Elastic anisotropy and thermal properties of extended linear chain compounds MV$_2$Ga$_4$ (M = Sc, Zr, Hf) from ab-initio calculations

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Abstract

MV$_2$Ga$_4$ (M = Sc, Zr, Hf) compounds belong to an emerging class of materials showing a unique combination of unusual superconducting behavior with extended linear chains in the crystal structure. In order to gain insights into its mechanical and thermal properties, we have performed first-principles electronic-structure calculations in the framework of the Density Functional Theory (DFT). From the calculated second-order elastic constants, we have systematically shown that the extended vanadium chain substructures indeed give rise to an anisotropic regime in the elastic and mechanical moduli. The high density of valence and conduction electrons along the linear vanadium chains leads to a directional dependence of the reciprocal linear compressibility. Young’s modulus and shear modulus. Poisson’s ratio for several elongation directions is also drastically affected by the presence of extended V chains. If the elongation is along the V chains, all compounds exhibit practically the same Poisson ratio in directions perpendicular to it, further highlighting the importance of the V chains to the mechanical properties. Moreover, based on our results, we have discussed the possible consequences of the elastic anisotropy on the superconducting properties of the compounds. Finally, using the Debye-Grüneisen approximation, our calculations of thermal properties show a good agreement with the available experimental low temperature heat capacity data above the superconducting critical temperature.

Keywords: Anisotropic elasticity, Ab-initio calculations, Mechanical behavior, Superconductivity, Extended linear chain compounds

1. Introduction

The discovery of new materials drives the technology to an entirely new plethora of applications and possibilities. To harness their potential, it is essential to develop a fundamental understanding of the basic physics that governs their behavior. One of the most interesting class of materials, with crucial applicabilities, are the superconductors. Since their discovery in 1911 by Kamerlingh Onnes, and the first successful microscopic theory proposed in the seminal work by Bardeen, Cooper and Schrieffer (BCS) in 1957 [1], superconducting materials have been used in medical, energy and transport applications, electronic devices, quantum interference sensors, and as high-field electromagnets [2–8]. For a long time, novel types of superconducting materials have been found in contrast to what became known as conventional superconductors, which can be explained by BCS-type signatures. In particular, a new type-II electron-phonon superconductor at 4.1 K was recently discovered with composition HfV$_2$Ga$_4$ [9]. This compound is interesting and atypical since it exhibits a possible multiband superconducting effect, which fundamentally consists of the opening of two or more superconducting gaps at the Fermi surface below the critical superconducting temperature ($T_c$) [10]. In fact, HfV$_2$Ga$_4$ is one of the first examples of a non-heavy fermion material with double-jumps in the specific heat, and the two-gap superconductivity is supported by first-principle calculations, that show electrons arising from distinct bands in disconnected sheets of the Fermi surface with very different electronic characters [9, 11]. In addition, it was theoretically predicted that the ScV$_2$Ga$_4$ compound is presumably another example of a two-band electron-phonon superconductor with an even higher $T_c$ than HfV$_2$Ga$_4$ [11].

Attached to the unusual superconducting behavior that deviates from the more conventional BCS-theory signatures, the arrangement of atoms in the HfV$_2$Ga$_4$ compound is such that V atoms form directional bonds with one another so that the structure, as a whole, achieves extended linear 1D highly-populated (by electrons) V-d chains that command the density of states at the Fermi level ($E_F$). Extended (or “infinite”, as some authors prefer) linear chain compounds, despite known for quite some time, are a relatively recent topic of interest, having been systematically investigated only in the last few years in the literature [12]. Those compounds generally exhibit useful electrical, magnetic, superconducting, thermal and optical anisotropic properties, as seen, for instance, in Hg$_{3-\delta}$AsF$_6$ and Hg$_{3-\delta}$SbF$_6$ compounds [13–16]. Their anisotropy occurs due to the high density of conduction electrons on the Hg chains, which act as one-dimensional metals [17]. Transition metal chain substructures were also reported in several compounds within the YbM$_2$Al$_2$-prototype (the same prototype of MV$_2$Ga$_4$ materials, with M = Sc, Zr, Hf), but most efforts were focused on chemical bonding and electronic properties [18–21]. There is, therefore, a lack of information on the effect of the extended linear chains on the mechanical properties of such compounds. Moreover, ab-initio calculations of mechanical properties are a challenging but promising simulation technique that can be used with advantage to probe the potential of new materials [22].

In this work we have shown, using Density Functional Theory (DFT)-based methods, that the extended linear vanadium...
chains in the MV\textsubscript{2}Ga\textsubscript{4} (M = Sc, Zr, Hf) compounds indeed give rise to an anisotropic regime in the elastic and mechanical moduli. From the calculated second-order elastic constants and the Debye-Grüneisen quasi-harmonic approximation, we have evaluated the mechanical and thermal properties, as well as the directional dependence of linear compressibility, shear and Young’s modulus, Poisson’s ratio, and sound velocities in the crystal structure. Similar methodologies have been extensively employed in the literature to obtain mechanical and thermal properties for widely different classes of materials [23–29], which point to the importance of the topic and its high potential to promote and motivate future studies. On the same footing, it is possible that other extended linear chain compounds present similar elastic anisotropy trends as the compounds studied here, pointing to a general behavior of this class of materials.

2. Computational Methods

Ab-initio calculations were performed using the Quantum ESPRESSO computational package [30] within the framework of Density Functional Theory (DFT) in the Kohn-Sham scheme [31], employing scalar-relativistic optimized norm-conserving Vanderbilt pseudopotentials [32]. The Exchange and Correlation (XC) functional employed was the Generalized Gradient Approximation (GGA) [33] in the parametrization due to Perdew-Burke-Ernzerhof (PBE) [34]. We have used a wave-function energy cut-off of 220 Ry (1 Ry = 13.6 eV), and four times that value for the charge density energy cut-off. The Monkhorst-Pack scheme [35] was used for a 1728 \textit{k}-point sampling in the first Brillouin zone. Self-consistent-field (SCF) calculations were carried out using Marzari-Vanderbilt cold smearing [36] of 0.002 Ry, and the damped quick-min Verlet ion dynamics algorithm was applied for structural relaxation [37]. All lattice parameters and internal degrees of freedom were relaxed in order to guarantee a ground-state convergence of 10\textsuperscript{-5} Ry in total energy and 0.5 mRy/\textit{a}_{0} (\textit{a}_{0} \approx 0.529 \text{Å}) for forces acting on the nuclei. In a previous work [11] we used an all-electron approach, instead of the pseudopotential methodology applied here, in order to obtain the ground-state electronic properties for the HfV\textsubscript{2}Ga\textsubscript{4} and ScV\textsubscript{2}Ga\textsubscript{4} compounds. We found no appreciable differences either in the density of states or in the band structure plots when we compared the two techniques, which we take as an indication of the validity of the present methodology and of the choice of pseudopotentials.

