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ELECTRONIC AND OPTICAL PROPERTIES OF SbSBr, SbSI AND SbSeI*

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ABSTRACT

Electronic band structures of the ternary semiconductors SbSBr and SbSeI have been obtained by using the empirical pseudopotential method (EPM) to fit our measured optical reflectivity data and earlier gap measurements. An SbSI band structure has been determined by fitting to earlier reflectivity and Raman spectroscopic data, and the results agree better with the data than do the results of an earlier preliminary EPM calculation. Above the SbSI conduction band minimum are secondary minima located midway along the ΓZ and ΓX symmetry lines. These minima may in part be responsible for the observed microwave oscillation (Gunn effect) in this crystal. Similar minima in SbSBr and SbSeI are reported, suggesting these crystals might also show microwave properties. The total densities of states are presented.

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The ternary semiconductors SbSBr, SbSI and SbSeI have attracted considerable attention in recent years, in part because of observed phase transitions,¹ anisotropy,² piezoelectric behavior,³ nonlinear optical behavior⁴ and photoconductivity.⁵ Furthermore, microwave oscillation (the Gunn effect) has also been observed in SbSI.⁶ The purpose of the present communication is to report the electronic and optical properties of these crystals.

Details of the growth, sample preparation and room-temperature reflectance measurements will be presented in a more detailed later publication.

The empirical pseudopotential method (EPM) has already been discussed in detail elsewhere.⁷ The essence of the EPM is that the potentials of the constituent atoms are expanded in plane waves. The coefficients of these expansions are empirically adjusted to fit the experimental results. Additional details pertinent to the specific application of the EPM to the present orthorhombic crystals is given in a previously reported EPM calculation for SbSI by Fong et al.⁸ The lattice constants and atomic locations are given in Wyckoff.⁹

The theoretical and experimental optical reflectivity spectra are shown in Fig. 1. The measured SbSI spectra reported by Fong et al.⁸ are for polarizations parallel and perpendicular to the shortest crystal axis. The present SbSBr and SbSeI measurements are unpolarized.

The theoretical reflectivity agreement with the SbSI data is generally better than that obtained in the calculation by Fong et al.⁸ (not shown). In the present results, the potential associated with

the Sb atom is about 0.03 rydberg less attractive on the average than in their results, so there is greater transfer of charge from the Sb to the S and I atoms. The present I and S potentials are nearly the same as the earlier calculation. The main improvement over the earlier calculation is in the shape of the structure near 2 eV in the parallel-polarized reflectivity. In the earlier result⁸ the theoretical structure is a smooth, rounded peak, while the present peak shows the same type of sub-structure as in the data: a shoulder about 0.1 eV below a sharp peak at 2 eV. The appearance of these two separate structures, instead of the single rounded peak found by Fong et al⁸, is associated with the increased separation of unoccupied S and Sb states caused by the elevation of the Sb potential. For the perpendicular polarization, the main improvements over the earlier results⁸ is in the location of the lowest peak, which is about 0.25 eV too low in their results. In the present results, the location of this peak agrees to 0.05 eV with the measured location.

The measured spectra of SbSBr and SbSeI each show three main structures. Each of the theoretical spectra also show three structures and the locations of these structures agree to the order of 0.2 eV with the locations in the data. The largest discrepancy between the results is found in the heights of the lowest-energy structure near 2.5 eV in SbSBr. The strong peak at 2.37 eV in the data finds correspondence to only a weak shoulder at 2.55 eV in the theory.

A common feature of the theoretical and experimental spectra is the location of either a peak or a shoulder within 0.5 eV above the threshold of optical transitions. These structures also share a

common origin: about 70% of the strength of each structure arises from transitions from chalcogenide sp states in the top valence band to antimony sp states in the bottom conduction band. The remaining peaks in the various spectra do not share well-defined common origins; details regarding their specific origins are available on request.

