

LATTICE DYNAMICS OF ROCKSALT STRUCTURE OF PbS UNDER PRESSURE

Timothy Chibuike Chibueze

Department of Physics and Astronomy, University of Nigeria, Nsukka Enugu State.

Abstract

PbS has been extensively studied due its great potential application in solar cells among others. In this work, we have investigated the effect of pressure on the phonon dynamical properties of the rocksalt structure of PbS using density functional theory. The phonon dispersion relation and phonon density of states show that the structure is stable at zero pressure. Increase in pressure induces a phonon softening at the symmetry X point, phonon energy gap and increase in the frequency of both the acoustic and optical modes. Below the lattice constant of 5.44 Å, there is presence of imaginary phonon frequency at the symmetry X point which signifies instability in the structure at such high pressure.

Keywords: rocksalt structure, phonon, PbS, stability

1. Introduction

Lead (II) sulphide has received numerous experimental and theoretical attention in research for application in solar cell [1-6] due to its band gap. It is observed that it is a direct band gap semiconductor with a band gap in the range which optimum efficiency for application as solar absorber in solar cells according to Shockley-Queisser limit [7]. PbS has been synthesized using various experimental techniques. First principles methods has been employed also in investigating its electronic and structural properties [12]. It crystallizes into a cubic NaCl structure ($a=b=c$) in the space group Fm-3m (space group number 225). It has the Sulphur atom (S) and Lead atom (Pb) at the origin (0, 0, 0) and center (0.5, 0.5, 0.5) of the cell respectively. The dependence of mechanical properties on the number of k-points has been studied earlier [8]. Recent progress in density functional theory [9] makes it possible to predict accurate and reliable vibrational properties based on dynamical model of

lattice. Because for first-principles calculations of vibrational properties all input data is entirely based on structure of crystal and number of atoms within crystal. Vibrational properties such as phonon density of states and phonon dispersion curves play an important role in explaining the numerous number of material properties like thermal expansion coefficient at finite temperature, specific heat, propagation of sound waves, change of phase and thermal conduction. Phonon properties of rocksalt PbS have been studied both theoretically [10-12] and experimentally [13]. To the best of our knowledge, there is no theoretical investigation of the lattice dynamical properties using the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE). GGA-PBE has been proven to give better results for chalcogenide based compounds than local density approximation (LDA) [14, 15] and that used in Ref [12] and therefore gives better theoretical interpretation and predictions of these materials. Hence, in the present study, we have employed the method to investigate the lattice dynamical properties of the rocksalt structure of bulk PbS under pressure in order to determine its pressure dynamical stability limit.

2. Theoretical Details

We employ Kohn-Sham equation within the framework of Density Functional Theory (DFT) in our calculations. We performed ab-initio DFT non-spin polarized calculations in the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) [16]. For these calculations, plane-wave self-consistent field (PWSCF) method, as implemented in the Quantum-Espresso program package [17] was used. Plane wave basis sets were used to represent wave functions and density of valence electrons with kinetic energy and augmented density cutoff of 40 Ry and 400 Ry respectively.

Corresponding Author: Timothy C.C., Email: timothy.chibueze@unn.edu.ng, Tel: +2348068002470

Journal of the Nigerian Association of Mathematical Physics Volume 53, (November 2019 Issue), 117 – 122

At this cutoff, the total energy is converged to within 1 mRy/atom. Scalar relativistic ultra soft pseudo-potentials [18] were used to describe the interaction between ions and valence electrons. Pb 6s, 6p,5d and S 3s, 3p are treated as valence orbitals. Brillouinzone integration was done over 8 x 8 x 8 k-point grid sampled by Monkhorst-Pack scheme [19]. The optimization criteria for the ionic geometry relaxation was 0.0001 Ry for total energy and 0.001Ry/au for the Hellmann-Feynman forces. The experimental lattice parameters for PbS is obtained from Ref.[1] as 5.935 Å. Linear response method proposed by Baroni et al [20], a technique which uses density functional perturbation theory [21] to compute directly dynamical matrix on already calculated grid of q points. Fourier transform is then applied on these dynamical matrices to determine interatomic force constant in real space. Dynamical matrices for phonon dispersion relations were calculated at a 4x4x4 grid of q-points.



