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X-Ray Photoemission from Sodium and Lithium*

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X-ray photoelectron spectra of Na and Li metals were obtained in ultrahigh vacuum. Rich plasmon structures were observed on all peaks. Both the photoemission and Auger peaks showed large extra-atomic relaxation energies. A simple "equivalent-cores" screening model predicts extra-atomic relaxation energies in good agreement with experiment. The Na valence band shows approximately a $E^{(1/2)}$ behavior, as would be expected for a nearly-free-electron metal, but is somewhat anomalous.

We have observed x-ray photoelectron spectra from clean surfaces of sodium and lithium. They show multiple plasmon-satellite structure on all peaks, with plasmon energies $\hbar\omega_p$ (bulk)/$\hbar\omega_p$ (surface), in good agreement with theory. Large extra-atomic relaxation[1] energies of ~ 5 eV on core lines and ~15 eV on Auger lines were clearly identified. These are in excellent agreement with a simple screening model.[2,3] The sodium valence-band spectrum was observed. It has approximately the expected free-electron $E^{1/2}$ dependence observed in x-ray emission,[4] but both the Fermi-energy position and the shape of the valence-band edge are anomalous.

The measurements were made with a Hewlett-Packard 5950A ESCA spectrometer, using monochromatized Al $K\alpha_{1,2}$ x rays, modified for ultrahigh-vacuum work. A sodium film was evaporated from 99.99%-pure material onto an aluminum substrate and studied at 8×10^{-11} Torr. A Li film was evaporated from 99.95% material onto chromium and studied at 2×10^{-10} Torr. Carbon and oxygen 1*s* lines from possible surface contamination were undetectable.

Figure 1 shows the Na-1*s* and Li-1*s* lines with their characteristic plasmon-loss structures. The Na-1*s*, Na-2*s*, Na-2*p*, and Li-1*s* lines each show a surface-plasmon loss peak, plus 5, 4, 3, and 2 bulk-plasmon peaks, respectively. Plasmon frequencies ω_p are set out in Table I. The Na ω_p (bulk) values agree quite well with electron-loss results.[5-10] They also definitely favor the free-electron-plasma-model prediction of $(4\pi ne^2/m)^{1/2}$ over the core-polarization corrected values[5,11] in sodium. For lithium our $\hbar\omega_p$ (bulk) values are intermediate between those of Kunz[5] and of Fellenzer,[9] and lower than theory. The ratio [ω_p (bulk)/ω_p (surface)] is quite close to the theoretical $\sqrt{2}$, although the surface-plasmon peaks are poorly resolved.

Core-level binding energies relative to the Fermi level, E_B^F, and to the vacuum level $E_B^V = E_B^F$ + (work function), are set out in Table II. The Fermi energy E_F (Au) was determined from the spectrum of a single crystal of gold. It was checked by evaporating sodium directly onto gold and comparing core-level positions. For both Na and Li, the core-level E_B^F values based on E_F (Au) agree very well with x-ray edges.[4] The E_B^V results are systematically lower than E_B values for free atoms, as estimated either from optical[12] plus x-ray[13] data or from theoretical free-atom values.[14] The latter two are in excellent agreement (Table II). These results appear to provide particularly clear examples of extra-atomic relaxation. The last column in Table II gives estimates of extra-atomic relaxation shifts from a simple "equivalent-cores"

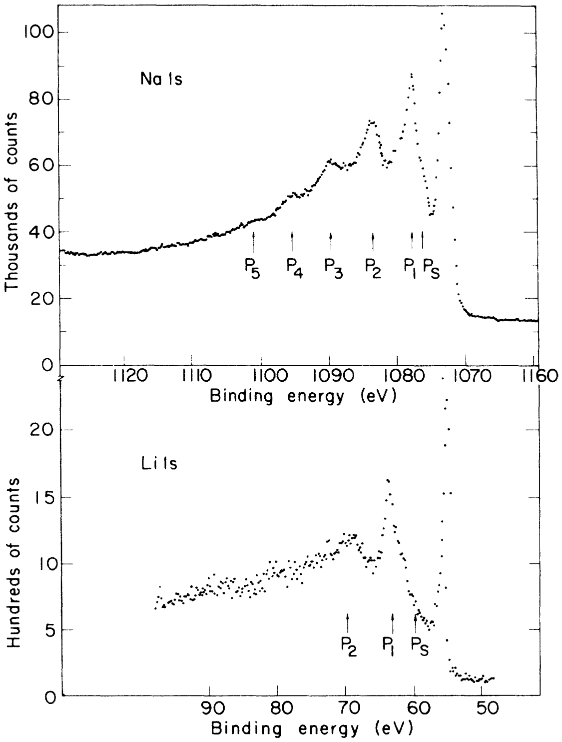

FIG. 1. Sodium and lithium 1*s* lines, with characteristic plasmon structure. The Li P_1 peak is slightly enhanced in this spectrum from Na 2*s* contamination.

