

Mechanical stability and elastic properties of new quaternary alloys

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In this research paper, newly found quaternary alloys of the type A_2BCD_4 are investigated. The bulk and shear modulus of these crystals are calculated by means of the stiffness tensor, which is obtained through the stress tensor procedure. From the stiffness tensor, the crystals are subjected to the elastic stability criteria to assess whether these alloys are truly stable. DFT is implemented with QuantumEspresso, using PBE pseudopotentials for all elements involved.

I. INTRODUCTION

Recently new quaternary alloys of the type A_2BCD_4 were found to be stable according to energetic considerations based on density functional theory (DFT). It is the goal of this paper to assess whether or not these crystals also meet the Born stability criteria based on mechanical considerations. To this end, the stiffness tensor is generated using the well-known stress tensor procedure in DFT. From this, estimates for the bulk- and shear modulus are made as well. There are a variety of elements that make up these alloys, the elements of type A, being K-Rb-Cs, belong to the alkali metals, while elements of type B can belong to the alkali- or alkaline earth metals. Elements of type C can be found in group 4A and 5A, while type D elements are found in group 6A of the periodic table. Before properties can be accurately derived, a convergence test for all crystals is done to make sure no noise is calculated and that the results are actually relevant, whilst keeping computational times as low as possible. Once finished, the energy of the crystal is minimized by optimizing the geometry of the unit cell while relaxing the atoms. Here-after the stress-tensor procedure is initiated to compute the stiffness tensor, from which the desired properties can be derived.

II. DFT PREPARATION

A. Convergence Testing

All crystals were subjected to an independent convergence test, this implies that the K-mesh, cutoff for charge density (ecutrho) and cutoff for wavefunctions (ecutwfc) were fine-tuned. To this end, the K-mesh was increased with the suggested values of the used PBE pseudopotentials until the hydrostatic pressure deviated no more

than 3 kbar from the previous value. The effect of changing the ecutwfc parameter, whilst keeping the ecutwfc/ecutrho ratio constant, on the hydrostatic pressure was investigated. Lastly, the said ratio was checked to see if it had effect on this same property.

B. Geometry Optimization

To check for energetic stability, and to give sense to stress-strain interaction, the crystal structures need to be optimized with respect to their total energy. All crystals started from a tetragonal lattice and all resulted in triclinic lattice structures with $a = b \neq c$; $\alpha = \beta \neq 90^\circ$ and $\gamma \approx 90^\circ$. An example can be seen in Figure 1 where the Rb_2NaPSe_4 crystal is shown after geometrical optimization.

III. COMPUTING THE PROPERTIES

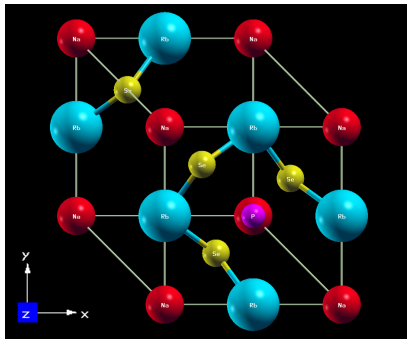
A. Theoretical background

It is possible to write down the generalization of Hookes law - for anisotropic materials - in matrix formalism using the Voigt notation. Since the stress and strain tensors are symmetric, it is possible to write the (3x3) matrix representations as (6x1) vectors, without the loss of information:

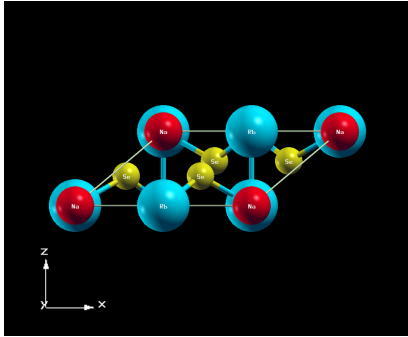
$$\begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{xy} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} \end{bmatrix} \rightarrow \begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{xz} \\ \sigma_{xy} \end{bmatrix}$$

$$\begin{bmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{xy} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{xz} & \epsilon_{yz} & \epsilon_{zz} \end{bmatrix} \rightarrow \begin{bmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \epsilon_{zz} \\ 2\epsilon_{yz} \\ 2\epsilon_{xz} \\ 2\epsilon_{xy} \end{bmatrix}$$

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(a) XZ plane



(b) XZ plane

FIG. 1: Visual representation from different planes of the $\text{Rb}_2\text{NaPSe}_4$ crystal after geometry optimization.

