Study of Elastic Anisotropy of Compounds RhBiX (X = Hf, Ti and Zr)

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Abstract

The study shows the minimum and maximum values of Young's modulus, Poisson's ratio and shear modulus of compounds RhBiHf, RhBiTi and RhBiZr at zero pressure using ELATE software. Anisotropy parameters A_G and A^U for RhBiTi are slightly greater than the respective values of these parameters for RhBiHf and RhBiZr. The ratios of maximum to minimum values of Young's modulus (E_{max}/E_{min}), linear compressibility (β_{max}/β_{min}), shear modulus (G_{max}/G_{min}) and Poisson's ratio (ν_{max}/ν_{min}) for RhBiTi are 1.12, 1.00, 1.14 and 1.26, respectively. The investigation shows the spatial dependence of Young's modulus, linear compressibility, Poisson's ratio and shear modulus of compound RhBiTi through polar plots.

Keywords: Elastic, Anisotropy, Young's Modulus, Linear Compressibility, Shear Modulus.
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Introduction

Half-Heusler compounds have been given attention, as they are likely to be promising thermoelectric energy materials [1-5]. Half-Heusler compounds are considered suitable thermoelectric materials [1-5]. Wei *et al.* [5] studied the properties of compounds RhBiX (X = Hf, Ti and Zr) within density functional theory using the WIEN2k Code [6]. Carrete *et al.* [7] and Feng *et al.* [8] also studied the thermal conductivities of these Half-Heusler compounds. Half-Heusler compounds XYZ exhibit crystal structure with space group $F\bar{4}3m$ [5, 8-10]. The reported optimized lattice constants are 6.406 Å, 6.444 Å and 6.265 Å for RhBiHf, RhBiZr and RhBiTi, respectively [5]. As per Wei *et al.* [5], RhBiHf is a direct band gap semiconductor. Compound RhBiHf has direct band gap of 0.33 eV [5]. Compound RhBiZr is an indirect band gap semiconductor with a band gap of 1.06 eV [5]. Thermoelectric parameters (such as power factor, Seebeck coefficient, etc.) for compounds RhBiX (X=Hf, Ti and Zr) were studied by Wei *et al.* [5]. At 300K, reported [5] lattice thermal conductivities of RhBiHf, RhBiZr and RhBiTi are 7.71 WmK^{-1}, 10.15 WmK^{-1} and 10.60 WmK^{-1}, respectively. By ratio of bulk modulus to shear modulus, compounds RhBiX (X = Hf, Ti and Zr) are expected to have ductile nature, as predicted by Wei *et al.* [5]. The computation of forces induced by small displacements was carried out by Wei *et al.* [5] using VASP software [11-17]. To the best of my knowledge, elastic anisotropy of the compounds RhBiHf, RhBiZr and RhBiTi has not yet been explored. For the design and fabrication of thermoelectric devices, elastic anisotropy plays a key role in determining the preferred orientation of the crystals. The elastic analysis provides the knowledge of the flexibility limit of device material to bend or stretch without losing the optimum functionality. The degree of malleability allows for thermoelectric devices to be designed from the point of view of adaptability for ideal applications. The durability of thermoelectric devices may decrease with repeated bending or stretching. From the point of view of long-term stability, the investigation of the elastic anisotropy of these compounds would be beneficial for the design of devices.

Computational details

Wei *et al.* [5] calculated the values of elastic constants C_{11}, C_{12} and C_{44} of RhBiHf, RhBiTi and RhBiZr using first-principles methods. Simulations were conducted within density functional theory [18-20] using GGA functional PBE [21, 22] by Wei *et al.* [5]. In the present investigation, values of elastic constants C_{ij} of compounds RhBiX (X = Hf, Ti and Zr) have been taken from the reported work of Wei *et al.* [5]. Using these values of elastic stiffness constants [5], the Voigt-Reuss-Hill scheme [23-25] bulk modulus, shear modulus and Young's modulus are

Table 1: Using values of elastic constants C_{ij} of compounds RhBiX (X = Hf, Ti and Zr) [5], calculated[a] values of bulk modulus K (in GPa unit), shear modulus G (in GPa unit) and Young's modulus E (in GPa unit) of compounds RhBiX at zero pressure.

