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Electronic properties of spin excitation in multiferroics with a spinel structure: first principles calculation

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ABSTRACT

In the present work, the structural, electronic and mechanical properties of LiVCuO_4 and LiCu_2O_4 spinel type multiferroics have been investigated by means of first principles calculations. The spin polarized generalized gradient approximation has been used for modeling exchange-correlation effects. The structural optimization of these multiferroics compounds has been performed by using VASP-code, and the lattice parameters and magnetic moments have been calculated. From our calculation, it has been determined that the LiVCuO_4 compound is a narrow band gap semiconductor, while the LiCu_2O_4 compound is metallic in nature. Considering the spin states from the electronic band structure and density of the state (DOS) of the LiVCuO_4 compound, it has been identified that $E_g=1.87$ eV for spin up and $E_g=0.37$ eV for spin down. The second-order elastic constants have been calculated, and the other related quantities have also been estimated in the present work.

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1. Introduction

Recently, researchers have focused on LiMVO_4 ($M = \text{Cu, Ni, Co, Zn, Mg, Be}$) materials that can be used for rechargeable lithium cathode materials to increase the energy density and decrease costs. LiCuVO_4 material is understood as a one-dimensional superconductor as a result of the electrical conductivity and heat transfer measurements obtained at low temperature [1–4]. Formulated ternary AB_2O_4 oxides are spinel structural materials. Spinel structural materials according to the distribution of atoms A and B on the lattice sites can be classified into two distinct kinds deemed normal and inverse spinel, respectively. The atoms A and B are characterized as normal spinel by occupying the tetrahedral and octahedral sites, respectively, while some of the B atoms, the A and the remaining B atoms are characterized as reverse spinel by occupying tetrahedral and octahedral sites, respectively [5]. Since spinel structure materials are considered as battery materials, magnetic materials, superhard materials and luminescent materials, these materials have wide and very important application areas [6–8].

Multiferroics are materials where in ferroelectric and ferromagnetic properties are exhibited in a single phase. Since magnetization cannot be controlled by an electric field in a single phase, the coupling between ferromagnetic and ferroelectric is so weak that it cannot contribute to the magnetic transition. Therefore, many multiferroics have a low Curie temperature. Ferromagnetism and ferroelectric loss occur due to weak coupling and a low Curie temperature. Therefore, multiferroic-ferrite composites can be synthesized as a result of high Curie temperature and suitable ferromagnetic-ferroelectric coupling. As a result of the work done, it has been reported that the elastic coupling between multiferroites and spinel ferrites may be formed by epitaxial or layered alignment [9, 10].

In the past, some detailed studies on the structural and magnetic properties of these spinel-type multiferroic compounds have been made [4, 5, 11–15]. Lafontaine et al. [11] experimentally investigated the structural properties of orthorhombic LiCuVO_4 at room temperature. Prokofiev et al. [12] discussed the magnetic properties of the LiCuVO_4 compound using magnetic susceptibility measurements. Kumar et al. [13] investigated the magnetic properties of Zn, Co, and Mn doped LiCuVO_4 compound with neutron diffraction and X-ray photoemission. They observed that the antiferromagnetic correlation of the compound was increased when doped with Zn and Co, and it was stimulated when the ferromagnetic order was doped with Mn. Kazakopoulos et al. [4] studied the characterization of the LiCuVO_4 compound prepared at 530°C by solid state reaction method. Kegler et al. [14] discussed the anisotropy effects on magnetic resonance spectra in the distorted reverse spinel LiCuVO_4 compound using EPR and NMR measurements. Santos et al. [15] investigated the structural and magnetic properties of spinel-structured Co_2MnO_4 compound doped with a different conformation of bismuth by X-ray diffraction. Heng-Nan et al. [5] obtained Raman vibration modes and Raman shifts corresponding to these modes under different pressure of the reverse spinel-structured LiCuVO_4 compounds by Raman spectroscopy measurements. As far as we know, the physical properties (structural, mechanical, and optical properties) of these compounds have not been studied theoretically until now. In this work, we have investigated the structural, mechanical, and electronic properties of the LiCuVO_4 and LiCu_2O_4 compounds.

