

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

X-RAY PHOTOMISSION FROM SODIUM AND LITHIUM

### Permalink

<https://escholarship.org/uc/item/8v245254>

### Authors

Kowalczyk, S.P.

Ley, L.

McFeely, F.R.

et al.

### Publication Date

1973-04-01

X-RAY PHOTOEMISSION FROM SODIUM AND LITHIUM

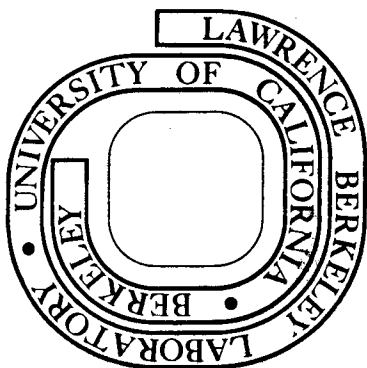
S. P. Kowalczyk, L. Ley, F. R. McFeely,  
R. A. Pollak, and D. A. Shirley

April 1973

Prepared for the U. S. Atomic Energy Commission  
under Contract W-7405-ENG-48

**For Reference**

Not to be taken from this room



## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

X-RAY PHOTOEMISSION FROM SODIUM AND LITHIUM\*

S. P. Kowalczyk, L. Léy, F. R. McFeely, R. A. Pollak<sup>†</sup>, and D. A. Shirley

Department of Chemistry and  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, California 94720

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.

- - -

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  $\hbar\omega_p(\text{bulk})/\hbar\omega_p(\text{surface})$  in good agreement with theory. Large extra-atomic relaxation<sup>1</sup> energies of  $\sim 5$  eV on core lines and  $\sim 15$  eV on Auger lines were clearly identified. These are in excellent agreement with a simple screening model.<sup>2,3</sup> The sodium valence-band spectrum was observed. It has approximately the expected free-electron  $E^{1/2}$  dependence observed in x-ray emission,<sup>4</sup> 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  $8 \times 10^{-11}$  Torr. A Li film was evaporated from 99.95% material onto chromium and studied at  $2 \times 10^{-10}$  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  $\omega_p$  are set out in Table I. The Na  $\omega_p$  (bulk) values agree quite well with electron-loss results.<sup>5-10</sup> They also definitely favor the free-electron plasma model prediction of  $(4\pi n e^2/m)^{1/2}$  over the core-polarization corrected values<sup>5,11</sup> in sodium. For lithium our  $\hbar\omega_p$  (bulk) values are intermediate between those of Kunz<sup>5</sup> and of Fellenzer,<sup>6</sup> and lower than theory. The ratio  $\omega_p$  (bulk)/ $\omega_p$  (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  $E_B^V = E_B^F + (\text{work function})$ , 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.<sup>4</sup> The  $E_B^V$  results are systematically lower than  $E_B$  values for free atoms, as estimated either from optical<sup>12</sup> plus x-ray<sup>13</sup> data or from theoretical free-atom values.<sup>14</sup> 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<sup>3</sup> that assumes complete screening in the atomic cell, using Mann's<sup>15</sup> Slater integrals. In this model the Li 1s shift, for example, would be given by

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

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<sup>2</sup> 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 <sup>1</sup>D line,

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

Free-atom Auger energies were estimated, using optical and x-ray data, both from one-electron binding energies<sup>2</sup> (Columns 4 and 6) and from NaII and NaIII states<sup>12</sup> (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.<sup>4,16</sup> 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.<sup>17</sup> The reduced valence-band width was  $3.1 \pm 0.1$  eV if measured from the high-energy edge, or  $2.5 \pm 0.1$  eV if measured from  $E_F(\text{Au})$ . The latter value agrees well with the x-ray emission data of Crisp and Williams.<sup>16</sup> 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<sup>16,18-20</sup> and attributed to the Nozieres-De Dominicis singularity.<sup>21</sup>

It is unusual, however, both in the position of the valence band relative to  $E_F(\text{Au})$  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.

† Present Address: IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598.