The full second-order elastic stiffness tensor was obtained using the ElaStic code [38]. In the energy approach, the elastic constants result from a set of deformations imposed on the reference ground-state structure, in the framework of the Lagrangian Theory of Elasticity [39]:

\[
c_{\alpha\beta} = \frac{1}{V_{0}} \left. \frac{\partial^{2}U}{\partial \eta_{\alpha} \partial \eta_{\beta}} \right|_{\eta=0},
\]

where \(U\) is the total energy due to the deformation, \(V_{0}\) is the volume of the undeformed ground state structure and \(\eta_{\alpha}, \eta_{\beta}\) are Lagrangian strains, expressed in Voigt notation. The MV\textsubscript{2}Ga\textsubscript{4} compounds crystallize in a body-centered tetragonal structure, having therefore six independent second-order elastic constants, as shown below in matrix form:

\[
\mathbf{C} = \begin{pmatrix}
    c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\
    c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\
    c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\
    0 & 0 & 0 & c_{44} & 0 & 0 \\
    0 & 0 & 0 & 0 & c_{44} & 0 \\
    0 & 0 & 0 & 0 & 0 & c_{66}
\end{pmatrix}
\]

Therefore, in the ElaStic code we have used six different deformation types for each ground-state compound, with a maximum absolute intensity of \(\eta_{\text{max}} = 0.05\) for the Lagrangian strain, and 15 distorted structures with strain intensities between \(-\eta_{\text{max}}\) and \(+\eta_{\text{max}}\) for each deformation type, a total of 90 deformations per compound.

3. Results and Discussion

3.1. Elastic stiffness and compliance tensors

MV\textsubscript{2}Ga\textsubscript{4} (M = Sc, Zr, Hf) compounds crystallize in the same body-centered tetragonal structure as the YbMo\textsubscript{2}Al\textsubscript{4} prototype (space group I4/mmm, \#139, Pearson symbol tI14) [40]. The crystal structure is such that the M sites, at the 2\textit{a} (0, 0, 0) Wyckoff positions, are surrounded by V and Ga sites at 4\textit{d} (0, 1/2, 1/4) and 8\textit{h} (0, 0.303, 0.303, 0), respectively, in a cage-like structure, in such a way that the vanadium sites form extended linear chains in the \(c\)-direction. A stacking of three unit cells along the \(c\) axis is schematically illustrated in Figure 1. In the present work, the initial crystal structure was built based on experimental crystallographic data [9, 40], and then optimized as described in Sec. 2. The calculated lattice parameters and the 8\textit{h} degree of freedom (\(\xi_{\text{Ga}}\)) are shown in Table 1. The slight dissimilarity of at most 1% in the optimized lattice parameters and atomic positions in comparison with experimental data reinforce the validity of the computational methods employed.

The six calculated second-order elastic constants necessary to specify the elastic stiffness tensor for a body-centered tetragonal crystal are listed in Table 2. The related elastic compliance constants \(s_{\alpha\beta}\) are presented in Table 3, obtained by matrix inversion of the stiffness tensor:

\[
\sigma_{\alpha} = c_{\alpha\beta} \varepsilon_{\beta} \quad \Leftrightarrow \quad \varepsilon_{\alpha} = s_{\alpha\beta} \sigma_{\beta}
\]

in which \(1 \leq \alpha, \beta \leq 6\) and, as in the rest of the work, Einstein’s tensorial implicit, equal indices sum notation was employed. It is seen that the elastic constants in Table 2 do not obey the Cauchy conditions \(c_{12} = c_{66}\) and \(c_{13} = c_{44}\), an indication that the strength does not come from central forces. This, naturally, is a consequence of the symmetry of the structure, since, with the

| Compound      | \(a\) (Å) | \(c\) (Å) | \(\xi_{\text{Ga}}\) |
|---------------|----------|----------|------------------|
| ScV\textsubscript{2}Ga\textsubscript{4} | 6.421 | 5.135 | 0.3003 |
|              | 6.432 | 5.216 | 0.3030 |
| ZrV\textsubscript{2}Ga\textsubscript{4} | 6.379 | 5.140 | 0.3026 |
|              | 6.462 | 5.207 | 0.3030 |
| HfV\textsubscript{2}Ga\textsubscript{4} | 6.458 | 5.206 | 0.3030 |
|              | 6.432 | 5.190 | 0.3030 |
by Mouhat and Coudert [42]: using the four necessary and sufficient conditions established for the atomic positions are not centers of inversion [41].

exception of the the M sites (occupied by Sc, Zr or Hf), the atomic positions are not centers of inversion [41].

For tetragonal crystals, the elastic stability can be verified using the four necessary and sufficient conditions established by Mouhat and Coudert [42]:

\[ c_{11} > |c_{12}|, \]
\[ 2c_{13}^2 < c_{33}(c_{11} + c_{12}), \]
\[ c_{44} > 0, \quad c_{66} > 0. \]

All of the conditions listed above are fulfilled by the elastic constants in Table 2, a result that point to the mechanical stability of the MV$_2$Ga$_4$ (M = Sc, Zr, Hf) compounds.

The elastic constants $c_{ab}$ also provide straightforward information about the elastic response to different applied stress conditions in single crystals. For instance, $c_{11}$ and $c_{33}$ represent the resistance to uniaxial deformation along the [100] and [001] directions, respectively, while $c_{44}$ is related to the resistance to a pure shear deformation on $(hk0)$ planes. One can verify in Table 2 that ScV$_2$Ga$_4$ and HfV$_2$Ga$_4$ are slightly more resistant under uniaxial stress along the $z$ direction than along the $x$ or $y$ axis, while ZrV$_2$Ga$_4$ has practically the same resistance in both these orientations. ZrV$_2$Ga$_4$ also has the largest $c_{44}$ elastic constant, which indicates an appreciable shear modulus in the plane normal to the extended vanadium chains, as will be seen in more detail in section 3.3.

