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Authors

Martinez, G.
Schluter, M.
Cohen, Marvin L.

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G. Martinez, M. Schluter, and Marvin L. Cohen

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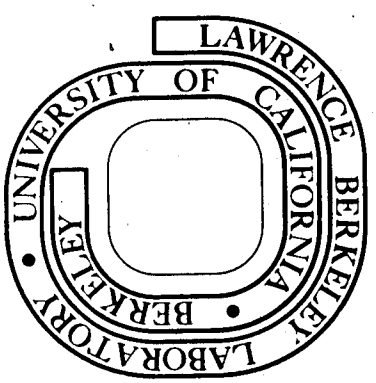

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Synchrotron Radiation Measurements and Calculation of Core - to Conduction Level Transitions in Lead Chalcogenides*

G. Martinez†, M. Schlüter‡ and Marvin L. Cohen
Department of Physics, University of California and
Inorganic Materials Research Division,
Lawrence Berkeley Laboratory, Berkeley, California 94720
and
R. Pinchaux, P. Thiry, D. Dagneaux and Y. Petroff§
Laboratoire de Physique des Solides -
University of Paris VI and L.U.R.E. (Orsay)

Abstract

New high resolution reflectivity measurements on PbSe and PbTe using synchrotron radiation (18-26 eV) are studied using improved EPM band structure models to determine the angular momentum character of the final conduction band states. Detailed analysis reveals that the reflectivity threshold is shifted to lower energies by 0.8 eV compared to results derived from photoemission and low energy reflectivity data. Electron-hole interactions are suggested as a possible explanation for this shift.

New reflectivity measurements on PbSe and PbTe, using synchrotron radiation give, for the first time, very detailed

information about transitions in the 18-26 eV energy range. In this range we primarily expect to see transitions from the cation core d-levels into conduction states.[1] Since the core levels retain their atomic like character in the solid, i.e. they are essentially dispersionless, these transitions add new important information about the nature of conduction band states. Depending upon the angular momentum character of the core level, the core to conduction band transitions "filter out" specific angular momentum states of the conduction bands. In particular, if the initial state is a d-like core state and if the f-character of the conduction band is small or non-existent, then we obtain from reflectivity measurements the density of p-states in the conduction bands weighted by transition matrix elements. These measurements therefore represent a very powerful tool to investigate the conduction band structure. In the present paper only transitions from lead 5d-levels are discussed.

The reflectivity measurements are made using synchrotron radiation generated by the storage ORSAY ring (536 MeV and 35 mA). The monochromator has a resolution of 0.5 Å with a 1200 l/mm platinum grating. The detector (an E.M.I. electron multiplier) is connected to a digital voltmeter and the information is sent to a small Varian computer. The source stability allows us to take the derivatives $dR/d\lambda$ and $d^2R/d\lambda^2$ with a very high signal to noise ratio. The crystals of PbSe and PbTe were cleaved in air and mounted

in an ultra vacuum (10^{-10} mm Hg) reflectometer. Figures 1 and 2 contain the room temperature reflectivity (a) of PbSe and PbTe and the second derivative $d^2R/d\lambda^2$ (b) between 18 and 26 eV. The second derivative allows the detection of weak structures in the reflectivity with high precision. (Shoulders or peaks in R appear as dips in $d^2R/d\lambda^2$).

To perform an actual calculation of the reflectivity we need to know the energies and wavefunctions of the lead 5d core levels in addition to the conduction band structures. We assumed the lead 5d core states to be atomic-like with wavefunctions well represented by non-interacting orbitals[2] and energies to be determined empirically. The final state conduction band wavefunctions are taken from new improved EPM calculations which are in excellent agreement with optical experiments up to 15 eV.[3] The pseudo wavefunctions are orthogonalized to the core states and normalized. This procedure proved necessary for the calculation of momentum matrix elements which involve localized core states. This approach increases the transition matrix elements by about a factor of 4 and subsequently increases the imaginary part of the dielectric function $\varepsilon_2(\omega)$ as calculated in a usual way, by about one order of magnitude. A detailed description of the orthogonalization procedure is given in reference (3). With the aforementioned approximations for the d levels, matrix elements and conduction states, $\varepsilon_2(\omega)$ can be calculated and these contributions are added to a weak and almost

structureless background originating from valence to conduction band transitions. To determine the reflectivity it is first necessary to obtain the real part of the dielectric function $\varepsilon_1(\omega)$. This was done using a Kramers-Kronig transformation including all interband contributions at lower energies. In figures 1(a) and 2(a) we compare the calculated reflectivity with the experimental spectra taken on PbSe and PbTe. The theoretical and experimental spectra are aligned at the transition threshold energies. The following discussion of the spectra holds qualitatively for both lead salts. To facilitate this discussion we present in figure 3, the conduction band structure of PbTe as obtained in reference 3.