Compound	K_V	K_R	K_H	G_V	G_R	G_H	E_V	E_R	E_H
RhBiHf	126.78	126.78	126.78	49.15	48.98	49.06	130.57	130.18	130.37
RhBiTi	124.90	124.90	124.90	39.20	39.05	39.13	106.47	106.10	106.29
RhBiZr	122.99	122.99	122.99	51.46	51.41	51.43	135.48	135.37	135.43

[a]Using computational ELATE software [26, 27].

Table 2: Using values of elastic constants C_{ij} of compounds RhBiX (X = Hf, Ti and Zr) [5], calculated[b] lowest and largest values of Young's modulus E (in GPa unit), linear compressibility β [in $(\text{TPa})^{-1}$ unit], Poisson's ratio ν (unitless) and shear modulus G (in GPa unit) of compounds at zero pressure.

Compound	G_{min}	G_{max}	E_{min}	E_{max}	$\beta_{min} = \beta_{max} = \beta$	ν_{min}	ν_{max}
RhBiHf	46.77	52.72	124.95	138.89	2.63	0.293	0.370
RhBiTi	37.20	42.21	101.52	113.81	2.67	0.319	0.402
RhBiZr	50.18	53.38	132.52	139.89	2.71	0.298	0.338

[b]Using computational ELATE software [26, 27].

Table 3: Using values mentioned in Table 1 and Table 2, elastic anisotropy parameters: ratio of largest to lowest values of Young's modulus E, linear compressibility β, shear modulus G and Poisson's ratio ν for compounds RhBiX (X = Hf, Ti and Zr). Elastic anisotropy parameters A_K, A_G and A^U for compounds RhBiX.

Compound	Anisotropy						
	$\frac{E_{max}}{E_{min}}$	$\frac{\beta_{max}}{\beta_{min}}$	$\frac{G_{max}}{G_{min}}$	$\frac{\nu_{max}}{\nu_{min}}$	A_K	A_G	A^U
RhBiHf	1.11	1.00	1.13	1.26	0.00	0.0017	0.0174
RhBiTi	1.12	1.00	1.14	1.26	0.00	0.0019	0.0192
RhBiZr	1.06	1.00	1.06	1.13	0.00	0.0005	0.0048

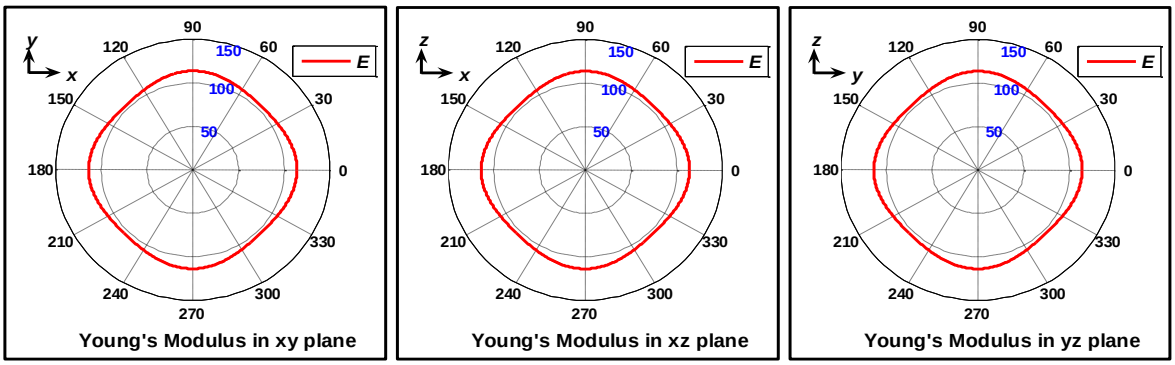

Figure 1: Spatial variation (polar plot) of Young's modulus E (in GPa unit) of RhBiTi.