Figure 1: RocksaltPbS crystal structure. The blue atoms are the sulphur atoms while the red atoms are the Lead atoms. On the left (a) is the conventional unit cell while on the right (b) is the 3x3x3 repeated cell to show the full arrangement of the atom in a bulk like case.

Table 1: The phonon properties of rocksalt structure of PbS. E_g is the phonon energy gap. TA, LA, TO and LO represent transverse acoustic, Lateral acoustic, transverse optical and lateral optical phonon modes respectively.

Lattice constant (Å)	E_g (cm ⁻¹)	Symmetry k-point	TA (cm ⁻¹)	LA (cm ⁻¹)	TO (cm ⁻¹)	LO (cm ⁻¹)
6.01	0.0	Γ	0.0 0.0	0.0	38.91 65.05 ^a , 63.7 ^b	184.29 223.49 ^a , 210.48 ^b
		X	44.79	88.49	103.61, 175.88	215.38
5.87	0.0	L	47.31 49.37 ^a , 51.04 ^b	102.77 101.74 ^a , 108.07 ^b	182.19 194.13 ^a , 193.47 ^b	225.46 237.83 ^a , 243.50 ^b
		Γ	0.0	0.0	86.76	123.63
		X	48.07, 55.81	98.14	136.83, 201.92	235.60
		L	58.08	111.34	208.75	245.16
5.71	14.215	Γ	0.0	0.0	124.80	184.61
		X	40.98, 64.94	109.12	171.37, 229.71	257.16
		L	69.41	121.37	237.55	266.96
5.60	45.69	Γ	0.0	0.0	167.86	271.85
		X	33.93, 75.95	117.44	198.32, 250.32	274.48
		L	78.05	128.99	259.24	283.93
5.44	75.0	Γ	0.0	0.0	211.07	307.50
		X	16.43, 91.43	131.31	242.62, 287.26	304.52
		L	92.62	141.43	294.41	313.45
5.29	98.32	Γ	0.0	0.0	244.22	333.20
		X	-40.96, 105.16	142.71	281.31, 320.23	333.89
		L	105.84	154.32	328.42	342.08

^aReference [13]

^bReference [12]

3. Result and Discussion

We first optimized our structural parameters and obtained a lattice constant of 6.01 angstrom which is in good agreement with 6.007 Å obtained by Bencherif et al [11]. Our result is 1% higher than the experimental result. This is typical of GGA result because it tends to overestimate the lattice parameter. The model of rocksaltPbS is shown in Figure 1. Using the optimized lattice parameter, we calculated the phonon dispersion relation and phonon density of states (PHDOS). Since we used two atoms in our unit cell, we obtained total of six phonon modes, three been acoustic and the remaining three optical (Figures 2-7). We repeated our calculations for various lattice constants smaller than that of the optimized value and which corresponds to various pressures. The various phonon mode frequencies for the symmetry points were calculated for all the lattice constants considered and are recorded in Table I. Our result (calculated at temperature of 0K) agrees fairly with the experimental result of Elcombe et al [13] obtained at the temperature of 300K but slightly disagrees with the theoretical result of Zhang et al [12]. For example, at the equilibrium lattice parameter (zero pressure), we obtained the frequency of 225.46 cm^{-1} for lateral optical phonon at L (0.5,0.5,0.5) symmetry k-point. This is in better agreement with the value of 237.83 cm^{-1} obtained experimentally by Elcombe et al [13] at temperature of 300 K than the theoretical value of 243.50 cm^{-1} obtained by Zhang et al [12] at absolute zero temperature. It is observed that as the pressure increases, the frequency of the optical phonon increases across all the symmetry points. Also the transverse acoustic phonon mode which is two-fold degenerate at the symmetry point X splits into two non-degenerate branches whose energy difference increases with pressure at the symmetry point X; while one of the transverse acoustic branches reduces in frequency (generally called phonon softening), the other increases in frequency. Below about lattice constant of 5.44 Å, the lower transverse acoustic branch approaches the frequency of zero and at the lattice constant of about 5.29 Å, it collapses below the frequency of zero thereby signifying failure in stability of the structure (see Figure 7). In general, increase in pressure increases the frequency of the acoustic phonon modes at other symmetry points. We also observe that at the equilibrium lattice constant, there is sort of overlap in the frequency of the phonon acoustic phonon modes and the optical phonon modes. As we increase the pressure, there is a point where we observe a finite phonon energy gap between the acoustic and optical modes which increases with pressure. The range of energy occupied by the optical phonon also becomes reduced as pressure increases

