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X-RAY PHOTOEMISSION FROM SODIUM AND LITHIUM*

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April 1973

Abstract:

XPS spectra of Na and Li metals were obtained in ultrahigh vacuum. Rich plasmon structures were observed. Both photoemission and Auger peaks showed large extra atomic relaxation energies. The Na valence band shows approximately the expected $E^{1/2}$ shape, but it is somewhat anomalous.

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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 1s lines from possible surface contamination were undetectable.

Figure 1 shows the Na 1s and Li 1s lines with their characteristic plasmon loss structures. The Na 1s, Na 2s, Na 2p, and Li 1s 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,[6] 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" model[3] that assumes complete screening in the atomic cell, using Mann's[15] Slater integrals. In this model the Li 1s shift, for example, would be given by

$$\Delta E = E_B(\text{atom}) - E_B^V \cong \frac{1}{2}\,\mathcal{F}(1s\ 2s)_{\text{Beryllium}} \quad ,$$

where $\mathcal{F} = (F^0 - \frac{1}{2}G^0)$ 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 strongly supports this model.

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

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

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 NaII and NaIII 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 hours. 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 Nozieres-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.

FOOTNOTES AND REFERENCES

*Work performed under the auspices of the U. S. Atomic Energy Commission.

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FIGURE CAPTIONS

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

Fig. 2. Sodium KLL Auger spectrum, with plasmons.

Fig. 3. Sodium valence band. The data has 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]	$E(P_2)$	$E(P_3)$	$E(P_4)$	$E(P_5)$	$\overline{E(P)}$[b]	$E(P_S)$	$\overline{E(P)}/E(P_S)$	$E(P)_{th}$	$E(P)^*_{th}$[c]	$E(P)_e$[d]	$E(P_S)_e$[d]
Na 1s	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[5,e]	5.58[5]	5.71(10)[5]	3.85(10)[5]
Na 2s	5.9(1)	5.8(1)	5.8(2)	5.8(1)	--	5.80(2)	4.1(1)	1.41			5.85(5)[6]	3.82(10)[6]
Na 2p	5.8(1)	5.9(1)	5.7(2)	--	--	5.77(6)	4.0(2)	1.44			5.87[7]	4.01(17)[7]
Na VB	6.0(2)	5.0(3)	--	--	--	5.5(2)	4.0(3)	1.38			5.4(2)[8]	
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 1s	7.5(3)	7.3(3)	--	--	--	7.4(2)	5.0(3)	1.48	8.02[5]	7.96[5]	7.12(10)[5]	4.20(10)[5]
											8[9]	4.6[9]
												5.2[10]

[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] Superscripts denote references in text.

Table II. Binding, Auger, and Relaxation Energies (eV)

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

[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 Ref. 14.

[d] Estimated from binding energies, without relaxation.

[e] From data in Refs. 12 and 13.

[f] Estimated as in Ref. 3.

[g] Estimated as in Ref. 2.

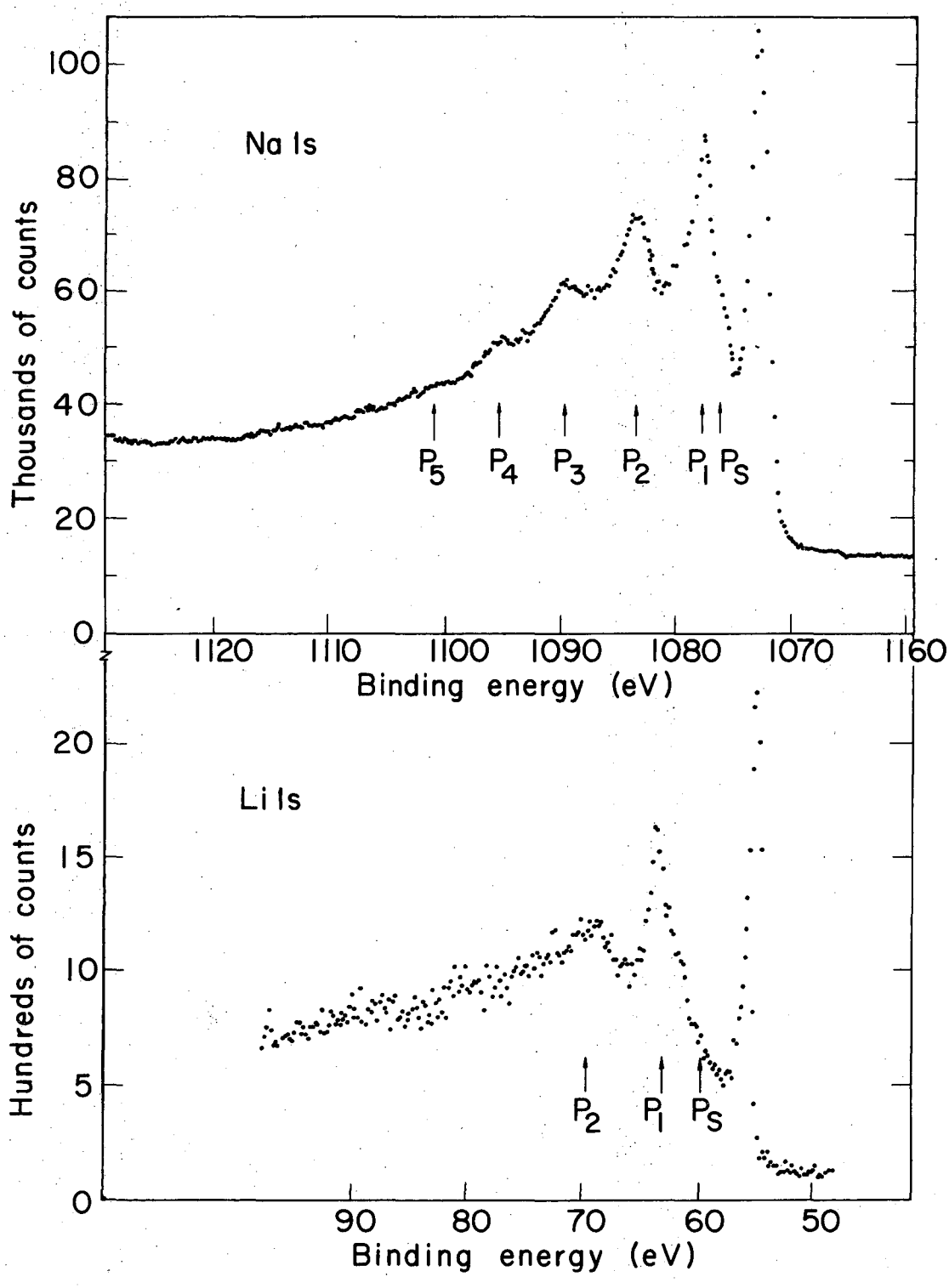
Na 1s
Thousands of counts
100
80
60
40
20
0
P5
P4
P3
P2
P1
PS
1120
1110
1100
1090
1080
1070
1160
Binding energy (eV)
Li 1s
Hundreds of counts
20
15
10
5
0
P2
P1
PS
90
80
70
60
50
Binding energy (eV)
XBL 734-2752