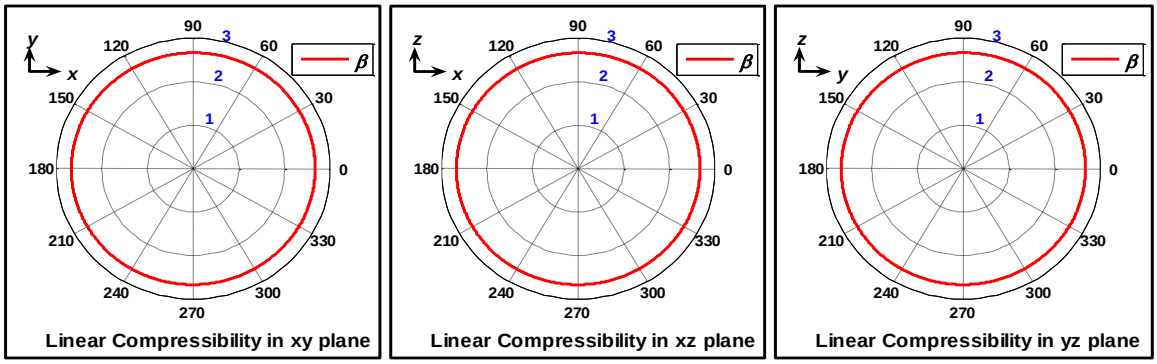

Figure 2: Spatial variation (polar plot) of linear compressibility [in $(\mathrm{TPa})^{-1}$ unit] of RhBiTi.

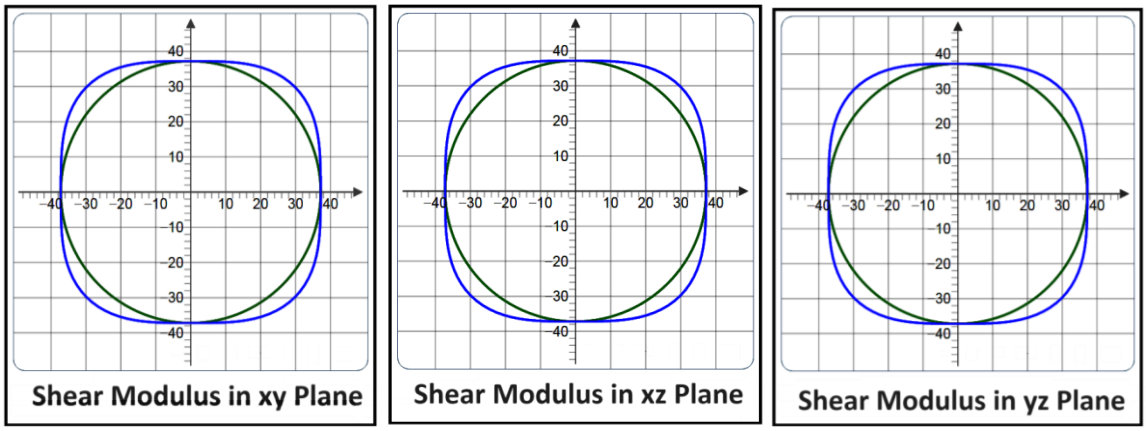

Figure 3. Spatial variation of shear modulus (in GPa unit) of RhBiTi using computational ELATE software [26, 27].

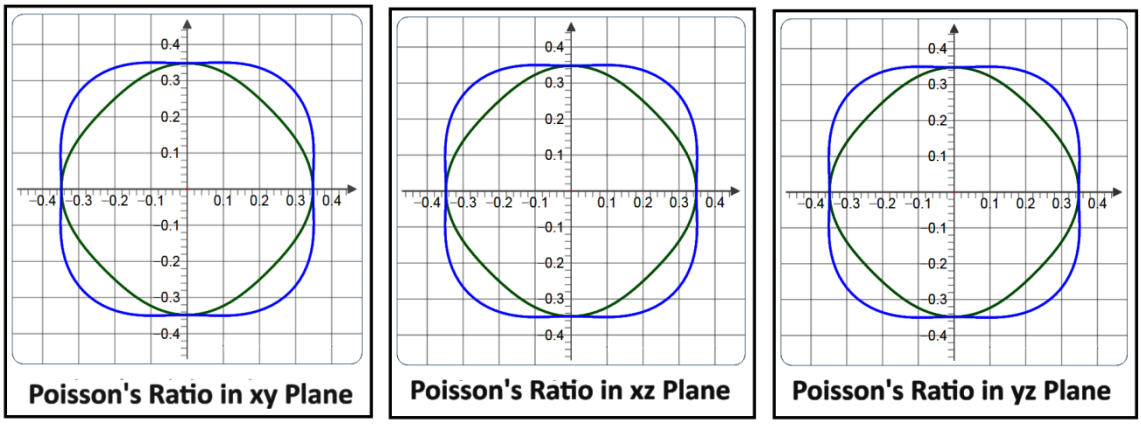

Figure 4. Spatial variation of Poisson's ratio of RhBiTi using computational ELATE software [26, 27].

