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Electronic Energy Band Structure of SnS_2 and SnSe_2

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Abstract

The local empirical pseudopotential method is used to calculate the electronic band structure of SnS_2 and SnSe_2 . The pseudopotential form factors for the constituent elements, Sn, S, and Se are determined from previous pseudopotential calculations for other crystals. Slight adjustments were made to give the correct fundamental gaps. A group theoretical study of the symmetry properties of these crystals is included. The imaginary part of the dielectric function, $\epsilon_2(\omega)$, is calculated for SnS_2 . Some comparison is made between the theory and the existing experimental data.

I. Introduction

Compounds with layer structure show a wide range of electronic properties--from insulator to metal.¹ We concentrate here on two semiconducting tin chalcogenides, SnS_2 and SnSe_2 . The semiconducting characteristics of SnSe_2 was predicted by Mooser and Pearson.² This prediction was verified experimentally by Busch et al.³ and Asanabe⁴ from conductivity, Hall effect and thermoelectric measurements. The first reflectivity data was reported by Greenway and Nitsche⁵ in the range of 0.05 - 12.0 eV with polarization perpendicular to the \vec{c} -axis of the SnS_2 crystal. Their results give a shoulder at 3.8 eV and other structure at 4.9, 5.8, 6.9 and 7.6 eV. The indirect fundamental optical absorption edges were determined to be at 2.07 and 0.97 eV for SnS_2 and SnSe_2 respectively by Domingo et al.⁶ These authors also determined the forbidden direct gaps at 2.88 eV for SnS_2 and at 1.63 eV for SnSe_2 . Recently, Lee and Said⁷ measured the absorption coefficient

for SnSe_2 and determined the indirect energy gap at 1.03 eV.

The first energy band calculations for SnS_2 and SnSe_2 were reported by AuYang and Cohen.⁸ Their results have several errors. The group theory was done incorrectly resulting in errors both in the symmetry assignments and in the calculated band structures. This work supersedes reference 8. In the present work the band structures were calculated using methods similar to reference 8. Because the most reliable experimental data relate only to the fundamental energy gaps, we determine the pseudopotential form factors by making small adjustments in the extracted known form factors from other pseudopotential calculations to give the experimental values for the band gaps. The paper is arranged as follows: In Section II, we give a group theoretical analysis for the crystals. The method of calculation, the results, and comparisons with the experimental data are discussed in Section III.

II. Group Theoretical Analysis

The crystals, SnS_2 and SnSe_2 , crystallize in the CdI_2 type structure. The Bravais lattice of the structure is hexagonal. There is one molecule, e.g. CdI_2 , per primitive cell. If one chooses the origin of the cell at the Cd-atom, then the coordinates of the two I-atoms are given by $\pm \vec{u}$, where $\vec{u} = \left(\frac{a}{3}, \frac{2a}{3}, \frac{c}{4} \right)$. The first two components in \vec{u} are along two vectors \vec{a} and \vec{b} in the x-y plane placed 120° apart (Fig. 1), and the third component is along the vector \vec{c} in the \vec{z} -direction. a and c are the usual lattice constants for the hexagonal structure.

The point group associated with CdI_2 structure is D_{3d} .⁹ There are 12 symmetry operations which leave the crystal invariant. They are: the identity operator E , two three-fold rotations ($2C_3$) about the \vec{c} -axis, three two-fold

rotations ($3C_2'$) about the axes in the x-y plane and perpendicular to the sides of the hexagon (Fig. 1), the inversion operator i , two three-fold rotations about the \vec{c} -axis followed by an inversion ($2iC_3$), and three two-fold rotations followed by an inversion ($3iC_2'$). The last three operations are equivalent to $3\sigma_d$, the reflection in a "diagonal" plane¹⁰ (Fig. 1).

The first Brillouin zone of the hexagonal unit cell is also a hexagonal prism which is shown in Fig. 2b. The two shortest reciprocal lattice vectors \vec{A} and \vec{B} in the x-y plane determined from \vec{a} , \vec{b} and \vec{c} are shown in Fig. 2a. The small groups associated with symmetry points and symmetry lines of the BZ are discussed as follows: The group at Γ is obviously D_{3d} . One can easily show that A has the same symmetry properties at Γ . For example, in Fig. 2b, $\vec{\Gamma A}$ is transformed to $\vec{\Gamma A'}$ under inversion. However, the difference between $\vec{\Gamma A}$ and $\vec{\Gamma A'}$ is $\vec{AA'}$ which is a reciprocal lattice vector with length $2\pi/c$, $\vec{\Gamma A}$ and $\vec{\Gamma A'}$ are therefore equivalent. The symmetry operators associated with M and L are the identity operator, E; a two-fold rotation about an axis containing $\vec{\Gamma M}$, C_2 ; a reflection, σ_h , about plane containing $\vec{\Gamma A}$ and perpendicular to $\vec{\Gamma M}$; and the inversion operator, i . The group associated with these two points is C_{2h} .¹¹ Points K and H have the same symmetry operators as Γ and A except for the operators involving i , the inversion operator. They are associated with the group D_3 . Vectors along the lines Σ , R and U are invariant under the identity operator E, and σ_h defined for points M and L. These two operators form a group C_{1h} . The group associated with vectors along Δ is C_{3v} . Finally, T' and S' belong to C_2 . A summary of the groups for various

symmetry points and symmetry lines is listed in Table I. The character tables for two important small groups at $\Gamma(A)$ and $M(L)$ and the compatibility relations are given in Table II.

To study the optical properties of these two crystals, one has to measure the spectra by polarizing the incident light along and perpendicular to the \vec{c} -axis. The selection rules for the optical transitions are calculated for these two different polarizations. We give our results in Table III.

III. Calculations and Results

The method of calculation has been described elsewhere.⁸ We just give a few important expressions to define the form factors.

The local pseudopotential Hamiltonian neglecting spin-orbit interaction has the form

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) . \quad (1)$$

The weak pseudopotential $V(\vec{r})$ is expanded in the reciprocal lattice

$$V(\vec{r}) = \sum_{\vec{G}} V(\vec{G}) e^{i\vec{G} \cdot \vec{r}} \quad (2)$$

and

$$V(\vec{G}) = \frac{1}{\Omega_{\text{cell}}} \int_{\text{cell}} V(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} d^3 r = \frac{1}{\Omega_{\text{cell}}} \left[\Omega_{\text{Sn}} V^{\text{Sn}}(\vec{G}) + \right. \quad (3)$$

$$\left. + 2\Omega_{\text{S}} V^{\text{S}}(\vec{G}) \cos(\vec{G} \cdot \vec{u}) \right]$$

where Ω_{cell} is the unit cell volume of the crystal under consideration.