3.2. Polycrystal mechanical properties

Once the set of independent elastic stiffness and compliance constants for single crystals are known, we can calculate the mechanical properties of a polycristalline aggregate using the Voigt-Reuss-Hill (VRH) approximation. In the Voigt approach an uniform strain is assumed, while Reuss considers an uniform applied stress. Hill [43] has shown that the measured moduli for the aggregate always lie in between the Voigt and Reuss procedures, therefore proposing the bulk ($B$) and shear ($G$) moduli of the polycrystalline material as the arithmetic average of Voigt (upper) and Reuss (lower) bounds:

\[ B_H = \frac{1}{2} (B_V + B_R), \]
\[ G_H = \frac{1}{2} (G_V + G_R). \]

with $B_V$, $G_V$, $B_R$, and $G_R$, for body-centered tetragonal structures, given respectively by

\[ B_V = \frac{2c_{11} + c_{33} + 2(c_{12} + 2c_{13})}{9}, \]
\[ G_V = \frac{2c_{11} + c_{33} - (c_{12} + 2c_{13}) + 3(2c_{44} + c_{66})}{15}, \]
\[ B_R^{-1} = 2s_{11} + s_{22} + 2(s_{12} + 2s_{13}) \]
\[ G_R^{-1} = \frac{4(2s_{11} + s_{33}) - (s_{12} + 2s_{13}) + 3(2s_{44} + s_{66})}{15}. \]

Furthermore, Young’s modulus ($E$) and Poisson’s ratio ($\nu$) are obtained in terms of the bulk and shear modulus using the isotropic theory of elasticity [44]:

\[ E = \frac{9BG}{3B + G}, \]
\[ \nu = \frac{3B - 2G}{2(3B + G)}. \]

Following the VRH approximation, the mechanical properties according to Voigt, Reuss and Hill approaches were calculated and are listed in Table 4. We verify that all MV$_2$Ga$_4$ compounds have the same order of magnitude regarding mechanical moduli, indicating that the element on the 2a site in the structure has only a weak influence on the mechanical properties when we take the overall scenario into account. The larger...
difference between them is observed in ZrV$_2$Ga$_4$, which has the largest values for bulk, shear and Young’s moduli. The obtained bulk modulus, which indicates the resistance of a solid to a hydrostatic external pressure, reveals that ZrV$_2$Ga$_4$ has the most significant resistance to volume change under pressure.

The $B/G$ ratio can be used to predict the ductility of a material [45], and has been extensively used for this purpose in the recent literature [26, 28, 46, 47]. A $B/G$ ratio higher than the critical value 1.75 indicates a significant ductile material, while $B/G < 1.75$ usually means that the material is brittle. As shown in Table 4, all the compounds are essentially brittle, consistent with Poisson’s ratio values smaller than 0.26. It is known that the Poisson’s ratio is a good indicative of the degree of covalent bonds, telling also in advance about the ductility and brittleness of a polycrystalline material [48].

### 3.3. Anisotropy of elastic properties

In several materials, the degree of anisotropy in the single crystal elastic properties is essential to unravel the macroscopic behavior of a solid, even in the polycrystalline state [49]. As previously discussed, extended linear chain compounds usually present strong anisotropy. Therefore, it is reasonable that mechanical moduli also comes up with an outward directional dependence directly related to the elements of the stiffness tensor. Given its importance to applications, considerable efforts have been made to develop parameters able to quantify the extent of anisotropy in elasticity [50–52]. Most recently, Ranganathan et. al [53] proposed a new universal index to quantify a single crystal elastic anisotropy:

$$A^U = 5 \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6.$$  \hspace{1cm} (13)

$A^U$ is identically zero for locally isotropic single crystals, and deviations from zero point out the degree of elastic anisotropy of the material. Using the values in Table 4 we see that ZrV$_2$Ga$_4$, despite possessing the highest mechanical moduli values, has the smallest universal anisotropy index, around 0.28. HfV$_2$Ga$_4$ presents an index equal to 0.38, revealing a considerable directional dependence. The strongest elastic anisotropy, thought, is reached by ScV$_2$Ga$_4$, which has a value of 0.42 for $A^U$. The main contribution for $A^U$ in the MV$_2$Ga$_4$ compounds comes from the shear moduli, taking into account the large difference between the $G_V$ and $G_R$ values according to Voigt and Reuss approximations, as seen in Table 4.

At the same time, the directional dependence of the reciprocal linear compressibility ($B_c$) and Young’s modulus ($E$) can be most easily visualized in the form of 3D spherical plots. In the full fourth-rank tensorial notation, these are given, respectively, by [54, 55]

$$B_c^{-1}(\vec{l}) = s_{ijkl}l_il_j$$ \hspace{1cm} (14)

$$E^{-1}(\vec{l}) = s_{ijkl}l_il_jl_kl_m$$  \hspace{1cm} (15)

in which $1 \leq i, j, k, m \leq 3$ and $\vec{l}$ = $(l_1, l_2, l_3)$ is a unit vector defining the tension direction. For instance, we can adopt

$$\vec{l} = \left( l_1 \atop l_2 \atop l_3 \right) = \left( \cos \varphi \sin \theta \atop \sin \varphi \sin \theta \atop \cos \theta \right)$$ \hspace{1cm} (16)

using the usual azimuthal ($\varphi$) and polar ($\theta$) angles in spherical coordinates shown schematically in Figure 2.

We take the opportunity to make a remark about the reciprocal linear compressibility coefficient $B_c$, since there seems to be a certain degree of confusion in the literature regarding this material property. Some authors equate it to the bulk modulus of the single crystal along a given direction. This interpretation lacks physical meaning, since the bulk modulus is essentially a non-directional quantity, different from the linear compressibility ($B_c^{-1}$), which is indeed a directional property that tells the linear contraction along a given direction resulting from a hydrostatic external pressure [55]. That explains the fact that the “bulk modulus” spherical plots of some authors show values around three times higher than tabulated values found in the same reference (see refs. 25, 27, 28, for instance).

Returning to Eqs. (14) and (15) applied to a body-centered tetragonal system and reverting to Voigt’s notation [55], we can rewrite $B_c^{-1}(\vec{l})$ and $E^{-1}(\vec{l})$ along a given direction $\vec{l}$ as

$$B_c^{-1}(\vec{l}) = (s_{11} + s_{12} + s_{13}) (l_1^2 + l_2^2) + (2s_{13} + s_{33}) l_3^2,$$

$$E^{-1}(\vec{l}) = s_{11} (l_1^2 + l_2^2) + s_{33} l_3^2 + (2s_{13} + s_{44}) (l_1^2 + l_2^2) l_3^2 + (2s_{12} + s_{66}) l_3^2 l_1 l_2.$$  \hspace{1cm} (17)

The resulting spherical plots for the reciprocal linear compressibility and Young’s modulus as a function of the crystallographic orientation are shown in Figure 3(a-f). In the plots,
Figure 3: Surface spherical plots showing the directional dependence of the reciprocal linear compressibility $B_c$ (a-c) and Young’s modulus $E$ (d-f) for the $\text{MV}_2\text{Ga}_4$ ($M = \text{Sc}, \text{Zr}, \text{Hf}$). Values in GPa.

colours indicate the magnitude of the moduli, going in ascending scale from blue to red. The reciprocal linear compressibility plots show only a weak anisotropy, presenting a quasi-spherical profile. As with any chain, the extended linear $V$ chains are weaker against compression and, therefore, the $B_c$ plots are slightly flattened in the [001] direction, as seen in Figures 3(a-c).

