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Conduction-electron screening and surface properties of Cs metal

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In Cs $5p$ core-electron photoemission spectra obtained with He resonance radiation, the response from the first atomic layer is well resolved and shifted 228 meV from the bulk line at 11.79 eV. The singularity index of the conduction-electron screening response is 0.18, i.e., comparable to the values close to 0.20 obtained for the other alkali metals. In contrast, the edge exponent of the Cs $5p$ absorption edge is only $\frac{1}{6}$ that of the Na $2p$ edge and is incompatible with the phase shifts deduced from the Cs singularity index. This result sharpens a long-standing problem regarding the interpretation of the emission and absorption edges.

Both emission¹ and absorption-edge² experiments at the Cs $5p$ threshold have recently given results which suggest that the conduction-electron screening in Cs is quantitatively different from that in the other alkali metals. The emission edge fails to show the peaking found in the spectra of the outermost p edge of the other alkali metals.¹ The absorption edge does show the expected peaking, but yields an edge exponent α_0 of only 0.064 (Ref. 2) compared to values 4–6 times larger obtained for Na.³ Since the edge exponent and the core-hole screening singularity index α are related parametrically through the Friedel phase shifts, a determination of α should shed some light on the hypothetical unique character of Cs. The singularity index has the advantage over the edge exponent of being largely insensitive to small-scale structure in the density of states near the Fermi cutoff, greatly simplifying the analysis. Photoemission studies of the Cs $5p$ level are, however, very surface sensitive, because the photoelectron mean free path is comparable to the lattice constant. As a result the bulk information is obtained from a small number of atomic layers near the surface, excluding only the outermost layer, which yields a resolved signal.

The Cs surfaces were prepared by the deposition of Cs vapor from a commercial SAES Getters source onto a Cu(111) surface cooled to 90 K. The Cu surface had been previously cleaned by argon-ion sputtering and annealing. The base pressure in the experimental chamber was 1×10^{-10} -Torr, and rose in the mid- 10^{-9} -Torr range during alkali-metal deposition. Most of that pressure rise is due to the alkali-metal vapor. Since a buildup of suboxide became detectable in runs exceeding 4 h, even at pressures in the 10^{-10} -Torr range, data acquisition was restricted to 2 h after sample preparation. The photoemis-

sion spectra were obtained with both He I (21.22 eV) and He II (40.81 eV) resonance radiation. The electron energies were measured with a Vacuum Science Workshop 50-mm hemispherical analyzer with 1-mm slits, typically operated with a 10-V pass energy for a nominal resolution of 100 meV.

A wide-scan spectrum taken with He II radiation and a 10-V pass energy is shown in Fig. 1. The two sharp lines near 12-eV binding energy are the $5p_{3/2}$ response from the bulk and surface. The stronger line at larger binding energy is the response from the first atomic layer, the

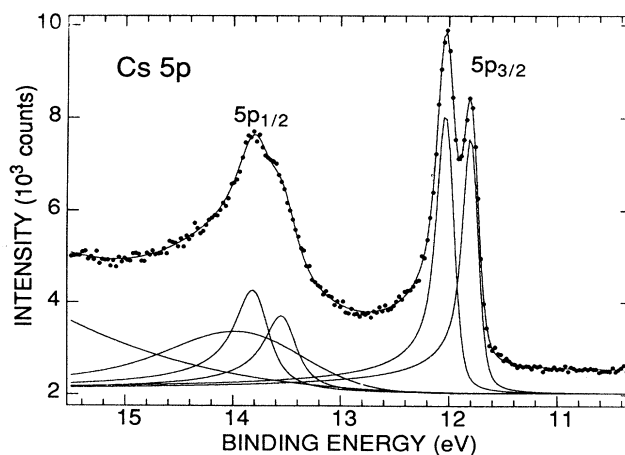


FIG. 1. Cs $5p$ photoemission spectra from a Cs surface at 100 K taken with He II resonance radiation. The line through the data and the components are the result of a least-squares fit described in the text.

weaker line that from atoms in the second and deeper layers. The fact that two well-resolved lines are obtained indicates that even the second atomic layer is largely bulklike, i.e., the perturbation provided by the truncation of the crystal is confined to the first atomic layer. The unresolved complex of lines at 13.8 eV contains the corresponding $5p_{1/2}$ emission as well as the broad surface plasmons of the $5p_{3/2}$ lines. The surface plasmons of the $5p_{1/2}$ lines contribute to the rising background at large binding energy. Expanded views of the $5p_{3/2}$ region taken, respectively, with He I and He II radiation are shown in Figs. 2 and 3.