Ω_{Sn} and Ω_{S} are volumes per atom in SnS_2 . We truncate the expansion in \vec{G} at

$|\vec{G}_{\max}|^2 = \frac{59}{4} \left(\frac{2\pi}{a} \right)^2$. This limits the expansion to 16 nonvanishing pseudopotential form factors for Sn and 15 for S. Equation (1) is then solved by expanding the periodic part of the Bloch state in plane waves. The cutoff energies as defined in reference 12 are $E_1 = 9.1$ and $E_2 = 25.1$, which give the convergence of energy gaps at Γ , M and L to the order of 0.1 eV. The size of the matrix is about 55×55 . There are roughly 190 plane waves contributing to the Löwdin perturbation scheme as modified by Brust.¹³ Because of the fact that the best known data for these two compounds are the forbidden indirect and direct energy gaps, we simply adjust (slightly) the scaled potentials of Sn, S and Se from other calculations as discussed in reference 8 to fit these experimental data. The comparison of the resulting elemental pseudopotential form factors from the present calculations and the extracted ones from other calculations are shown in Fig. 3. The form factors are normalized to the following volumes: 67.50 \AA^3 for Sn and S; and 76.67 \AA^3 for Se. The pseudopotential form factors are given in Table IV. The $|\vec{G}|^2$'s are in units of $\left(\frac{2\pi}{a_{\text{ZB}}} \right)^2$, where $a_{\text{ZB}} = \sqrt{2}a$. We use the form factors obtained by Animalu and Heine¹⁴ for Sn, because their results give the form factors at large $|\vec{G}|$. For S and Se, we compare the results of present calculations with the results obtained by Cohen and Bergstresser¹² (CB) and Walter and Cohen¹⁵ (WC).

The symmetry properties of crystals of the CdI_2 structure allow us to diagonalize the pseudopotential Hamiltonian on a mesh which is $\frac{1}{12}$ of the Brillouin zone. The total number of points in the mesh is 225. The band structure along symmetry lines are plotted in Fig. 4a and Fig. 4b for SnS_2 and SnSe_2 respectively. There are three points for SnS_2 along U such that

the lowest conduction band energies are 0.2 eV less than the corresponding value at L. If this were the case, then the indirect fundamental transition would be an allowed transition. This is not consistent with the experimental results.⁶ Furthermore, it is very difficult to push up the lowest conduction band along U by changing the form factors. We use a technique discussed by Cahn and Cohen¹⁶ to calculate the lowest conduction band energy at these points by using $m^* = 0.98 m$. In SnSe_2 , there are two points which cause the same difficulty. It is resolved by the same method.

These band structure calculations are considered to be preliminary because of a lack of sufficient experimental data, especially for SnSe_2 . Therefore, we calculate the $\epsilon_2(\omega)$, the imaginary part of the dielectric function, for SnS_2 only. Using the results of the energy band structure calculation, we evaluate $\epsilon_2(\omega)$ by

$$\epsilon_{2\parallel}(\omega) = \frac{4\pi^2 e^2 \hbar}{m^2 \omega^2} \sum_{\vec{k}} \sum_{c,v} |\langle u_{c,\vec{k}} | \nabla_{\parallel} | u_{v,\vec{k}} \rangle|^2 \delta(\omega_{cv} - \omega) \quad (4)$$

$$\epsilon_{2\perp}(\omega) = \frac{4\pi^2 e^2 \hbar}{2m^2 \omega^2} \sum_{\vec{k}} \sum_{c,v} |\langle u_{c,\vec{k}} | \nabla_{\perp} | u_{v,\vec{k}} \rangle|^2 \delta(\omega_{cv} - \omega) \quad (5)$$

where $\epsilon_{2\parallel}$ and $\epsilon_{2\perp}$ are $\epsilon_2(\omega)$ with light polarized parallel and perpendicular to the \vec{c} -axis. $u_{c,\vec{k}}$ and $u_{v,\vec{k}}$ denote the periodic part of the conduction band and valence band pseudowavefunctions at \vec{k} . ∇_{\parallel} and ∇_{\perp} are the gradient operators parallel and perpendicular to the \vec{c} -axis. The results for $\epsilon_{2\parallel}(\omega)$ and $\epsilon_{2\perp}(\omega)$ are plotted in Fig. 5.

The fundamental gap is indirect and forbidden for both compounds. The experimental values⁶ are 2.07 and 0.97 eV for SnS₂ and SnSe₂ respectively; the corresponding values from the calculations are 2.19 and 0.91 eV. Both these transitions are from Γ to L, and are forbidden transitions. The calculated lowest direct gaps for SnS₂ and SnSe₂ are 3.15 and 1.75 eV. They occur at M and are forbidden by parity. The forbidden direct gaps measured by Domingo *et al.*⁶ are 2.88 (SnS₂) and 1.62 eV (SnSe₂). The theoretical and experimental results for the lowest energy gaps therefore agree quite well. A summary is given in Table V. The structures in $\epsilon_{21}(\omega)$ occur at 3.9, 4.8, 5.4, 5.8, and 6.8 eV. They correlate quite well with the experimental reflectivity⁵ curve with structure at 3.8, 4.9, 5.8, and 6.9 eV. There is no experimental optical data for SnS₂ with light polarized along the \vec{c} -axis. We summarize the structure in $\epsilon_2(\omega)$ and the measured reflectivity in Table VI.

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Figure Captions

- Figure 1 The primitive translation vectors, \vec{a} and \vec{b} , and some of the symmetry operations of the crystal in the x-y plane.
- Figure 2a The two shortest reciprocal lattice vectors \vec{A} and \vec{B} in the x-y plane.
- Figure 2b The first Brillouin zone for CdI₂ structure.
- Figure 3a Comparison of pseudopotential form factors for Sn. AH is Ref. 14.
- Figure 3b Comparison of pseudopotential form factors for S. WC is Ref. 15.
CB is Ref. 12.
- Figure 3c Comparison of pseudopotential form factors for Se. WC is Ref. 15.
CB is Ref. 12.
- Figure 4a Band structure of SnS₂.
- Figure 4b Band structure of SnSe₂.
- Figure 5 Calculated $\epsilon_2(\omega)$ for SnS₂.