We can relate the Voigt stress and strain vectors by a 6×6 elasticity matrix, which is a specific representation of the stiffness tensor C , whose elements are called elastic constants. Writing this down, we obtain the generalized Hooke's law in Voigt notation:

$$\begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{xz} \\ \sigma_{xy} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{bmatrix} \begin{bmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \epsilon_{zz} \\ 2\epsilon_{yz} \\ 2\epsilon_{xz} \\ 2\epsilon_{xy} \end{bmatrix}$$

It is important to note that this is a tensor equation, which means it is invariant to a change of coordinate system. Once one of the three tensors in Hooke's law is represented by its matrix-representation in a chosen coordinate system, one must keep in mind that all other tensors must be represented in this specific system. That is why the elasticity matrix was denoted as a specific representation of the stiffness tensor C . Concise: the stiffness tensor is invariant, the elastic constants are not.

In essence, the stress and strain tensors are rank 2 covariant tensors σ_{ij} and ϵ_{ij} respectively, which relate to a (3×3) matrix representation in a three dimensional coordinate system. Hooke's law, for an anisotropic material, then requires a rank 4 tensor C_{ijkl} to relate these second order tensors (dependency on all 4 indices), which has a

Property	Equation
Bulk modulus Voigt average, K_V	$9K_V = (C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{23} + C_{31})$
Bulk modulus Reuss average, K_R	$1/K_R = (s_{11} + s_{22} + s_{33}) + 2(s_{12} + s_{23} + s_{31})$
Shear modulus Voigt average, G_V	$15G_V = (C_{11} + C_{22} + C_{33}) - (C_{12} + C_{23} + C_{31}) + 3(C_{44} + C_{55} + C_{66})$
Shear modulus Reuss average, G_R	$15/G_R = 4(s_{11} + s_{22} + s_{33}) - 4(s_{12} + s_{23} + s_{31}) + 3(s_{44} + s_{55} + s_{66})$

FIG. 2: Relation between the Bulk and Shear moduli and the elasticity matrix. The Voigt estimates are an upper bound while the Reuss estimates are a lower bound [2].

$(3 \times 3 \times 3 \times 3)$ matrix representation. The tensor equation:

$$\sigma_{ij} = C_{ijkl} \epsilon_{kl}$$

Taking advantage of symmetries, one can rewrite the $(3 \times 3 \times 3 \times 3)$ representation into a (6×6) matrix representation, with use of the Voigt notation for stress and strain tensors. The independent variables of C are then further reduced to 21, because it is symmetric in this representation. This results in the generalized Hooke's law (cfr. supra). A full mathematical description can be found in the paper of P. Helnwein [1].

The properties that will be calculated are the Voigt and Reuss averages for the bulk and shear modulus, and are given in Figure 2, which stems from the paper by M. de Jong, W. Chen et al. [2]. It is clear from the discussion above that the derived properties will depend on the choice of the coordinate system. In this project, the triclinic lattice parameters, the deformations, the stresses and the strains - and therefore the elastic constants - are expressed in a cartesian coordinate system. This is conform the description by *IEEE* [3]: *The elastic, piezoelectric, and dielectric properties of a piezoelectric material are characterized by a knowledge of the fundamental constants referred to a rectangular coordinate system fixed relative to the crystallographic axes*. It seems important to use this orthogonal set-up, because the expressions for the bulk and shear modulus are mainly dependent on the upper quadrant values of the elasticity matrix, which carry a relation between normal stresses and strains in the chosen coordinate system. This is good when one recalls that the bulk modulus is defined by introducing a pressure difference, which introduces normal stresses and strains.

B. DFT procedure

To obtain the elastic coefficients in the previously mentioned coordinate system, six independent deforma-

tions are introduced into the geometry-optimized crystals, which are given at the end of this section. Hereafter, the atoms in the crystals are relaxed and the remaining stresses are acquired in Voigt representation. The strains that result from these deformations do not require DFT, and are calculated by means of the Green-Lagrange strain tensor:

$$E = 1/2(F^T F - I)$$

Where F denotes the deformation matrix, and I the identity matrix. This method of calculating the strain tensor was chosen over the strain tensor calculated by the Bilbao Crystallographic Server, for the simple reason that the latter is not expressed in the same coordinate system as the cartesian one defined by the in-and output of QuantumEspresso. From the previous theoretical discussion it is clear that these strains would result in useless elasticity calculations. After transforming the strains into Voigt notation, a system of 6 independent generalized Hookes law relations is obtained, as described in the theory section, which allows calculation of the elasticity matrix. The latter will not be symmetric because of the presence of numerical noise, and because the calculation was overfitted with 36 data points whilst only 21 were needed (the symmetry was not fixed beforehand).

$$F_1 = \begin{bmatrix} 1 + \delta_1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} F_2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 + \delta_1 & 0 \\ 0 & 0 & 1 \end{bmatrix} F_3 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 + \delta_1 \end{bmatrix}$$

$$F_4 = \begin{bmatrix} 1 & \delta_2 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} F_5 = \begin{bmatrix} 1 & 0 & \delta_2 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} F_6 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & \delta_2 \\ 0 & 0 & 1 \end{bmatrix}$$

FIG. 3: The six independent deformations used in this study. δ_1 was set to 0.01 and δ_2 was set to 0.03.