The solid line through the data points in all three figures is the result of a least-squares fits with a model function in which the emission lines are represented by the Doniach-Šunjić⁴ (DS) line shape. Past experience has shown that this function provides a satisfactory representation of the effect of conduction electron screening in core-electron photoemission from simple metals.⁵ In the model function the bulk and surface lines were given independent Gaussian widths, which include phonon and instrumental contributions. The spin-orbit components of a given doublet were constrained to have the same Gaussian width. The $5p_{3/2}$ and $5p_{1/2}$ lines were given independent lifetime Lorentzian widths, but those of bulk and surface were assumed to be the same, since the *OVV* Auger and *OOV* Coster-Kronig rates should be comparable in both. In the fits shown the singularity index α was assumed to be the same for all lines. The surface plasmons were represented by an additional line with independent parameters. The inelastic background was represented by a sloping line and a power-law term. It makes only small contributions in the region of the $5p_{3/2}$ lines, see Figs. 2 and 3, where much of the line-shape information was obtained.

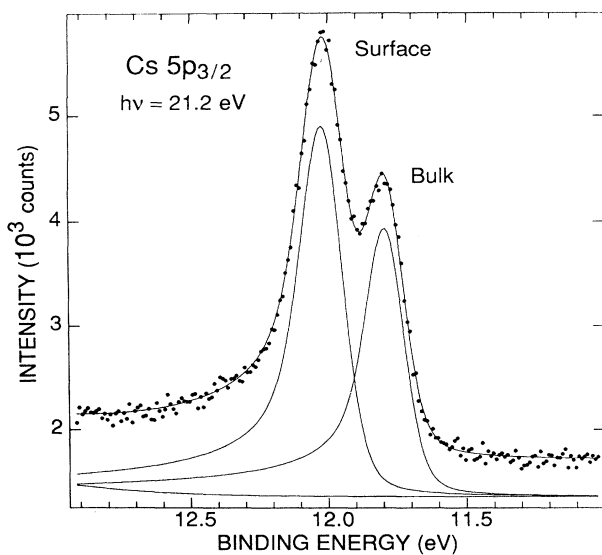


FIG. 2. Cs $5p_{3/2}$ photoemission spectrum taken with He I radiation, fitted by two DS lines with identical lifetime width and singularity index.

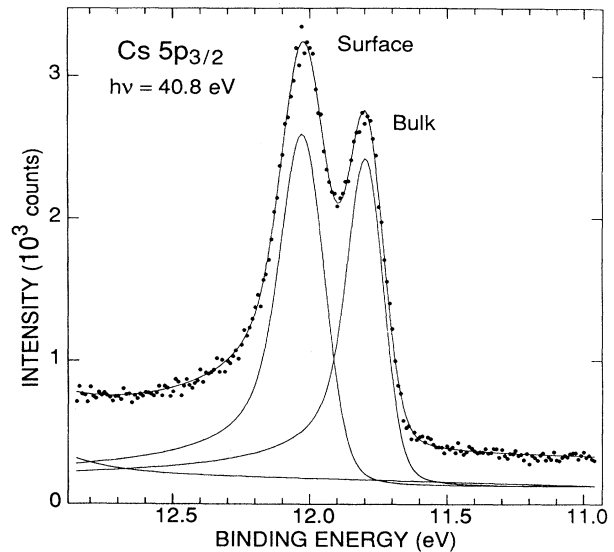


FIG. 3. Cs $5p_{3/2}$ photoemission spectrum taken with He II radiation, fitted as in Fig. 2.

The least-squares analysis yields the following results.