Table Captions

- Table I Small groups associated with various symmetry points and symmetry lines in the Brillouin zone.
- Table IIA Character tables for groups D_{3d} and C_{2h} .
- Table IIB Compatibility relations for various symmetry points in the Brillouin zone.
- Table III Selection rules for allowed transitions.
- Table IV Pseudopotential form factors in Ryd.
- Table V Summary of fundamental energy gaps for SnS_2 and $SnSe_2$.
- Table VI Summary of main structure in the calculated $\epsilon_{21}(\omega)$ for SnS_2 and the measured reflectivity.

Table I

Symmetry points and lines	$\Gamma, A,$	K, H	Δ	M, L	Σ, R, U	T', S'
Group	D_{3d}	D_3	C_{3v}	C_{2h}	C_{1h}	C_2

Table IIA

D_{3d}		E	$2C_3$	$3C_2'$	i	$2iC_3$	$3iC_2' = 3\sigma_d$
	Γ_1	1	1	1	1	1	1
	Γ_2	1	1	-1	1	1	-1
	Γ_3	2	-1	0	2	-1	0
	$\Gamma_{1'}$	1	1	1	-1	-1	-1
z	$\Gamma_{2'}$	1	1	-1	-1	-1	1
x,y	$\Gamma_{3'}$	2	-1	0	-2	1	0

C_{2h}		E	C_2	σ_h	i
	M_1	1	1	1	1
z	$M_{1'}$	1	1	-1	-1
	M_2	1	1	-1	1
x,y	$M_{2'}$	1	-1	1	-1

Table IIB

$\Gamma(A)$			
$\Gamma_1(A_1)$	Δ_1	$\Sigma_1(R_1)$	$T_1(S_1)$
$\Gamma_2(A_2)$	Δ_2	$\Sigma_2(R_2)$	$T_2(S_2)$
$\Gamma_1'(A_1')$	Δ_2	$\Sigma_2(R_2)$	$T_1(S_1)$
$\Gamma_2'(A_2')$	Δ_1	$\Sigma_1(R_1)$	$T_2(S_2)$
$\Gamma_3, \Gamma_3'(A_3, A_3')$	Δ_3	$\Sigma_1 + \Sigma_2 (R_1 + R_2)$	$T_1 + T_2 (S_1 + S_2)$

$M(L)$			
$M_1(L_1)$	U_1	$\Sigma_1(R_1)$	$T_1'(S_1')$
$M_1'(L_1')$	U_2	$\Sigma_2(R_2)$	$T_1'(S_1')$
$M_2(L_2)$	U_2	$\Sigma_2(R_2)$	$T_2'(S_2')$
$M_2'(L_2')$	U_1	$\Sigma_1(R_1)$	$T_2'(S_2')$

$K(H)$			
$K_1(H_1)$	P_1	$T_1(S_1)$	$T_1'(S_1')$
$K_2(H_2)$	P_1	$T_2(S_2)$	$T_2'(S_2')$
$K_3(H_3)$	P_3	$T_1 + T_2 (S_1 + S_2)$	$T_1' + T_2' (S_1' + S_2')$

Table III

Perpendicular polarizations:

$$\begin{aligned}
 & \Gamma_1(A_1) \leftrightarrow \Gamma_{3'}(A_{3'}) , \quad \Gamma_2(A_2) \leftrightarrow \Gamma_{1'}(A_{1'}) , \quad \Gamma_{2'}(A_{2'}) \leftrightarrow \Gamma_3(A_3) , \\
 & \Gamma_3(A_3) \leftrightarrow \Gamma_{3'}(A_{3'}) . \\
 & M_1(L_1) \leftrightarrow M_{2'}(L_{2'}) , \quad M_{1'}(L_{1'}) \leftrightarrow M_2(L_2) . \\
 & \Delta_1 \leftrightarrow \Delta_{3'} , \quad \Delta_3 \leftrightarrow \Delta_{3'} . \\
 & P_1 \leftrightarrow P_3 . \\
 & K_1(H_1) \leftrightarrow K_3(H_3) , \quad K_3(H_3) \leftrightarrow K_{3'}(H_{3'}) , \quad K_{3'}(H_{3'}) \leftrightarrow K_3(H_3) . \\
 & \Sigma_1(U_1) \leftrightarrow \Sigma_1(U_1) , \quad \Sigma_2(U_2) \leftrightarrow \Sigma_2(U_2) .
 \end{aligned}$$

Parallel polarizations:

$$\begin{aligned}
 & \Gamma_1(A_1) \leftrightarrow \Gamma_{2'}(A_{2'}) , \quad \Gamma_{1'}(A_{1'}) \leftrightarrow \Gamma_3(A_3) , \quad \Gamma_3(A_3) \leftrightarrow \Gamma_{3'}(A_{3'}) . \\
 & M_1(L_1) \leftrightarrow M_{1'}(L_{1'}) , \quad M_2(L_2) \leftrightarrow M_{2'}(L_{2'}) . \\
 & \Delta_1 \leftrightarrow \Delta_1 , \quad \Delta_3 \leftrightarrow \Delta_3 . \\
 & P_1 \leftrightarrow P_1 , \quad P_3 \leftrightarrow P_3 . \\
 & K_1(H_1) \leftrightarrow K_3(H_3) , \quad K_{3'}(H_{3'}) \leftrightarrow K_{3'}(H_{3'}) . \\
 & \Sigma_1(U_1) \leftrightarrow \Sigma_2(U_2) .
 \end{aligned}$$

Table IV

\vec{G}	SnS ₂		SnSe ₂	
	V _{Sn} [*] (Ryd.)	V _S (Ryd.)	V _{Sn} (Ryd.)	V _{Se} (Ryd.)
(001)	-0.117		-0.0985	
(100)	- .0362	- .126	- .048	- .125
(002)	- .0208	- .0987	- .0386	- .086
(101)	- .0185	- .081	- .0358	- .071
(102)	.0181	- .0237	.0096	- .0338
(003)	.0247	- .0088	.0173	- .0098
(210)	.0322	.0019	.0222	.0018
(211)	.0318	.0091	.0222	.0098
(103)	.0294	.0146	.0251	.0124
(200)	.0273	.019	.0236	.0153
(212)	.0265	.0205	.0236	.0167
(201)	.0261	.0217	.0229	.0178
(004)	.0241	.0225	.0214	.0178
(202)	.0193	.0201	.0185	.015
(104)	.0145	.0158	.0159	.0132
(213)	.0145	.0158	.0159	.0132

* All V's normalized to the respective unit hexagonal cell volume.