Since the locations of the theoretical peaks agree to the order of 0.2 eV with the experimental locations, the relative locations of the energy bands are probably also accurate to the order of 0.2 eV. These energy bands are shown in Fig. 2. Because the band structures were obtained by fitting to only the optical energy range of the reflectivity data, we may regard as accurate only those bands for which the valence-to-conduction band separations are in the optical energy range. These are the only bands shown in Fig. 2.

In the SbSBr band structure, the valence band maximum is slightly displaced from the usual location of the maximum (at Γ) in semiconductors. However, this maximum is only 0.05 eV above the energy at Γ . Since the uncertainty in the present energy bands is of the order of 0.2 eV, these results cannot rule out the possibility that the actual valence band maximum is at Γ . The conduction band minimum for SbSBr is at the S symmetry point. The fundamental gap is thus indirect, with a value 2.18 eV. This is in excellent agreement with the gap (2.22 eV) reported by Pikka and Fridkin.¹⁰

In SbSI, the gap is 2.11 eV and is indirect, from Γ to S. Recent Raman spectroscopic measurements by Shen¹¹ yielded values of 2.05 eV and 2.20 eV for perpendicular and parallel polarizations, respectively. The average of these measurements, 2.12 eV, is in

excellent agreement with the theory. The data¹¹ indicates that the gap is direct, but since the uncertainty in the bands is about 0.2 eV, the present results should not be regarded as inconsistent with the data. Indeed, the smallest direct gap (2.28 eV), at the S symmetry point, is only 0.17 eV larger than the indirect gap, suggesting that the gap measured by Shen¹¹ may have been at S.

In SbSeI, the gap is 1.67 eV and is also indirect, from Γ to S. This is in good agreement with the data (1.71 eV) reported by Pikka and Fridkin.¹⁰ The gap, however, is significantly smaller than in SbSBr and SbSI. The reason for this difference is discussed below.

Among all of the constituent atoms Sb, S, Se, I and Br, the Sb atom is the least electronegative. (Thus, the lowest unoccupied states would originate from the Sb sp states from which an electron has been transferred to the halide.) On the other hand, since the halides are the most electronegative, the occupied sp states of I or Br are expected to lie the farthest below the top of the valence bands. The largest portion of the occupied states at the gap must therefore come from the sp states of the chalcogenides and the remaining states of Sb.¹² Compared to Se, the S atoms are more electronegative. Therefore, the bonds between S and Sb should be more ionic than the ones between Se and Sb. Consequently, the gaps in the former crystals (SbSBr and SbSI) should be larger than the one in SbSeI. These gaps are shown in the total densities of states in Fig. 3.

The small arrows in Fig. 2 show the location of secondary minima in the lowest conduction band. SbSI, in which microwave oscillations have already been observed,⁶ shows two minima, one at 0.25 eV and

another at 0.55 eV above the conduction band minimum at S. The first is roughly midway along the ΓX symmetry line, and the second is about midway along the ΓZ line. In SbSBr, there are also two secondary minima, located in roughly the same locations as in SbSI. In the lowest SbSeI conduction band there is one second minima, midway between Γ and Z.

The existence of secondary minima in the lowest conduction band of semiconductors is certainly no guarantee of the existence of the Gunn effect. These minima, however, are an essential first requirement, and the present band structures strongly suggest that this requirement is met in the as-yet untested crystals of SbSBr and SbSeI.

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12. A preliminary SbSI charge density calculation reported at the Washington APS meeting in April, 1976, clearly showed that these states form a covalent bond with some of the Sb states. The remainder of the electrons of Sb atoms are transferred to the I atoms to form an ionic bond.

FIGURE CAPTIONS

FIGURE 1. Theoretical and experimental optical reflectivities of SbSI, SbSBr and SbSeI. Only the top four valence bands, and the bottom four conduction bands were used in the calculations.

FIGURE 2. Empirical pseudopotential band structures of SbSI, SbSBr and SbSeI. The smallest valence-to-conduction band gap is indicated by the long arrows in each band structure. The smaller arrows indicate the locations of second minima in the lowest conduction band.