From Knight shift measurements[4] and from pseudopotential calculations[3] we know that the bottom of the conduction band at L is dominated by Pb states having 6 $p^{1/2}$ character. Transitions from the highest core d levels ($5d^{5/2}$) are therefore forbidden at this band edge. The first transitions which we expect to be allowed appear at slightly higher energy for transitions into conduction states near Σ. This shifts the onset of core $5d^{5/2}$ transitions to the conduction band to higher energies by about 0.8 eV (for PbTe) and 1.0 eV (for PbSe) at 300°K with respect to the minimum energy at L. The first prominant peak at 20 eV for PbSe and 19.6 eV for PbTe originates from transitions from the $5d^{5/2}$ level into several closely spaced energy bands above the critical point at Σ. The individual transitions can be identified with

structure in the measured second derivative reflectivity spectrum as summarized in Table 1.

This group of transitions, which is followed by a gap results from the existence of a finite energy interval of about 2 eV width in the conduction bands at which transitions from the $5d^{5/2}$ core levels are allowed, i.e. those with strong lead $6p^{3/2}$ character. Transitions from the lower core d-levels ($5d^{3/2}$) start at about 20.6 eV for PbTe and 20.8 eV for PbSe. Unlike the $5d^{5/2}$ case these transitions involve states at the conduction band edge at L. Thus for transitions from the core $5d^{3/2}$ level the onset coincides with the band edge. Taking the spin orbit splitting for the lead core d-states to be 2.65 eV as determined by XPS and UPS measurements[5] and considering the shifts of 0.8 eV (PbTe) and 1 eV (PbSe) respectively for the onsets of the $5d^{5/2}$ transitions, we obtain an energy separation of the two thresholds for transitions from $5d^{5/2}$ and $5d^{3/2}$ levels of about 1.85 eV and 1.65 eV respectively in very good agreement with the reflectivity data. This result confirms the assumption, which is based on selection rules that the $5d^{5/2}$ transitions start at the $\Sigma(6)$ band edge (where 6 refers to the 6th band). Transitions from the $5d^{3/2}$ levels into the $6p^{3/2}$ conduction states are also allowed. They give rise to the shoulder or peak in the reflectivity at 22.8 eV for PbSe and 22.6 eV for PbTe. These structures however, are also due to transitions from $5d^{5/2}$ to higher conduction bands around Γ_8^-.

The relative heights of the two main peaks in the reflectivity can be explained by the different number of allowed transitions from the spin orbit split core d-levels: there exist 12 transitions from $5d^{5/2}$ into $6p^{3/2}$ and 16 transitions from $5d^{3/2}$ into $6p^{3/2}$ and $6p^{1/2}$. This relative strength is not reproduced in our calculation which is probably due to the approximation made in using the atomic wavefunctions. We finally note that the total density of conduction states is nearly constant[3] thus indicating that the observed peak structures are dominated by matrix elements effects, i.e. the structure represents the strongly varying atomic character of conduction states.

Very interesting problems arise when attempting to locate the core d-levels on an absolute energy scale using X-ray (XPS) or ultraviolet (UPS) photoemission spectroscopy results.[5] The reference energy in these measurements is either taken to be the Fermi level or some significant structure in the valence bands. The combination of these data with low energy optical measurements allows independent determination (compared to synchrotron radiation measurements) of the energy separation between core-levels and known structure in the conduction bands. In particular we can use the $\Sigma(5)$ to $\Sigma(6)$ transition which has been observed at 300°K in the near infrared region at 1.24 eV for PbTe and 1.54 eV for PbSe.[6] The energy at 300°K of the $\Sigma(5)$ critical point falls at most 50 meV for PbTe[7] and 200 meV for PbSe[8] below the