A strong elastic anisotropy, on the other hand, is observed from the Young’s modulus plots. The degree of deviation from the isotropic spherical shape points to the directionality of the material properties. A large resistance to elastic deformation is observed in the [110] direction, consistent with the fact that the (001) plane in the $\text{MV}_2\text{Ga}_4$ compounds has the higher planar density in the crystal, mainly due to the Hf–Ga bonds along [110]. In addition, as demonstrated by Rovati and Cazzani [49], the elastic response of tetragonal solids is intrinsically restricted by symmetry considerations and can be classified in 12 different and well-defined classes. As a consequence, it seems to be a fairly common feature in a great number of real single crystals with tetragonal symmetry that the Young’s modulus in directions within the (110) plane assumes higher values [49]. However, the Young’s modulus is also high along the [001] direction for the $\text{MV}_2\text{Ga}_4$ compounds, despite having a lower planar density at the (hk0) planes. The reason for this is directly linked to the presence of extended linear vanadium chains along the $c$-direction. For instance, it is easy to realise from the spherical plots that the anisotropy of Young’s modulus along the [001] direction in $\text{ZrV}_2\text{Ga}_4$ is less prominent than that of $\text{HfV}_2\text{Ga}_4$ and $\text{ScV}_2\text{Ga}_4$. This is in agreement with our previous analysis of the universal elastic anisotropy index, higher for $\text{ScV}_2\text{Ga}_4$ and $\text{HfV}_2\text{Ga}_4$ and lower for $\text{ZrV}_2\text{Ga}_4$. Therefore, we can conclude that the extended linear chains indeed play a fundamental role in the mechanical properties and anisotropy indices.

To provide an even more straightforward picture about the directional dependence of Young’s modulus, a few planar projections are illustrated in Figures 4(a-c) for directions in the (100), (001) and (110) crystallographic planes. The anisotropy coming from the extended linear vanadium chains is well visualized in the (100) plane, showing a larger resistance to uniaxial stress among the reasoning that the Young’s modulus along the [001] direction than the [010] direction. It’s also clear that $\text{ZrV}_2\text{Ga}_4$ presents the largest values for Young’s modulus, independent of the crystallographic orientation, and also the smallest anisotropy regime among all considered structures. The directional dependence for $\text{SeV}_2\text{Ga}_4$ and $\text{HfV}_2\text{Ga}_4$ is quite similar in the (001) plane, but the effect of the extended
linear chains is felt in the (100) and (110) planes. As observed in a previous work [11], the valence and conduction electronic density along the vanadium chains is larger for ScV4Ga4 than HfV2Ga4 and, therefore, the V–V bonds are stronger in the former compound, explaining its higher Young’s modulus along the [001] direction.

It is harder to analyze the anisotropy in Poisson’s ratio, since it depends not only on the elongation direction, but also on which normal direction one is interested in. Therefore, 3D plots such as those shown in Figures 3(a–f) are not possible. On the other hand, we can analyse the effect of longitudinal elongation along a few selected directions in the form of polar plots. In fourth-rank tensor notation, Poisson’s ratio is given by [54]

$$\nu(\vec{l}, \vec{n}) = \frac{\sigma_{ijkl} n_i l_j}{E l_k m_l}$$

where the normal direction $\vec{n}$ can be defined by the angle $\psi$ in a plane perpendicular to $\vec{l}$, as shown in Figure 2. Algebraically we can write $\vec{n}$ as

$$\vec{n} = \left( n_1, n_2, n_3 \right) = \left( \begin{array}{c}
-\cos \varphi \cos \theta \sin \psi - \sin \varphi \cos \psi \\
-\sin \varphi \cos \theta \sin \psi + \cos \varphi \cos \psi \\
\sin \theta \sin \psi
\end{array} \right)$$

In Voigt’s notation for body-centered tetragonal structures, Poisson’s ratio for the normal direction $\vec{n}$, when the elongation happens along direction $\vec{l}$, can be written as [56]:

$$\nu(\vec{l}, \vec{n}) = \frac{s_{ijkl} n_i l_j}{E l_k m_l} = s_{11}(l_1^2 n_1^2 + l_2^2 n_2^2) + s_{12}(l_1^2 n_1^2 + l_2^2 n_2^2) +$$

$$+ s_{13}(l_3^2 + n_3^2 - 2l_3^2 n_3^2) + s_{33}l_3^2 n_3^2 +$$

$$+ s_{44}(l_1 n_1 + l_2 n_2)(l_1 n_1 + l_2 n_2) + s_{66} l_1 n_1 n_2$$

Using this strategy, Poisson’s ratios resulting from three different elongation directions are shown in Figure 5(a–c). In Figure 5(a), the elongation is along the [100] direction, and the Poisson’s ratio is measured in the [0kl] family of directions perpendicular to it. It is readily seen that the Poisson’s ratio is quite large (close to 0.5) in the [010] direction. It should be kept in mind that, although the Poisson’s ratio is limited to the interval $-1 \leq \nu \leq 0.5$ for isotropic materials, there is no such restriction when we consider deformation of single crystals [57]. Still, a value close to 0.5 indicates that areas in (001) planes are only weakly affected by elongation along the [100] direction. The behavior is drastically different in the [001] crystallographic orientation, where $\nu$ is quite small, around 0.15 for all compounds. This indicates that the dimensions along the tetragonal fourfold symmetry axes (i.e., the c-axis) are only slightly affected by elongation in the [100] direction. We readily see the effect of the extended linear chains as the explanation for this characteristic, since a contraction in the c-direction would mean a shortening of the directional V–V bonds, enormously affecting the energy density of the deformed structure. It is important to notice that this contraction in the c-direction, being the effect of an elongation along [100], happens without stress in the contraction direction. This is different from the case shown in Figures 3(a–c), that come from an applied isostatic pressure, in which the [001] direction is the most affected. Moreover, we see that $\text{ZrV}_2\text{Ga}_4$ has the lowest Poisson’s ratio in the [010] direction, while $\text{ScV}_2\text{Ga}_4$ has the lowest value in the [001] direction. Since, as we mentioned previously, $\text{ScV}_2\text{Ga}_4$ has the highest electronic density along the extended linear V chains, is expected that it will be the most resistant against V–V bond length alterations.

Figure 5(b) shows Poisson’s ratio values when the elongation happens in the [110] direction, that is, in directions normal to the highest Young’s modulus directions in the crystal. In this case, all three compounds behave in a similar manner, with low Poisson’s ratio values, in the range 0.09–0.22. The values for the [001] direction are similar to those in Figure 5(a), for the reasons explained in the preceding paragraph. In the [110] crystallographic orientation, the values are even smaller, a consequence of the high resistance along this direction.

