Accurate Electronic, Transport, and Structural Properties of Disodium Sulfide (Na_2S)

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Abstract

We present the results of ab initio, self-consistent calculations of electronic, transport, and structural properties of a cubic phase of disodium sulphide (Na_2S). Our calculations employed a local density approximation (LDA) potential and the linear combination of Gaussian orbital (LCGO) formalism. The implementation of the LCGO followed the Bagayoko, Zhao, and Williams (BZW) method, as enhanced by Ekuma and Franklin (BZW-EF). Our results include electronic energy bands, effective masses pertinent to transport properties, total (DOS) and partial (pDOS) densities of states, and the bulk modulus. Our calculated, direct band gap, at the Γ point, is 2.831 eV while the bulk modulus is 37.02 GPa. It is hoped that experimental studies will soon be done on this material. Their findings are expected to confirm our theoretical predictions (as was the case for c-InN and c-Si_3N_4).

Background

Na_2S is used in a number of applications as an oxygen scavenger. One such application is the development of photographs. Na_2S is used to prevent the oxidation of development solutions.

Na_2S is a major component of the kraft process in paper manufacturing.

Experimental work on the electronic properties of Na_2S is lacking.

Methods

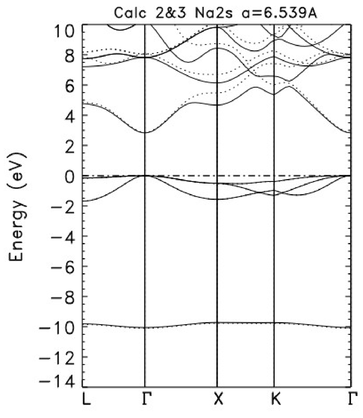
- The BZW-EF method uses successive, self-consistent calculations with increasingly larger basis sets. The basis set of a given calculation is that of the one before it augmented by one orbital.
- We compare the occupied energies of consecutive calculations.
- This process continues until we find three consecutive calculations that give the same occupied energies. This means that the occupied energies have reached their absolute minima.
- Among the three calculations, the one with the smaller basis set provides the DFT (Density Functional Theory) description of the material. The basis set for that calculation is referred to as the optimal basis set.
- The BZW method avoids basis sets much larger than the optimal one, due to the artificial (i.e., unphysical) lowering of some unoccupied energies by virtue of the Rayleigh theorem.

Results

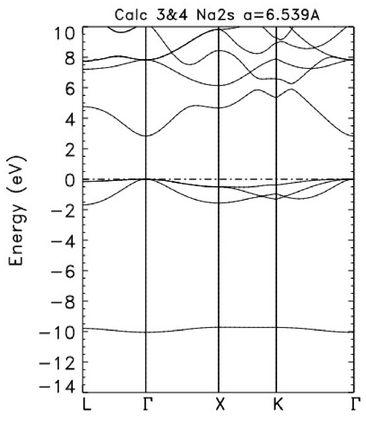
Table 1: Sucessive calculations of the band structure of Na_2S at the room temperature lattice constant to determine the optimal basis set. Valence orbitals and the calculated band gap are provided.

Calc #	Na^+ val orbitals	S^{2-} val orbitals	# val func	Band gap
1	Na: $2s^22p^63s^0$	S: $3s^23p^6$	28	3.009 eV
2	Na: $2s^22p^63s^0\mathbf{3p^0}$	S: $3s^23p^6$	40	2.869 eV
3	Na: $2s^22p^63s^03p^0\mathbf{3d^0}$	S: $3s^23p^6$	60	2.831 eV
4	Na: $2s^22p^63s^03p^03d^0$	S: $3s^23p^6\mathbf{3d^0}$	70	2.830 eV
5	Na: $2s^22p^63s^03p^03d^0\mathbf{4p^0}$	S: $3s^23p^63d^0$	82	2.830 eV
6	Na: $2s^22p^63s^03p^03d^04p^0$	S: $3s^23p^63d^0\mathbf{4s^0}$	84	2.821 eV

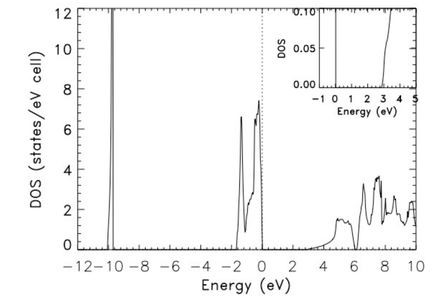
Band structures from Calculations 2(---) and 3(__). The occupied energies are almost the same; the unoccupied energies are clearly different with those from 3 lower than their corresponding ones from 2.



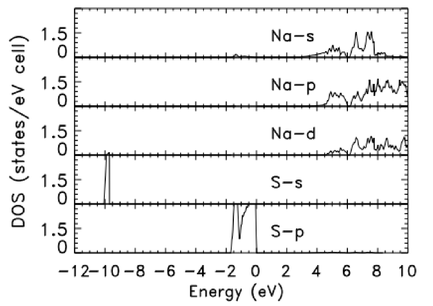
Band structures from calculations 3(---) and 4 (__). The occupied energies are identical. Even the unoccupied energies are the same up to 10eV. Calculation 5 gives the same occupied energies. Calculation 3 gives the DFT description of the material.



Total convergence is observed, not only of the occupied bands, as expected by theory, but also of unoccupied bands up to 10eV. Calculation 3 gives the DFT description of the material and all other properties are calculated using the outputs of Calculation 3.



Density of states of Na_2S as obtained from the bands from Calculation 3. The calculated band gap is 2.831 eV.



Partial density of states of Na_2S, as obtained from the electronic structure from Calculation 3.

The upper valence bands are mainly from sulfur p and the lower valence ones are mainly from sulfur s. The low laying unoccupied bands are made of hybridized sodium s, p, and d.

Conclusions

- We calculated a direct (Γ – Γ) band gap of 2.831 eV for Na_2S. This result is qualitatively similar to other theoretical ones but is quantitatively different enough to be significant. No experimental results appear to exist.
- Our density of states and partial density of states are also similar, qualitatively, to other theoretical results. Again, we could not find any experimental data for comparison.
- Our total energy versus lattice constant calculations also matched the existing body of work within reasonable tolerances.
- We calculated the bulk modulus to be 37.02 GPa which, according to statements in the literature, is a value in agreement with the experimental one of 49.00GPa.
- Further research is needed. In particular, future, experimental studies are expected to confirmed of DFT BZW-EF results.

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