Int. J. Medicine and Occupational Health and Safety Sciences, 1, 2 (2023)

DOI: 10.5281/zenodo.10430972

IJMOHSS

An Investigation on Physical Properties of $NiAs_2$ Crystal: An Ab-initio Study

Saniye Ilgin OLMEZ[a], Emel Kilit DOGAN[a]* and Sinem Erden GULEBAGLAN[b]

[a] Van Yüzüncü Yıl University, Department of Physics, 65080 Van, Turkey

[b]Van Yüzüncü Yıl University, Van Vocational School, Department of Electric and Energy, 65080 Van, Turkey

ABSTRACT

The physical properties of $NiAs_2$ compound is examined theoretically in this study. The study is performed by using Abinit computer programme which depends on Density Functional Theory (DFT). The volume optimization is performed in order to obtain theoretical lattice parameters and atomic positions in unit cell of $NiAs_2$. The electronic properties are revealed by obtaining the electronic band structure and Density of States graphs of this compound. The elastic properties are investigated by calculating the elastic stiffness constants. Finally, the thermodynamic properties of $NiAs_2$ compound are investigated. All calculations of this study are performed under Generalized Gradient Approximation (GGA).

Keywords: *$NiAs_2$, DFT, Electronic properties, Elastic Properties, Thermodynamic properties.*

*Corresponding author: e-mail: ekilit@yyu.edu.tr and ORCID: https://orcid.org/0000-0001-7609-7206

Int. J. Medicine and Occupational Health and Safety Sciences, 1, 2 (2023)

DOI: 10.5281/zenodo.10430972

IJMOHSS

$NiAs_2$ Kristalinin fiziksel özellikleri üzerine bir araştırma: Bir Temel İlkeler Çalışması

Saniye Ilgin Ölmez[a], Emel Kilit Doğan[a]* and Sinem Erden Gulebağlan[b]

ÖZET

Bu çalışmada $NiAs_2$ bileşiğinin fiziksel özellikleri teorik olarak incelenmiştir. Çalışma Yoğunluk Fonksiyonel Teorisine (YFT) dayanan Abinit bilgisayar programı kullanılarak gerçekleştirilmiştir. $NiAs_2$'nin birim hücresindeki teorik örgü parametrelerini ve atomik konumlarını elde etmek için hacim optimizasyonu gerçekleştirilmiştir. Bu bileşiğin elektronik bant yapısı ve Durum Yoğunluğu grafikleri elde edilerek elektronik özellikleri ortaya çıkarılmıştır. Elastik özellikler, elastik sertlik sabitleri hesaplanarak araştırılmıştır. Son olarak $NiAs_2$ bileşiğinin termodinamik özellikleri araştırılmıştır. Bu çalışmanın tüm hesaplamaları Genelleştirilmiş Gradyan Yaklaşımı (GGA) altında yapılmıştır.

Anahtar kelimeler: *$NiAs_2$, YFT, Elektronik özellikler, Elastik özellikler, Termodinamik özellikler.*

Int. J. Medicine and Occupational Health and Safety Sciences, 1, 2 (2023)

DOI: 10.5281/zenodo.10430972

IJMOHSS

INTRODUCTION

Nickel occurs in nature as oxides, sulfides and silicates. We can list the nickel minerals as cloanthite, milerite, pentlandite, nickelin, and garnienite. Many nickel-containing materials are the subject of research for many researchers [1-4]. Wei and et al. examined the thermoelectric properties of $NiAs_2$, $PdAs_2$ and $PtAs_2$ materials with DFT using the VASP simulation program [5]. They concluded that $NiAs_2$, $PdAs_2$ and $PtAs_2$ materials are promising thermoelectric materials. Donohue et al. experimentally investigated the Fe, Co, Ni diphosphide and diarsenide phases of Cu and Pd [6]. They revealed the lattice parameter for Pyrite-type $NiAs_2$. Ho et al. studied the possibility and kinematics of the water-splitting process of Penta-NiAs monolayer [7]. Qian et al. investigated some properties of two-dimensional binary $PdAs_2$, PdP_2, NiP_2, $NiAs_2$, PtP_2 and $PtAs_2$ structures and concluded that the band gap values of these structures are between 0.3 and 0.8 eV [8]. Stassen et al. revealed by experimentally investigating the atomic positions of $NiAs_2$ in the orthorhombic crystal structure [9]. Additionally, its structural properties were determined by the neutron diffraction method [10]. Bachhuber et al. examined the phase stability of NiN_2, NiP_2, $NiAs_2$, $NiSb_2$ and $NiBi_2$ crystals and calculated their structural properties [11].

