

## Electronic structure of alkaline-earth selenides

Ravindra Pandey, Phillip Lepak, and John E. Jaffe

*Department of Physics, Michigan Technological University, Houghton, Michigan 49931*

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The electronic band structures of MgSe, CaSe, and SrSe have been calculated by the Hartree-Fock method with correlation corrections included. Our results are compared to optical data on these rocksalt-structure insulators predicting that CaSe is a direct-gap material while both MgSe and SrSe are indirect-gap materials.

Alkaline-earth chalcogenides are an important group of technological materials with applications in the area of luminescent devices.<sup>1</sup> In selenides, SrSe has been proposed as host material for infrared-sensitive devices. Both CaSe and SrSe doped with Pb have also been explored for their luminescence properties.<sup>2</sup>

Electronic structure of alkaline-earth oxides and sulfides has recently been the subject of our investigation<sup>3</sup> (hereafter referred to as part I) with an aim to providing a basis for the interpretation of their optical spectrum. Extension of the work to alkaline-earth selenides is now a logical next step. In this Brief Report, we will concentrate on calculation of the band structure focusing on the nature of energy gaps in selenides.

The all-electron local-orbitals Hartree-Fock method including correlation is used to perform band-structure calculations. Both long-range and short-range correlation effects are included by means of the virtual-polaron approximation and a cluster orbital relaxation approximation, respectively. For a detailed discussion of this method, we refer to part I. It is to be noted here that these selenides have the face-centered-cubic (rocksalt) structure with lattice constant of 5.449 Å for MgSe, 5.933 Å for CaSe, and 6.246 Å for SrSe.

The correlated Hartree-Fock energy bands for MgSe, CaSe, and SrSe are shown in Figs. 1–3. The qualitative features in these band structures are found to be very

similar to those in oxides and sulfides. For example, anion  $p$  orbitals form the upper valence band. In all the cases, the valence-band maximum occurs at the  $\Gamma$  point. On the other hand, the minimum in conduction band occurs at the  $X$  point for MgSe, at the  $\Gamma$  point for CaSe, and at the  $K$  point  $[(4\pi/a)(0.75, 0.75, 0)]$  for SrSe. Thus CaSe is predicted to be direct band-gap material while both MgSe and SrSe are predicted to be indirect gap materials. Our calculation finds the Hartree-Fock direct band gap of 12.0, 11.6, and 11.3 eV for MgSe, CaSe, and SrSe, respectively. The correlation corrections (on the order of 2.5 eV) reduce the gap to 9.9, 8.6, and 7.9 eV for MgSe, CaSe, and SrSe, respectively. The energy gaps at high symmetry points are given in Table I along with the results of the augmented plane-wave calculation based on local-density approximation (APW-LDA) for CaSe and SrSe. No band-structure calculation has been reported for MgSe.

Experimentally, the optical absorption<sup>4</sup> of thin films of MgSe, CaSe, and SrSe at 77 K and the optical reflectivity<sup>5</sup> of single crystals of CaSe and SrSe at 2 K have been reported and Table II displays the data for the major peaks. The band gap is taken to be the energy of the lowest-energy absorptivity or reflectivity peak plus the exciton binding energy. The experimental values for the band gaps are then estimated to be about 5.7 for MgSe, 5.0 for CaSe, and 4.7 for SrSe. As for the overall

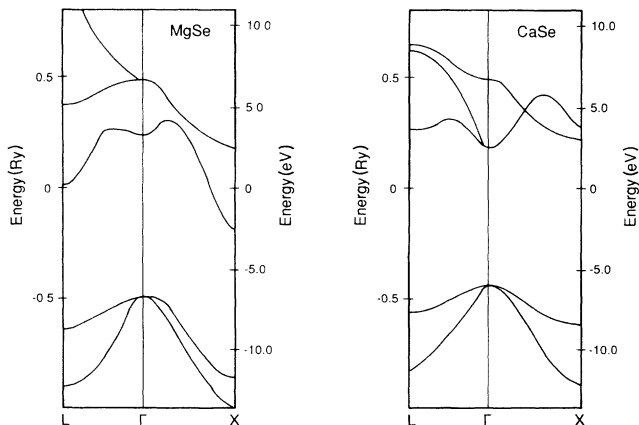


FIG. 1. Correlated energy bands for MgSe and CaSe.

TABLE I. Energy gaps (in eV) at high-symmetry points for selenides. Bold numbers represent the minimum values of the gap.

	Energy gap				
	Direct gap		Indirect gap		
	$\Gamma$	$X$	$L$	$(\Gamma-X)$	$(\Gamma-L)$
MgSe					
This work	9.93	9.06	9.30	<b>4.14</b>	7.20
CaSe					
This work	<b>8.56</b>	11.60	11.27	9.16	9.61
APW calculation <sup>a</sup>		4.89	3.85		
SrSe					
This work	7.92	9.79	10.24	<b>7.66<sup>b</sup></b>	8.65
APW calculation <sup>a</sup>	4.57	4.48		3.81	

<sup>a</sup>Reference 5.