valence band edge. The lead $5d^{5/2}$ levels have been found from recent high resolution UPS measurements or previous XPS measurements[5] at 18.25 ± 0.1 eV below the valence band edge for both lead salts. We thus obtain for the $5d^{5/2} \rightarrow \Sigma(6)$ threshold energies:

$$\Delta E\ (PbTe) = 18.25 + 1.24 - 0.05 = 19.45\ (\pm 0.1)eV$$

$$\Delta E\ (PbSe) = 18.25 + 1.54 - 0.20 = 19.70\ (\pm 0.1)eV$$

Comparing these energies to the threshold energies ($\Delta E(PbTe)$ = 18.65 eV and $\Delta E(PbSe)$ = 18.8 eV) measured in our experiment we find a characteristic shift in the reflectivity data of about 0.8 eV toward lower energies.

This shift is too large to be attributed to finite resolution effects or experimental errors. It therefore must arise from the difference in the nature of synchrotron radiation reflectivity measurements and photoemission spectroscopy. One possible explanation might invoke excitonic effects. Electron-hole interaction may play a role in synchrotron radiation reflectivity measurements but not in photoemission measurements. Excitonic effects with characteristic energies of the order of the observed shift (0.8 eV) would necessarily involve a large number of conduction bands, so that individual assignments to critical points and an interpretation in terms of classical excitons, would not be justified. Moreover, the comparison of the experimental and the calculated reflectivity seems to indicate that the electron-hole interaction results in a rather uniform shift

of all structures with some deformations but without the appearance of new exciton-like peaks at lower energy. Though electron-hole correlation effects seem to be a very appealing explanation of the observed energy shift, quantitative calculations are needed for a better understanding. Finally we shall notice that other possible effects, like e.g. relaxation effects or final state interactions in the photoemission process should be considered before final conclusions can be drawn.

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† On leave from University of Paris VI, France on NATO fellowship. Permanent address: Laboratoire de Physique des Solides, Université Paris VI - 4 place Jussieu, 75 Paris 5°, France.

‡ Swiss National Science Foundation Postdoctoral Fellow.

§ U.S. National Science Foundation fellow.

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Table Caption

Assignment of minima in λ the experimental second derivative of the reflectivity to individual core-conduction band transitions. The energy zeros are taken at the respective reflectivity thresholds at $\Sigma(6)$ corresponding to 18.65 eV for PbTe and 18.8 eV for PbSe. Σ_1' and Δ' stand for regions in K-space around Σ and Δ respectively. P is the critical point with coordinates (0.625, 0.46, 0) which also gives rise to the highest peak in ε_2 (see Ref. 3). Δ'' is a region around the point (1.00, 0.2, 0.2).

Table 1

PbSe			PbTe		
Transition	Theory	exp	Transition	Theory	exp
$d^{5/2} \rightarrow \Sigma(6)$	0	0	$d^{5/2} \rightarrow \Sigma(6)$	0	0
$d^{5/2} \rightarrow \Lambda(7)$	0.70	0.68	$d^{5/2} \rightarrow \begin{cases}\Sigma(7) \\ \Sigma'(7)\end{cases}$	$\begin{matrix}0.70 \\ 1.20\end{matrix}$	0.92
$d^{5/2} \rightarrow \begin{cases}\Sigma(7) \\ \Sigma'(7)\end{cases}$	1.20	1.24	$d^{5/2} \rightarrow \Lambda(7,8)$	1.55	1.58
$d^{3/2} \rightarrow L(6)$	1.75	1.85	$d^{3/2} \rightarrow L(6)$	1.97	1.99
$d^{3/2} \rightarrow \Sigma(6)$	2.55	2.60	$d^{3/2} \rightarrow \Sigma(6)$	2.55	2.58
$d^{3/2} \rightarrow \begin{cases}\Delta(6) \\ P(6)\end{cases}$	$\begin{matrix}3.05 \\ 3.45\end{matrix}$	2.82	$d^{3/2} \rightarrow \begin{cases}\Delta(6) \\ P(6)\end{cases}$	3.15	2.85
$d^{3/2} \rightarrow \begin{cases}\Sigma'(6) \\ \Lambda(6)\end{cases}$	3.95 ± 0.1	4.02	$d^{3/2} \rightarrow \begin{cases}\Sigma'(6) \\ \Lambda(6)\end{cases}$	3.65	3.46
$d^{5/2} \rightarrow \Delta'(6)$	4.55		$d^{3/2} \rightarrow \Delta'(6)$	4.05	3.98
$d^{5/2} \rightarrow \Gamma(10)$ $d^{3/2} \rightarrow \Gamma(6)$	4.85	4.57	$d^{3/2} \rightarrow \Gamma(6)$	4.50	4.36
--	--	5.62	$d^{3/2} \rightarrow \Delta''(6)$	5.65	5.30 ± 0.2
$d^{3/2} \rightarrow \Delta''(7)$	6.45 ± 0.2	6.33 ± 0.1			