computed by means of computational ELATE software [26, 27]. The lowest values of quantities Young's modulus, linear compressibility, Poisson's ratio and shear modulus of compounds RhBiX at zero pressure are also computed using computational ELATE software. The largest values of these elastic quantities are also computed. Elastic anisotropy parameters are calculated for these compounds. The spatial dependence of Poisson's ratio and shear modulus are investigated by means of computational ELATE software.

Results and discussion

Wei *et al.* [5] reported elastic stiffness constants C_{11} = 181.18 GPa, C_{12} = 96.76 GPa, and C_{44} = 37.20 GPa for RhBiTi and C_{11} = 194.16 GPa, C_{12} = 87.41 GPa, and C_{44} = 50.18 GPa for RhBiZr. Elastic stiffness constants are C_{11} = 197.07 GPa, C_{12} = 91.64 GPa, and C_{44} = 46.77 GPa for RhBiHf as calculated by Wei *et al.* [5]. The bulk modulus and shear modulus of compounds RhBiX (X = Hf, Ti and Zr) were reported by Wei *et al.* [5]. The Young's modulus and Poisson's ratio of these compounds RhBiX were also reported [5].

Table 1 shows the calculated values of quantities bulk modulus, shear modulus and Young's modulus of compounds RhBiX (X = Hf, Ti and Zr) at zero pressure as

per the Voigt-Reuss-Hill scheme [23-25]. Using elastic stiffness constants C_{ij} for RhBiX as reported by Wei *et al.* [5], these elastic moduli (shown in Table 1) are computed by means of computational ELATE software [26, 27]. For the calculation of elastic anisotropy, Voigt and Reuss elastic moduli [23, 24] of compounds RhBiX are calculated in this work. The values of quantities bulk modulus, shear modulus and Young's modulus of compounds RhBiX (X = Hf, Ti and Zr) as computed by Wei *et al.* [5] and the respective elastic moduli values (K_H, G_H and E_H in Table 1) are almost the same.

All these three compounds have sufficiently high values of bulk modulus. It is clear from Table 1 that the values of bulk modulus of these compounds are not much different from each other. Table 1 shows that compound RhBiTi has the lowest value of shear modulus among these compounds. There is about 31% difference in the value of shear modulus between RhBiZr and RhBiTi. It is evident from Table 1 that the value of Young's modulus is the lowest for RhBiTi among these compounds. As per the Voigt-Reuss-Hill scheme [23-25], Young's modulus E_H of RhBiTi is 106.29 GPa. Thus, Table 1 shows the ample mechanical strength of these compounds RhBiX.

In terms of elastic compliance constants (S_{ij}), Young's modulus E along the unit vector l_i for the cubic crystal may be shown as [28].

$$E = \left[S_{11} - 2\left(S_{11} - S_{12} - \frac{1}{2} S_{44} \right)\left(l_1^2 l_2^2 + l_2^2 l_3^2 + l_1^2 l_3^2 \right) \right]^{-1} \quad (1)$$

where the direction cosines are denoted by l_1, l_2 and l_3.

The directional linear compressibility β for cubic crystal may be shown as [28].

$$\beta = S_{11} + 2S_{12} \quad (2)$$

Using the values of elastic stiffness constants C_{ij} [5], computed lowest and largest values of Young's modulus, linear compressibility, Poisson's ratio and shear modulus of compounds RhBiHf, RhBiTi and RhBiZr at zero pressure are shown in Table 2. For calculations of these values (shown in Table 2), ELATE software [26, 27] is utilized. For linear compressibility, there is no variation in its value for each compound. Variations in the values of shear modulus of RhBiHf, RhBiTi and RhBiZr are 12.7%, 13.5% and 6.4%, respectively, concerning their respective minimum values. The maximum percentage changes in the values of Young's modulus of compounds RhBiHf, RhBiTi and RhBiZr are 11.2%, 12.1% and 5.6%, respectively, with reference to their respective minimum values. It is obvious that RhBiZr has a lower percentage change in the quantities of shear modulus and Young's modulus in comparison to those of RhBiHf and RhBiTi. The variation in the value of Poisson's ratio is nearly 26% each for RhBiHf and RhBiTi, whereas it is 13.4% for RhBiZr relative to their respective minimum values.