Table V

Optical Transitions	Material	Domingo et al ⁶ (exp)	Lee and Said ⁷	Fong-Cohen
Forbidden Indirect Transitions	SnS ₂	2.07 eV		2.19 eV (Γ _{1'} →L ₁)
	SnSe ₂	0.97	1.03 eV	0.91 (Γ _{1'} →L ₁)
Forbidden Indirect Transitions	SnS ₂	2.88		3.15 (M ₂ →M ₁)
	SnSe ₂	1.62		1.75 (M ₂ →M ₁)

Table VI

Structure in Reflectivity	Structure in $\epsilon_{21}(\omega)$	Identification Main Transitions
3.8 eV	3.9 eV	$M_0 \Gamma_3' \rightarrow \Gamma_1$
	4.0	Volume effect 7→9, 8→9
4.9	4.9	Volume effect 6→9, 7→9, 8→9
	5.4	6→9, 7→9, 7→10, 8→10
5.8	5.7	6→9, 7→9, 7→10, 8→10
6.9	6.8	6→10, 7→10, 8→10, 7→11, 8→11

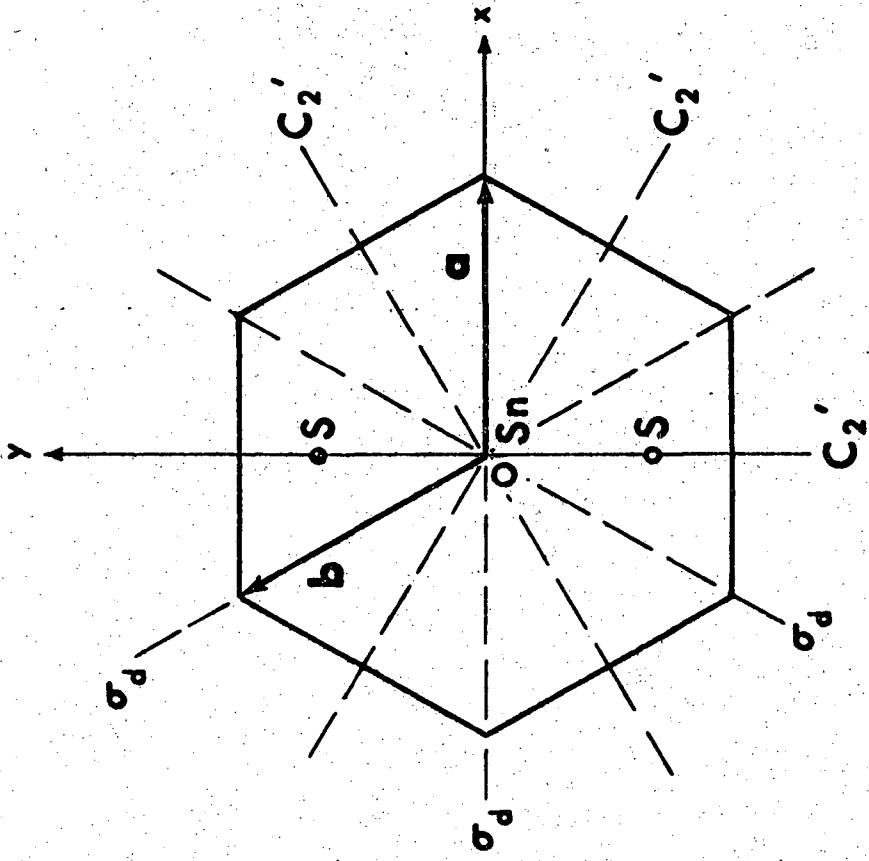
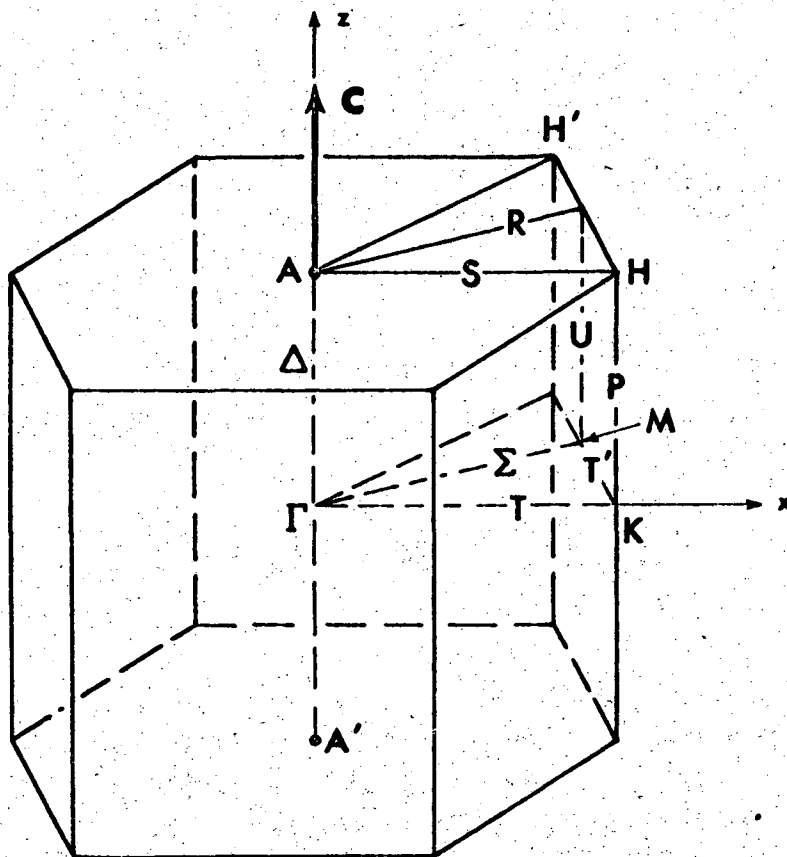
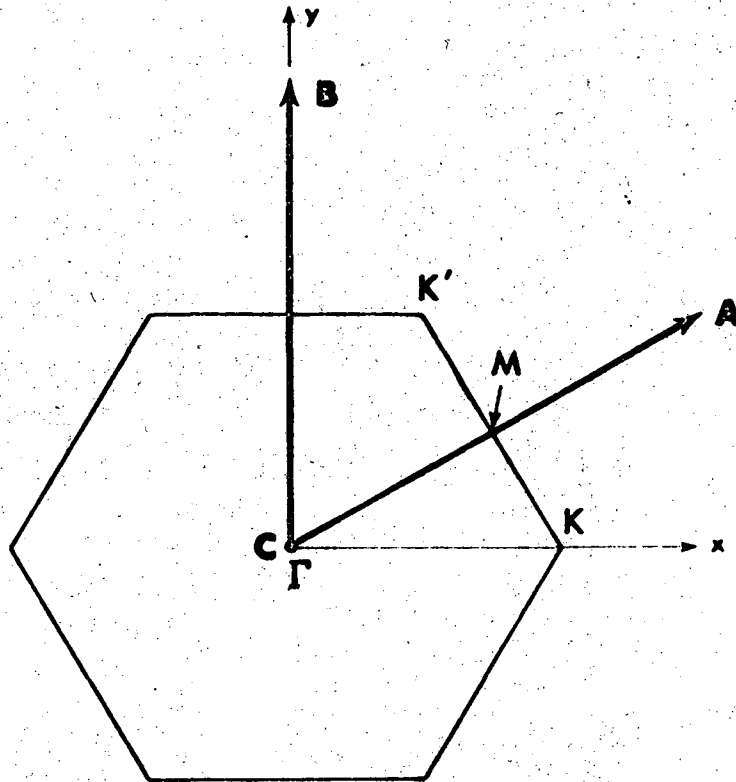


