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CALCULATION OF THE SURFACE DENSITY OF ELECTRONIC STATES IN LEAD

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ABSTRACT

We present a tight-binding calculation of the local surface density of states for the (001) surface of lead. It is based on a simple phenomenological interpolation scheme which replaces the one-dimensional bulk density of states normal to the surface by a surface adapted curve. The integration over the two-dimensional Brillouin zone is performed numerically. The calculation explains qualitatively differences observed between experimental X-ray photoemission density of states and bulk-value calculations in both s-like and p-like bands.

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The tight-binding approach to the study of the electronic properties of surfaces has recently become quite popular[1-5]. This has been prompted by the realization that the bulk properties of Group IV and III-V semiconductors and d-band metals may be adequately described by tight-binding theory[3-7].

The calculations of the local surface density of states (LSDOS) have used two basic approaches, those in which no recourse to Bloch's theorem was made[8-9] and those in which Bloch's theorem was used in the two dimensions in which it still applies.

In the second approach -- the one we use here -- the crystal is regarded as being comprised of infinite two-dimensional layers. The basis states are then characterized by a two-dimensional wave vector $\vec{k}$ and a layer index $\underline{n}$, i.e.

$$|\alpha,n,\vec{k}\rangle = N_2^{-1/2} \sum_{\vec{R}} e^{i\vec{k}\vec{R}_i} u_{\alpha n}(\vec{r}-\vec{R}_i) \qquad (1)$$

where the index α indicates the particular atomic state on the atom at site $\vec{R}_i$ in layer $\underline{n}$, consisting of N_2 atoms. The LSDOS (layer n=0) is then given by

$$N_3(E,0) = -\pi^{-1}\sum_{\alpha\vec{k}} \mathrm{Im}\ \langle\alpha,0,\vec{k}|G|\alpha,0,\vec{k}\rangle \ . \qquad (2)$$

The Green's function matrix element above is then found[4] from Dyson's equation

$$\varepsilon^{-1}\ \underset{\approx}{G} = \underset{\approx}{\mathbf{1}} + \underset{\approx}{H}\ \underset{\approx}{G} \ . \qquad (3)$$

This equation can be solved exactly with the aid of a transfer matrix $\underset{\approx}{T}(\vec{k})$

$$\sum_{\alpha''} \langle\alpha,\vec{k}|T|\alpha''\vec{k}\rangle\ \langle\alpha'',n,\vec{k}|G|\alpha',0,\vec{k}\rangle$$

$$= \langle\alpha,(n+1),\vec{k}|G|\alpha',0,\vec{k}\rangle \ . \qquad (4)$$

It should be noted that $\underset{\approx}{T}(\vec{k})$ is a function of $\vec{k}$, has the dimensions (νxν), where ν is the number of α bands included in the calculation, and, most important of all, is independent of <u>n</u>. This allows one to reduce to a finite number the infinite set of coupled equations (3).

The difficulty in the above calculations are those inherent in handling large numbers of (νxν) matrices and its attendant algebra. As a consequence, most calculations are modelistic in nature and include usually a very small

number of bands, e.g. four for Si and Ge[5], five or six for transition metals[10].

In addition to the many band problem mentioned above, surface tight-binding calculations suffer from a fundamental difficulty. The introduction of a surface in an otherwise infinite three-dimensional lattice has three different effects: (a) the topology and coordination number of atoms at the surface is altered; (b) there is in most cases a rearrangement and/or a reconstruction of the surface; and (c) as a consequence of (a) and (b) the numerical values of the hamiltonian matrix elements change significantly. This last effect causes some problems in tight-binding approaches where most matrix elements are not calculated from first principles but fitted or adjusted to give bulk band structures obtained from other methods.

In the calculation we present here, we attempt to construct a model which is easily adaptable to a large hamiltonian without requiring large scale computation. No attempt is made to deal with reconstructed or significantly relaxed surfaces and consequently no change in the surface potential is included. Our aim is thus to examine the nature and magnitude of the topological and coordination number effects alone on the LCDOS corresponding to a realistic bulk hamil-

tonian. We have chosen to calculate these effects for the (001) surface of Pb. Our choice is guided by the facts that: (i) McFeely et al.[11] have recently constructed a tight-binding hamiltonian which adequately describes both bulk de Haas-van Alphen data[12] and X-ray photoemission experiments[13]; and (ii) the (001) surface of Pb is not known to reconstruct and the relaxation effects, based on charge density arguments, are expected to be small[14].