2. Method of calculation

In all of our calculations that were performed using the ab-initio total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) [16–19] that was developed within the density functional theory (DFT) [20], the exchange-correlation energy function is treated within a spin polarized GGA (generalized gradient approximation) by the density functional of Perdew et al. [21]. The potentials used for the GGA calculations take into account the $1p^22s^1$ valence electrons of each Li-, $3p^63d^{10}4s^1$ valence electrons of each Cu-, $2s^22p^4$ valence electrons of each O-, and $3p^63d^34s^2$ valence electrons of each V- atoms. When including a plane-wave basis up to a kinetic-energy cutoff equal to 20.36 Ha for LiCu_2O_4 and 23.38 Ha for Li(VCu)O_4 , the properties investigated in this work are well converged. The Brillouin-zone integration was performed using special k points sampled within the Monkhorst-Pack scheme [22]. We

Table 1. The calculated equilibrium lattice parameters (a, b, and c) together with the experimental values and total magnetic moment (μ , in $\mu_B/\text{f.u.}$) for LiVCuO_4 and LiCu_2O_4 compounds

Material	a (Å)	b (Å)	c (Å)	V_0 (Å ³)	μ	Refs.
LiVCuO_4	5.687	5.796	9.011	297.02	2.00	Present
	5.662	5.809	8.758	288.0		Exp. [11]
	5.652	5.800	8.745	286.68		Exp. [13]
					1.84-1.97	Exp. [12]
					1.88	Exp. [23]
LiCu_2O_4	5.631	5.919	8.318	277.17	2.82	

Table 2. The calculated elastic constants (in GPa) for LiVCuO_4 and LiCu_2O_4 compounds

Material	Reference	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}
LiVCuO_4	Present	294.3	89.1	92.7	371.1	136.7	151.1	55.2	121.1	82.5
LiCu_2O_4	Present	190.8	88.6	79.8	208.4	101.8	265.9	37.4	78.4	64.1

found that a mesh of $8 \times 8 \times 8$ k points and $7 \times 7 \times 7$ k point for LiCu_2O_4 and Li(VCu)O_4 , respectively was required to describe the structural, mechanical, and electronic properties.

3. Result and discussion

LiCuVO_4 and LiCu_2O_4 compounds have an orthorhombic structure with the Imma (No. 74) space group. There are 4 molecules (28 atoms) in the unit cell of this crystal structure. Before starting the calculations, we performed the optimization process using the experimental structural parameters (lattice constants and atomic positions) for these compounds. The calculated lattice parameters are given in Table 1 together with the experimental values. The lattice parameters calculated for the LiCuVO_4 compound are in good agreement with the experimental values [11, 13] approx. 0.1–1.5%. The total magnetic moments obtained for LiCuVO_4 and LiCu_2O_4 are 2.00 and 2.82, respectively. The magnetic moment value obtained for the LiCuVO_4 compound is close to the μ_{eff} values [12, 23] obtained experimentally (see Table 1).

Elastic constants are important parameters because they give information about the structural stability of a material. The elastic constants given in Table 2 are calculated using the “strain-stress” technique [24]. Unfortunately, there are no experimental and theoretical results to be compared with the obtained results. Elastic constants calculated for both compounds provide the mechanical stability conditions specified in the Ref. [25, 26]. The C_{11} , C_{22} and C_{33} elastic constants show resistance to the linear compression in the a-, b-, and c- directions, respectively. The C_{22} value for the LiCuVO_4 compound is higher than the C_{11} and C_{33} values. Therefore, the b-axis can be less compressible. The C_{33} value for the LiCu_2O_4 compound is higher than the C_{11} and C_{22} values, so the c axis can be less compressible.