In this study, the structural, electronic, elastic and thermodynamic properties of cubic $NiAs_2$ crystal were performed using DFT. It is thought that the results obtained for $NiAs_2$ crystal will support future experimental or theoretical studies.

MATERIALS and METHODS

The calculations of all physical properties of $NiAs_2$ compound were performed by DFT within Generalized Gradient Approximation using ABINIT [12] computer programme. As a norm conserving pseudopotentials, theself-consistent Fritz Haber Institute-type[13] with the Troullier-Martins scheme [14] isused. To be able to compute the Kohn-Sham equations [15] the conjugate gradient minimization method [16] is used. The Perdew-Burke-Ernzerhof [17] functions are used for solve the exchange-correlation effects. The plane waves were taken in to accountas the basis set. The value of cut-off energy was calculated as 1088.45 eV. The Monkhorst-Pack mash grid is chosen as12x12x12 [18].

RESULTS AND DISCUSSION

In this paper the physical properties of $NiAs_2$ compound is investigated theoretically. First of all, the theoretical lattice parameters and the atomic positions of atoms in its unit cell are calculated by performing a volume optimization by DFT under Generalized Gradient Approximation (GGA). This optimization results with the relationship between volume of unit cell and the total energy of the compound in its ground state. Total energy vs. volume graph is

DOI: 10.5281/zenodo.10430972

given in Figure 1. The volume is in the ground state calculated as 1336.9 $Bohr^3$. The lattice parameters of the unit cell of $NiAs_2$ are equal to each other (since $NiAs_2$ compound is in cubic structure) and calculated as 11.0165 Bohr. This value is very close to the value obtained from the literature [19] that is equal to 10.9363 Bohr.