The bulk unit cell compatible with a (001) surface has translation vectors

$$\vec{t}_1 = \frac{a}{2}(1,1,0); \quad \vec{t}_2 = \frac{a}{2}(1,-1,0); \quad \vec{T} = \frac{a}{2}(0,0,2) \qquad (5)$$

which has a volume $\Omega = (a^3/2)$ and contains two atoms. The corresponding reciprocal lattice vectors are

$$\vec{g}_1 = \frac{2\pi}{a}(1,1,0); \quad \vec{g}_2 = \frac{2\pi}{a}(1,-1,0); \quad \vec{G} = \frac{2\pi}{a}(0,0,1) \ , \qquad (6)$$

resulting in a (001) surface adapted Brillouin zone (BZ) which is a square prism and has a volume equal to half that of the bulk BZ. The bulk density of states remaps into this new BZ by a 2 to 1 band correspondence. If we include 6s and 6p states in our calculation, $\nu = 8$ in the

surface adapted BZ. The two-dimensional BZ (2BZ) is a square, equal to the cross section of the (001) adapted BZ.

The bulk density of states $N_3(E)$ can be thought of as obtained from

$$N_3(E) = \sum_{\underset{\sim}{k}} N_1(E,\vec{k}) \tag{7}$$

where N_1 is a one-dimensional density of states corresponding to all allowed energy levels with fixed $\vec{k}$ parallel to the surface; the summation in (7) extends over the 2BZ.

In (7), $N_1(E,\vec{k})$ considered as a function of E for fixed $\vec{k}$, has the classical one-dimensional singularities of the $(E-E_1)^{-1/2}$ or $(E_2-E)^{-1/2}$ type as seen on the left hand side of Fig. 1. These singularities may appear at the bottom and top of the band, but they must also appear in the middle, as shown in Fig. 1(b). It is a good approximation to treat $N_1(E,\vec{k})$ in the bulk as the superposition of one or more bands of the form

$$N_1(E,\vec{k}) = \frac{F}{\pi W} (1-x^2)^{-1/2}, \tag{8}$$

where

$$W \equiv \frac{1}{2}[E_T(\vec{k}) - E_B(\vec{k})] \quad ,$$
$$x \equiv [E - E_B(\vec{k}) - W]/W \quad , \tag{9}$$

$E_B(\vec{k})$ is the lowest energy of a given single-valued subband, $E_T(\vec{k})$ the corresponding highest value and F is the fraction of the one-dimensional k-space involved in that subband ($0<F\leqslant 1$). As an example F = 1 in Fig. 1(a), while in Fig. 1(b), $F_1 = 0.2$ and $F_2 = 0.8$ for the two single-valued subbands involved.

It has been repeatedly shown[2,4] that LSDOS's have no one-dimensional van Hove singularities, and that the resulting curves are smooth and go smoothly to zero at their boundaries. The development of van Hove singularities[2] is gradual and is only fully completed in the limit $n \to \infty$.

We have introduced a phenomenological density of state function which has these characteristics

$$N_1(E,\vec{k};\zeta) = \frac{2F\zeta(\zeta-1)(1-x^2)^{1/2}}{\pi W[\zeta^2-4(\zeta-1)x^2]} \tag{10}$$

where W, x and F have the same meaning as before, and the parameter ζ

$$2 \leq \zeta < \infty$$

describes the varying shape. The bulk curve (8) is obtained for $\zeta = 2$, while for $\zeta \to \infty$ we obtain

$$N_1(E,\vec{k},\zeta\to\infty) = \frac{2F}{\pi W}(1-x^2)^{1/2} , \qquad (11)$$

which adequately describes the LSDOS. Intermediate values of ζ should describe other layers within small distances from the surface. Replacement of (10) into (7) gives $N_3(E;\zeta)$, which gives various local densities of states; in particular, $N_3(E;\zeta\to\infty)$ yields the approximate LSDOS we are looking for.