Other polycrystalline elastic properties (Young’s modulus, Poisson’s ratio, anisotropic factors, sound velocities, the Debye temperature) of polycrystalline bulk modulus and isotropic Shear modules obtained from the Voigt-Reuss-Hill (VRH) approach [27–29] are calculated and given in Table 3 and Table 4. In general, hardness is known as a material parameter that resists elastic and plastic deformation, this parameter is bulk modulus (B) or shear modulus (G). It can be said that the ionic character is dominant

Table 3. The calculated isotropic bulk modulus (B , in GPa), shear modulus (G , in GPa), Young's modulus (E , in GPa) and Poisson's ratio for LiVCuO_4 and LiCu_2O_4 compounds

Material	Reference	B_R	B_V	B_H	G_R	G_V	G_H	E	ν	G/B	B/G
LiVCuO_4	Present	137.4	161.5	149.5	69.0	85.0	76.7	197.0	0.28	0.51	1.95
LiCu_2O_4	Present	131.0	133.9	132.5	57.7	62.3	60.0	156.4	0.30	0.45	2.21

Table 4. The calculated anisotropic factors, sound velocities (v_t , v_l , v_m) the Debye temperatures for LiVCuO_4 and LiCu_2O_4 compounds

Material	Reference	A_1	A_2	A_3	$A_{\text{comp}}(\%)$	$A_{\text{shear}}(\%)$	$v_t(\text{m/s})$	$v_l(\text{m/s})$	$v_m(\text{m/s})$	θ_D (K)
LiVCuO_4	Present	0.849	1.947	0.677	8.061	10.722	4301	7792	4792	649
LiCu_2O_4	Present	0.504	1.159	1.155	1.102	3.840	3556	6691	3973	551

in the atomic bonding from the calculated Poisson's ratio ($\nu=0.28$ for LiCuVO_4 and $\nu=0.30$ for LiCu_2O_4) [30–32]. It can also be seen from the G/B ratio (0.51 for LiCuVO_4 and 0.45 for LiCu_2O_4) where the ionic character dominates (covalent if $G/B \approx 1.1$, ionic if $G/B \approx 0.6$). The Young's modulus (E) is a measure of the stiffness and if the E value is high, the material is stiffer. The Young's modulus value (197.0) calculated for the LiCuVO_4 compound is higher than the value (156.4) of the LiCu_2O_4 compound, so the LiCuVO_4 compound is expected to be stiffer. If the B/G ratio is less (high) than 1.75, the material is brittle (ductile) [33, 34]. According to the B/G value, both compounds are ductile.

The elastic anisotropies (A_1 , A_3 , A_3) calculated for LiCuVO_4 and LiCu_2O_4 compounds and the percentages of anisotropy in the compression and shear are given in Table 4. The LiCuVO_4 compound exhibits low anisotropy compared to the LiCu_2O_4 compound. For materials, the $A_{\text{comp}}(\%)$ and $A_{\text{shear}}(\%)$ values can range from zero (isotropic) to 100% representing the maximum anisotropy [35]. The $A_{\text{comp}}(\%)$ and $A_{\text{shear}}(\%)$ calculated for the LiCuVO_4 compound are higher than the LiCu_2O_4 compound. The Debye temperature and sound velocities [36–38] calculated for these compounds are given in Table 4. The calculated Debye temperature value (649 K) for LiCuVO_4 is higher than the calculated Debye temperature value (551K) for LiCu_2O_4 . Generally, the Debye temperature is small for soft materials and large for hard materials. Therefore, it can be said that both compounds are hard materials, but the LiCuVO_4 compound is harder than the LiCu_2O_4 compound.