Figure 1



Figures 2a and 2b

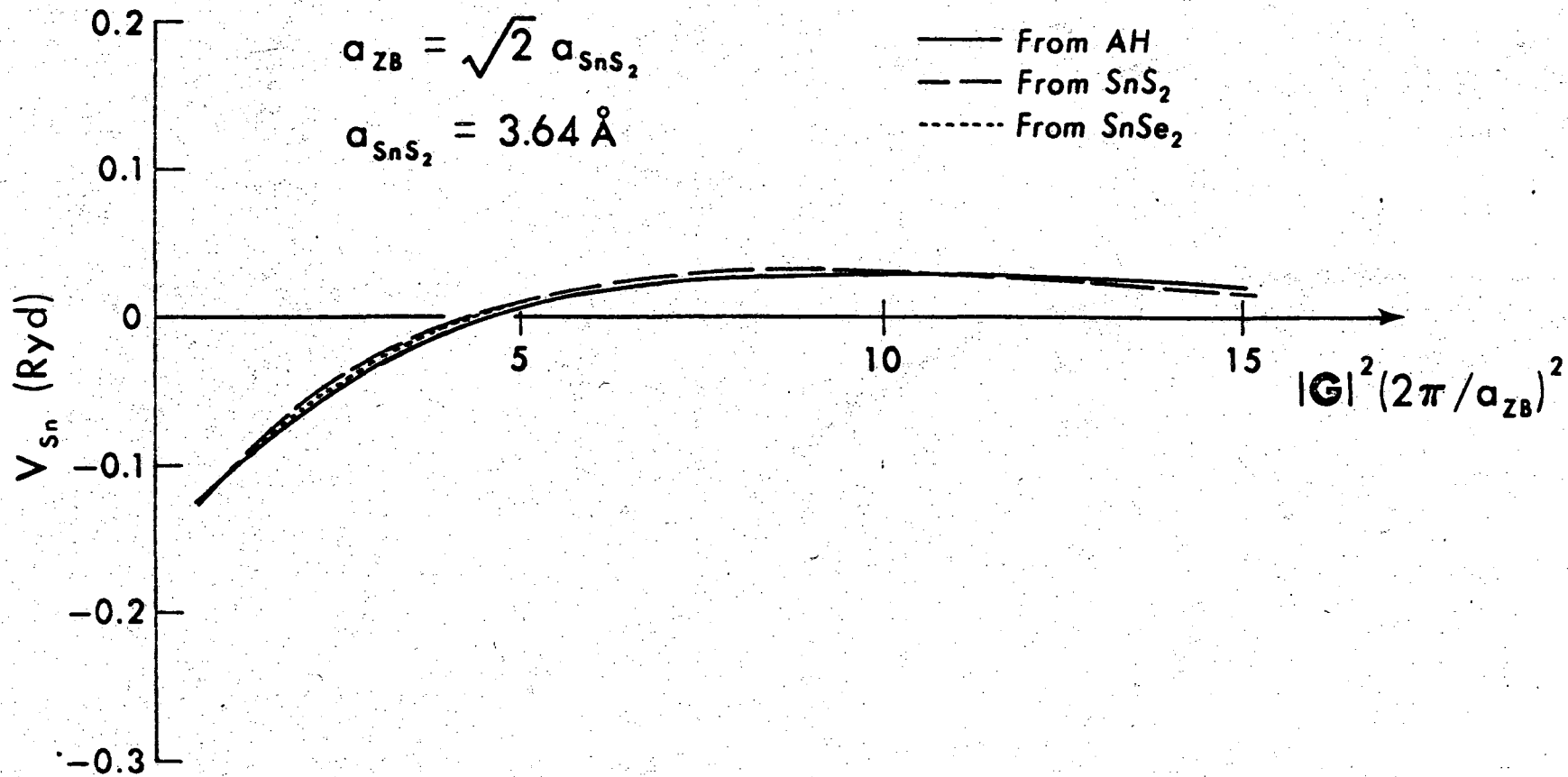


Figure 3a

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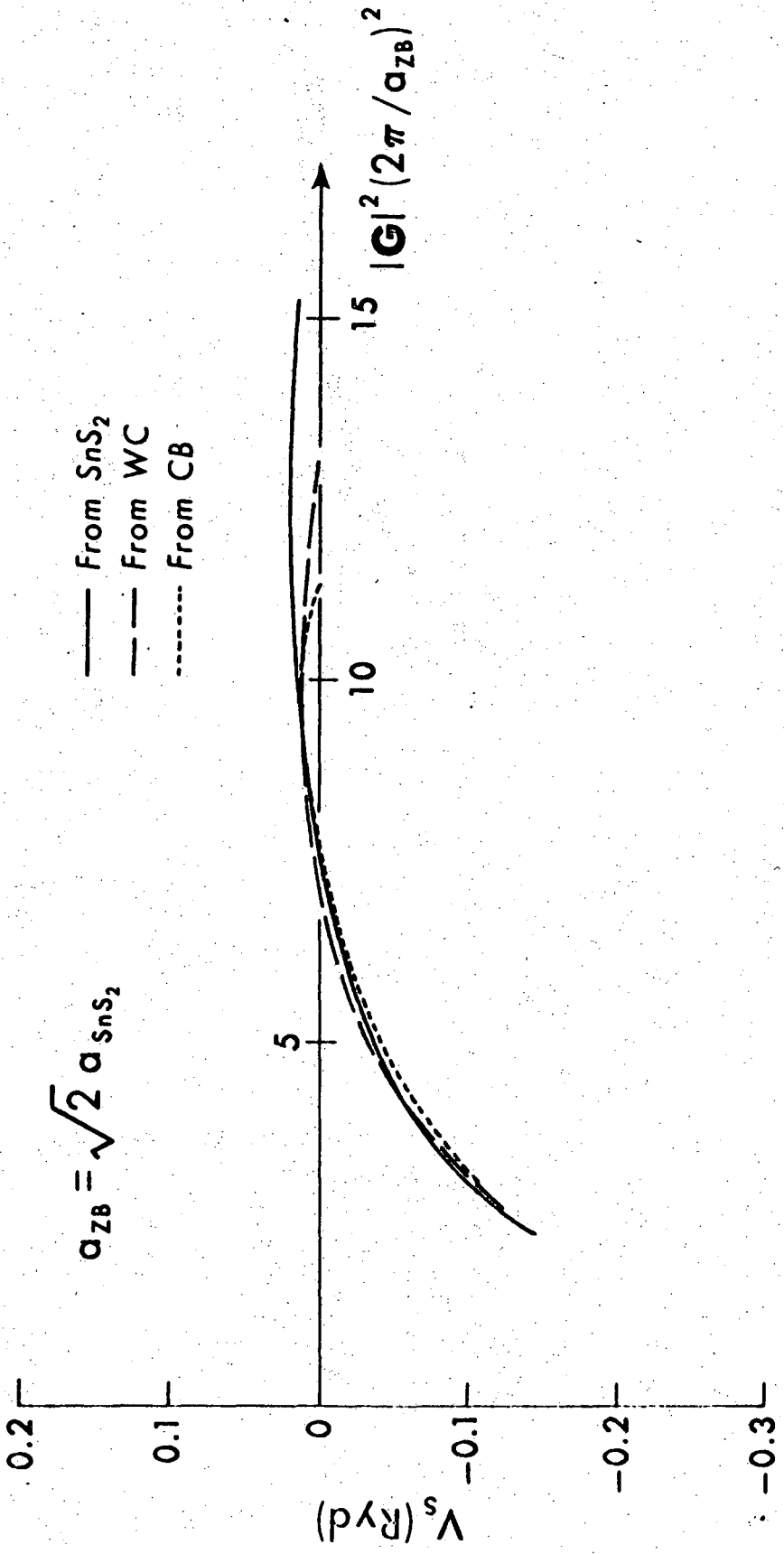