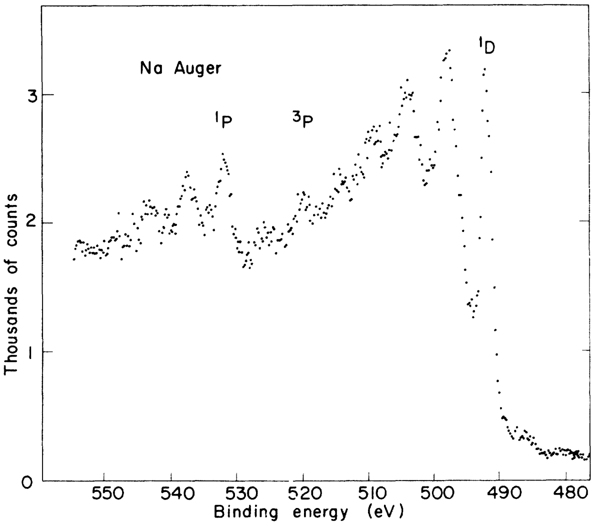

FIG. 2. Sodium *KLL* Auger spectrum, with plasmons.

model[3] that assumes complete screening in the atomic cell, using Mann's[15] Slater integrals. In this model the Li 1*s* shift, for example, would be given by

$$\Delta E = E_B\,(\text{atom}) - E_B^V \cong \tfrac{1}{2}\,\mathfrak{F}(1s\;2s)_{\text{Beryllium}}\ ,$$

where $\mathfrak{F} = (F^0 - \frac{1}{2}G^0)$ is the two-electron interaction between the K hole and the screening electron. The very good agreement of the last column in Table II with the preceding two columns strongly supports this model.

Auger energy shifts from extra-atomic relaxation are even larger, because two holes are screened

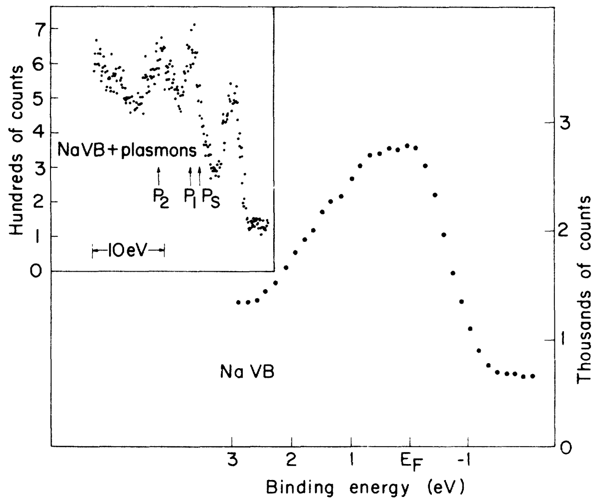

FIG. 3. Sodium valence band. The data have been treated by adding four channels and then performing a sliding linear fit to three adjacent points. Insert shows a wider unsmoothed scan, with plasmons.

TABLE I. Plasmon energies (eV).