Spin-polarized electronic band structures and density of states have been calculated using the GGA approach for both compounds in the orthorhombic structure and given in Figs. 1–3. The high symmetry points (Γ - T- S- W- R) of the Brillouin zone are used in electronic band structure calculations. Fermi level is selected as the zero energy level although it is not specified in Fig. 1. The E_g values for both compounds are determined from the electronic band structure data. LiCuVO_4 compound is a narrow band gap (0.13 eV-indirect) semiconductor in nature and the LiCu_2O_4 compound is also metallic. Considering the spin polarized electronic band structure of the LiCuVO_4 compound, it has been identified as $E_g=1.87$ (indirect) eV for spin up and $E_g=0.37$ (indirect) eV for spin down (see Fig. 1a). The valence band maximum (VBM) of the LiCuVO_4 compound is located at the S point, while the conduction band minimum (CBM) is located almost midway between W- Γ . In the spin polarized LiCuVO_4 compound, VBM for spin

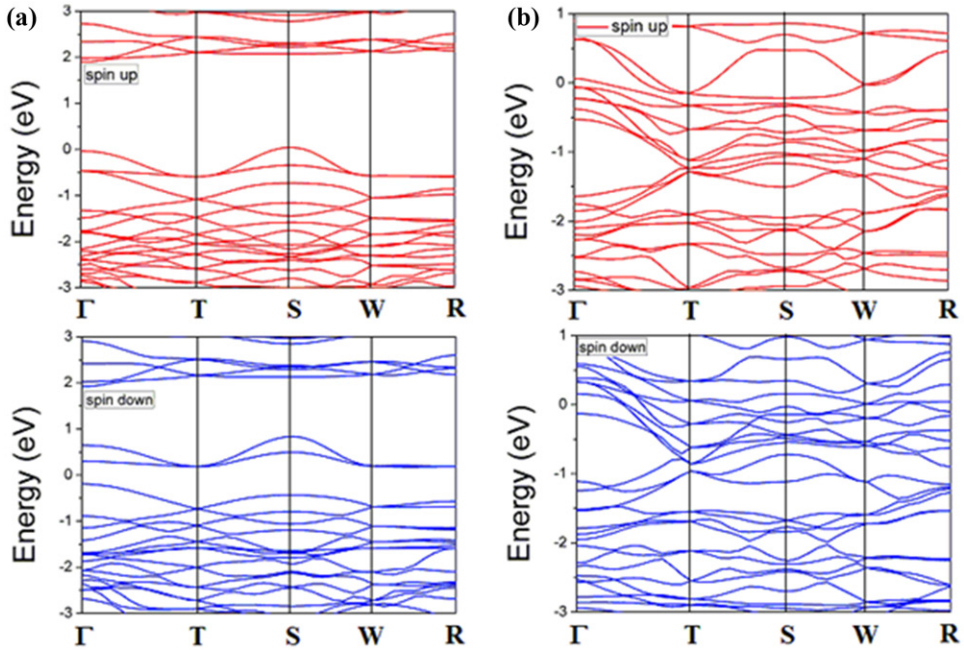


Figure 1. The calculated electronic band structures for the spin up and spin down of a) LiCuVO_4 and b) LiCu_2O_4 compounds.