We performed the calculation outlined above by numerically sampling 245 points in the irreducible (1/8)th of the 2BZ. We calculated the one-dimensional band structure for each of these points, located the corresponding $E_B(\vec{k})$ and $E_T(\vec{k})$ maxima and evaluated the LSDOS by performing numerically the summation over the 2BZ.

Figure 2 shows curves for $\zeta = 2$, 3, 4 and 1000. The

left hand side curves show the generic $N_1(E,\vec{k};\zeta)$ curves given by (10); the right hand side curves give the corresponding $N_3(E;\zeta)$. The upper graphs $\zeta = 2$ depict the local density of states for a bulk atom, deep inside the metal; the lower graph $\zeta = 1000$ describes the LSDOS. The other two rows show intermediate cases. Each $N_3(E;\zeta)$ displays the characteristic splitting of the s (lower) and p (upper) bands of lead.

We note the following important features of the spectrum. First, we note the evolution of the s-band shape. In the bulk, the maximum in $N_3(E)$ is at the band edge at (-6.72) eV. Following this "spike" in the region between the band onset and $\sim$(-8.0) eV the position of an apparent M_1 type van Hove singularity, $N_3(E)$ is fairly constant. In progressing to the surface, the van Hove singularities are obviously destroyed, and this proves to have a dramatic effect on the band shape. The spike at the band onset gradually falls, and the M_1 singularity in the bulk evolves into a peak in $N_3(E)$.

In examining the p bands we focus our attention on two peaks in $N_3(E)$ which we label P_1 and P_2. The peak P_1, centered at $\sim$(-2.2) eV in the bulk $N_3(E)$ has a square-shaped top, arising from nearby M_1 and M_2 van Hove singularities.

In progressing to the surface we see very much the same phenomenon as in the s-band. The M_1 point evolves into a sharp peak in $N_3(E)$. The other edge of the peak, characterized by the M_2 singularity, gradually loses intensity in progressing to more surface-like $N_1(E)$ shapes, so that at the surface limit it is a practically indistinguishable shoulder on the high-energy side of P_1.

The peak labeled P_2 in Fig. 2 is also square-shaped and is separated from the strong peak at $E > 0.8$ eV by a distinct valley. In progressing from bulk to surface, this peak gradually becomes more rounded, and the valley disappears. It is interesting to note that for intermediate values of ζ this peak is somewhat less sensitive to the form of $N_1(E)$ than either P_1 or the s band.

The over all difference in shape of the lead surface and bulk $N_3(E)$ suggests that some of these effects may manifest themselves in the photoemission data of Ley et al.[13]. If an inelastic scattering length of $\sim$15 Å is assumed, up to 20% of the photoemission intensity can arise from the surface layer.

In Fig. 3 we show the experimental results of Ley et al.[13] along with the simulated photoemission spectrum calculated from the bulk band structure by McFeely et al.[11],

and a simulation of the surface contribution calculated by us on the basis of the $N_3(E;\ \zeta=1000)$ curve in Fig. 2. The largest discrepancy with experiment in each case is the height ratio of the two peaks P_1 and P_2 in the p bands. Experimentally $(P_2/P_1)_{exp} = 0.86$; the calculation with bulk density of states $\zeta = 2$ yields $(P_2/P_1)_{bulk} = 0.66$ while a LSDOS calculation ($\zeta=1000$) produces a ratio $(P_2/P_1)_{surface} = 0.83$. Our LSDOS calculation accounts for 85% of the discrepancy between experiment and bulk calculation.

In addition, the experimental s-band shape is in much closer agreement with the surface layer calculation. This is particularly interesting since, as can be seen from an inspection of Fig. 2, the s-band shape calculated for the intermediate values of ζ do all resemble the surface layer shape rather than the bulk shape. Since these intermediate $N_1(E)$ functions correspond to layers near the surface, a more substantial fraction of the photoemission intensity should reflect this form. The persistence of the effect of the surface on the s band shapes in layers near the surface is an interesting analogy to the Group IV semiconductors, in which the s-bands are far more sensitive (and for a longer range) to topological variations than are the p-bands[15].

