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PSEUDOPOTENTIAL BAND STRUCTURE OF SOLID SOLUTIONS SnS_xSe_{2-x} †*

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ABSTRACT

A very satisfying agreement with the experimental optical data is obtained from a priori pseudopotential calculations for SnS_xSe_{2-x} solid solutions. The band structure of $SnSe_2$ is also computed and previous results for SnS_2 are improved.

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The electronic band structure of SnS_2 has recently been calculated by Fong and Cohen[1] and by Mula and Aymerich[2]. Fong and Cohen[1] also evaluated the electronic band structure of $SnSe_2$. Both papers make use of the pseudopotential method, the main difference between them being the approach used to evaluate the ionic form factors. The choice between the a priori method[3),4)] used by Mula and Aymerich and the empirical method used by Fong and Cohen could be regarded essentially as a matter of taste, both methods giving quite satisfactory answers to the experimental results; however, a substantial difference comes out when one computes the band structure of a solid solution. In fact, the a priori approach introduces in a natural way the non-linear variation of the pseudopotential with respect to the composition and allows, therefore, a reliable interpretation of the behaviour of the physical properties. In the present paper we shall exploit this feature to analyse the optical properties of solid solutions SnS_xSe_{2-x}.

We recall now that, in the first application of the a priori version of the pseudopotential method to a solid solution, Jones and Lettington[4] used as pseudopotential form factors those obtained by renormalizing the dielectric screening of the model potential of Heine and Abarenkov[5], by means of a Penn-type dielectric function.

We use here a slightly different approach to determine the ionic form factors. In the last few years, in fact, a number of E.P.M. calculations[6] were successfully performed on several materials and a number of data for the pseudopotentials of many elements are now available. Looking at these results we built up our curves for the form factors of Sn, S, and Se by graphical interpolation of existing data (the model potentials included) which were made comparable by proper volume and dielectric function renormalization.

In Fig.1 we report the form factors of S, and of Se normalized to the dielectric constant and the atomic volume of cubic zinc sulphide and cubic zinc selenide, respectively. The form factors of Sn normalized to the volume and the dielectric constant of grey tin are given in Fig.1 of Ref.3.

The a priori version of the pseudopotential method in the virtual crystal approximation gives the following expression of the one-electron potential in the unit cell of the solid solution SnS_xSe_{2-x}:

$$V(q)^{sol_x} = \frac{1}{\varepsilon_{sol_x}(q)\,\Omega_{sol_x}} \left\{ \begin{matrix} \text{Grey tin} \\ \varepsilon(q) \end{matrix} \begin{matrix} \text{Grey tin} \\ \Omega_0 \end{matrix} \begin{matrix} \text{Sn} \\ S(\underline{q}) \end{matrix} \begin{matrix} \text{Sn} \\ F(q) \end{matrix} + \begin{matrix} \text{S,Se} \\ S(\underline{q}) \end{matrix} \times \right.$$

$$\left. \times \left[x \begin{matrix} \text{ZnS} \\ \varepsilon(q) \end{matrix} \begin{matrix} \text{ZnS} \\ \Omega_0 \end{matrix} \begin{matrix} \text{S} \\ F(q) \end{matrix} + (2-x) \begin{matrix} \text{ZnSe} \\ \varepsilon(q) \end{matrix} \begin{matrix} \text{ZnSe} \\ \Omega_0 \end{matrix} \begin{matrix} \text{Se} \\ F(q) \end{matrix} \right] \right\} . \qquad (1)$$

In expression (1) q depends on the composition via the lattice constant which is taken as varying linearly with x. Ω_{sol_x} is the volume of the unit cell of the solution SnS_xSe_{2-x}. Ω_0^A is the atomic volume of the semiconductor A.

By diagonalization of the pseudohamiltonian (we took $E_1 = 3.8$, $E_2 = 8.0$) we obtained the band structure of our solutions for several values of x.

In Fig.2 we report our results for the transitions $\Gamma_4 - \Gamma_1$, $\Gamma_4 - L_1$, $\Gamma_4 - M_1$, which are the lowest ones for the whole range of composition of the solution. As we can see from Fig.2, the energies of these transitions change non-linearly with x as a consequence of non-linear variation of the potential. In the same figure we report the lowest gap determined from the transmission measurements performed by Lee, Said, Davis and Lim[7]. The excellent agreement of our results with the experimental data goes further if one looks at the details of the experiment. For the entire range of composition the absorption coefficient of the solid solutions SnS_xSe_{2-x} shows the same feature of the absorption coefficient of SnS_2. We suggest that the contribution of more than one transition, which explains the behaviour of the fundamental edge of SnS_2,[2] is the mechanism which determines the absorption curves of the solutions SnS_xSe_{2-x} for each x value.