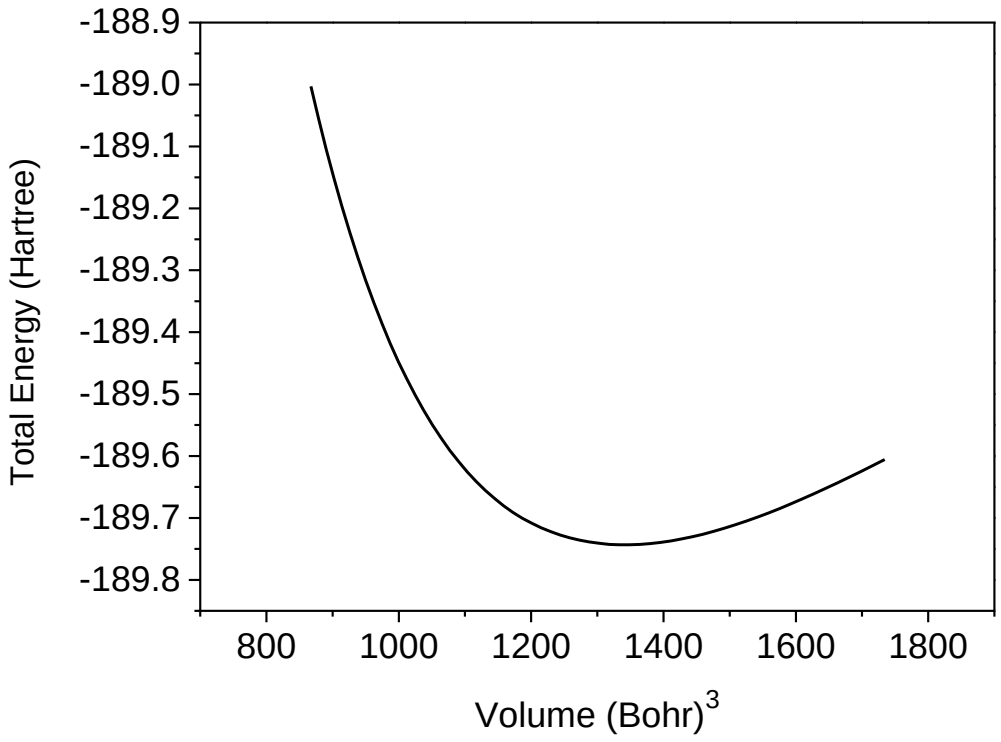

Figure 1. The total energy vs. volume graph of $NiAs_2$ with GGA

After volume optimization the calculations were continued with electronic properties. The electronic band structure and DOS graphs are plotted and given in Figure 2. In Figure 2, the left part gives the electronic band structure and the right part gives the Density of States (DOS) of the compound. The two graphs are matched in order to make easy to compare them. The Fermi level is matched with 0 eV. There is no band gap around the Fermi level. Therefore, it is clear that this material is in metallic structure with high electronic conduction property. It is also clear that the electronic band structure graph and DOS graph are in a good agreement. In the band structure part of Figure 2, it is seen that the electronic bands below Fermi level are valence bands and above ones are conduction bands. In the valence bands there are also some core electron levels which are seen between -10 and -16 eV.

After revealing the electronic properties, we focused on the elastic properties of $NiAs_2$ compound. For this purpose, we calculated the elastic stiffness constants. By using the elastic stiffness constants (Table 1) one can calculate Bulk, Shear and Young Modulus, Poisson ratio and Flexibility coefficient (Table 2).

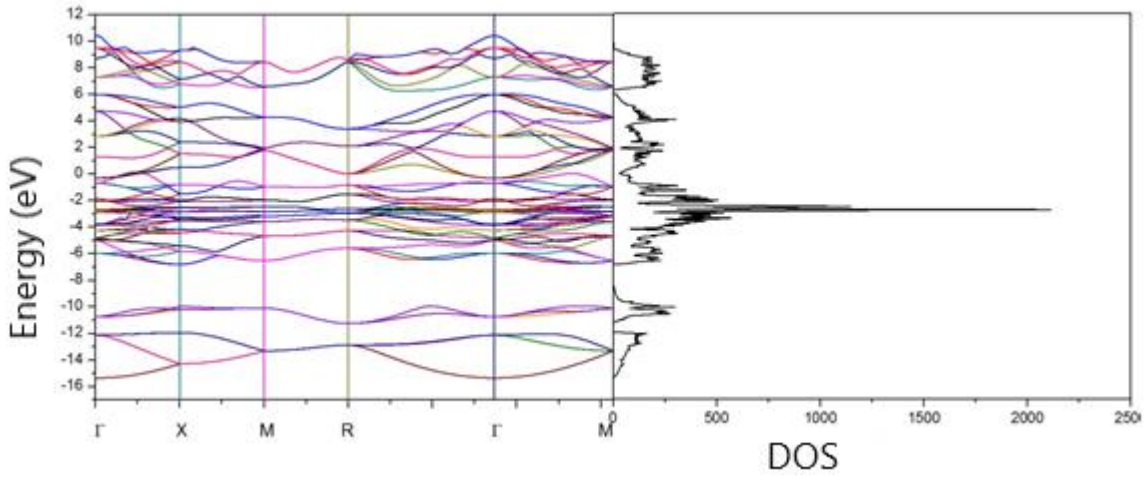

Figure 2. The electronic band structure (left part) and the Density of States (right part) of the $NiAs_2$ compound.