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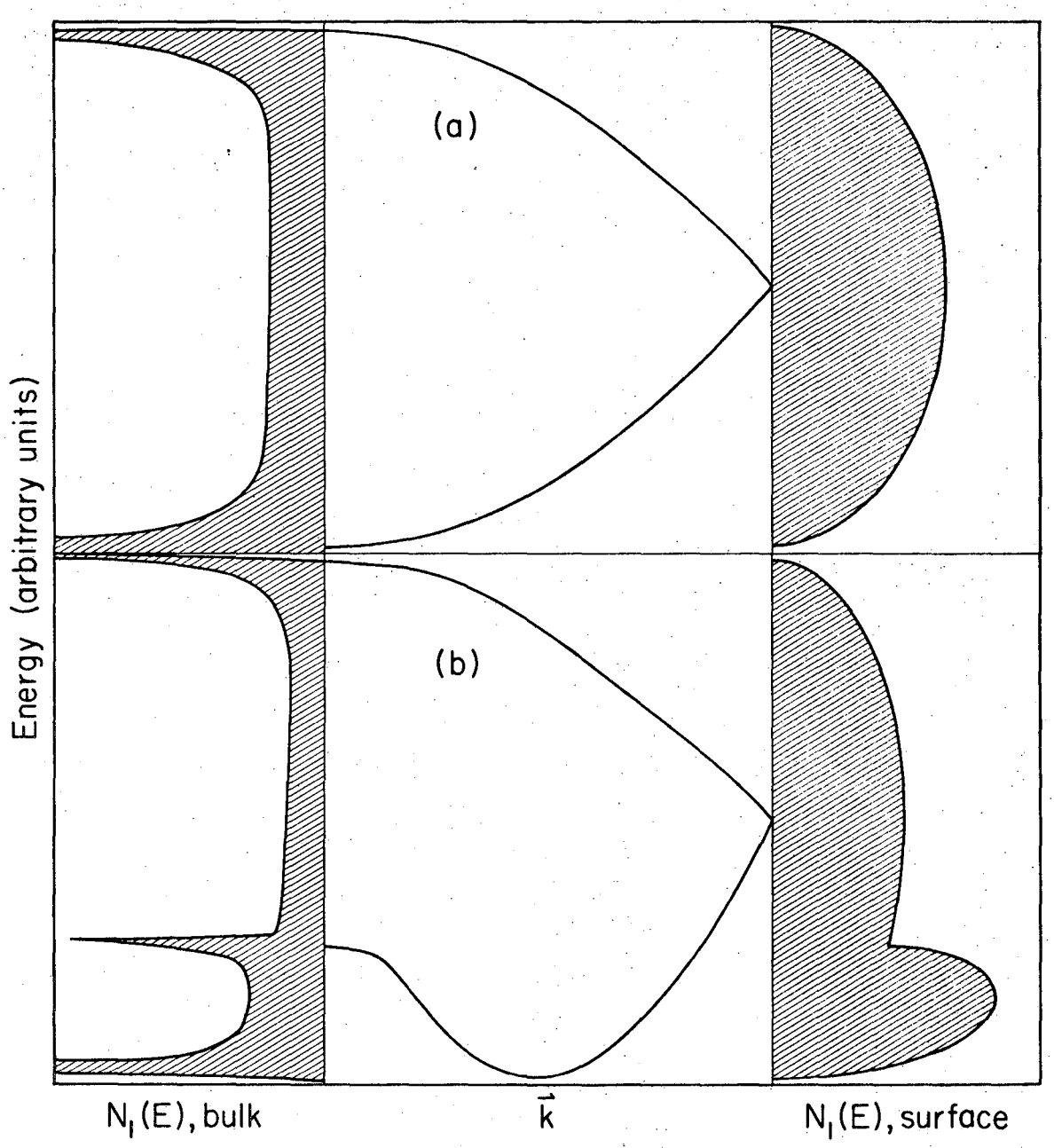
FIGURE CAPTIONS

Fig. 1: Typical band shapes. The bulk one-dimensional DOS is shown on the left-hand side. The corresponding LSDOS is depicted on the right.

Fig. 2: The parametrized DOS's. The left-hand side gives the various one-dimensional curves used in the calculation. The right-hand side shows corresponding LDOS for lead. The upper curves are for $\zeta = 1000$, i.e. the surface layers. The lower curves are for $\zeta = 2$, the bulk. Intermediate values are also shown.