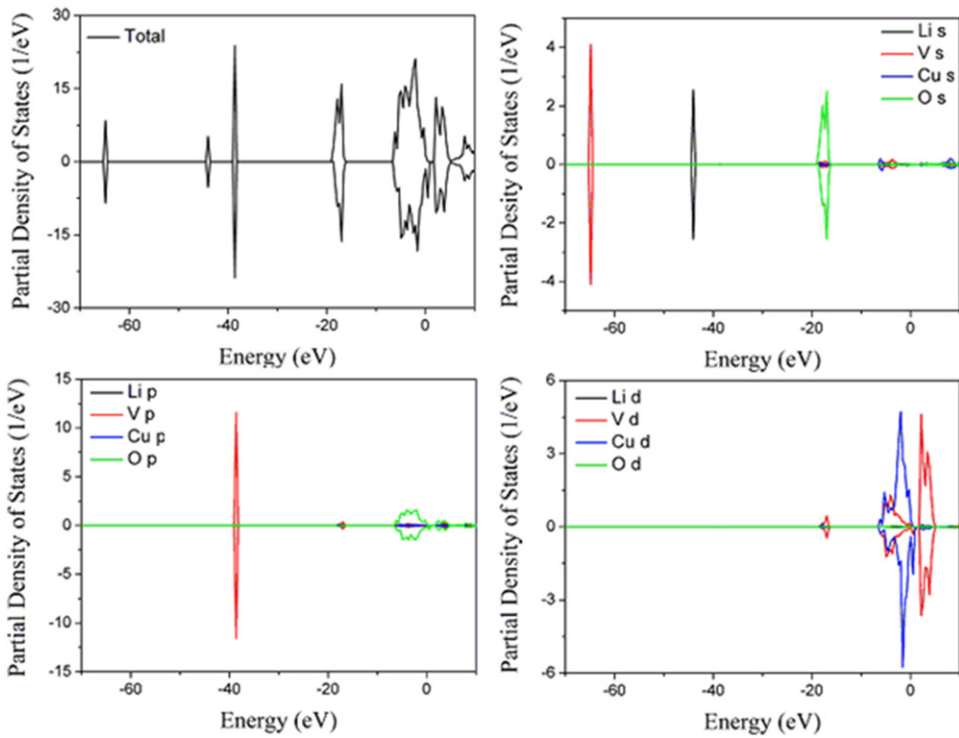


Figure 2. The spin-polarized total and projected density of states for LiCuVO_4 compound.

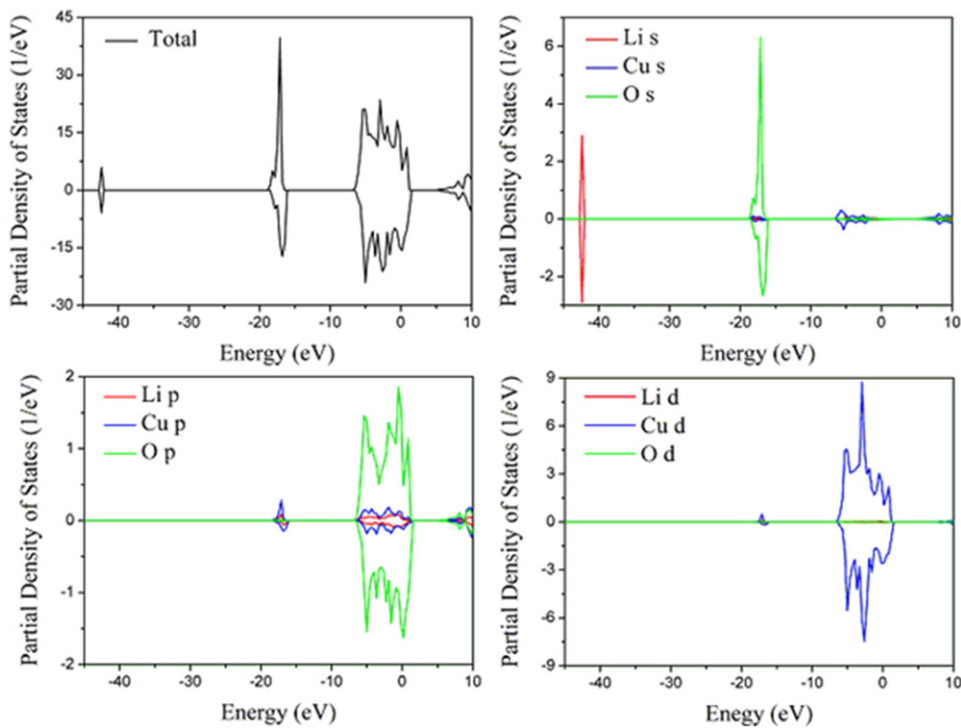


Figure 3. The spin-polarized total and projected density of states for LiCu_2O_4 compound.

up is located at the S point and CBM is located at the Γ point, while VBM for spin down is located at the S point and CBM is located almost midway between W- Γ .