Fig. 1

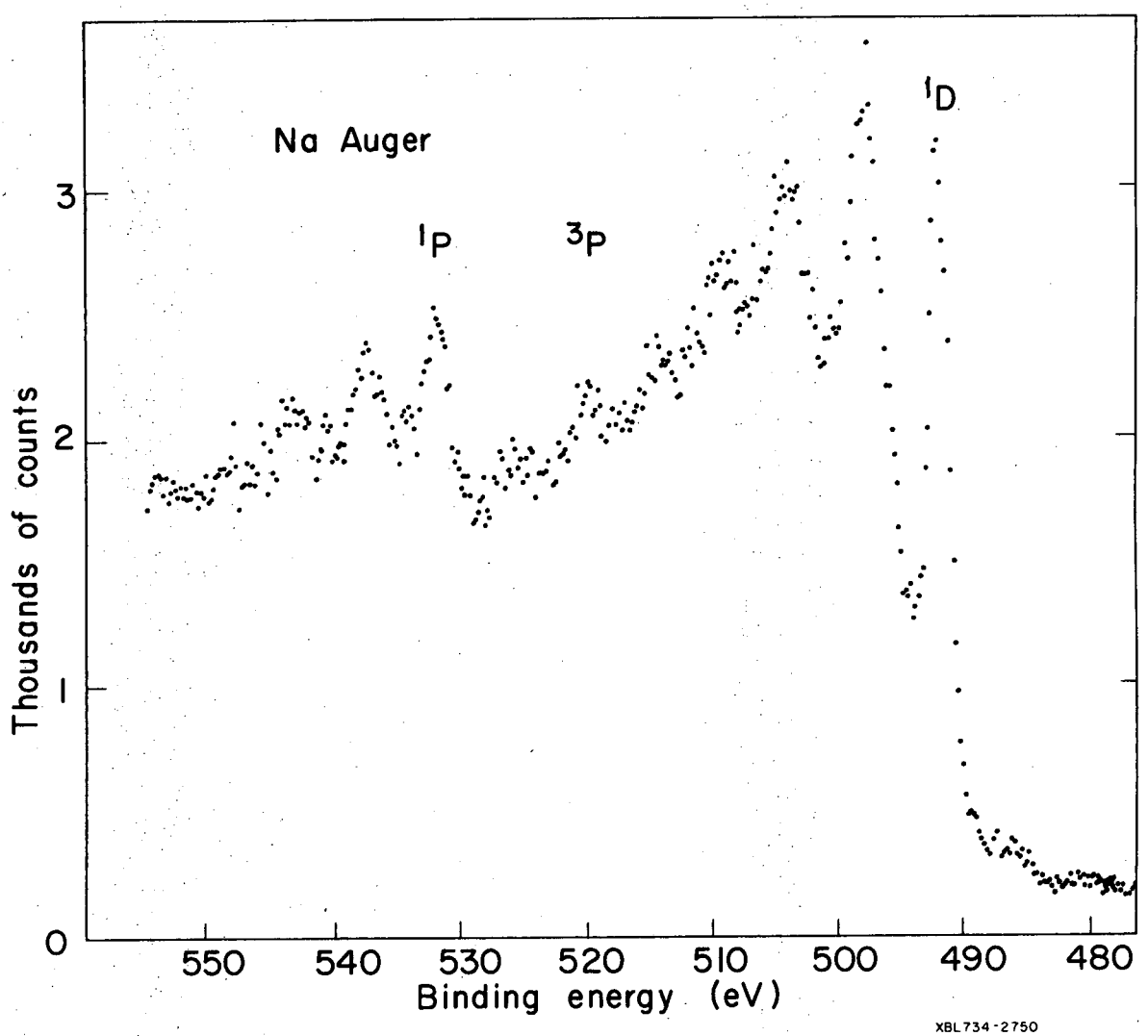
Na Auger
^1P
^3P
^1D
Thousands of counts
0
1
2
3
550
540
530
520
510
500
490
480
Binding energy (eV)
XBL734-2750