FIGURE 3. The total densities of states of SbSI, SbSBr and SbSeI.

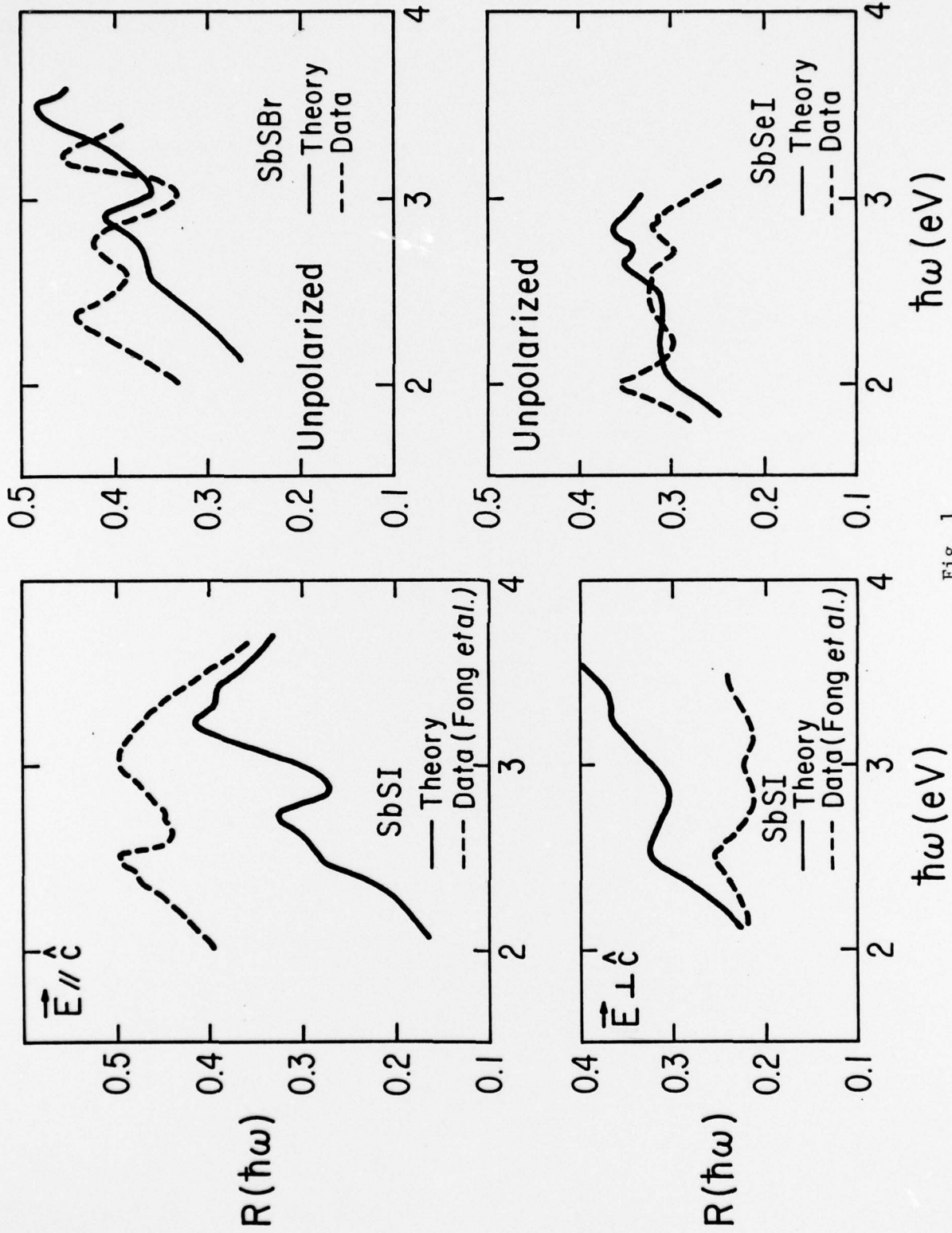