Table 3 reveals the various elastic anisotropy parameters. The ratios of largest to lowest values of Young's modulus, shear modulus and Poisson's ratio of compounds RhBiX are represented in Table 3.

There are different ways to represent elastic anisotropy. The elastic anisotropy parameters (A_K and A_G) may be represented in the following way [29, 30]:

$$A_G = \frac{G_V - G_R}{G_V + G_R} \quad (3)$$

$$A_K = \frac{K_V - K_R}{K_V + K_R} \quad (4)$$

It is evident from Table 3 that the value of the elastic anisotropy parameter A_K for each compound RhBiX (X = Hf, Ti and Zr) is zero. The value of the elastic anisotropy parameter A_G for compound RhBiZr is lower than those of compounds RhBiHf and RhBiTi.

Ranganathan et al. [31] defined the universal elastic anisotropy index (A^U) in the following way:

$$A^U = \frac{K_V}{K_R} + 5\frac{G_V}{G_R} - 6 \quad (5)$$

The value of A^U of compound RhBiZr is 0.0048. The values of A^U of compounds RhBiHf and RhBiTi are 0.0174 and 0.0192, respectively.

Figure 1 shows the spatial variation of Young's modulus E (in GPa unit) of RhBiTi. Spatial variation of linear compressibility [in $(TPa)^{-1}$ unit] of RhBiTi is shown in Figure 2.

The spatial variation of shear modulus (in GPa unit) of RhBiTi is illustrated in Figure 3. For the Poisson ratio of RhBiTi, spatial variation is represented in Figure 4. For plotting, Figure 3 and Figure 4, convention as described by Marmier et al. [32] is implemented.

In order to plot Figure 1 to Figure 4, elastic constants C_{11}, C_{12} and C_{44} of RhBiTi as reported by Wei *et al.* [5] are used as input parameters.

Conclusion and Future Prospective

The present study reveals the elastic anisotropy of compounds RhBiX (X = Hf, Ti and Zr). The shear modulus of RhBiHf varies from 46.77 GPa to 52.72 GPa. The maximum change in values of shear modulus of RhBiHf, RhBiTi and RhBiZr are 12.7%, 13.5% and 6.4%, respectively, with reference to their respective minimum

values. Directional Young's modulus of RhBiTi varies from 101.52 GPa to 113.81 GPa. Compound RhBiZr has a lower percentage change in Young's modulus in comparison to those of RhBiHf and RhBiTi. The values of the universal elastic anisotropy index (A^U) for RhBiTi and RhBiZr are 0.0192 and 0.0048, respectively. From the point of view of mechanical stability, the results of the present investigation may be utilized for the preferred orientation of crystals for the fabrication of devices using these compounds. In this calculation, our elastic anisotropy results depend on the values of elastic constants. As far as the experimental values of the elastic constants of these compounds are concerned, to the best of my knowledge, these values are not known. The computed elastic constants may vary significantly with computed lattice parameters. The calculated elastic constants by the first principle method also depend on the used exchange-correlation functional. Hence, our elastic anisotropy results are also dependent on the used PBE functional in the reported work of Wei et al. Nevertheless, the low order of values of the universal elastic anisotropy index of these compounds clearly indicates that the order of elastic anisotropy would be low. Our results may be validated by future experimental research. Elastic properties of compounds RhBiX (X=Hf, Ti and Zr) with doping of appropriate elements may be investigated in future research to reveal the possibilities of appropriate utilization of these compounds in devices. Future research may shed light on investigations of pressure-dependent elastic properties.