1. D. A. Shirley, Chem. Phys. Letters 16, 220 (1972).
2. S. P. Kowalczyk, R. A. Pollak, F. R. McFeely, L. Ley, and D. A. Shirley, Phys. Rev. B, to be published.
3. L. Ley, S. P. Kowalczyk, F. R. McFeely, R. A. Pollak, and D. A. Shirley, Phys. Rev. B, to be published.
4. D. H. Tombouliau, Handbuch der Physik XXX, ed. by S. Flügge (Springer-Verlag, Berlin, 1957), p. 246; and references therein.
5. C. Kunz, Phys. Letters 15, 312 (1965).
6. J. B. Swan, Phys. Rev. 135, A1467 (1964).
7. J. L. Robins and P. E. Best, Proc. Roy. Soc. 79, 110 (1962).
8. R. E. Palmer and S. E. Schnutterly, Phys. Rev. B4, 2329 (1971).
9. H. Fellenzer, Z. Physik 165, 419 (1961).
10. I. Lindau, H. Löfgren, and L. Walldin, Phys. Letters 36A, 293 (1971).
11. D. Pines, Elementary Excitations in Solids (W. A. Benjamin, 1963).
12. C. E. Moore, "Atomic Energy Levels", NBS Circular 467 (1949).
13. J. A. Bearden, Rev. Mod. Phys. 39, 78 (1967).
14. K. Siegbahn, et al., Nova Acta Regiae Soc. Sci. Upsaliensis Ser. IV, Vol. 20 (1967). Appendix II.
15. J. B. Mann, "Atomic Structure Calculations I. Hartree-Fock Energy Results for the Elements Hydrogen to Lawrencium", LA-3690, TID 4500.
16. R. S. Crisp and S. E. Williams, Phil. Mag. 6, 625 (1961).
17. F. S. Ham, Phys. Rev. 128, 2524 (1962).
18. C. Kunz, R. Haensel, G. Keitel, P. Schreiber, and B. Sonntag, NBS Special Publication 323 (1971), p. 275.



19. G. D. Mahan, Phys. Rev. 163, 612 (1967).
20. G. D. Mahan, NBS Special Publication 323 (1971), p. 253.
21. P. Nozieres and C. T. De Dominicis, Phys. Rev. 178, 1097 (1969).

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 <sup>5,e</sup>	5.58 <sup>5</sup>	5.71(10) <sup>5</sup>	3.85(10) <sup>5</sup>					
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) <sup>6</sup>	3.82(10) <sup>6</sup>			
Na 2p	5.8(1)	5.9(1)	5.7(2)	--	--	5.77(6)	4.0(2)	1.44							5.87 <sup>7</sup>	4.01(17) <sup>7</sup>	
Na VB	6.0(2)	5.0(3)	--	--	--	5.5(2)	4.0(3)	1.38									5.4(2) <sup>8</sup>
Auger <sup>1</sup> D (KL <sub>23</sub> L <sub>23</sub> )	5.7(2)	5.7(2)	5.7(3)	--	--	5.7(1)	--	--									
Auger <sup>1</sup> P (KL <sub>1</sub> L <sub>23</sub> )	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 <sup>5</sup>	7.96 <sup>5</sup>	7.12(10) <sup>5</sup>	4.20(10) <sup>5</sup>					
													8 <sup>9</sup>	4.6 <sup>9</sup>			
															5.2 <sup>10</sup>		

<sup>a</sup>Energy of peak N - Energy of peak N - 1.

<sup>b</sup>Average of all the bulk plasmon energies.

<sup>c</sup>Free electron theory corrected for core polarization.

<sup>d</sup>Other measurements.

<sup>e</sup>Superscripts denote references in text.

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

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

<sup>a</sup>Binding energy or kinetic energy relative to  $E_F$ (Au).

<sup>b</sup>Work-function corrections of 2.3 eV (Na) or 2.4 eV (Li) were made.