Elastic stiffness constants are actually rank 4 tensors, but by using matris notation [20] they can be shown with two indices. However, they are still rank four tensors. These constants have 36 components in matris notation. Since there is symmetry property between the components of elastic stiffness constants and the symmetry property of cubic structures, the number of independent components decreases to three, i.e. $C_{11}(= C_{22} = C_{33})$, $C_{12}(= C_{13} = C_{23})$ and $C_{44}(= C_{55} = C_{66})$. The rest of the components of elastic stiffness constants are equal to zero.

Table 1. Elastic stiffness constants of $NiAs_2$

Elastic Stiffness Constants (GPa)	$NiAs_2$
C_{11}	479.34
C_{12}	78.98
C_{44}	117.85

Bulk modulus gives information about resistance of a material to a compression. The Bulk modulus of $NiAs_2$ is 212.43 GPa (Giga Pascal), which is a quiet high value. The Shear Modulus is the ratio of shear stress to the shear strain. Stress is force (that causes deformation of a material) per unit area. Strain is the measurement of deformation of a material. The value of Shear modulus for this component is calculated as 145.92 GPa. Young Modulus is about compressive stiffness when the force is applied longitudinally, which is computed as 356.2 GPa for $NiAs_2$ compound. Poisson ratio and Flexibility coefficient give the state of a material elastically as if it is fragile or elastic material.

If the calculated Poisson ratio is smaller than 0.26 that means this material is fragile material. If the value is bigger than 0.26, the material is said to be elastic material. Also, if the value of Flexibility coefficient is smaller than 1.75 the material is fragile otherwise it is elastic material. Table 2, shows that Poisson ratio and Flexibility coefficient are smaller than their critical values. Therefore, $NiAs_2$ is a fragile material.

Table 2. Elastic properties of $NiAs_2$

Elastic Properties (Units)	$NiAs_2$
Bulk Modulus (GPa)	212.43
Shear Modulus (GPa)	145.92
Young Modulus (GPa)	356.2
Poisson Ratio (-)	0.221
FlexibilityCoefficient (-)	1.456

Finally, the thermodynamic properties of $NiAs_2$ are revealed.While examining the thermodynamic properties, the phonon contributions to the entropy (Figure 3), heat capacity under constant volume (Figure 4), and Helmholtz free energy(Figure 5) and internal energy of the $NiAs_2$ crystal are calculated and plotted the relevant graphs as a function of temperature. Mathematical expressions of phonon contributions to Helmholtz free energy, internal energy,heat capacity under constant volume and entropy under the harmonic approach[21, 22], are given in the following equations.

$$\Delta F = 3nNk_BT\int_0^{\omega_L} ln\left(2sinh\frac{\hbar\omega}{2k_BT}\right)g(\omega)d\omega, \qquad (1)$$

$$\Delta E = 3nN\frac{\hbar}{2}\int_0^{\omega_L}\omega cot\left(\frac{\hbar\omega}{2k_BT}\right)g(\omega)d\omega, \qquad (2)$$

$$Cv = 3nNk_B\int_0^{\omega_L}\left(\frac{\hbar\omega}{2k_BT}\right)^2 sc^2h^2\left(\frac{\hbar\omega}{2k_BT}\right)g(\omega)d\omega, \qquad (3)$$

$$S = 3nNk_B\int_{\times g(\omega)d\omega}^{\omega_L}\left[\frac{\hbar\omega}{2k_BT}cot\frac{\hbar\omega}{2k_BT} - ln\left(2sinh\frac{\hbar\omega}{2k_BT}\right)\right] \qquad (4)$$

Here, k_B is Boltzman constant.

The entropy behaviour with respect to temperature is given in Figure 3. As seen from the figure, entropy, as expected, shows an increasing feature with respect to temperature.The constant-volume specific heat of a material is the amount of heat energy required to increase the temperature of its unit mass by one degree. From Figure 4, it is seen that the specific heat of $NiAs_2$ reaches its limit value which is equal to 296 J/(mol.K) at 791 K.