References

1. Wei, J., Yang, L., Ma, Z., Song, P., Zhang, M., Ma, J., Yang, F. and Wang, X., 2020. *Review of current high-ZT thermoelectric materials*. Journal of Materials Science, 55(27), pp.12642-12704. https://doi.org/10.1007/s10853-020-04949-0
2. Fu, C., Bai, S., Liu, Y., Tang, Y., Chen, L., Zhao, X. and Zhu, T., 2015. *Realizing high figure of merit in heavy-band p-type half-Heusler thermoelectric materials*. Nature Communications , 6(1), p.8144. https://doi.org/10.1038/ncomms9144
3. Zhu, H., Mao, J., Li, Y., Sun, J., Wang, Y., Zhu, Q., Li, G., Song, Q., Zhou, J., Fu, Y., He, R., Tong, T., Liu, Z., Ren, W., You, L., Wang, Z., Luo, J., Sotnikov, A., Bao, J., Nielsch, K., Chen, G., Singh, D.J. and Ren, Z., 2019. *Discovery of TaFeSb-based half-Heuslers with high thermoelectric performance*. Nature Communications, 10(1), p.270. https://doi.org/10.1038/s41467-018-08223-5
4. Graf, T., Klaer, P., Barth, J., Balke, B., Elmers, H.J. and Felser, C., 2010. *Phase separation in the quaternary Heusler compound CoTi(1− x)MnxSb–A reduction in the thermal conductivity for thermoelectric applications*. Scripta Materialia, 63(12), pp.1216-1219. https://doi.org/10.1016/j.scriptamat.2010.08.039
5. Wei, J., Guo, Y. and Wang, G., 2023. *Exploring structural, mechanical, and thermoelectric properties of half-Heusler compounds RhBiX (X= Ti, Zr, Hf): A first-principles investigation*. RSC Advances, 13(17), pp.11513-11524. https://doi.org/10.1039/D3RA01262J
6. Blaha, P., Schwarz, K., Tran, F., Laskowski, R., Madsen, G.K.H. and Marks, L.D., 2020. WIEN2k: *An APW+ lo program for calculating the properties of solids.* The Journal of Chemical Physics, 152(7), p. 074101. https://doi.org/10.1063/1.5143061
7. Carrete, J., Li, W., Mingo, N., Wang, S. and Curtarolo, S., 2014. Finding Unprecedentedly *Low-Thermal-Conductivity Half-Heusler Semiconductors via High-Throughput Materials Modeling*. Physical Review X, 4(1), p.011019. https://doi.org/10.1103/PhysRevX.4.011019
8. Feng, Z., Fu, Y., Zhang, Y. and Singh, D.J., 2020. *Characterization of rattling in relation to thermal conductivity: Ordered half-Heusler semiconductors*. Physical Review B, 101(6), p.064301. https://doi.org/10.1103/PhysRevB.101.064301
9. Ma, J., Hegde, V.I., Munira, K., Xie, Y., Keshavarz, S., Mildebrath, D.T., Wolverton, C., Ghosh, A.W. and Butler, W.H., 2017. *Computational Investigation of Half-Heusler Compounds for Spintronics Applications*. Physical Review B, 95(2), p.024411. https://doi.org/10.1103/PhysRevB.95.024411
10. Graf, T., Felser, C. and Parkin, S.S.P., 2011. *Simple rules for the understanding of Heusler compounds. Progress in Solid State Chemistry*, 39(1), pp.1-50. https://doi.org/10.1016/j.progsolidstchem.2011.02.001
11. Kresse, G. and Hafner, J., 1993. *Ab initio molecular dynamics for liquid metals*. Physical Review B, 47(1), pp.558-561. https://doi.org/10.1103/PhysRevB.47.558
12. Kresse, G. and Hafner, J., 1993. *Ab initio molecular dynamics for open-shell transition metals*. Physical Review B, 48(17), pp.13115-13118. https://doi.org/10.1103/PhysRevB.48.13115
13. Kresse, G. and Hafner, J., 1994. *Ab initio molecular-dynamics simulation of the liquid-metal–amorphous-semiconductor transition in germanium.* Physical Review B, 49(20), pp.14251-14269. https://doi.org/10.1103/PhysRevB.49.14251