Finally, Poisson’s ratio for elongation along the [001] direction is shown in Figure 5(c). In this case, the tetragonal symmetry imposes transverse isotropy in Poisson’s ratio for directions in the (001) plane [58], in which case Eq. (21) reduces to

$$\nu[001][hk0] = -\frac{s_{13}}{s_{33}}$$

resulting in the circles shown in Figure 5(c). In the scale of the figure, it is impossible to separate the curves for the three compounds, but they are slightly different: 0.1812 for $\text{ScV}_2\text{Ga}_4$, $\text{ZrV}_2\text{Ga}_4$, and $\text{HfV}_2\text{Ga}_4$.
0.1816 for ZrV$_2$Ga$_4$, and 0.1815 for HfV$_2$Ga$_4$. This apparent coincidence is again explained by the presence of extended linear V chains: the V–V and V–Ga bonds are those responsible for most of the contraction (or resistance against it) along directions perpendicular to the c-axis, regardless of the atom occupying the M sites. It should be noticed that this equivalence of Poisson’s ratio for elongation along the fourfold symmetry axes is not found among other tetragonal systems [26], which, one more time, points to the peculiarity of extended linear chain compounds.

We can adopt a similar procedure to investigate the anisotropy in the shear modulus, which, in fourth-rank tensorial notation, is given by [54]

$$G^{-1}(\hat{l}, \hat{n}) = 4s_{ijkl}l_il_jn_kn_l$$  \hspace{1cm} (23)

For a tetragonal body-centered structure using Voigt’s matrix notation, the last equation amounts to

$$G^{-1}(\hat{l}, \hat{n}) = 4s_{11}(l_1^2n_1^2 + l_2^2n_2^2) + 4s_{12}(l_1l_2n_1n_2) + 8s_{13}(l_1n_1 + l_2n_2)(l_3n_3) + s_{44}(l_1n_2 + l_2n_1)^2 + s_{44}[(n_1^2 + n_2^2)l_3^2 + (l_1^2 + l_2^2)n_3^2 + 2(l_1n_1 + l_2n_2)n_3]$$  \hspace{1cm} (24)

Polar representations for selected stress states are shown in Figures 6(a–c). Shear modulus in the (100) plane, i.e., for \( \hat{n} = [0kl] \) and \( \hat{l} \) parallel to the x-axis, is shown in Figure 6(a). It is seen that a larger shear modulus is found in the [010] direction, that is, for shear in the y-direction. All three compounds exhibit a lower resistance against shear when \( \hat{n} = [001] \), a result that comes from the fact that \( s_{66} < s_{44} \) for the three compounds. With applied uniaxial stress in the [110] direction, as shown in Figure 6(b), the situation is reversed: higher shear modulus for \( \hat{n} = [001] \) (which is the same as in Fig. 6a) than for a direction normal to it, [110]. The lower shear modulus in this case can be accounted for by the higher atomic density in the (110) planes, favouring slip. Finally, for \( \hat{l} = [001] \), that is, along the fourfold symmetry axes, the transverse isotropy of tetragonal lattices reduces Eq. (24) simply to

$$G[001][hk0] = \frac{1}{s_{44}} = c_{44}$$  \hspace{1cm} (25)

resulting in the concentric circles shown in Figure 6(c). Therefore, as mentioned at the end of Sec. 3.1, it is natural that ZrV$_2$Ga$_4$, possessing the higher \( c_{44} \) value, is the compound with the higher shear modulus on the (001) plane.

3.4. Sound velocity and Debye temperature

The anisotropy can also be evaluated by means of the sound velocities in an elastic medium. The pure longitudinal and transverse modes for elastic waves in single crystals are essentially dictated by its symmetry [59]. For instance, a tetragonal symmetry implies that the principal directions along which elastic waves can propagate in pure longitudinal and transverse modes are [001], [100] and [110]. In all other crystallographic orientations the propagating waves are either quasi-transverse or quasi-longitudinal. In the propagating directions for a tetragonal lattice the sound velocities can be written simply as:

- [100] direction:
  $$\upsilon_l = \sqrt{c_{11}/\rho}; \quad \upsilon_{l+} = \sqrt{c_{44}/\rho}; \quad \upsilon_{l-} = \sqrt{c_{66}/\rho}.$$  \hspace{1cm} (26)

- [001] direction:
  $$\upsilon_l = \sqrt{c_{33}/\rho}; \quad \upsilon_{l+} = \sqrt{c_{66}/\rho}; \quad \upsilon_{l-} = \sqrt{c_{11}/\rho}.$$  \hspace{1cm} (27)

- [110] direction:
  $$\upsilon_l = \sqrt{(c_{11} + c_{12} + 2c_{66})/2\rho}; \quad \upsilon_{l+} = \sqrt{c_{44}/\rho}; \quad \upsilon_{l-} = \sqrt{(c_{11} - c_{12})/2\rho}.$$  \hspace{1cm} (28)

where \( \rho \) is the mass density, \( \upsilon_l \) is the longitudinal sound velocity, and \( \upsilon_{l+} \) and \( \upsilon_{l-} \) are the first and second transverse acoustic modes, respectively.

Considering the expressions above, it is easy to verify that the sound velocities present similar elastic anisotropy as the second-order elastic stiffness constants, and smaller densities with higher elastic properties result in large propagating modes inside the crystal. The complete set of longitudinal and transverse acoustic modes along the principal axes was calculated and listed in Table 5. The elastic sound waves travel faster along the [110] longitudinal direction in ScV$_2$Ga$_4$, ZrV$_2$Ga$_4$
and HfV$_2$Ga$_4$ as an immediate consequence of the higher mechanical properties in that direction. In fact, ZrV$_2$Ga$_4$ is responsible for the strongest pure modes in all principal crystallographic orientations, except along the extended vanadium chains. Indeed, the large longitudinal sound velocity in [001] and [110] directions is responsible for the strongest pure modes in all principal crys-
tallographic orientations, except along the extended vanadium chains. Indeed, the large longitudinal sound velocity in [001] directions.

Table 5: Anisotropic sound velocities (in m/s) along the three principal axes of MV$_2$Ga$_4$ (M = Sc, Zr, Hf).

| Direction | [100] | [001] | [110] |
|-----------|-------|-------|-------|
| ScV$_2$Ga$_4$ | 5951.38 | 3659.90 | 4546.54 | 6268.77 | 4546.54 | 4546.54 | 6891.90 | 3659.90 | 2931.15 |
| ZrV$_2$Ga$_4$ | 6206.89 | 3698.39 | 4590.31 | 6145.31 | 4590.31 | 4590.31 | 7017.68 | 3698.39 | 3216.93 |
| HfV$_2$Ga$_4$ | 5262.57 | 3061.98 | 3922.32 | 5321.11 | 3922.32 | 3922.32 | 6023.88 | 3061.98 | 2606.17 |

Table 6: Longitudinal ($u_l$), transverse ($u_t$), and mean ($u_m$) sound velocities (in m/s), and Debye temperature $\Theta_D$ (in K) for the MV$_2$Ga$_4$ (M = Sc, Zr, Hf) compounds.

| Compound | $u_l$ | $u_t$ | $u_m$ | $\Theta_D$ |
|----------|-------|-------|-------|-----------|
| ScV$_2$Ga$_4$ | 6221.15 | 3683.89 | 4080.42 | 490.21 |
| ZrV$_2$Ga$_4$ | 6373.94 | 3818.91 | 4225.23 | 510.33 |
| HfV$_2$Ga$_4$ | 5381.91 | 3147.86 | 3490.67 | 416.39 |

Figure 6: Shear modulus (in GPa) for MV$_2$Ga$_4$ compounds (M = Hf, Sc, Zr) measured in normal directions to the longitudinal (a) [100], (b) [110] and (c) [001] directions.