DOI: 10.5281/zenodo.10430972

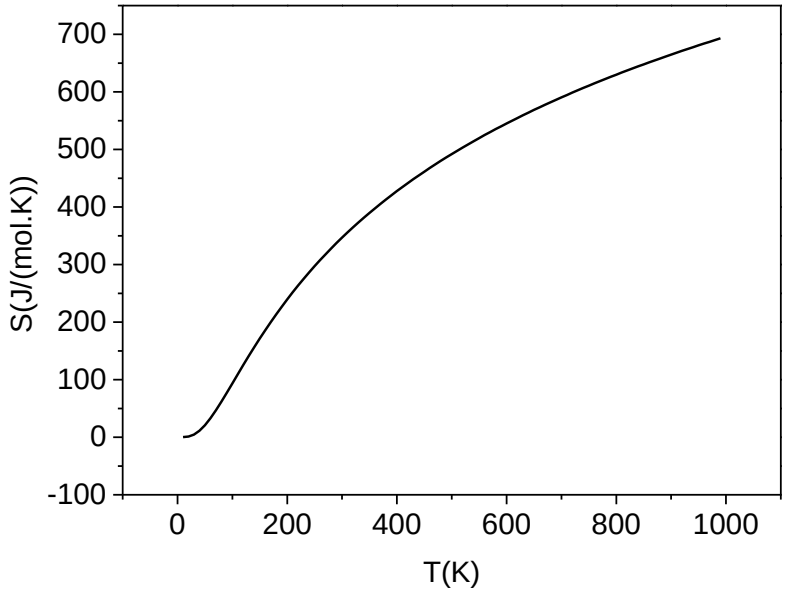

Figure 3. Entropy-temperature graph of $NiAs_2$ under GGA.

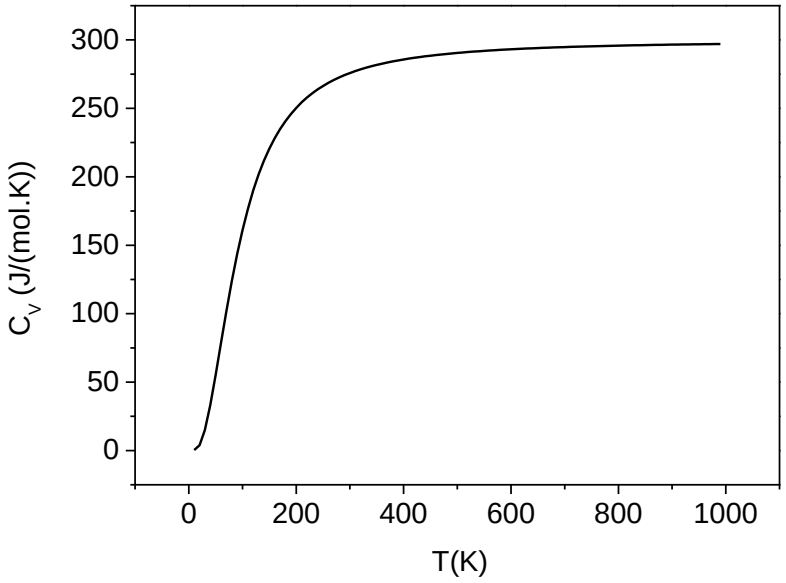

Figure 4. Heat capacity- temperature graph of $NiAs_2$ under GGA.