The spin polarized total and partial densities of states are calculated to analyze the basic electronic components of the band structures of the LiCuVO_4 and LiCu_2O_4 compounds and are given in Figs. 2 and 3, respectively. As shown in Figs. 2 and 3, there are 5 and 3 different energy ranges for the LiCuVO_4 and LiCu_2O_4 compounds below the Fermi level, respectively. The energy region between -39 and -37 eV is occupied by V p states while the lowest energy region of the LiCuVO_4 compound is occupied by V s states. The energy region between -45 and -44 eV for both compounds is occupied by Li s states. The energy region between -19 and -16 eV for both compounds is dominated by V p states with a small amount of Cu s states. The upper valence bands for both compounds can be divided into two parts: The higher energy region of the LiCuVO_4 compound is dominated by V d states, while the lower valence bands are dominated by the hybridization of V d and Cu d states. The lower valence bands of the LiCu_2O_4 compound are dominated by the hybridization of the O p and Cu d states by a slight hybridization of the Li p and Cu p states, while the upper valence bands are dominated by the hybridization of the O p and Cu d states (but the contribution from the states of Cu d is greater than the contribution from O p states). The lowest unoccupied conduction bands just above the Fermi level are dominated by the Cu d states of the LiCu_2O_4 compound while the LiCuVO_4 compound is dominated by the V d states.

4. Conclusion

In this work, the structural, electronic and mechanical properties of LiCuVO_4 and LiCu_2O_4 spinel type multiferroics have been calculated using the ab initio method. Spin polarized GGA approximation has been used in the calculations. The obtained lattice parameters values as a result of optimization are compared with the existing literature values, and it is seen that they are in agreement with these values. In electronic structure calculations, the LiCuVO_4 compound is indirect narrow gap semiconductor in nature and the LiCu_2O_4 compound is also a metallic character. The calculated elastic constants provide the mechanical stability conditions. In addition, the calculated mechanical properties (bulk modulus, Shear modulus, Poisson's ratio, Young's modulus etc.) indicate that these compounds are ionic, rigid, and isotropic materials.