Figure Captions

Figure 1. Reflectivity (a) and second derivative spectrum (b) for the measured reflectivity for PbSe. The theoretical reflectivity curve is indicated by the broken line. The assignments in part (b) are explained in Table 1.

Figure 2. Reflectivity (a) and second derivative spectrum (b) for the measured reflectivity for PbTe. The theoretical reflectivity curve is indicated by the broken line. The assignments in part (b) are explained in Table 1.

Figure 3. E P M conduction band structure of PbTe as obtained from Reference 3.

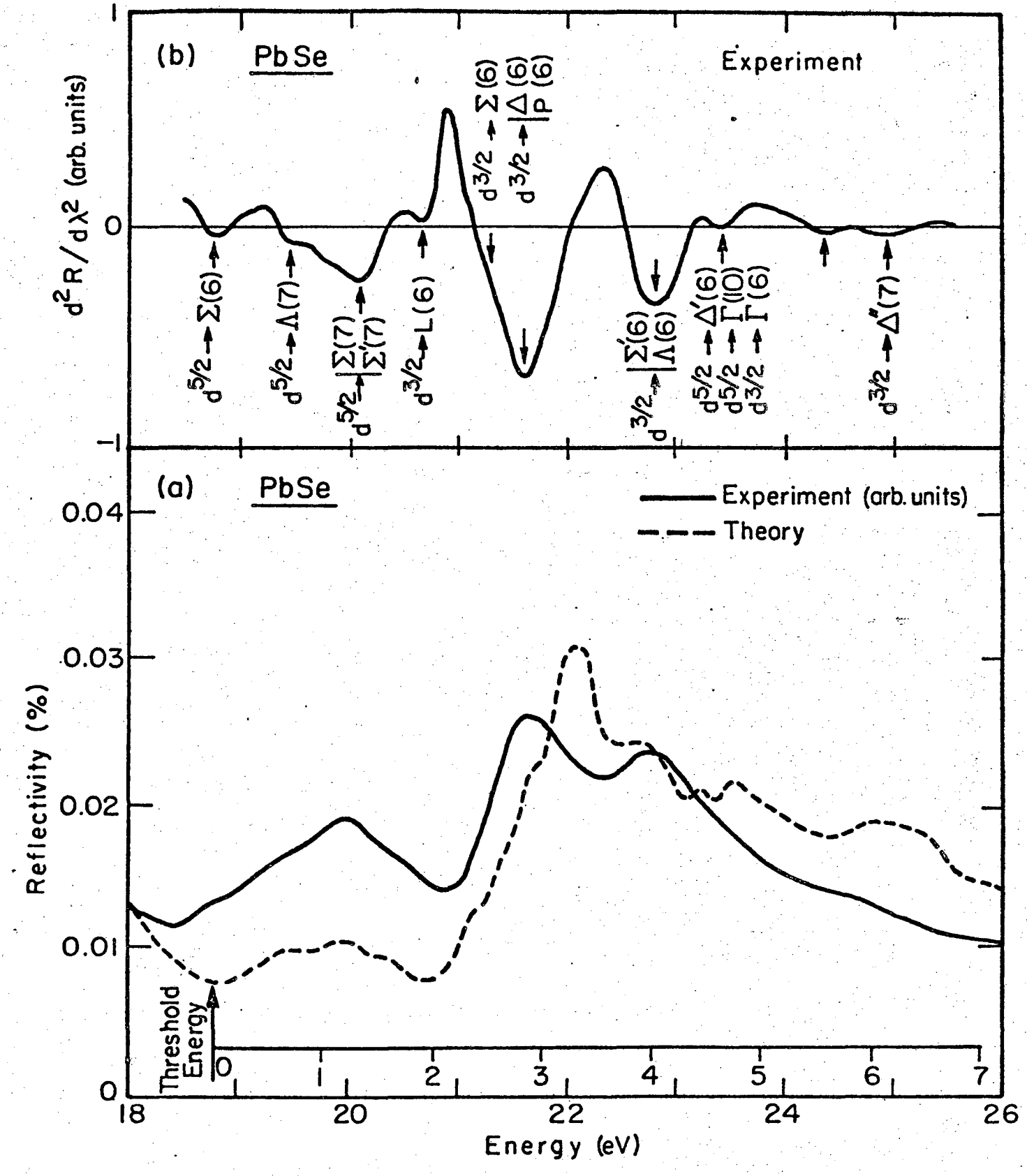

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Figure 1