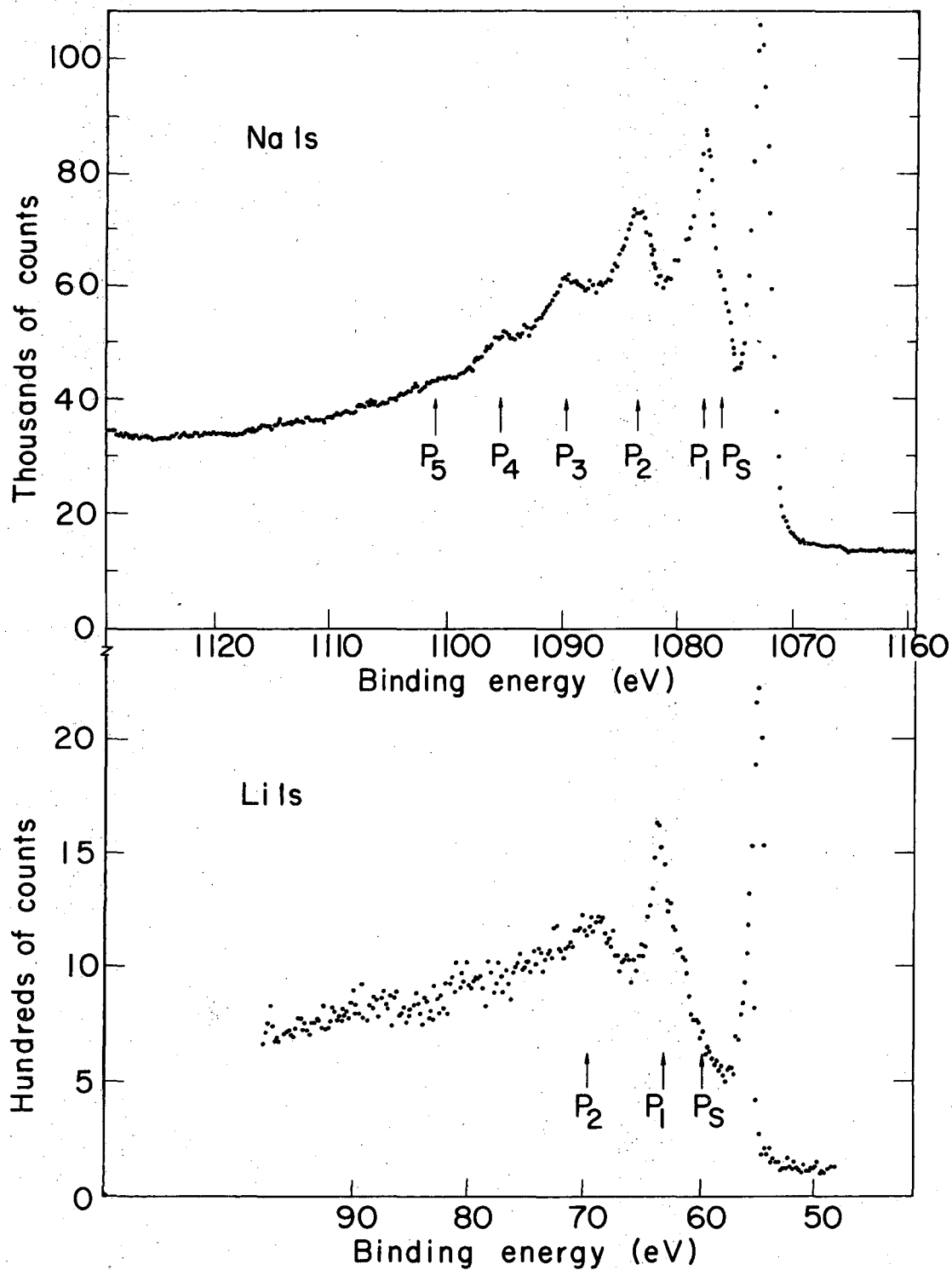
<sup>c</sup>From Ref. 14.

<sup>d</sup>Estimated from binding energies, without relaxation.

<sup>e</sup>From data in Refs. 12 and 13.