Figure 3b

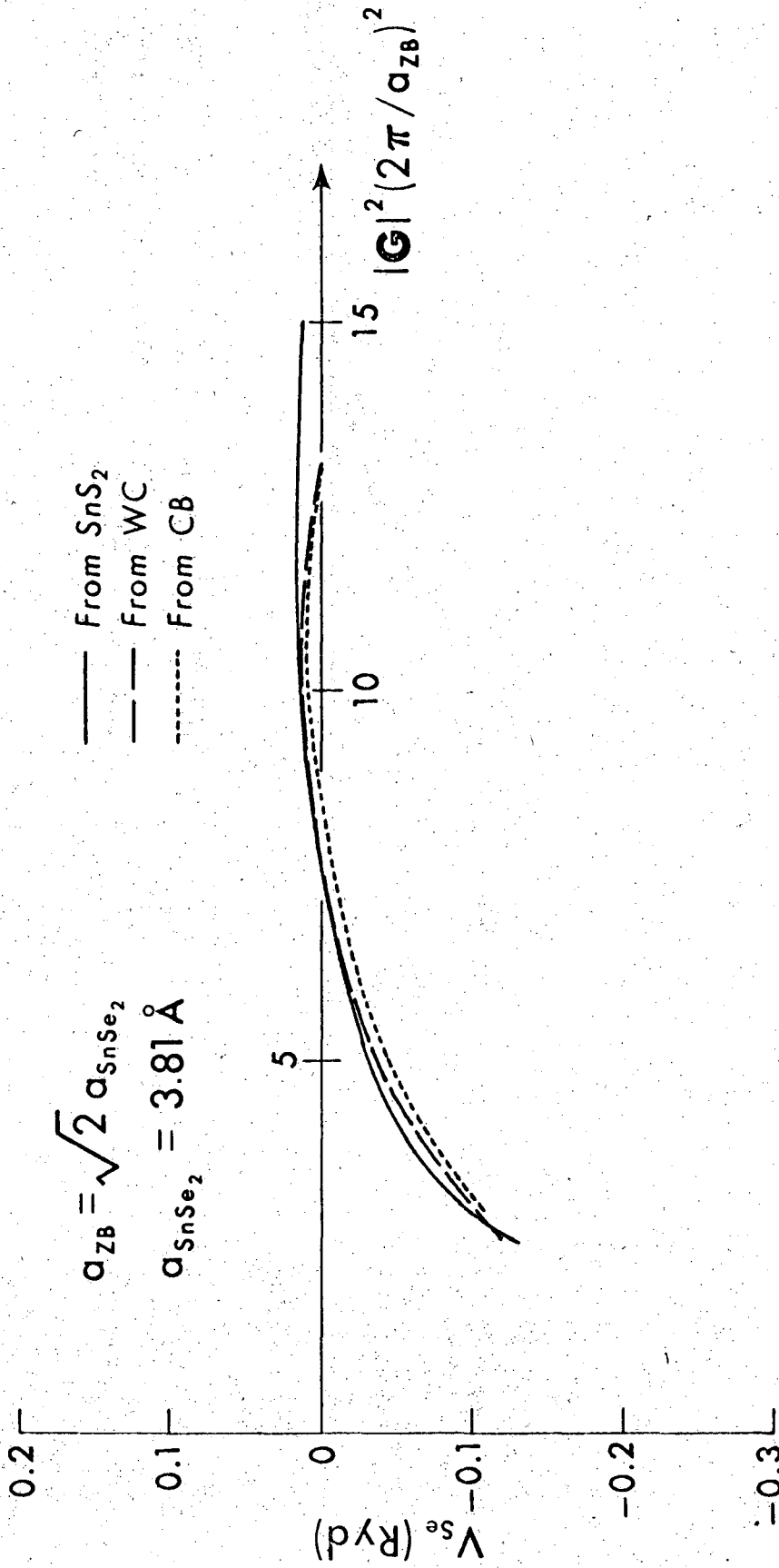


Figure 3c

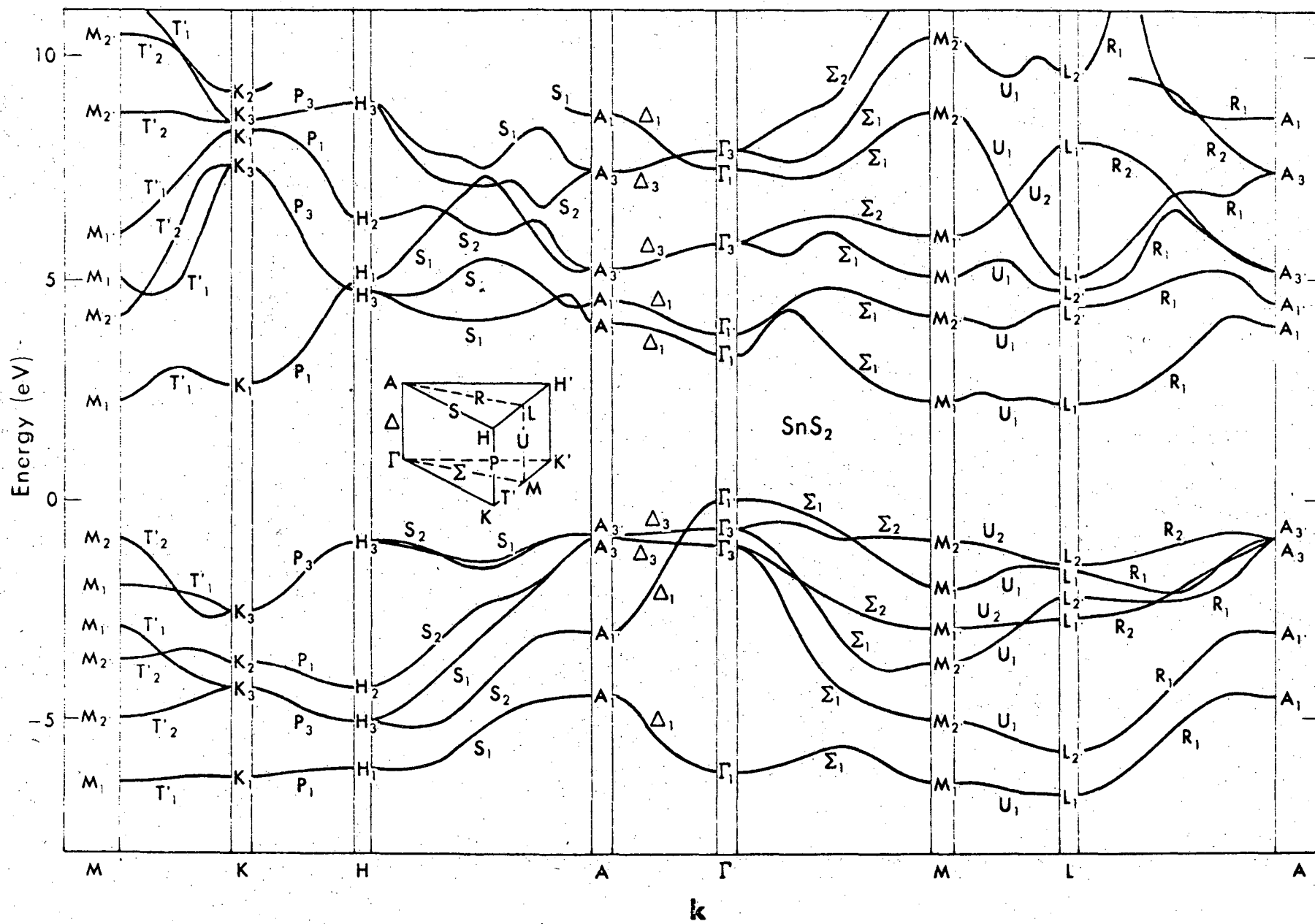