Fig. 2

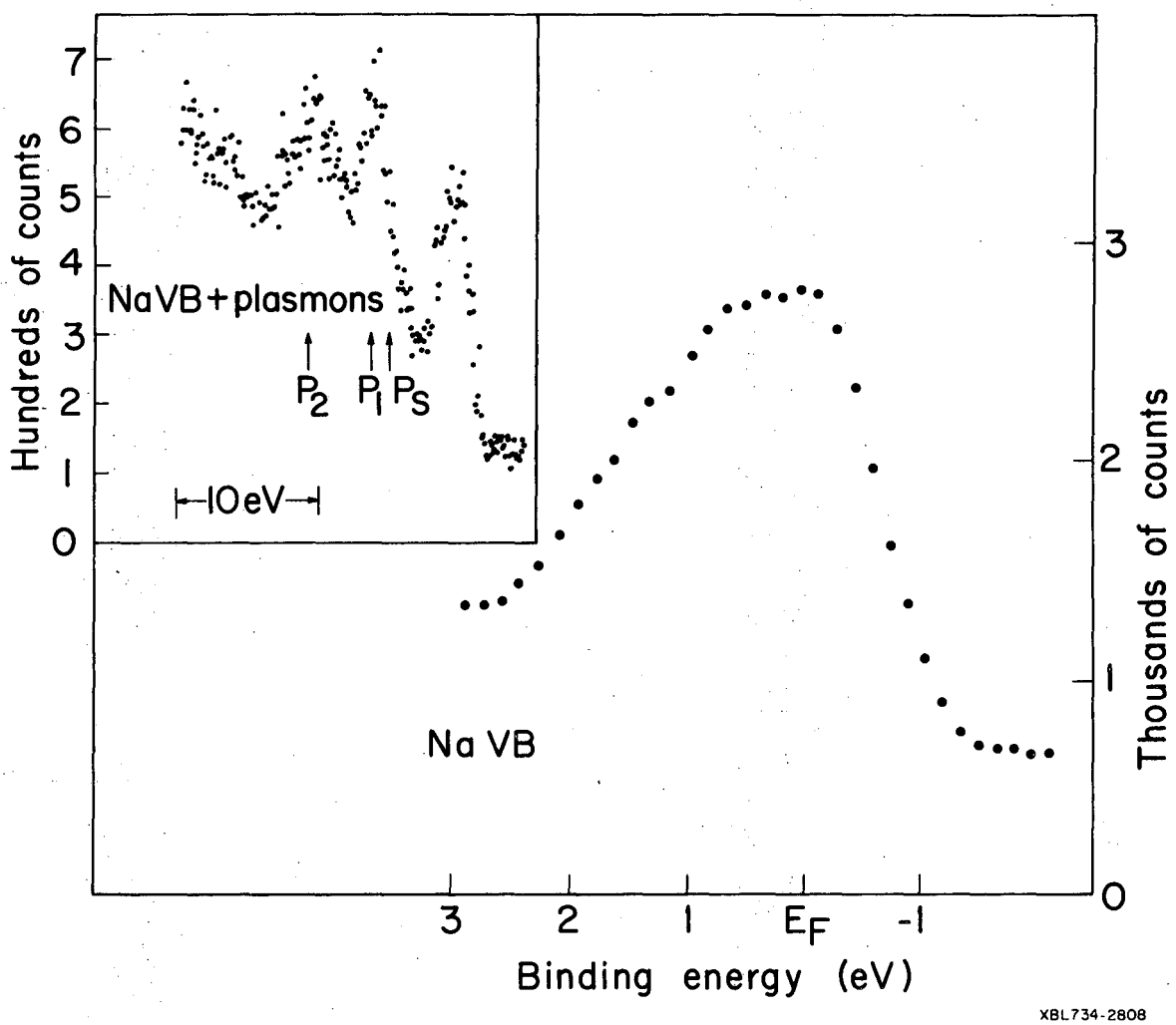
Hundreds of counts
7
6
5
4
3
2
1
0
NaVB+plasmons
P2
P1
PS
10eV
Na VB
3
2
1
EF
-1
Binding energy (eV)
Thousands of counts
3
2
1
0
XBL734-2808

Fig. 3

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