For the sake of completeness we report in Fig.3 the band structure of $SnSe_2$ along some symmetry directions.

In conclusion, we can say that the overall agreement with the experimental results shown by our calculations is a very strong evidence of the validity of our approach of evaluating the ionic form factors. As a consequence, we are very confident that the model proposed by Mula and Aymerich[2] to explain the behaviour of the fundamental edge of

SnS_2 is the most reliable one, and it applies to the solid solution SnS_xSe_{2-x} and to $SnSe_2$ as well. No definite conclusion can be reached, on the other hand, for the higher transitions because of the absence of experimental measurements of reflectivity both with parallel and perpendicular polarization of light with respect to the c-axis.

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FIGURE CAPTIONS

Figure 1

Part (a) Full line: form factors of S .
Stars: empirical form factors from Ref.8 and Ref.9.
Squares: empirical form factors from Ref.10.

Part (b) Full line: form factors of Se .
Stars: empirical form factors from Ref.8 and Ref.9.
Broken line: model potential of Heine and Abarenkov renormalized to ZnSe (see text).

Figure 2

Full lines: lowest energy gaps of solid solutions SnS_xSe_{2-x} versus composition x .
Stars: experimental data of Ref.7.

Figure 3

Band structure of $SnSe_2$.

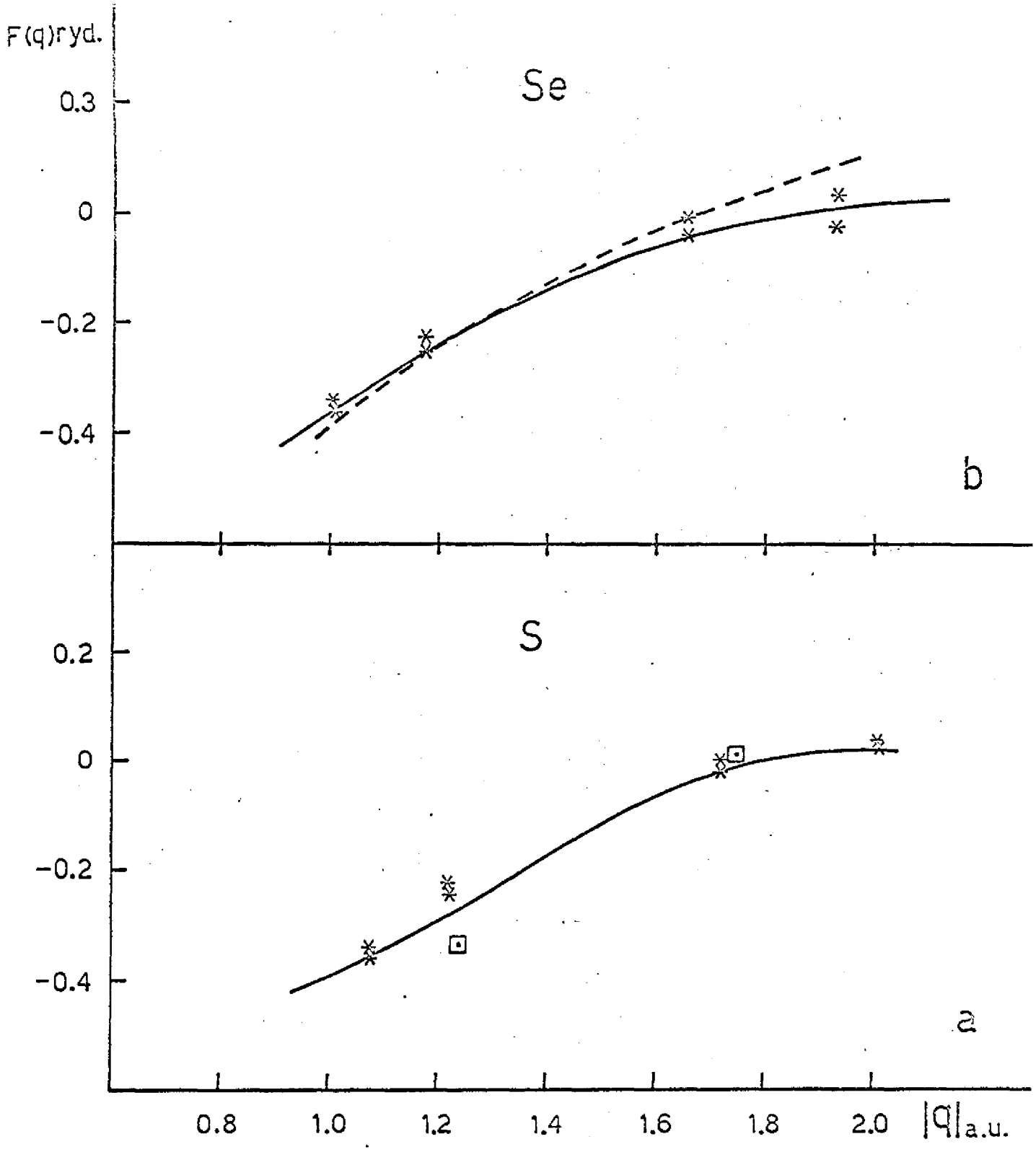

FIG 1

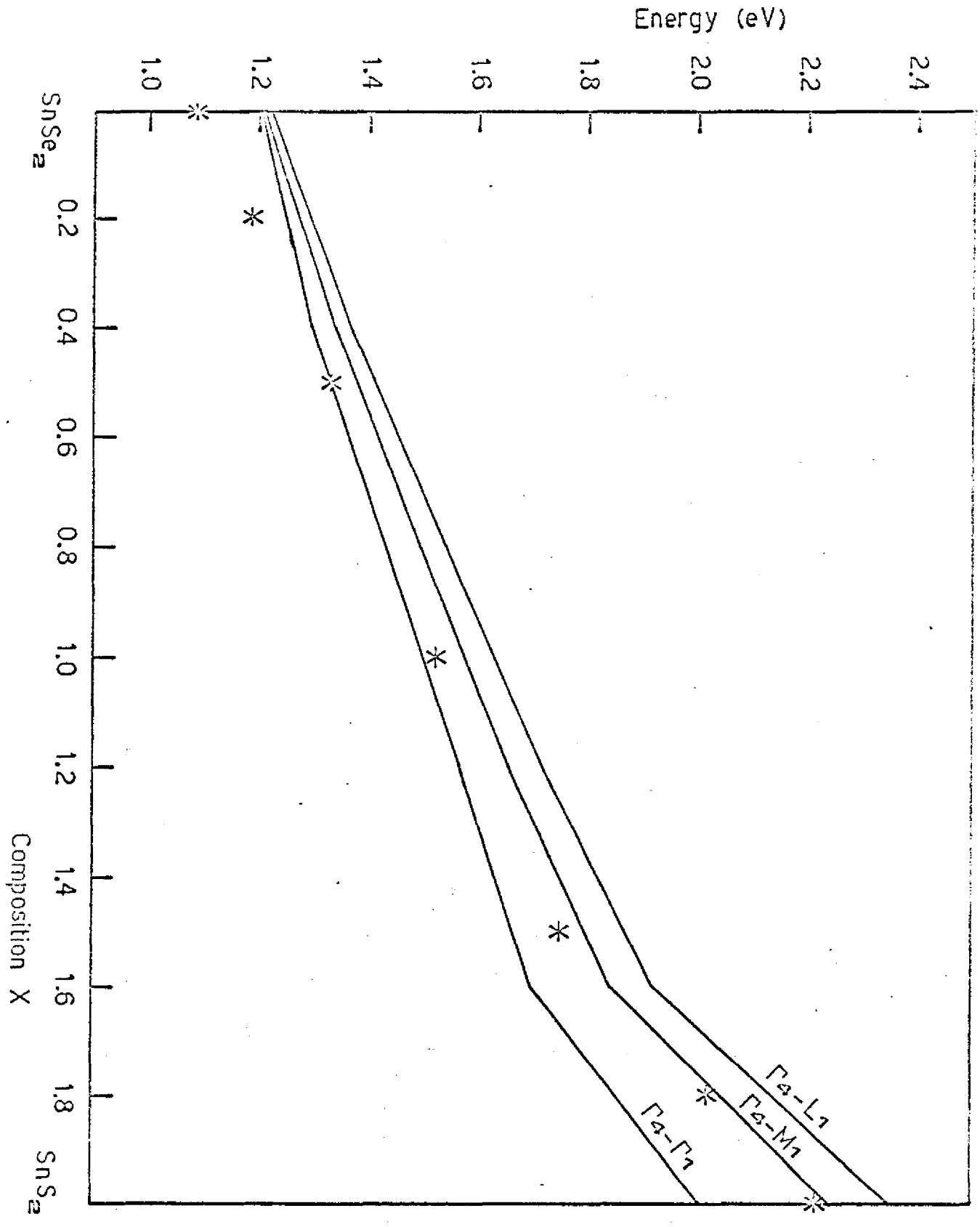
Energy (eV)
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
SnSe2
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
SnS2
Composition X
Γ4-L1
Γ4-M1
Γ4-Γ1