(1) The binding energy of the bulk $5p_{3/2}$ line was determined from a single spectrum (not shown) containing both the Fermi cutoff in the Cs conduction band excited by He I radiation and the Cs $5p$ core-level spectrum excited by He II. The energy separation of the Fermi edge and the $5p_{3/2}$ line is 7.80 eV. Subtracting this from the 19.59-eV energy difference between He II and He I radiation gives a Cs $5p_{3/2}$ binding energy of 11.79 ± 0.04 eV. This value is in excellent agreement with both the Cs $5p$ absorption-edge energy of 11.75 eV obtained from Fig. 5 of Ref. 6, and the Cs $5p$ emission edge at 11.8 eV in Fig. 8 of Ref. 1. It is also in agreement with the much less precise value of 11.8 ± 0.4 eV obtained by Petersen⁷ at higher photon energies. These values are, however, all distinctly smaller than those obtained more recently from photoemission with smaller photon energies.⁸⁻¹⁰ The determinations of Refs. 8 and 9, which range from 12.0 to 12.1 eV, are in error due to an unfortunate combination of low photon energy (small escape depth) and poor resolution. In those studies the unresolved surface line is responsible for most of the signal, so that the binding energy which was obtained is not representative of the bulk, but of the surface, which falls at 12.02 eV, see Fig. 1.

(2) The surface-atom core-level shift is 228 ± 5 meV. It is in reasonable agreement with two other determinations which gave shifts of 240 meV.^{1,10} (Note that the identification of bulk and surface are reversed in Fig. 3 of Ref. 10, but correct in Fig. 4.) Recent determinations for Na (Ref. 11) and Rb (Ref. 12) both gave surface-atom core-level shifts of 190 meV. The shift in Cs is consequently distinctly larger than those of the other alkali metals, except Li. Earlier work¹³ did give a larger shift for Na, one close to the present value for Cs. However, that determination is suspect because the data analysis gave erroneously small values for the spin-orbit splittings

of bulk and surface. Since the overall width of the spectrum depends on the sum of the spin-orbit splitting and the surface-atom core-level shift, it is likely that the shift is actually significantly smaller than the quoted value.

(3) The electron mean free path (escape depth) obtained from the intensities of the bulk and surface components in Figs. 2 and 3 are 4.8 Å at a kinetic energy of 9 eV and 5.5 Å at 29 eV. [For comparison, the lattice constant of bcc Cs is 6.07 Å, and the layer spacing in the (110) direction is 4.29 Å.] The escape depths in Cs are distinctly larger than those obtained for the lighter alkalis at comparable kinetic energies.¹¹⁻¹³ However, when normalized by the respective lattice constants they differ little, confirming the expected dependence on the conduction-electron density.

(4) The spin-orbit splittings for bulk and surface are 1.74 ± 0.03 and 1.77 ± 0.01 eV, respectively. The bulk splitting is less well determined because the bulk $5p_{1/2}$ line is not resolved from the stronger surface line. These splittings are in excellent agreement with the free-atom $5p$ spin-orbit splitting of 1.764 eV for the $5p^5 6s^2$ configuration,¹⁴ which is approximated by the screened final hole state in the photoemission experiment. Similar agreement was recently reported for the Rb $4p$ spin-orbit splitting.¹² Earlier photoemission studies^{8,9} have reported a splitting of 1.9 eV. This discrepancy was probably caused by the 2.1-eV surface plasmons of the $5p_{3/2}$ lines, which were not resolved from the $5p_{1/2}$ lines, resulting in an increased average shift, see Fig. 1.

(5) The singularity index was found to be 0.18 ± 0.01 , when bulk and surface components were constrained to have the same value. No significant improvement in the fit was obtained when bulk and surface indexes were given independent values. However, the fit is relatively insensitive to the singularity index of the bulk line, since the region which contains the relevant information is obscured by the surface component. The decision to assign identical values to the bulk and surface is based on recent theoretical results for sodium¹⁵ in which the bulk and surface singularity indexes are nearly identical. The value obtained for Cs is somewhat smaller than those of the other alkali metals, which cluster near 0.20.^{5,12} Among the alkali metals only Li has a distinctly larger singularity index of 0.24,⁵ because of the absence of d -phase shifts. The smaller singularity index of Cs indicates greater contributions from higher phase shifts.