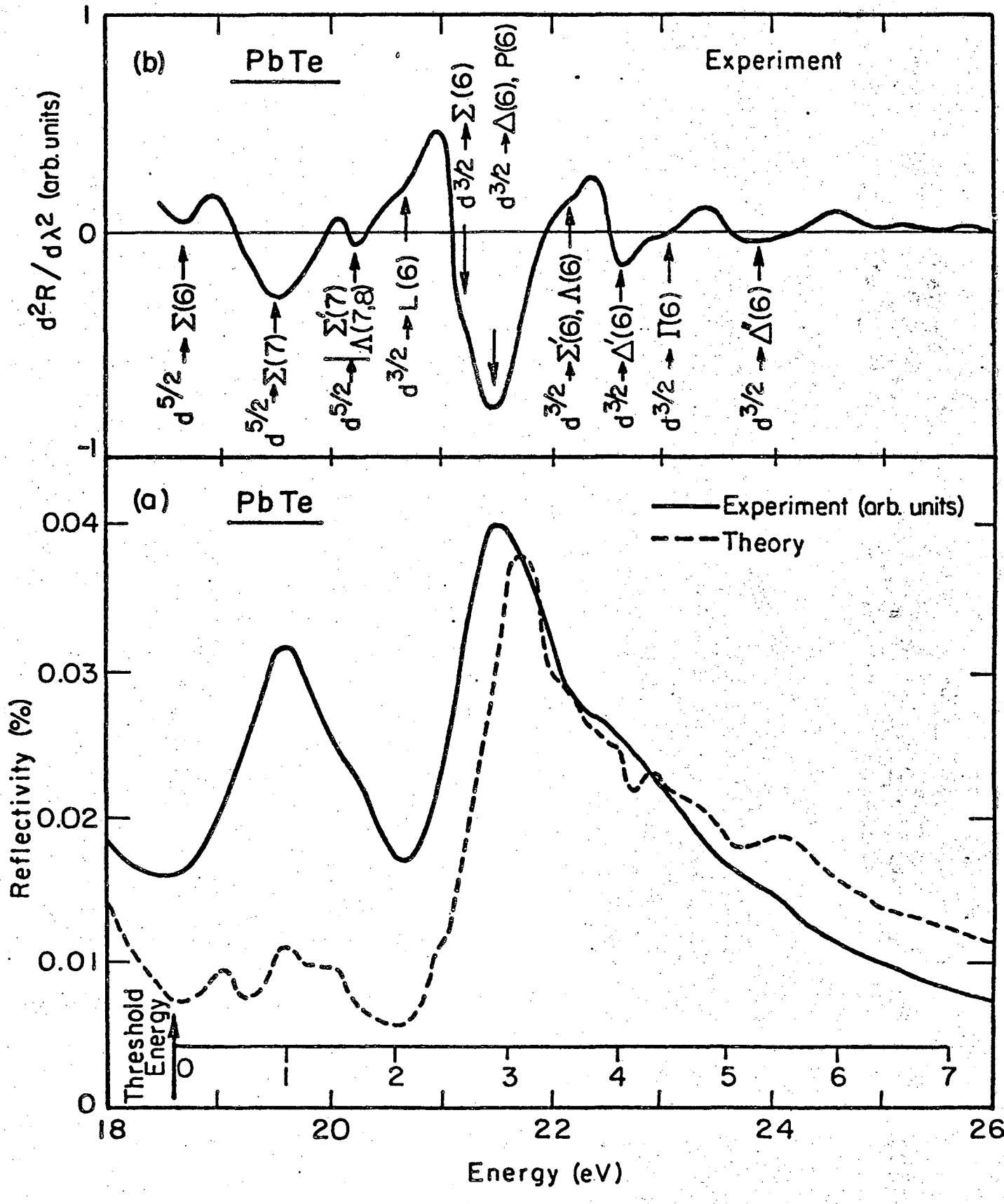

Figure 2

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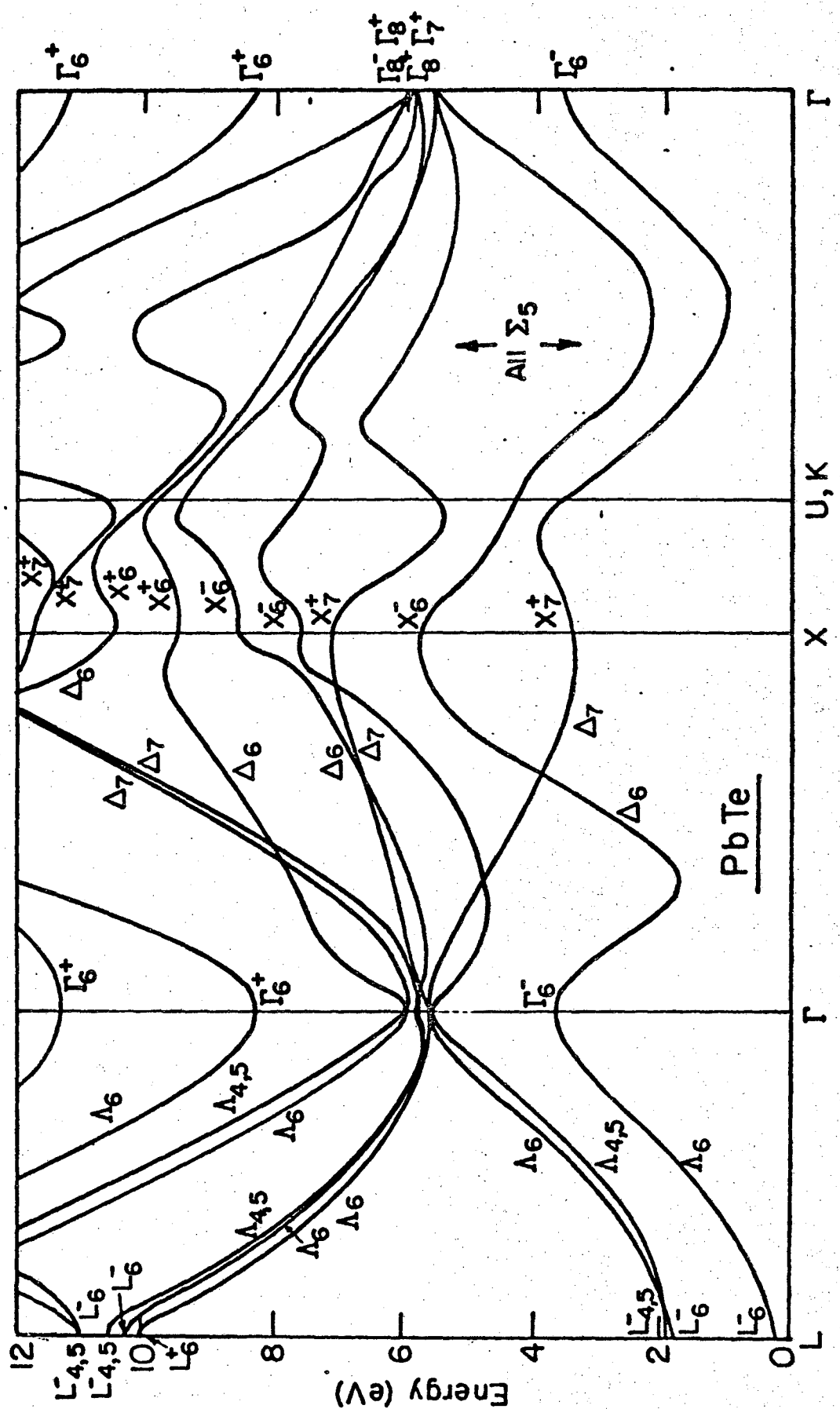

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Figure 3

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UNIVERSITY OF CALIFORNIA
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