IV. RESULTS

First of all, geometry optimization revealed that all the crystals are indeed energetically stable. Mechanical stability was probed with the Born stability criteria. One of these criteria states that all eigenvalues of the elasticity matrix should be larger than zero. When these were calculated for each crystal, it was noted that they all had at least one negative eigenvalue, of the order of -10 or larger. This means that although the crystals are energetically stable, they are not mechanically stable. This is reflected in the bulk and shear moduli calculated by the Voigt and Reuss estimates, which reveal a lot of negative values. After discarding the extreme values, marked in gray in Table I, which could be obtained by convergency or accuracy issues, the average of the upper and lower

bound from the crystals were compared to each other. $\text{Rb}_2\text{KSiSe}_4$ has the highest average bulk modulus while $\text{K}_2\text{MgSiSe}_4$ has the lowest one. As far as the shear modulus is concerned, $\text{Rb}_2\text{KSiSe}_4$ has the lowest average shear modulus while $\text{K}_2\text{MgSiSe}_4$ has the highest one.

Crystal	K_{Voigt} (GPa)	K_{Reuss} (GPa)	G_{Voigt} (GPa)	G_{Reuss} (GPa)
$\text{Cs}_2\text{MgSnSe}_4$	-14.12	-15.86	-7.20	-11.66
$\text{Cs}_2\text{CaSnSe}_4$	-3.10	0	-13.53	0
$\text{Cs}_2\text{MgGeSe}_4$	-16.53	-56.52	-13.22	-7.88
$\text{Cs}_2\text{CaGeSe}_4$	-12.74	-10.91	-9.35	-3.08
$\text{Cs}_2\text{BaSnSe}_4$	-10.74	-8.14	-6.13	-0.38
$\text{Cs}_2\text{BaGeSe}_4$	-81.20	0	-23.96	0
$\text{Cs}_2\text{SrGeSe}_4$	18.22	16.37	6.17	1.29
$\text{Cs}_2\text{SrSnSe}_4$	24.69	19.94	6.25	4.10
$\text{Cs}_2\text{RbAsSe}_4$	9.12	13.87	3.48	7.71
$\text{K}_2\text{BaSiSe}_4$	31.70	955.4	-1.44	7.00
$\text{K}_2\text{CaSiSe}_4$	53.70	-2792	22.85	172.2
$\text{K}_2\text{MgSiSe}_4$	-20.78	-30.99	-8.59	-14.56
$\text{K}_2\text{RbSiSe}_4$	-13.29	-12.83	-3.67	12.94
$\text{K}_2\text{SrSiSe}_4$	-22.47	-21.37	-7.02	-6.77
$\text{Rb}_2\text{CaSiSe}_4$	6.78	5.33	-7.08	-5.75
$\text{Rb}_2\text{BaSiSe}_4$	-3.90	-7.90	-5.94	8.50
$\text{Rb}_2\text{CsPSe}_4$	-10.25	-10.93	-3.79	9.53
Rb_2KPSe_4	28.80	23.03	-4.33	4.65
$\text{Rb}_2\text{KSiSe}_4$	32.63	34.71	-4.57	-19.13
$\text{Rb}_2\text{MgSiSe}_4$	9.08	14.35	-5.10	-11.29
$\text{Rb}_2\text{MgSiTe}_4$	1.65	4.49	-5.81	-10.15
$\text{Rb}_2\text{NaPSe}_4$	5.87	4.47	-5.36	-2.71
$\text{Rb}_2\text{SrSiSe}_4$	7.74	17.23	-11.12	-118.53

TABLE I: Calculated bulk- and shear moduli for all 23 crystals.

V. CRITICAL ASSESSMENT

We would like to conclude with a critical look on the procedure used to obtain the desired properties. As was stressed in the theoretical part, the elasticity matrix is dependent on the coordinate system that is used. We took quite some time to assess that the used coordinate systems in all of the tensor quantities of Hooke's law were represented in the same coordinate system, and to the best of our knowledge this was done correctly. We also postulated that the chosen orthogonal reference frame was correct for calculation of the bulk modulus, since a natural link arose between the Voigt and Reuss estimates and normal strains and -stresses. However, since we do not know the intricacies of the Voigt and Reuss averaging procedure, we cannot say with certainty that these results are indeed indicative for a correct estimation. As regard to numerical precision, the negative eigenvalues were too much below zero to assume stability might be present with higher precision calculations (provided that the procedure was correctly implemented).

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