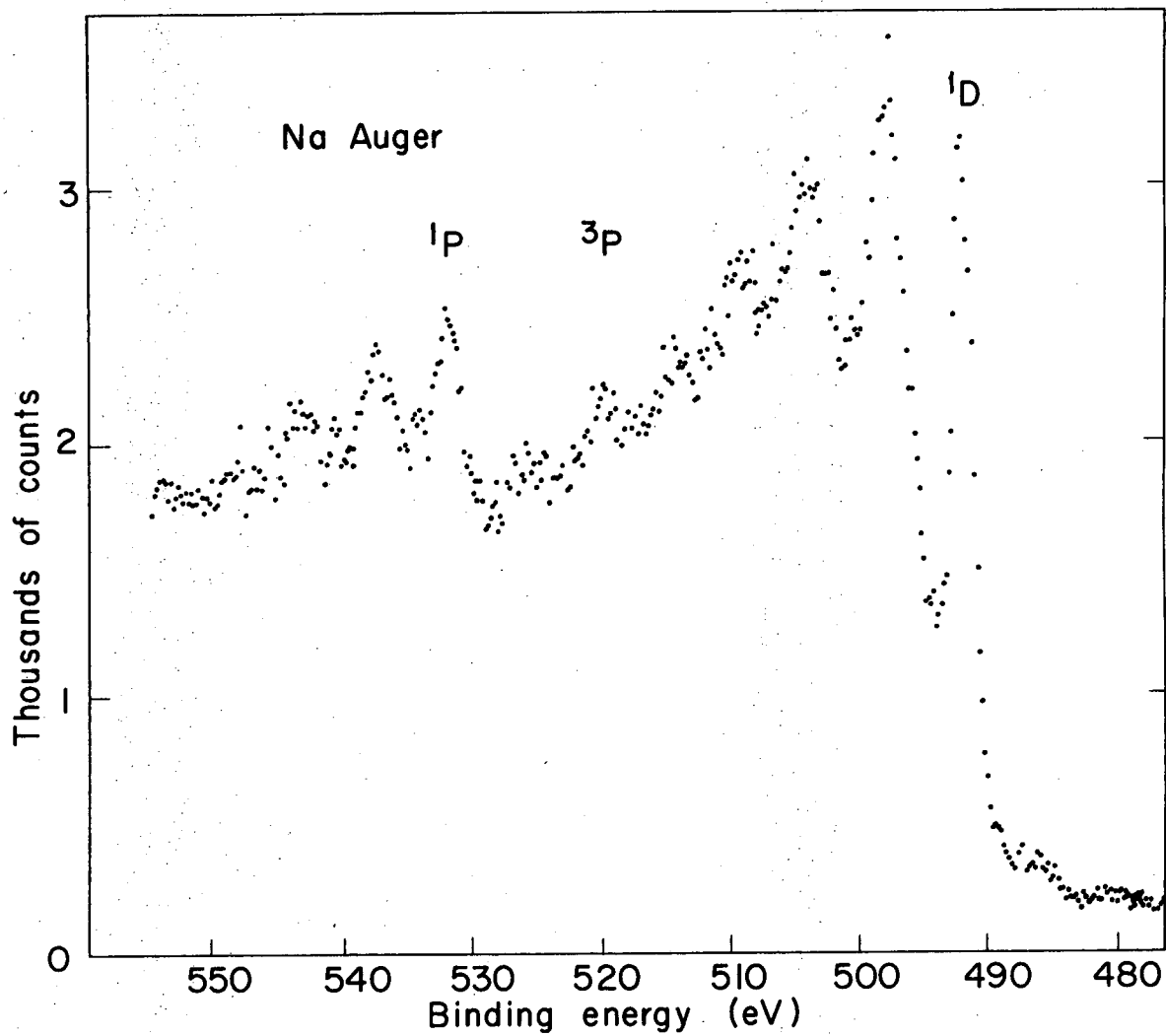
<sup>f</sup>Estimated as in Ref. 3.

<sup>g</sup>Estimated as in Ref. 2.



