B* **27**, 3160 (1983).

⁷D. Spanjaard, C. Guillot, M. C. Desjonquères, G. Tréglia, and J. Lecante, *Surf. Sci. Rep.* **5**, 1 (1985).

⁸D. M. Riffe, G. K. Wertheim, and P. H. Citrin, *Phys. Rev. Lett.* **63**, 1976 (1989).

⁹D. M. Riffe, G. K. Wertheim, and P. H. Citrin, *Phys. Rev.*

Lett. **67**, 116 (1991).

¹⁰G. K. Wertheim, D. M. Riffe, and P. H. Citrin, *Phys. Rev. B* **45**, 8703 (1992) show that in the alkali metals the surface singularity index is ~40% larger than the bulk value.

¹¹D. M. Riffe, G. K. Wertheim, D. N. E. Buchanan, and P. H. Citrin, *Phys. Rev. B* **45**, 6216 (1992).

¹²G. K. Wertheim, D. N. E. Buchanan, and J. E. Rowe, *Solid State Commun.* **77**, 903 (1991).

¹³S. Doniach and M. Šunjić, *J. Phys. C* **3**, 285 (1970).

¹⁴See, for example, D. A. Papaconstantopoulos, *Handbook of the Band Structure of the Elemental Solids* (Plenum, New York, 1986).

¹⁵G. K. Wertheim and D. N. E. Buchanan, *Phys. Rev. B* **43**, 13 815 (1991).

¹⁶N. V. Smith and G. B. Fisher, *Phys. Rev. B* **3**, 3662 (1971).