FIG. 2

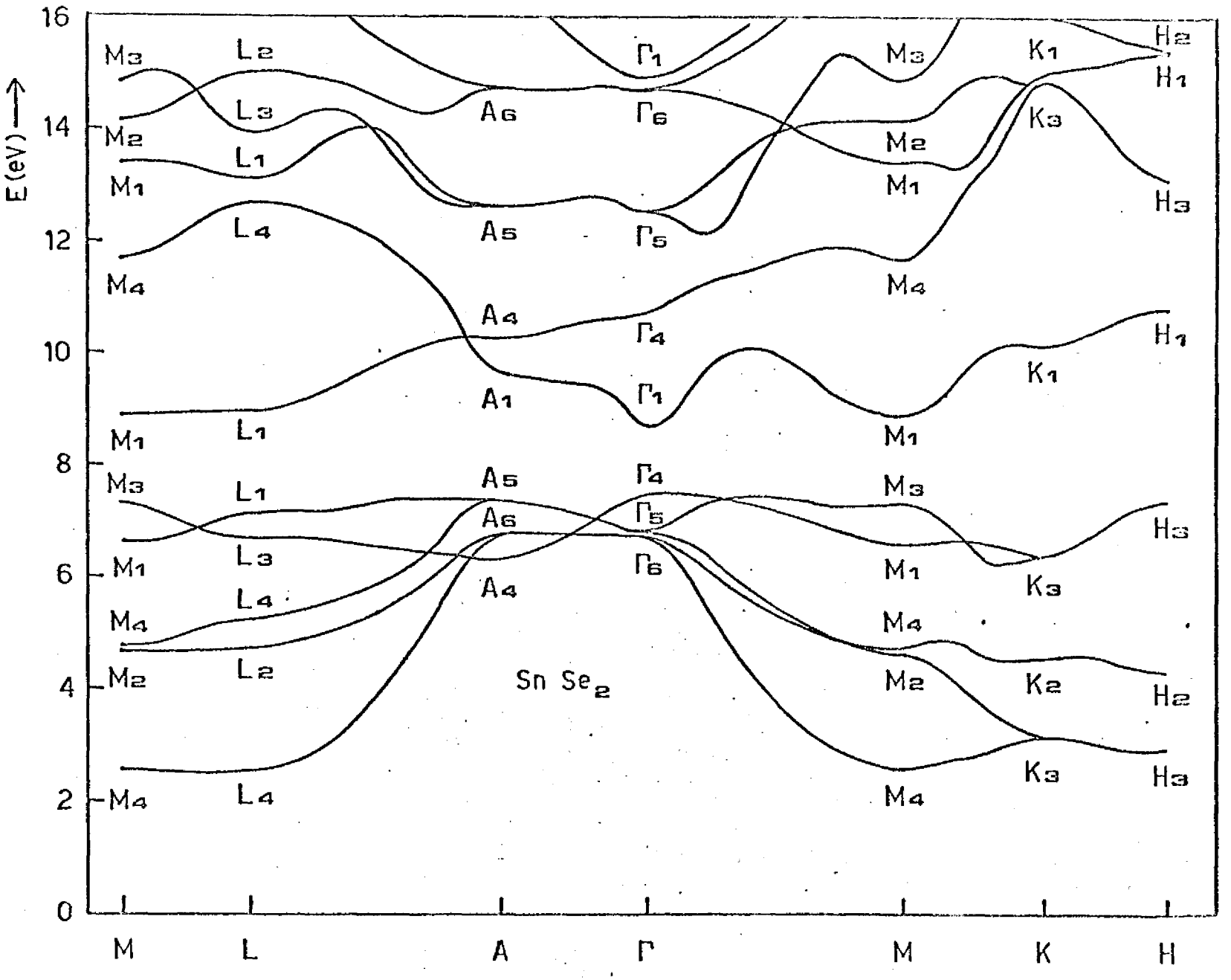
E (eV) ⟶
16
14
12
10
8
6
4
2
0
M
L
A
Γ
M
K
H
M3
M2
M1
M4
L2
L3
L1
L4
A6
A5
A4
A1
Γ1
Γ6
Γ5
Γ4
K1
K3
K2
H2
H1
H3
Sn Se2

FIG. 3

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