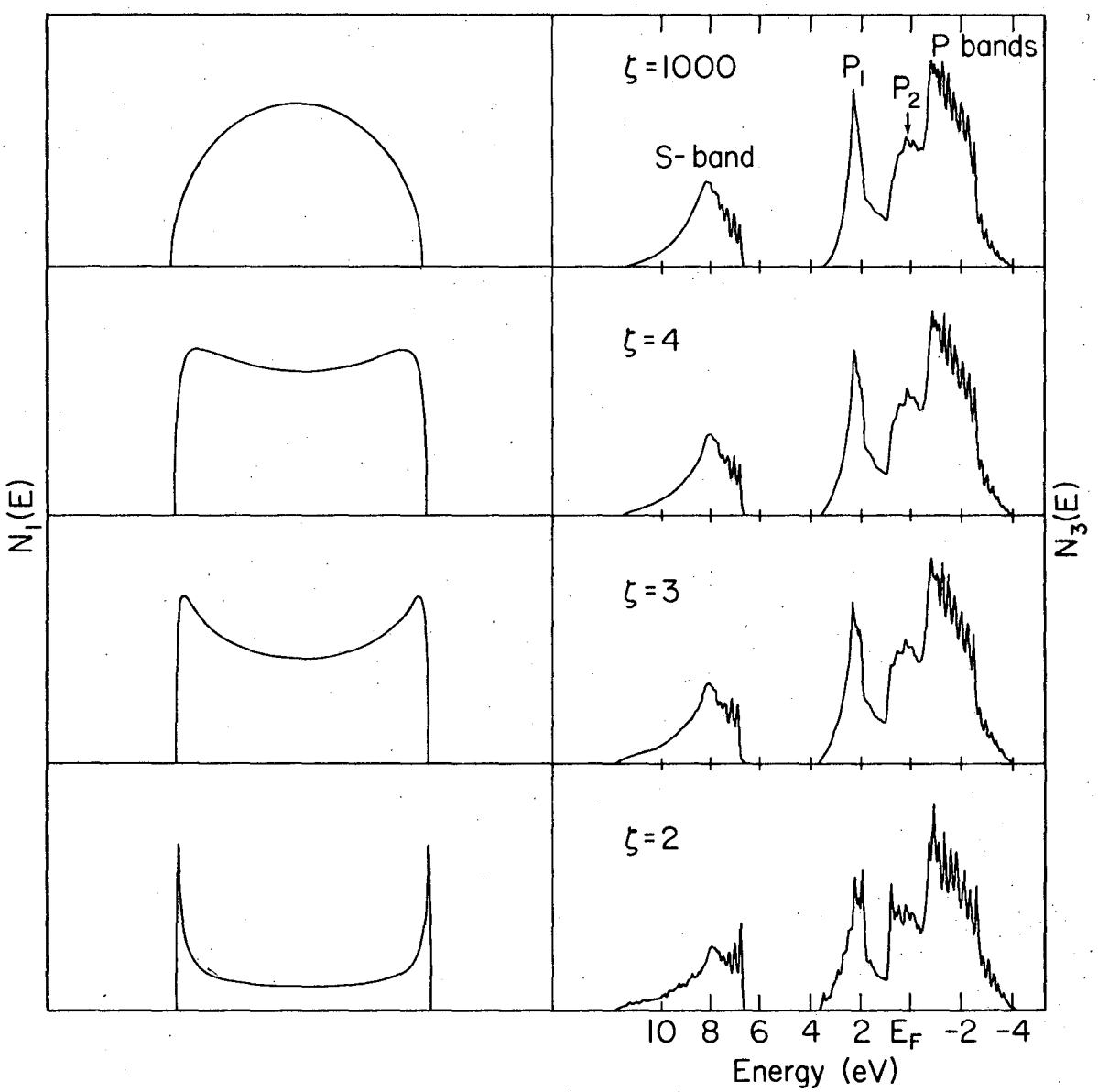
Fig. 3: The XPS spectra for lead. (a) The experimental results of Ref. 13; (b) the calculated spectrum for the bulk density of states from Ref. 11; (c) the present calculation using the LSDOS, $\zeta = 1000$.