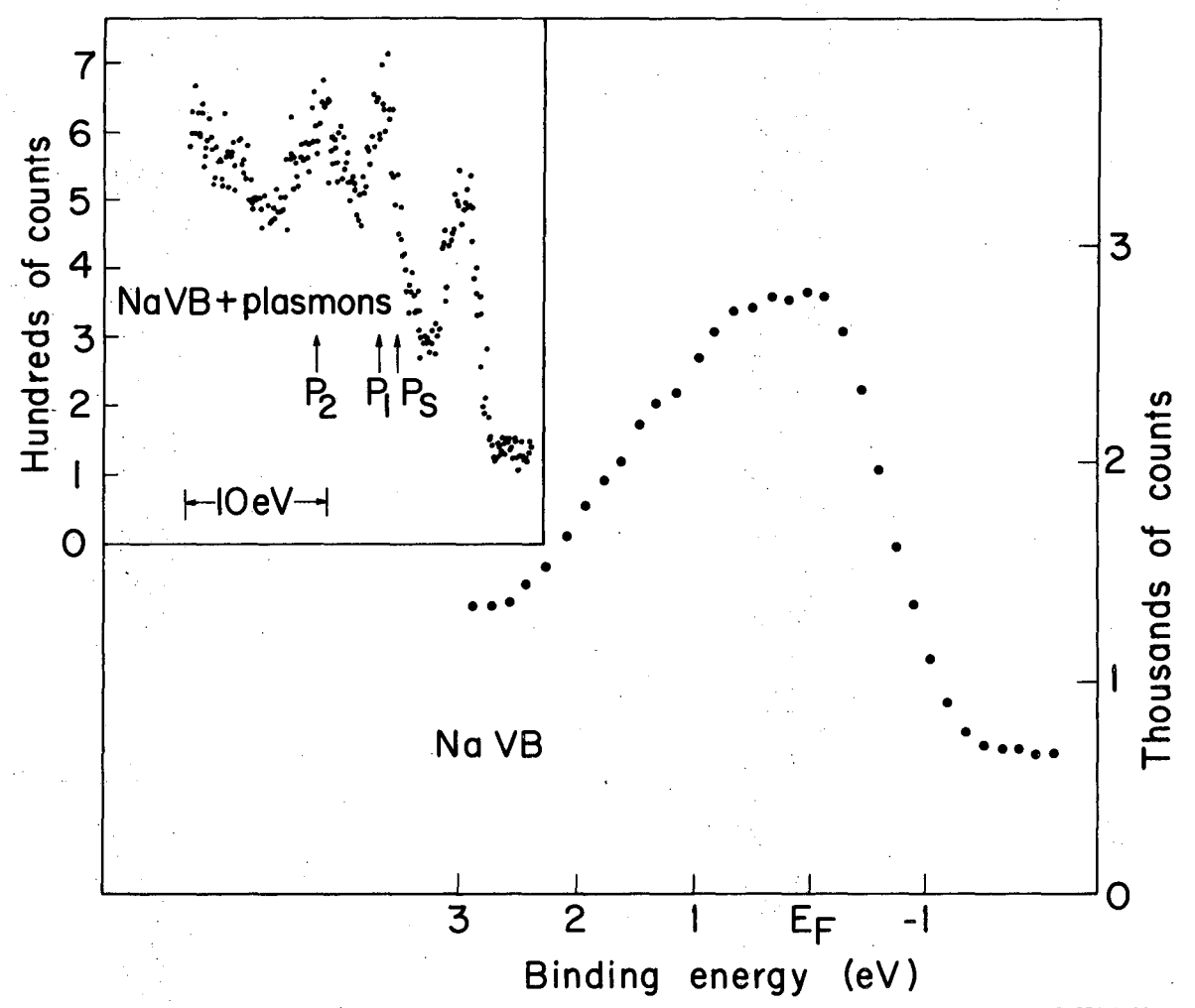
XBL 734-2752

Fig. 1



XBL734-2750

Fig. 2



XBL734-2808

Fig. 3

LEGAL NOTICE

*This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.*

TECHNICAL INFORMATION DIVISION  
LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720