Line	$E(P_1)$[a]	$E(P_2)$	$E(P_3)$	$E(P_4)$	$E(P_5)$	$\langle E(P)\rangle$[b]	$E(P_S)$	$\langle E(P)\rangle/E(P_S)$	$E(P)_{\text{th}}$	$E(P)^*_{\text{th}}$[c]	$E(P)_{\text{e}}$[d]	$E(P_S)_{\text{e}}$[d]
Na 1*s*	5.8(1)	5.8(1)	5.9(1)	5.9(2)	5.9(2)	5.83(4)	4.0(1)	1.45	5.95[e]	5.58[e]	5.71(10)[e]	3.85(10)[e]
Na 2*s*	5.9(1)	5.8(1)	5.8(2)	5.8(1)	···	5.80(2)	4.1(1)	1.41			5.85(5)[f]	3.82(10)[f]
Na 2*p*	5.8(1)	5.9(1)	5.7(2)	···	···	5.77(6)	4.0(2)	1.44			5.87[g]	4.01(17)[g]
Na VB	6.0(2)	5.0(3)	···	···	···	5.5(2)	4.0(3)	1.38			5.4(2)[h]	
Auger ^1D $(KL_{23}L_{23})$	5.7(2)	5.7(2)	5.7(3)	···	···	5.7(1)	···	···				
Auger ^1P (KL_1L_{23})	5.5(3)	5.9(3)	···	···	···	5.7(2)	···	···				
Li 1*s*	7.5(3)	7.3(3)	···	···	···	7.4(2)	5.0(3)	1.48	8.02[e]	7.96[e]	7.12(10)[e]	4.20(10)[e]
											8[i]	4.6[i]
												5.2[j]

[a] Energy of peak N − energy of peak $N-1$.
[b] Average of all the bulk-plasmon energies.
[c] Free-electron theory corrected for core polarization.
[d] Other measurements.
[e] Reference 5.
[f] Reference 6.
[g] Reference 7.
[h] Reference 8.
[i] Reference 9.
[j] Reference 10.

TABLE II. Binding, Auger, and relaxation energies (eV).

Line	$E_{B,K}^{F}$ [a]	$E_{B,K}^{V}$ [b]	E^A(th)	E^A(opt)[c]	ΔE^A(th)	ΔE^A(opt)	ΔE^A(calc)
Na 1s	1071.7(1)	1074.0	1079[d]	1079.1	5.0	5.1	5.3[e]
Na 2s	63.4(1)	65.7	71.9[d]	71.1	6.2	5.4	5.0[e]
Na 2p	30.4(1)	32.7	36.6[d]	38.1	3.9	5.4	5.1[e]
Auger ^1D ($KL_{23}L_{23}$)	994.2(1)	991.9	975.8[f]	977.2	16.1	14.7	16.8[g]
Auger ^1P (KL_1L_{23})	954.7(1)	952.4	937.1[f]		15.3		16.8[g]
Li 1s	54.8(1)	57.2	···	64.9	···	7.7	6.4[e]

[a] Binding energy or kinetic energy relative to E_F (Au).
[b] Work-function corrections of 2.3 eV (Na) or 2.4 eV (Li) were made.
[c] From data in Refs. 12 and 13.
[d] From Ref. 14.
[e] Estimated as in Ref. 3.
[f] Estimated from binding energies, without relaxation.
[g] Estimated as in Ref. 2.

in the final state. Again a simple "equivalent-cores" screening model[2] predicts extra-atomic relaxation energies in (Table II, column 8) very good agreement with experiment. The sodium KLL Auger spectrum is shown in Fig. 2. The predicted energy in this case is, for the sodium ^1D line,

$$\Delta E_{ea} \cong \mathcal{F}(2p\,3s)_{\mathrm{Al}} + \mathcal{F}(2p\,3p)_{\mathrm{Al}} - \mathcal{F}(1s\,3s)_{\mathrm{Mg}}\ .$$

Free-atom Auger energies were estimated, using optical and x-ray data, both from one-electron binding energies[2] (columns 4 and 6) and from Na II and Na III states[12] (columns 5 and 7). These large Auger extra-atomic relaxation energies should be very useful in surface-physics studies.

The lithium valence-band cross section was too small to give usable spectra in 20 h. The valence-band spectrum of sodium (Fig. 3) agrees roughly in shape and width with the x-ray emission spectrum.[4,16] An approximate $E^{1/2}$ dependence of intensity on energy is observed, as expected, because sodium is the most free-electron-like of the alkali metals.[17] The reduced valence-band width was 3.1 ± 0.1 eV if measured from the high-energy edge, or 2.5 ± 0.1 eV if measured from E_F (Au). The latter value agrees well with the x-ray emission data of Crisp and Williams.[16] Of course, x-ray photoemission and x-ray emission and absorption are very different processes, and the spectra need not be identical. Our spectrum does not show the excitonic structure observed in x-ray emission[16,18–20] and attributed to the Nozières-De Dominicis singularity.[21] It is unusual, however, both in the position of the valence band relative to E_F (Au) and in the gradual slope of the valence-band edge. Both of these features may result from final-state relaxation accompanying photoemission from the valence bands. Further work is needed to clarify this question.

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