0 0 0 0 4 6 0 2 5 0 1



XBL 767-3180

Fig. 1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P bands
P1
P2
S- band
ζ=4
ζ=3
ζ=2
N1(E)
N3(E)
10 8 6 4 2 EF -2 -4
Energy (eV)
XBL 767-3181

Fig. 2

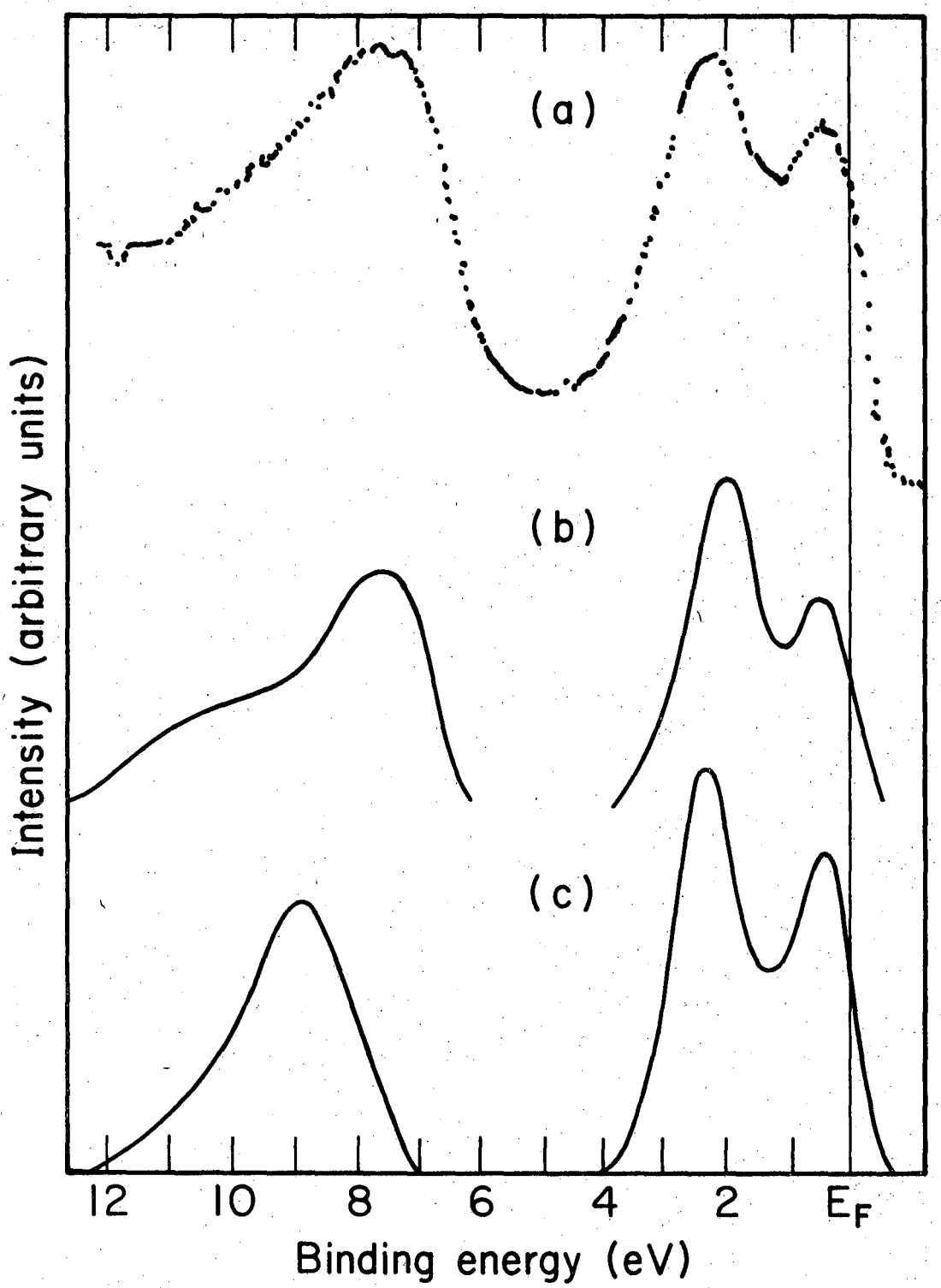

Fig. 3

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