Table 6: Longitudinal ($u_l$), transverse ($u_t$), and mean ($u_m$) sound velocities (in m/s), and Debye temperature $\Theta_D$ (in K) for the MV$_2$Ga$_4$ (M = Sc, Zr, Hf) compounds.

and HfV$_2$Ga$_4$ as an immediate consequence of the higher mechanical properties in that direction. In fact, ZrV$_2$Ga$_4$ is responsible for the strongest pure modes in all principal crystallographic orientations, except along the extended vanadium chains. Indeed, the large longitudinal sound velocity in [001] happens for ScV$_2$Ga$_4$. This is an interesting find: since ScV$_2$Ga$_4$ has the largest elastic anisotropy as a result of high populated V-chains along the c-direction, its atoms effectively interact with each other and consequently vibrate at higher frequencies like a tight rope, even ZrV$_2$Ga$_4$ presenting higher values for linear compressibility and Young’s modulus along that orientation. In a similar way, the transverse modes for the three compounds are almost the same. Thus we can clearly observe the influence of the extended linear chain substructures in single crystals regarding its mechanical response. Despite the fact that HfV$_2$Ga$_4$ shows a substantial elastic anisotropy as seen in the spherical and polar plots, as well as in the $A^U$ universal index, its heavier Hf atoms cause an appreciable impact on the compound density, leading to lower longitudinal and transverse modes for elastic waves. Therefore, the sound velocities obtained at different crystallographic orientations provide valuable information that tie together all conclusions we made about elastic anisotropy of the MV$_2$Ga$_4$ compounds.

Sound velocities are essential to characterize the elastic and thermal response of a given solid mostly because they are eas-

\[
\Theta_D = \frac{\hbar}{k} \left( \frac{6\pi^2}{V_{at}} \right)^{\frac{1}{3}} u_m. \tag{29}
\]

In the expression above, $u_l$ and $u_t$ are the longitudinal and transverse propagating modes, in which

\[
u_l = \sqrt{\frac{\lambda + 2\mu}{\rho}} \tag{31}
\]

and

\[
u_t = \sqrt{\frac{\mu}{\rho}}. \tag{32}
\]

with $\lambda$ and $\mu$ being the Lamé parameters, determined from Poisson’s ratio and bulk modulus:

\[
\lambda = \frac{3\nu}{1 + \nu} B \tag{33}
\]

and

\[
\mu = \frac{3}{2} \frac{1 - 2\nu}{1 + \nu} B. \tag{34}
\]
Applying this procedure, we have calculated the effective longitudinal, transverse and average sound velocities, as well as the related Debye temperature for each structure, which are presented in Table 6. Consistently with our previous analysis, ZrV₂Ga₄ assumes the highest modes, since its higher bulk modulus values lead to faster sound velocities. On the other hand, the ScV₂Ga₄ compound also reveals substantially large elastic wave velocities since, as discussed earlier, its high electronic density confers very effective modes.

The calculated Debye temperatures also support our previous results, since this quantity reflects to a certain extent the strength of the interatomic bonding. The calculated 416.39 K value for the Debye temperature of HfV₂Ga₄ is in excellent agreement with the 418.97 K value obtained in a recent experimental investigation [9]. We can also point out that ZrV₂Ga₄ and ScV₂Ga₄ should have better heat transfer properties than HfV₂Ga₄ since the thermal conductivity response is directly related to the average sound velocity [60].

At this point of the discussion, our attention is driven to the possible consequences that the above results will have on the superconducting properties. It is well-known that the critical temperature in which a electron-phonon superconductor undergoes a second-order phase transition from its normal state to a superconducting state, as calculated using McMillan’s formula, basically depends on the density of states at the Fermi level \(N(E_F)\), the strength of the electron-phonon coupling \(\lambda\), the Debye temperature \(\Theta_D\), and the electron-electron interaction constant (or Coulomb pseudopotential) \(\mu^*\) [11, 61]. The higher the first three parameters, the higher the critical superconducting temperature will be, while increasing the last parameter increases the electron scattering and, therefore, tends to reduce \(T_c\). Thus, we argue that the ZrV₂Ga₄ compound, once experimentally proved to be a superconductor, could present a critical temperature in which a electron-phonon superconductor underdi
ted the Sommerfeld approximation. Finally, the vibrational heat capacity is given by

\[
C_p^{\text{vib}}(p, T) = C_V^{\text{vib}}(p, T) + \alpha^2(p, T)B(p, T)V(p, T) \quad \text{(36)}
\]

where \(C_V^{\text{vib}}(p, T)\) is the vibrational heat capacity at constant volume, \(\alpha(p, T)\) is the volumetric thermal expansion coefficient, \(V(p, T)\) is the volume and \(B(p, T)\) is the isothermal bulk modulus. According to the Debye-Grüneisen approximation,

\[
C_V^{\text{vib}}(p, T) = 9NR \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad \text{(37)}
\]

in which \(R = 8.31451 \, \text{J} \, \text{mol}^{-1} \, \text{K}^{-1}\) is the universal gas constant, \(N\) is the number of atoms and the Debye temperature \(\Theta_D\) is considered volume dependent:

\[
\Theta_D(V) = \Theta_D(V_0) \left( \frac{V_0}{V} \right)^\gamma \quad \text{(38)}
\]

where \(\Theta_D(V_0)\) is the Debye temperature at 0 K and zero external pressure, as seen in the preceding section, and \(\gamma\) is the Grüneisen parameter, that can be written as [63]

\[
\gamma = g + \frac{1 + B'_p}{2}, \quad \text{(39)}
\]

with \(B'_p\) being the 0 K pressure derivative of the Bulk modulus at zero pressure, obtained from a fit to the ab-initio isotropic deformation data of an equation of state such as, for instance, the Birch-Murnaghan equation [69, 70]. The coefficient \(g\) can be fixed at \(g = 2/3\) if the aim is high-temperature data or \(g = 1\) for low temperatures [62]. The latter was the value adopted in this work.