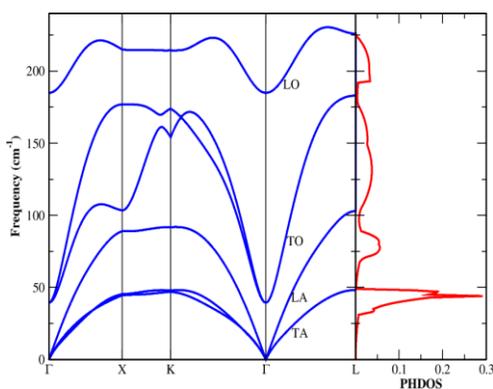


Figure 2: Phonon dispersion relation and phonon density of states (PHDOS) for rocksalt

PbS at lattice parameter of 6.01 Å. TA, LA, TO and LO represent transverse acoustic, lateral acoustic, transverse optical and lateral optical phonon modes respectively.

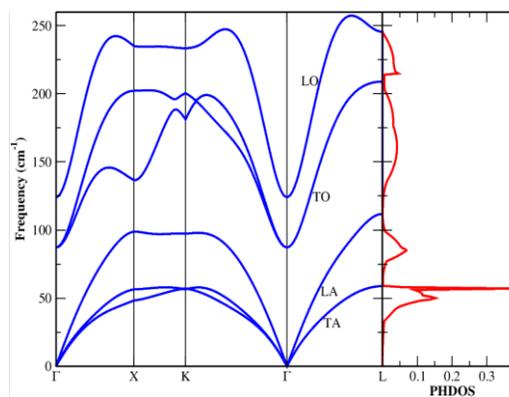


Figure 3: Phonon dispersion relation and phonon density of states (PHDOS) for rocksalt

PbS at lattice parameter of 5.87 Å. TA, LA, TO and LO represent transverse acoustic, lateral acoustic, transverse optical and lateral optical phonon modes respectively.

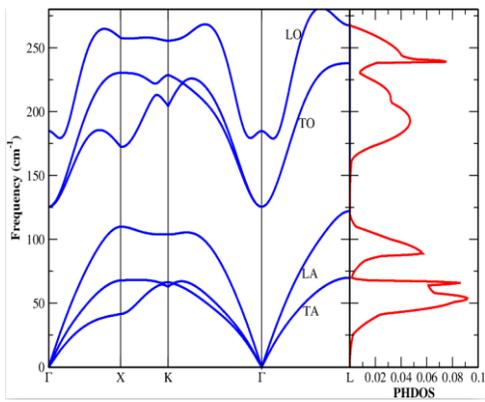


Figure 4: Phonon dispersion relation and phonon density of states (PHDOS) for rocksalt

PbS at lattice parameter of 5.71 Å. TA, LA, TO and LO represent transverse acoustic, lateral acoustic, transverse optical and lateral optical phonon modes respectively.

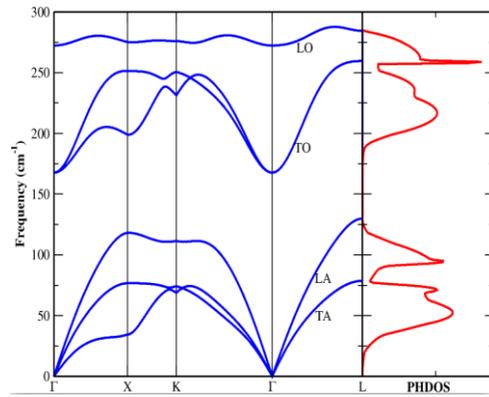


Figure 5: Phonon dispersion relation and phonon density of states (PHDOS) for rocksalt

PbS at lattice parameter of 5.60 Å. TA, LA, TO and LO represent transverse acoustic, lateral acoustic, transverse optical and lateral optical phonon modes respectively.