Fig. 1

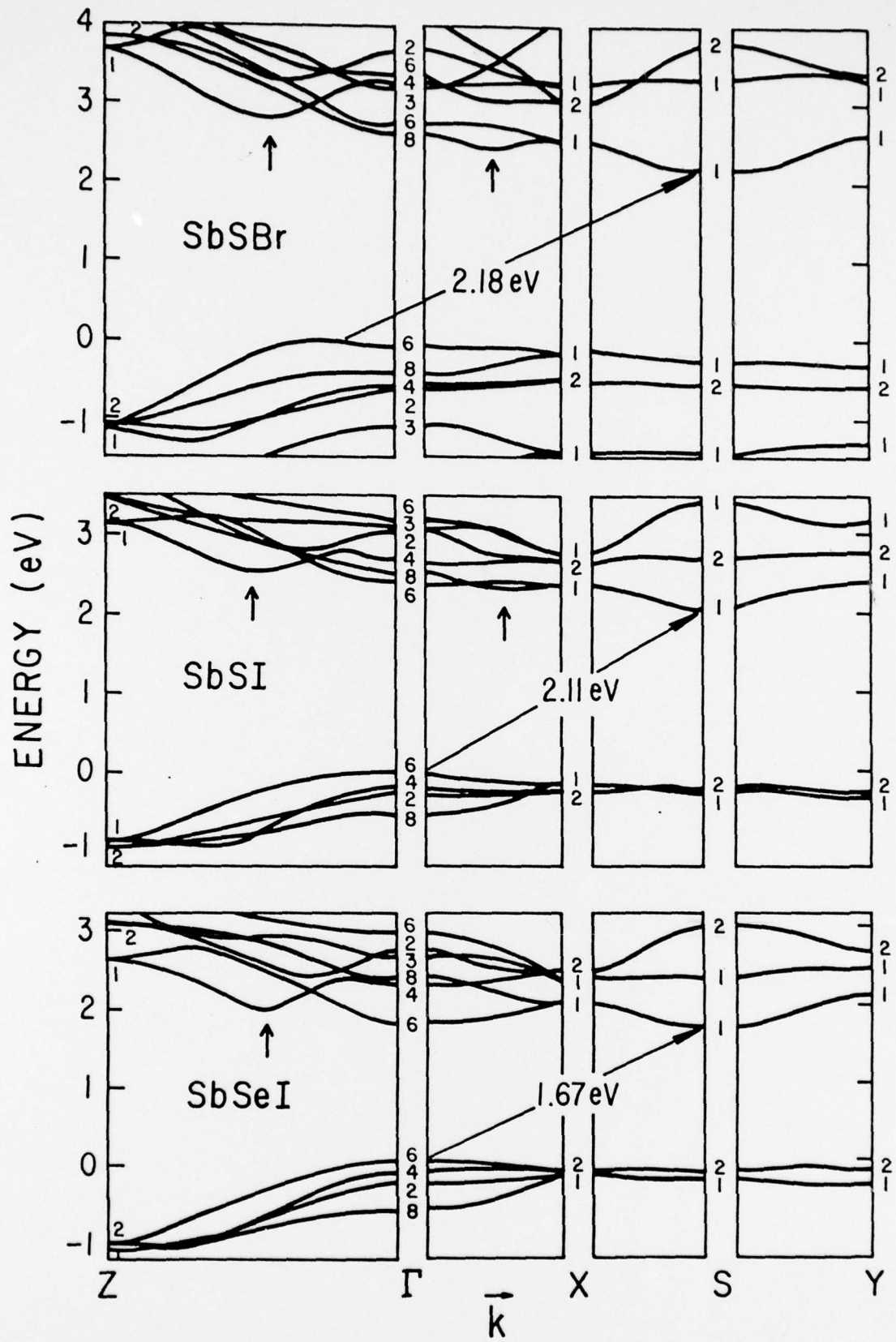


Fig. 2

TOTAL DENSITIES OF STATES