DOI: 10.5281/zenodo.10430972

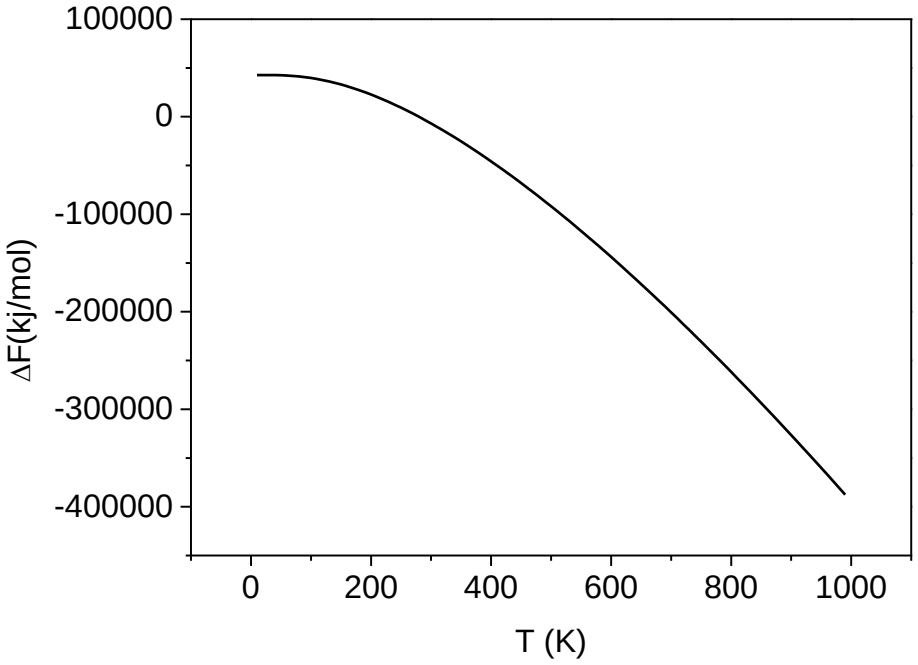

Figure 5. Helmholtz free energy- temperature graph of $NiAs_2$under GGA.

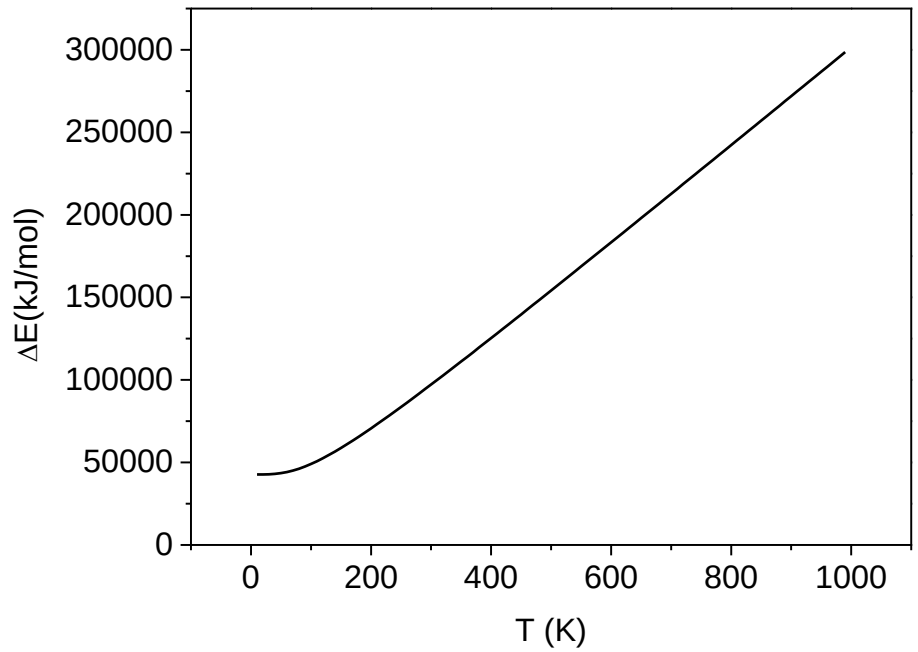

Figure 6. The internal energy- temperature graph of $NiAs_2$compound under GGA.

Since at zero Kelvin, the oscillations occur, at this temperature the free energy and the internal energy of $NiAs_2$ are different from zero. The value of Helmhotz free energy is 42698.68 kJ/mol and the value of internal energy is 42438.92 kJ/mol at zero temperature.

CONCLUSION

With this study, many physical properties such as structural, electronic, elastic and thermodynamic properties of $NiAs_2$ crystal were elucidated. All the calculations performed by DFT within Generalized Gradient Approximation. First, volume optimization is performed in order to find the theoretical values of lattice parameters of $NiAs_2$ compound. It is noticed after the electronic property calculations that $NiAs_2$ is in metallic structure. The electronic band structure and the density of states graphs are plotted. By the elastic property calculations, it is revealed that this compound is not elastic, it is fragile material. Lastly, the thermodynamic properties are shown by plotting the Helmholtz free energy, internal energy, entropy and specific heat graphs as a function of temperature.