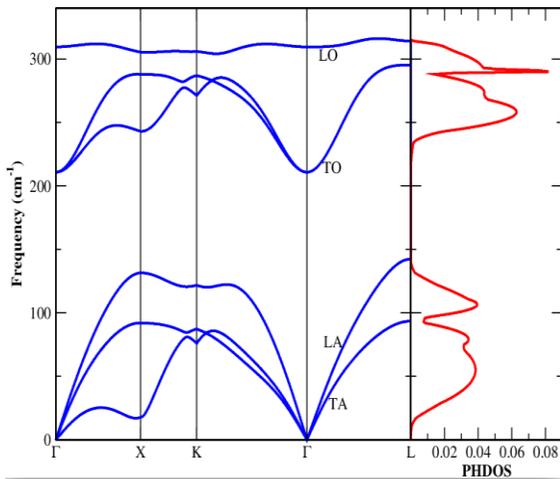


Figure 6: Phonon dispersion relation and phonon density of states (PHDOS) for rocksalt

PbS at lattice parameter of 5.44 Å. TA, LA, TO and LO represent transverse acoustic, lateral acoustic, transverse optical and lateral optical phonon modes respectively.

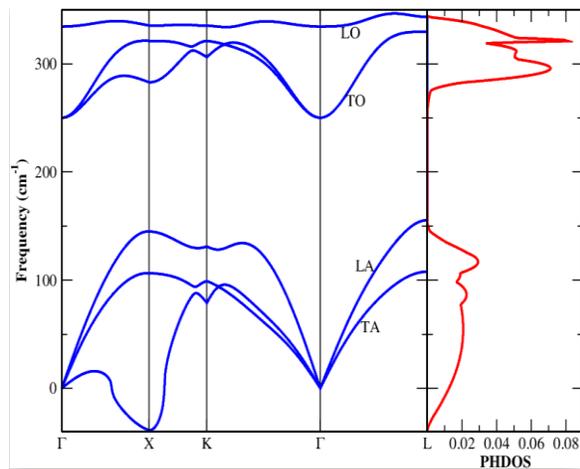


Figure 7: Phonon dispersion relation and phonon density of states (PHDOS) for rocksalt

PbS at lattice parameter of 5.29 Å. TA, LA, TO and LO represent transverse acoustic, lateral acoustic, transverse optical and lateral optical phonon modes respectively.

4. **Conclusion**

We have studied the phonon dynamical properties of rocksalt Lead (II) sulphide PbS using density functional theory. The structure is stable both at zero pressure and at finite pressure. However, at very high pressure corresponding to lattice constant of 5.29 Å, an imaginary frequency appears at the symmetry k-point X which signifies dynamical instability at such pressure. Unfortunately, we could not find any report on the pressure limit of the lattice dynamical stability of rocksalt PbS to compare our result with. Our result at equilibrium lattice parameter exposes overlap between the acoustic phonon and optical phonon suggesting that rocksalt PbS low thermal conductivity at ambient pressure. Also increase in phonon frequency and phonon energy gap is observed as pressure increases. We strongly recommend that rocksalt PbS may be very useful in applications that require moderately high pressure since they are dynamically stable at such pressure range.

Acknowledgement

We gratefully acknowledge the Centre for High Performance Computing (CHPC), Cape Town (South Africa) for providing computational resources.