Figure 4a

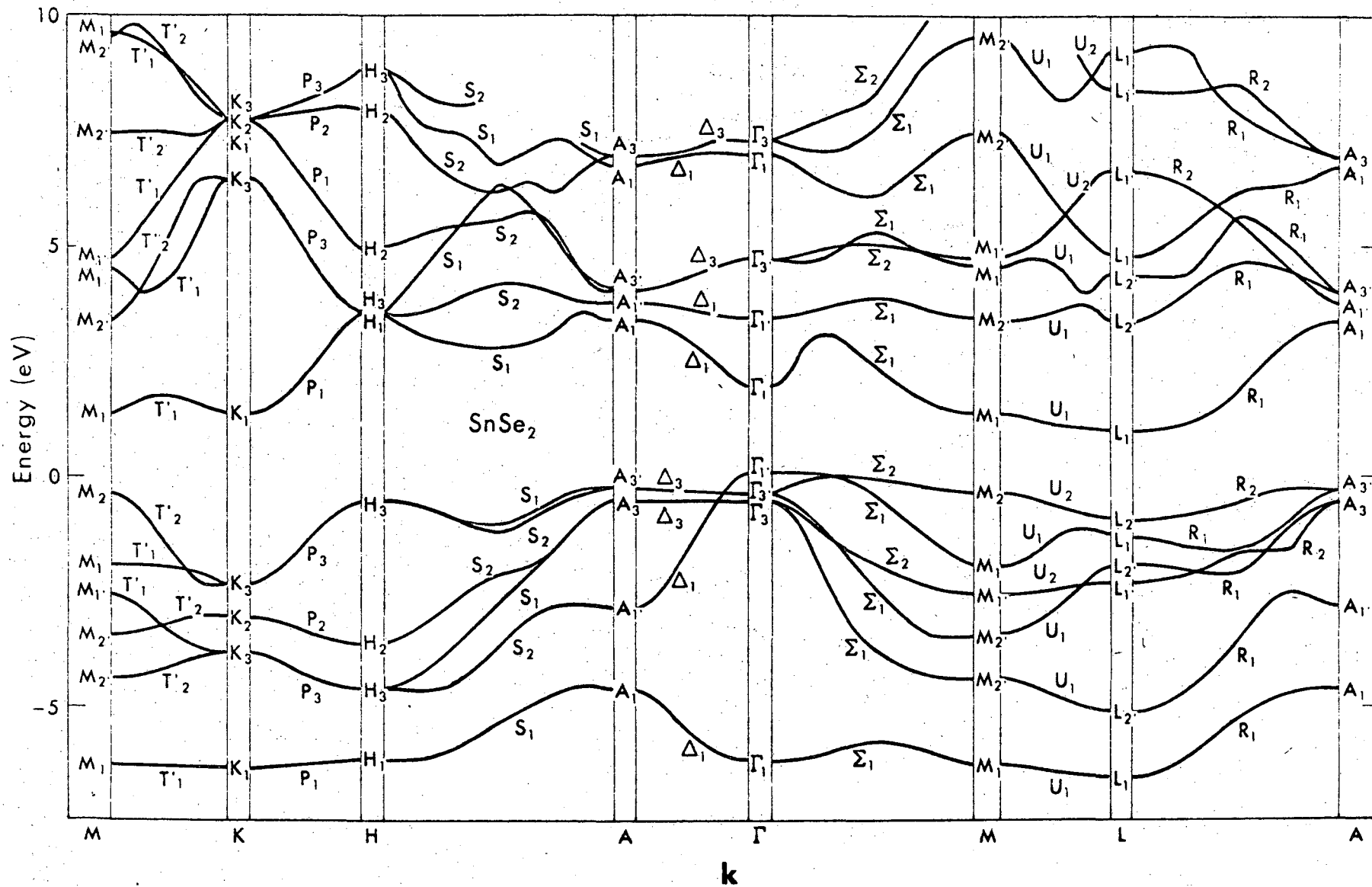


Figure 4b

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