Using the equations above, it is possible to calculate the temperature and pressure dependence of several quantities of interest. For instance, the volumetric thermal expansion is written as

\[
\alpha(p, T) = \frac{\gamma C_V^{\text{vib}}(p, T)}{B(p, T)V(p, T)} \quad \text{(40)}
\]

with the Bulk modulus given by

\[
B^{-1}(p, T) = -\frac{1}{V(p, T)} \left( \frac{\partial V}{\partial p} \right)_T \quad \text{(41)}
\]

Finally, the Young’s modulus is calculated using a result from the theory of elasticity of isotropic media:

\[
E(p, T) = \frac{3B(p, T)}{1 - 2\nu(p, T)} \quad \text{(42)}
\]

where \(\nu(p, T)\) is the Poisson’s ratio, which will be considered pressure- and temperature-independent in this work. Moreover,
we will only be interested in the zero external pressure case and, therefore, the crystal structure will expand due to thermal effects only.

The results of the calculations are shown in Figure 7(a-d). We limited the calculations to low temperatures since this is the region of interest and also because the method employed, as already discussed, is not precise enough outside this range. It is seen, as expected, that the material softens with increasing temperature, as observed by the lowering of Bulk and Young’s moduli in Figures 7(a) and (b), respectively. Since the Debye temperature for all compounds are similar, the thermal softening ratio is approximately the same in all cases.

The volumetric thermal expansion is shown in Figure 7(c). It is seen that ZrV$_2$Ga$_4$ is the compound presenting the lowest values, agreeing with the fact that it is the compound with the highest bulk modulus and, therefore, also the most resistant against variations in bond lengths. Finally, Figure 7(d) shows the heat capacity at constant pressure as a function of temperature. Again, since the Debye temperatures are quite close to one another, the three curves are very similar. The inset in Figure 7(d) shows a comparison to experimental data [9] for HfV$_2$Ga$_4$ in a $C_p/T$ vs. $T^2$ plot, highlighting the $T^3$ dependence of the heat capacity at low temperatures. In order to obtain the calculated curve, besides the DFT calculations, we took the value $\gamma_0 = 8.263$ mJ/mol K$^2$ for the Sommerfeld coefficient from the same experimental work [9]. Unfortunately, there are no data in the literature for the other compounds. The double jumps in the experimental curve, naturally, come from the second order transitions up to the critical temperature, around 4.1 K, that cannot be reproduced within the scope of conventional DFT calculations. It should be emphasized that our calculated $C_p$ curve for HfV$_2$Ga$_4$ shows a good agreement with the available experimental data [9] at low temperatures above $T_c$, considering the intrinsic limitations contained in the approximations required by the numerical methods.

4. Conclusions

In this work we have performed ab-initio calculations, based on DFT-methods, of elastic and thermal properties of extended linear chain compounds MV$_2$Ga$_4$ (M = Sc, Zr, Hf). From the independent set of elastic stiffness and compliance constants, we have evaluated the mechanical properties of the polycrystalline materials using the Voigt-Reuss-Hill approach. We found that ZrV$_2$Ga$_4$ has the largest values for bulk, shear and Young’s
modulus. Attached to this, the B/G ratio indicates that all compounds have a brittle character, which is consistent with the obtained Poisson’s ratio values. The universal elastic anisotropy index, as well as the directional dependence analysis of linear compressibility, Young’s modulus, Poisson’s ratio and shear modulus for different longitudinal and normal directions. For instance, the ZrV$_2$Ga$_4$ compound presents the strongest pure modes of elastic waves in all principal crystallographic orientations, except along the extended linear vanadium chains. In that direction, ScV$_2$Ga$_4$ exhibits the largest longitudinal sound velocity, a direct consequence of its highly populated V-chains.

From the calculated Debye temperatures and the high pure longitudinal and transverse modes for elastic wave velocities, which result in a more effective electron-phonon coupling in the structure, we also argue that ZrV$_2$Ga$_4$ could show a similar superconducting critical temperature, or even higher, than ScV$_2$Ga$_4$ (provided it is indeed a superconductor), a prediction that should be confirmed experimentally.

Finally, we believe that the approach and the results found in the present work will substantially advance our understanding of the properties in an emergent class of superconducting materials and extended linear chain compounds, forecasting and elucidating relevant parameters and motivating, as a guideline, future experimental investigations in similar or related systems.