References

- [1] Li Y, Wu H, Wu Y, Li Q. (2017)“Surfactant-assisted fabrication of PbSnanorice at low temperature in aqueous solution”Applied Phys. A 123, 491.
- [2] L. Wei, C. Jun-Fang, W. Teng, Electronic and elastic properties of PbS under pressure, (2010)Physica B: Condensed Matter 405 1279-1282.
- [3] R. S. Kane, R. E. Cohen, R. Silbey, Synthesis of PbSnanoclusters within block copolymer nanoreactors, (1996) Chem. Mater. 8 1919-1924.
- [4] J. M. Luther, H. Zheng, B. Sadtler, A. P. Alivisatos, Synthesis of PbSnanorods and other ionic nanocrystals of complex morphology by sequential cation exchange reactions, (2009)J. American Chem. Soc. 131 16851-16857.
- [5] M. Kowshik, W. Vogel, J. Urban, S. K. Kulkarni, K. M. Paknikar, Microbial synthesis of semiconductor PbSnanocrystallites, (2002) Advanced Materials, 14 815-818.
- [6] F. Gao, Q. Lu, X. Liu, Y. Yan, D. Zhao, Controlled synthesis of semiconductor PbSnanocrystals and nanowires inside mesoporous silica SBA-15 phase,(2001) Nano Letters, 1 743-748.
- [7] S. Rühle, Tabulated values of the Shockley–Queisser limit for single junction solar cells, (2016)Solar Energy, 130 139-147.
- [8] T.C Chibueze andA.O.E Animalu, First Principles investigation of the elastic constants and mechanical properties of the rocksalt structure of PbS,(2017) African J. Phys. 11 44-51.
- [9] G. Schreckenbach, P.J Hay,R.L Martin, Density functional calculations on actinide compounds: Survey of recent progress and application to [UO₂X₄]²⁻(X= F, Cl, OH) and AnF₆ (An= U, Np, Pu), , (1999)J. Computational Chem., 20 70-90.
- [10] Skelton, J. M., Parker, S. C., Togo, A., Tanaka, I., & Walsh, A. (2014). “Thermal physics of the lead chalcogenides PbS, PbSe, and PbTe from first principles”.Phys. Rev. B, 89 205203.
- [11] Y Bencherif, A Boukra,A Zaoui, M Ferhat, Lattice dynamics study of lead chalcogenides, (2011) Infrared Phys. Tech. 54 39-43.
- [12] Zhang, Y., Ke, X., Chen, C., Yang, J., and Kent, P. R. C. (2009). “Thermodynamic properties of PbTe, PbSe, and PbS: First-principles study”. Phys.Rev. B, 80, 024304.
- [13] M.M Elcombe, The crystal dynamics of lead sulphide, (1967)Proceed. Royal Soc. London.Series A. Math. Phys. Sci., 300 210-217.
- [14] Ceperley, D. M., & Alder, B. J. (1980). Ground state of the electron gas by a stochastic method. Phys. Rev. Lett. 45 566.
- [15] Perdew, J. P., &Zunger, A. (1981). “Self-interaction correction to density-functional approximations for many-electron systems”. Phys. Rev. B, 23 5048.
- [16] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple,(1996) Phys. Rev. Lett. 77 3865-3868.
- [17] Giannozzi P., Baroni S., Bonini N., Calandra M., Car R., Cavazzoni C., Ceresoli D., Chiarotti G.L., Cococcioni M., Dabo I., Corso A.D., de Gironcoli S., Fabris S., Fratesi G., Gebauer R., Gerstmann U., Gougoussis C., Kokalj A., Lazzeri M., Martin-Samos L., Marzari N., Mauri F., Mazzarello R., Paolini S., Pasquarello A., Paulatto L., Sbraccia C., Scandolo S., Sclauzero G., Seitsonen A.P., Smogunov A., Umari P., Wentzcovitch R.M. (2009).“QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials”. J. Phys.: Condens. Matter.21, 395502.
- [18] D. Vanderbilt, Soft self-consistent pseudopotentials in a generalized eigenvalue formalism, (1990) Phys. Rev. B. 41 7892-7895.

- [19] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, (1976) Phys. Rev. B. 13 5188-5192.
- [20] Baroni, S., DeGironcoli, S., Dal Corso, A. andGiannozzi, P. (2001). “Phonons and related crystal properties from density-functional perturbation theory”. Rev. Modern Phys. 73 515.
- [21] Gonze, X. and Lee, C. (1997). “Dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants from density-functional perturbation theory”. Phys. Rev. B, 55 10355.