Given an α of 0.18, the phase-shift-based relationships between the singularity index and the edge exponents require a strong peaking of the Cs O edge, corresponding to an exponent α_0 of 0.36. The absorption-edge data² do show such peaking, but a simple analysis gave an exponent α_0 of only 0.064. If d -phase shifts are neglected, this requires that the p -phase shift be 40% larger than the s -phase shift, an unlikely result for an alkali metal. Moreover, the corresponding singularity index α is 0.13, well outside the experimental range. The emission edge of Cs in Ref. 1 does not exhibit any discernible peaking, and no attempt was made to determine the edge exponent. Similar, though less extreme, discrepancies have arisen in the comparison of the photoemission line shape and the outer p edges of Na (Refs. 3, 5, 16, and 17) and

Rb.¹² These difficulties, including the inconsistent values of α_0 obtained from emission- and absorption-edge spectra, have given rise to a great deal of discussion,^{18,19} but no clarification has emerged. At this point it is not even clear whether they call for a more sophisticated theory or whether they can be resolved through more detailed analysis of the edge data.

(6) The natural widths Γ of the $5p_{3/2}$ and $5p_{1/2}$ components of the Cs $5p$ spin-orbit doublet are 35 ± 8 and 270 ± 60 meV. $\Gamma_{3/2}$ is in reasonable agreement with the width of 50 meV determined from the edge emission spectrum.¹ $\Gamma_{1/2}$ has not been previously determined. It has a relatively large uncertainty because of the overlap of the $5p_{1/2}$ lines with the broad surface plasmons of the $5p_{3/2}$ lines. The value of $\Gamma_{1/2}$ is sensitive to the shape of the plasmon, which was arbitrarily represented by a line with DS shape. The difference between the two lifetime widths is due to the *OOV* Coster-Kronig decay channel of the $5p_{1/2}$ hole. The *OOV* contribution is so much larger here than in the other alkali metals because of the larger spin-orbit splitting. In Rb, where this splitting is half as large (0.85 eV), the corresponding lifetime widths are 22 and 96 meV,¹² i.e., the *OOV* contribution is only $\frac{1}{3}$ as large. In Na, where the spin-orbit splitting is only 0.16 eV, i.e., less than one-tenth that of Cs, no difference between the widths of the two spin-orbit components has been detected in photoemission¹¹ or absorption-edge spectra.³

(7) The total Gaussian widths of the bulk and surface components are 130 and 155 meV. Subtracting an instrumental resolution of 100 meV in quadrature yields 83 ± 10 and 118 ± 20 meV. The uncertainty in the bulk value depends mainly on that of the instrumental resolution function, that of the surface value depends on the coupling between the Gaussian and the Lorentzian lifetime widths. The bulk width is in good agreement with the value determined from the emission edge,¹ which is ~ 80 meV at 100 K. The phonon width of the surface atoms has not been previously reported. The increased surface phonon width is in agreement with the softer modes perpendicular to the surface,²⁰ as found in Na.¹¹

The most significant result is that the conduction-electron singularity index α of Cs is quite comparable to those in Na, K, or Rb. From one point of view this is almost a necessary result, since the conduction bands of these simple metals have quite similar properties. From another, it is a major surprise, because the emission and absorption edges of Cs are less peaked than those of the lighter alkali metals and yield a smaller edge exponent. The fact that the singularity index of Na is in excellent agreement with theory⁵ suggests that the problem does not lie in the experimental values of α . The fact that the edge exponent of Cs requires a p -phase shift larger than the s -phase shift cast some doubt on the method used to determine that parameter. It is, of course, still possible that there is a more fundamental theoretical problem in the interpretation of the edge spectra.

In most other respects Cs is similar to the other alkali metals, yielding a surface-atom core-level shift only slightly larger than those of Na, K, and Rb, as well as enhanced surface phonon broadening similar to that of

Na. Minor discrepancies in the literature with regard to the $5p$ core-electron binding energy and spin-orbit splitting have been explained. It appears clear, based on the results for Rb and Cs, that the spin-orbit splitting of the outer p electrons of the alkali metals are closely equal to the free-atom spin-orbit splitting of the p^5s^2 state.

In the future it would be desirable to determine directly the singularity index of bulk Cs, using data taken at larger photon energy, where the surface atom peak should be much weaker. A full study of the temperature dependence of the phonon width would also be of interest.

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