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References

References

[1] Bardeen, J., Cooper, L.N., Schrieffer, J.R., Theory of superconductivity. Phys Rev 1957;108:1175.
[2] Tomita, M., Murakami, M., High-temperature superconductor bulk magnets that can trap magnetic fields of over 17 tesla at 29 K. Nature 2003;421(6922):517.
[3] Noi, M., Steurer, M., High-temperature superconductor fault current limiters: concepts, applications, and development status. Supercond Sci Technol 2007;20(3):R15.
[4] Tomsci, M., Rindfleisch, M., Yue, J., McFadden, K., Phillips, J., Sumpion, M.D., et al. Overview of MgB2 superconductor applications. Int J Appl Ceram Technol 2007;4(3):250.
[5] Malozemoff, A.P., Fleshler, S., Rupich, M., Thieme, C., Li, X., Zhang, W., et al. Progress in high temperature superconductor coated conductors and their applications. Supercond Sci Technol 2008;21(3):034005.
[6] Patti, M., Pallecchi, I., Bellingeri, E., Cimberle, M.R., Tropeano, M., Ferdeghini, C., et al. New Fe-based superconductors: properties relevant for applications. Supercond Sci Technol 2010;23(3):034003.
[7] Werfel, F., Floegel-Delor, U., Rothfeld, R., Kiedel, T., Goebel, B., Wippich, D., et al. Superconductor bearings, flywheels and transportation. Supercond Sci Technol 2011;25(1):014007.
[8] Schwartz, B., Superconductor applications: SQUIDs and machines; Ch. 21. Springer Science & Business Media; 2013.
[9] Santos, F.B., Correa, L.E., de Lima, B.S., Cigaroa, O.V., da Luz, M.S., Grant, T.W., et al. Unusual superconducting behavior in HfV$_2$Ga$_4$. Phys Lett A 2018;382:1065.
[10] Zehetmayer, M., A review of two-band superconductivity: materials and effects on the thermodynamic and reversible mixed-state properties. Supercond Sci Technol 2013;26(4):043001.
[11] Ferreira, P.P., Santos, F.B., Machado, A.J.S., Petrelli, H.M., Eleno, L.T.F., Insights into the unconventional superconductivity in HfV$_2$Ga$_4$ and ScV$_2$Ga$_4$ from first-principles electronic-structure calculations. Phys Rev B 2018;98:045126.
[12] Miller, J.S., Extended linear chain compounds; vol. 3. Springer Science & Business Media; 2012.
[13] Cutforth, B., Datars, W., Van Schyndel, A., Gillespie, R., Electrical conductivity of linear chain mercury compounds. Solid State Commun 1977;21(4):37.
[14] Chiang, C., Spal, R., Denenstein, A., Heeger, A., Miro, N., MacDiarmaid, A., Anomalous electrical properties of linear chain mercury compounds. Solid State Commun 1977;22(5):293.
[15] Koteles, E., Datars, W., Cutforth, B., Gillespie, R., Anisotropic optical reflectance of Hg$_2$SiF$_6$. Solid State Commun 1976;20(12):1129.
[16] Peebles, D.L., Chiang, C., Cohen, M.J., Heeger, A., Miro, N., MacDiarmaid, A., Optical properties of linear-chain mercury compounds. Phys Rev B 1977;15(10):4607.
[17] Brown, I., Datars, W., Gillespie, R., The infinite linear chain compounds Hg$_2$AsF$_6$ and Hg$_2$SbF$_6$. In: Miller, J.S., editor. Extended Linear Chain Compounds; vol. 3. 1983, p. 1.
[18] Mats, I., Matar, S.F., Rodewald, U.C., Vasyli, Z., Poettgen, R., SrAu4. 76In1. 24 with YbMo2Al4-type structure. Z Naturforsch, B: Chem Sci 2011;66(10):993.
[19] Matar, S.F., Poettgen, R., Electronic structure and bonding in Y1TI2Ga4 gallide with linear titanium chains and four-bonded gallium atoms. Z Naturforsch, B: Chem Sci 2013;68(1):23.
[20] Gerke, B., Niehaus, O., Hoffmann, R.D., Poettgen, R., Infinite linear zinc chains in AAu4Zn2 (A= Ca, Ce, Pr, Nd) with YbAl2Mo2 type structure. Z Anorg Allg Chem 2013;639(14):2575.
[21] Tappe, F., Matar, S.F., Schwickert, C., Winter, F., Gerke, B., Poettgen, R., Linear infinite cadmium chains in CaAu4Cd2 and other intermetallics with YbM0$_2$Al$_4$-type structure. Monatsh Chem 2013;144(6):751.
[22] Pokluda, J., Černý, M., Šob, M., Umeno, Y., Ab initio calculations of mechanical properties: Methods and applications. Prog Mater Sci 2015;73:127.
[23] Feng, J., Xiao, B., Wan, C., Qu, Z., Huang, Z., Chen, J., et al. Electronic structure, mechanical properties and thermal conductivity of Ln2Zn207 (Ln= La, Pr, Nd, Sm, Eu and Gd) pyrochlore. Acta Mater 2011;59(4):1742.
[24] Feng, J., Xiao, B., Chen, J., Du, Y., Yu, J., Zhou, R., Stability, thermal and mechanical properties of PtxAl$_y$ compounds. Mater Des 2011;32(6):3231.
[25] Feng, J., Xiao, B., Zhou, R., Pan, W., Clarke, D.R., Anisotropic elastic and thermal properties of the double perovskite slab–rock salt layer La$_3$SrAl$_2$O$_6$ (Ln = La, Nd, Sm, Eu or Dy) natural superlattice structure. Acta Mater 2012;60(8):3380.
[26] Feng, J., Xiao, B., Zhou, R., Pan, W., Anisotropy in elasticity and thermal conductivity of monazite-type REPO$_4$ (RE= La, Ce, Nd, Sm, Eu and Gd) from first-principles calculations. Acta Mater 2013;61(19):7364.
[27] Sun, L., Gao, Y., Xiao, B., Li, Y., Wang, G., Anisotropic elastic and thermal properties of titanium borides by first-principles calculations. J Alloys Compd 2013;579:457.
[28] Gao, X., Jiang, Y., Zhou, R., Feng, J., Stability and elastic properties of Y$_2$C binary compounds investigated by first principles calculations. J Alloys Compd 2014;587:819.
[29] Yang, J., Shahid, M., Zhao, M., Feng, J., Wan, C., Pan, W., Physical properties of La$_2$B$_2$O$_7$ (B = Zr, Sn, Hf and Ge) pyrochlore: First-principles calculations. J Alloys Compd 2016;663:834.
[30] Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. J Phys Condens Matter 2009;21:395502.
[31] Kohn, W., Sham, L.J., Self-consistent equations including exchange and correlation effects. Phys Rev 1965;140:A113.
[32] Schlüpf, M., Giggi, F., Optimization algorithm for the generation of onec
pseudopotentials. Comput Phys Commun 2015;196:36-44.
[33] Gross, E.K., Dreizler, R.M.. Density functional theory; vol. 337. Springer Science & Business Media; 2013.
[34] Perdew, J.P., Burke, K., Ernzerhof, M.. Generalized gradient approximation made simple. Phys Rev Lett 1996;77:3865.
[35] Monkhorst, H.J., Pack, J.D.. Special points for brillouin-zone integrations. Phys Rev B 1976;13:5188.
[36] Marzari, N., Vanderbilt, D., De Vita, A., Payne, M.C.. Thermal contraction and disordering of the Al(110) surface. Phys Rev Lett 1999;82:3296.
[37] Arias, T., Payne, M., Joannopoulos, J.. Ab initio molecular-dynamics techniques extended to large-length-scale systems. Phys Rev B 1992;45(4):1538.
[38] Goleborztkbar, R., Pavone, P., Spitaler, J., Puschnig, P., Draxl, C.. Elastic: A tool for calculating second-order elastic constants from first principles. Comp Phys Commun 2013;184:1861.
[39] Kantorovich, L.. Quantum theory of the solid state: an introduction; vol. 136. Springer Science & Business Media; 2004.
[40] Fornasini, M., Palenzona, A.. Crystal structure of the ternary RE Mo2Al4 phases (RE= Gd, Er, Yb). London, Oxford University Press; 1954.
[41] Born, M., Huang, K.. Dynamical Theory of Crystal Lattices. London: Oxford; 1992;45(4):1538.
[42] Monkhorst, H.J., Pack, J.D.. Special points for brillouin-zone integrations. Phys Rev B 1976;13:5188.
[43] Marzari, N., Vanderbilt, D., De Vita, A., Payne, M.C.. Thermal contraction and disordering of the Al(110) surface. Phys Rev Lett 1999;82:3296.
[44] Arias, T., Payne, M., Joannopoulos, J.. Ab initio molecular-dynamics techniques extended to large-length-scale systems. Phys Rev B 1992;45(4):1538.
[45] Goleborztkbar, R., Pavone, P., Spitaler, J., Puschnig, P., Draxl, C.. Elastic: A tool for calculating second-order elastic constants from first principles. Comp Phys Commun 2013;184:1861.
[46] Kantorovich, L.. Quantum theory of the solid state: an introduction; vol. 136. Springer Science & Business Media; 2004.
[47] Fornasini, M., Palenzona, A.. Crystal structure of the ternary RE Mo2Al4 phases (RE= Gd, Er, Yb). London, Oxford University Press; 1954.
[48] Monkhorst, H.J., Pack, J.D.. Special points for brillouin-zone integrations. Phys Rev B 1976;13:5188.