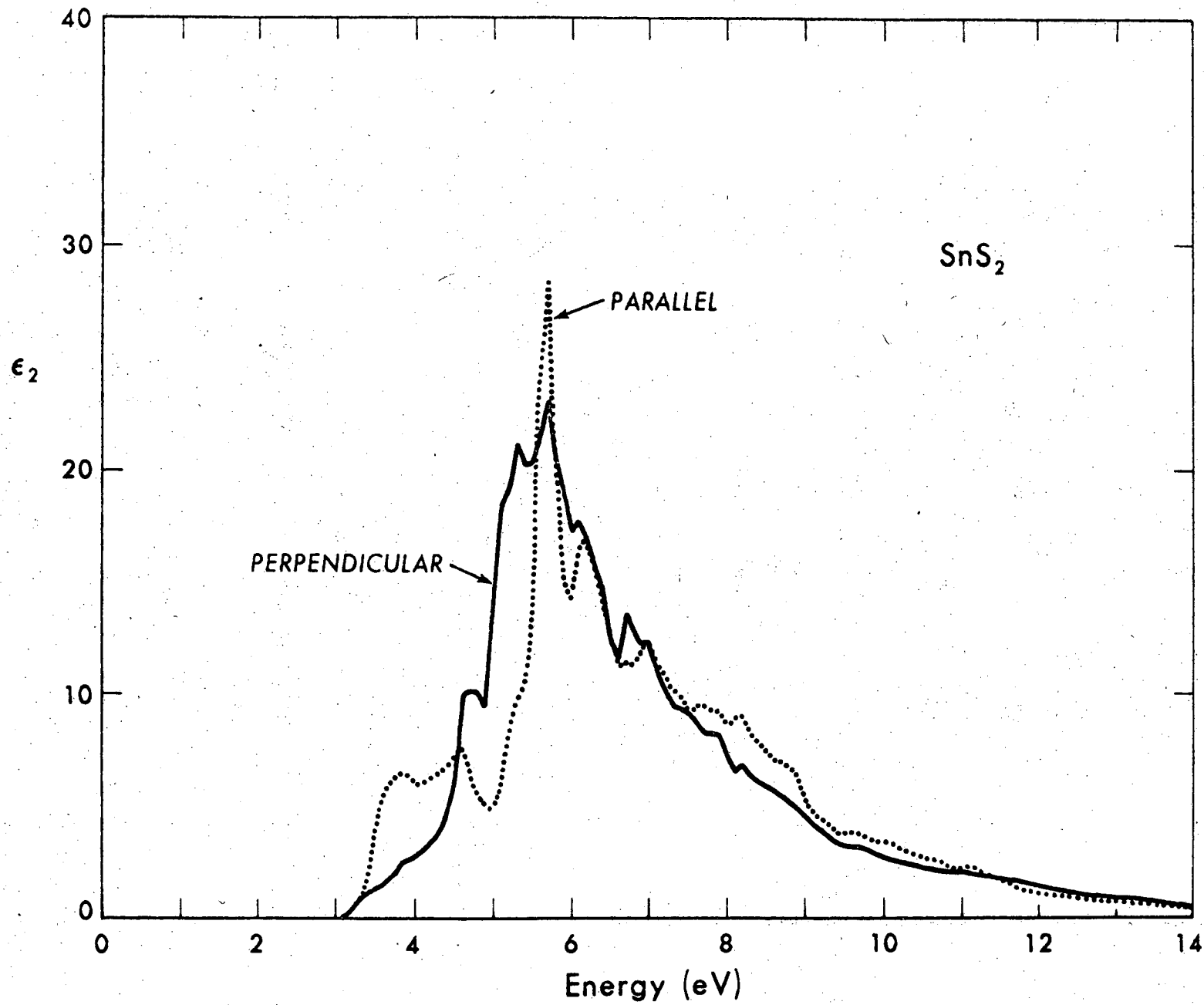


Figure 5

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