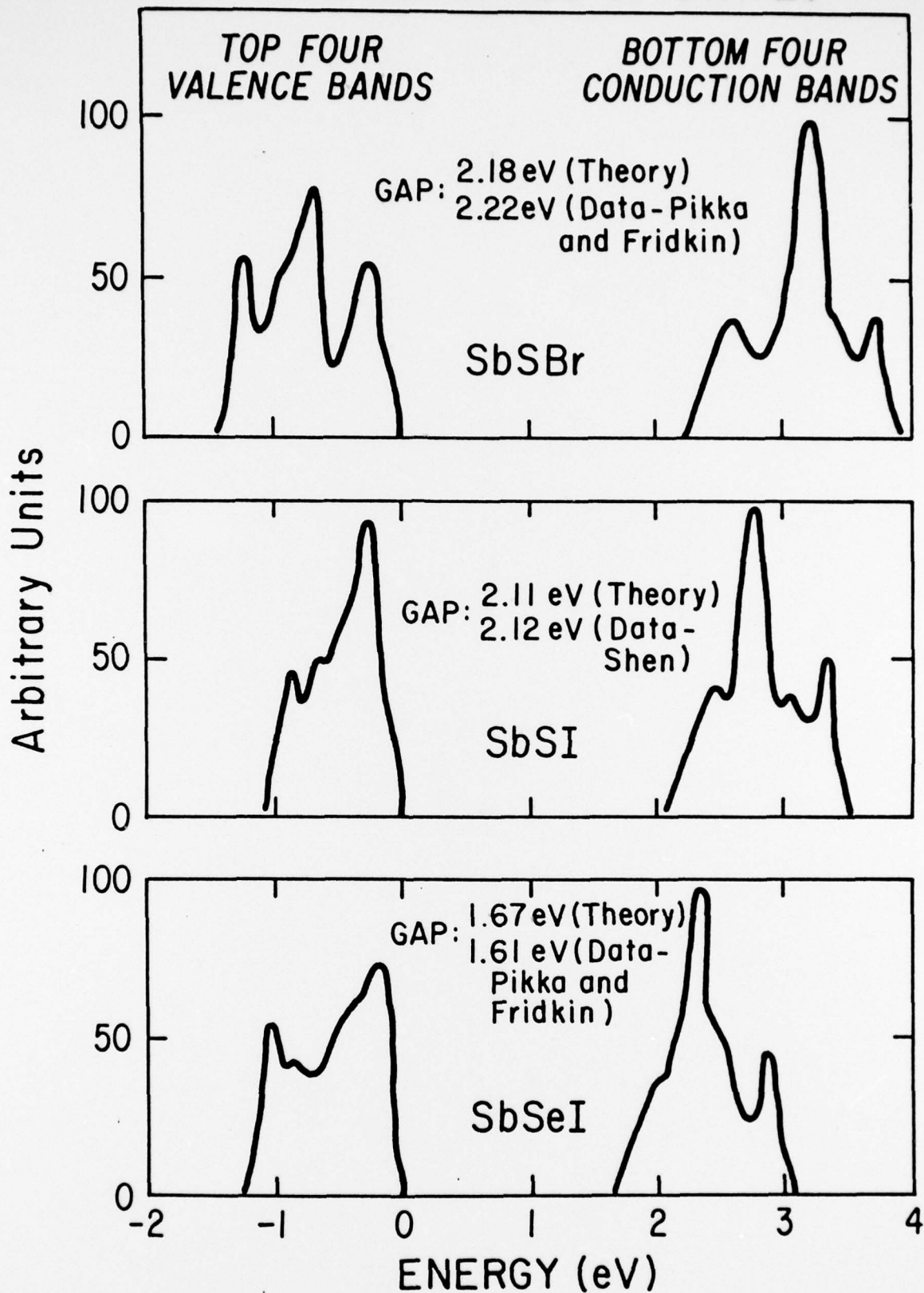


Figure 3

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