<sup>b</sup>Minimum in the lowest conduction band is at the  $K$  point.

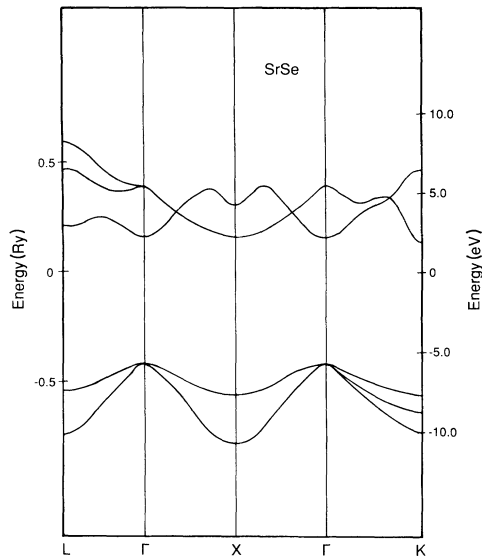


FIG. 2. SrSe: correlated energy bands.

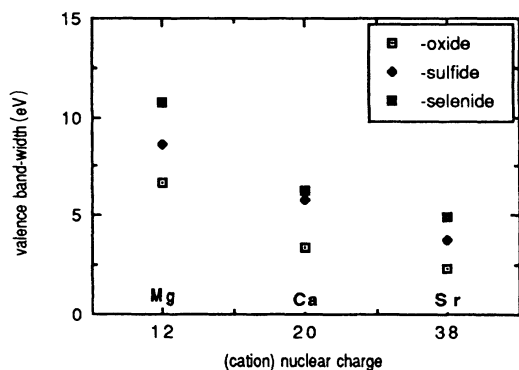


FIG. 3. Calculated (upper valence) band widths of alkaline-earth chalcogenides.

magnitudes of the band gaps, the calculations are therefore not in close agreement with experiment. This is consistent with the fact that the present method provides accurate values of gaps only for strongly ionic materials such as oxides. The agreement with experiment becomes

TABLE II. Experimental energies for the major peaks in the absorption-reflectivity spectrum of alkaline-earth selenides.

	Peak energies (eV)
MgSe	
absorption, <sup>a</sup> 77 K	5.60
CaSe	
absorption, <sup>a</sup> 77 K	4.87, 5.11
reflectivity, <sup>b</sup> 4 K	4.828, 5.056, 5.60
SrSe	
absorption, <sup>a</sup> 77 K	4.45, 4.70
reflectivity, <sup>b</sup> 2 K	4.387, 4.522, 4.639, 4.957, 5.40

<sup>a</sup>Thin film, Ref. 4.

<sup>b</sup>Single crystal, Ref. 5.

TABLE III. Valence-band widths (in eV) for selenides.

	MgSe	CaSe	SrSe
Se, 4 <i>p</i> band (upper valence)	10.7	6.25	4.9
Se, 4 <i>s</i> band	4.4	1.95	1.7
Se, <i>sp</i> band (total valence-band width)	22.6	18.1	16.6

less satisfactory as we move from oxides to sulfides to selenides. In comparison, the APW-LDA calculation predicts the gap to be about 3.85 and 3.81 eV for CaSe and SrSe, respectively.

Table III lists the calculated valence-band widths of these materials. The width decreases as we increase the nuclear charge of the cation, indicating that the wave function is more localized for SrSe than for MgSe. It is to be expected that valence-band states become more localized as a material becomes less covalent and more ionic, as it does when we increase the atomic number of the cation (Fig. 3).

In summary the band structure of selenides are found to exhibit the same qualitative features shown by oxides and sulfides. The lowest exciton is predicted to occur at the  $\Gamma$  point in CaSe and SrSe. The calculations predict that MgSe and SrSe are indirect gap materials while CaSe is a direct gap material.

<sup>1</sup>For a review, see R. Pandey and S. Sivaraman, *J. Phys. Chem. Solids* **52**, 211 (1991).

<sup>2</sup>N. Yamashita, T. Ohira, *et al.*, *J. Phys. Soc. Jpn.* **53**, 419 (1984); S. Asano, N. Yamashita, and Y. Nakao, *Phys. Status Solidi* **89**, 663 (1978).

<sup>3</sup>R. Pandey, J. Jaffe, and A. B. Kunz, *Phys. Rev. B* **43**, 9228 (1991).

<sup>4</sup>G. A. Saum and E. B. Hensley, *Phys. Rev.* **113**, B1019 (1959).

<sup>5</sup>Y. Kaneko and T. Koda, *J. Cryst. Growth* **86**, 72 (1988).