14. Kresse, G. and Furthmüller, J., 1996. *Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set*. Physical Review B, 54(16), pp.11169-11186. https://doi.org/10.1103/PhysRevB.54.11169
15. Kresse, G. and Furthmüller, J., 1996. *Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set*. Computational Materials Science, 6(1), pp.15-50. https://doi.org/10.1016/0927-0256(96)00008-0
16. Kresse, G. and Joubert, D., 1999. *From ultrasoft pseudopotentials to the projector augmented-wave method*. Physical Review B, 59(3), pp.1758-1775. https://doi.org/10.1103/PhysRevB.59.1758
17. Hafner, J., 2008. *Ab-initio simulations of materials using VASP: Density-functional theory and beyond*. Journal of Computational Chemistry, 29(13), pp.2044-2078. https://doi.org/10.1002/jcc.21057
18. Cramer, C.J., 2004. *Essentials of Computational Chemistry: Theories and Models*. 2nd ed. England: John Wiley & Sons Ltd.
19. Fermi, E., 1928. *Eine statistische Methode zur Bestimmung einiger Eigenschaften des Atoms und ihre Anwendung auf die Theorie des periodischen Systems der Elemente*. Zeitschrift für Physik, 48(1), pp.73-79. https://doi.org/10.1007/BF01351576
20. Thomas, L.H., 1927. *The calculation of atomic fields*. Mathematical Proceedings of the Cambridge Philosophical Society, 23(5), pp.542-548. https://doi.org/10.1017/S0305004100011683
21. Perdew, J.P., Burke, K. and Ernzerhof, M., 1996. *Generalized Gradient Approximation Made Simple*. Physical Review Letters, 77(18), pp.3865-3868. https://doi.org/10.1103/PhysRevLett.77.3865
22. Perdrew, J.P., Burke, K. and Ernzerhof, M., 1997. *Erratum: Generalized Gradient Approximation Made Simple* [Physical Review Letters, 77, 3865 (1996)]. Physical Review Letters, 78(7), p.1396. https://doi.org/10.1103/PhysRevLett.78.1396
23. Voigt, W., 1928. Lehrbuch der Kristallphysik. BG Teubner, Leipzig und Berlin.
24. Reuss, A. and Angew, Z., 1929. *Berechnung der Fliesgrenze von Mischkristallen auf Grund der Plastizatsberechnung fur Einkristalle*. Journal of Applied Mathematics and Mechanics, 9(1), pp.49–58. https://doi.org/10.1002/zamm.19290090104
25. Hill, R., 1952. *The Elastic Behaviour of a Crystalline Aggregate. Proceedings of the Physical Society*, Section A, 65(5), p.349-354. https://doi.org/10.1088/0370-1298/65/5/307
26. Gaillac, R., Pullumbi, P. and Coudert, F.X., 2016. *ELATE: An open-source online application for analysis and visualization of elastic tensors.* Journal of Physics: Condensed Matter, 28(27), p.275201. https://doi.org/10.1088/0953-8984/28/27/275201
27. http://progs.coudert.name/elate
28. Nye, J.F., 1985. *Physical Properties of Crystals: Their Representation by Tensors and Matrices*. New York: Oxford University Press Inc.
29. Chung, D.H. and Buessem, W.R., 1967. *The Elastic Anisotropy of Crystals*. Journal of Applied Physics, 38(5), pp.2010-2012. https://doi.org/10.1063/1.1709819
30. Chung, D.H. and Buessem, W.R., 1968. *Anisotropy in Single Crystal Refractory Compounds: Vol. 2*. (Eds. Vahldiek, F.W. and Mersol, S.A.), New York: Plenum Press. pp. 217–246
31. Ranganathan, S.I. and Ostoja-Starzewski, M., 2008. *Universal Elastic Anisotropy Index*. Physical Review Letters, 101(5), p.055504. https://doi.org/10.1103/PhysRevLett.101.055504
32. Marmier, A., Lethbridge, Z.A.D., Walton, R.I., Smith, C.W., Parker, S.C. and Evans, K.E., 2010. *ElAM: A computer program for the analysis and representation of anisotropic elastic properties*. Computer Physics Communications, 181(12), pp.2102-2115. https://doi.org/10.1016/j.cpc.2010.08.033.