Acknowledge

This paper is performed from the Master thesis entitled as “Investigation of the Structural, Electronic, Elastic, Dynamic and Thermodynamic properties of the $NiAs_2$ Crystal by Density Functional Theory” by Saniye Ilgin.

References

[1] R. Castroviejo, Pararammelsbergite (*prm*). In: A Practical Guide to Ore Microscopy—Volume 1. Springer, Cham. 2023

[2] S. M. Chernonozhkin, J. Mercadier, L. Reisberg, B. Luais, C. Zimmermann, C. Morlot, L. Salsi, A. Lecomte, O. Rouer, M. Brouand, A. Doney, P. Ledru, Geochimica et Cosmochimica Acta 280 (2020) 85-101.

[3]M. Singleton, P. Nash, Journal of Phase Equilibria 8 (1987) 419–422.

[4] E. H. El Ghadraoui, J. Y. Pivan, R. Guérin, M. Sergent, Materials Research Bulletin 23 (1988) 6-10.

[5] Q. L. Wei, H. Y. Yang, Y. Y. Wu, Y. B. Liu, Y. H. Nanomaterials 10 (2020) 204.

[6] P. C. Donohue, T. A. Bither, H. S. Young, Inorg. Chem. 7 (1968) 998-1001.

[7] T. H. Ho, H. C. Dong, V. Q. Bui, Y. Kawazoe, H. M. Le, Phys. Chem. Chem. Phys. 22 (2020) 18149-18154.

[8] S. Qian, X. Sheng, X. Xu, T. Wu, N. Lu, Z, Qin, J. Wang, C. Zhang, E. Feng, W. Huang, Y. Zhou, J. Mater. Chem. C 7 (2019) 3569-3575.

[9] W. N. Stassen, R. D. Heyding, Canadian Journal of Chemistry 46 (1968) 2059-2063.

[10] A. Kjekshus, T. Rakke, A. F. Andresen, Acta Chem.Scand. A 28 (1974) 9.

[11] F. Bachhuber, J. Rothballer, T. Söhnel, R. Weihrich, Journal of Chemical Physics 139 (2013) 214705.

[12] X. Gonze, J. M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G. M. Rignanese, L. Sindie, M. Verstrate, G. Zerah, F.Jollet, M. Torrent, A. Roy, M. Mikami, P. Ghosez, J. Y. Raty, and D. C. Allan, Computational Materials Science, 25 (2002) 478-492.

[13] M. Fuchs, M. Scheffler, Computer Physics Communications, 119 (1999) 67-98.

[14] N. Troullier, J. L. Martins, Physical Review B 43 (1991) 1993-2006.

DOI: 10.5281/zenodo.10430972

[15] W. Khon, L. J. Sham, Physical Review, 140 (1965) A1133-A1138.
[16] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, J. D. Joannopoulos, Reviews of Modern Physics, 64 (1992) 1045-1098.
[17] J. P. Perdew, K. Burke, M. Ernzerhof, Physical ReviewLetters, 77 (1996) 3865-3868.
[18] J. H. Monkhorst, J. D. Pack, Physical Review B 13 (1976) 5188-5192.
[19] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K. A. Persson, Apl. Materials. 1 (2013) 011002(1-11).
[20] J. F. Nye, Physical properties of crystals: their representation by tensors and matrices, Oxford University Press, United States, Chapter 8 1985
[21] C. Lee and X. Gonze, Phys. Rev. B 51 (1995) 8610.
[22] A. A. Maradudin E. M. Montroll, G. H. Weissand I. P. Ivatova, Solid StatePhysics, 2nd ed.,editedby H. E. Ehrenreich, F. Seitzand D. Turnbull. (Academic, New York, 1971), Chap 4.