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References

- [1] A. Kazakopoulos, and O. Kalogirou, Impedance spectroscopy study of LiCuVO_4 . *Solid State Ionics*. **179**(21-26), 936 (2008). DOI: [10.1016/j.ssi.2007.12.084](https://doi.org/10.1016/j.ssi.2007.12.084).
- [2] L.S. Parfen'eva *et al.*, Heat transport over nonmagnetic lithium chains in LiCuVO_4 , a new one-dimensional superionic conductor. *Phys. Solid State*. 2003; **45**(11): 2093. DOI: [10.1134/1.1626742](https://doi.org/10.1134/1.1626742).
- [3] L.S. Parfen'eva *et al.*, Electrical conductivity and permittivity of the one-dimensional superionic Conductor LiCuVO_4 . *Phys. Solid State*. 2004; **46**(6): 1027. DOI: [10.1134/1.1767238](https://doi.org/10.1134/1.1767238).
- [4] G. T. Fey, and D. L. Huang, Synthesis, characterization and cell performance of inverse spinel electrode materials for lithium secondary batteries. *Electrochim Acta*. **45**(1-2), 295 (1999). DOI: [10.1016/S0013-4686\(99\)00212-1](https://doi.org/10.1016/S0013-4686(99)00212-1).
- [5] L. Heng-Nan *et al.*, High-pressure effect on inverse spinel LiCuVO_4 : X-ray diffraction and Raman scattering. *Chin. Phys. B*. **22**(1), 016103 (2013). DOI: [10.1088/1674-1056/22/1/016103](https://doi.org/10.1088/1674-1056/22/1/016103).
- [6] W. F. J. Fontijn *et al.*, A consistent interpretation of the magneto-optical spectra of spinel type ferrites (invited). *J. Appl. Phys.* **85**(8), 5100 (1999).
- [7] A. Zerr *et al.*, Synthesis of cubic siliconnitride. *Nature*. **400**(6742), 340 (1999). DOI: [10.1038/22493](https://doi.org/10.1038/22493).
- [8] E. Martinez-Sanchez *et al.*, Cathodoluminescent characteristics of Sm-doped ZnAl_2O_4 nanostructured. *Phys. Stat. Sol. (a)*. **202**(1), 102 (2005). DOI: [10.1002/pssa.200406906](https://doi.org/10.1002/pssa.200406906).
- [9] M. Fiebig, Revival of the magnetoelectric effect. *J. Phys. D: Appl. Phys.* **38**(8), R123 (2005). DOI: [10.1088/0022-3727/38/8/R01](https://doi.org/10.1088/0022-3727/38/8/R01).
- [10] M. A. Nazir *et al.*, Structural, electrical, and dielectric properties of multiferroic-spinel ferrite composites. *J. Electron. Mater.* **45**, 1065 (2016). DOI: [10.1007/s11664-015-4286-3](https://doi.org/10.1007/s11664-015-4286-3).
- [11] M. A. Lafontaine, M. Leblanc, and G. Ferey, New refinement of the room-temperature of LiCuVO_4 . *Acta Cryst.* **C45**, 1205 (1989). DOI: [10.1107/S0108270189001551](https://doi.org/10.1107/S0108270189001551).
- [12] A. V. Prokofiev *et al.*, Structure, stoichiometry and magnetic properties of the low-dimensional structure phase LiCuVO_4 . *J. Solid State Chem.* **177**(9), 3131 (2004). DOI: [10.1016/j.jssc.2004.05.031](https://doi.org/10.1016/j.jssc.2004.05.031).

- [13] A. Kumar *et al.*, Structural and magnetic properties of quasi-dimensional doped LiCuVO₄. *J. Solid State Chem.* **208**, 120 (2013). DOI: [10.1016/j.jssc.2013.09.029](https://doi.org/10.1016/j.jssc.2013.09.029).
- [14] C. Kegler *et al.*, Magnetic resonance on LiCuVO₄. *Eur. Phys. J. B.* **22**(3), 321 (2001). DOI: [10.1007/s100510170109](https://doi.org/10.1007/s100510170109).
- [15] M. E. dos Santos *et al.*, Cation distribution and magnetic characterization of the multiferroic cobalt manganese Co₂MnO₄ spinel doped with bismuth. *J. Magn. Magn. Mater.* **329**, 53 (2013). DOI: [10.1016/j.jmmm.2012.09.070](https://doi.org/10.1016/j.jmmm.2012.09.070).
- [16] G. Kresse, and J. Hafner, Ab initio molecular dynamics for liquid metals. *Phys. Rev. B.* **47**(1), 558 (1993). DOI: [10.1103/PhysRevB.47.558](https://doi.org/10.1103/PhysRevB.47.558).
- [17] G. Kresse, and J. Furthmüller, Ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**(1), 15 (1996). DOI: [10.1016/0927-0256\(96\)00008-0](https://doi.org/10.1016/0927-0256(96)00008-0).
- [18] G. Kresse, and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B.* **59**(3), 1758 (1999). DOI: [10.1103/PhysRevB.59.1758](https://doi.org/10.1103/PhysRevB.59.1758).
- [19] G. Kresse, and J. Furthmüller, Efficient iterative schemes for ab initio total- energy calculations using a plane-wave basis set. *Phys. Rev. B.* **54**(16), 11169 (1996). DOI: [10.1103/PhysRevB.54.11169](https://doi.org/10.1103/PhysRevB.54.11169).
- [20] P. Hohenberg, and W. Kohn, Inhomogeneous Electron Gas. *Phys. Rev.* **136**, A1133 (1964).
- [21] J. P. Perdew, S. Burke, and M. Ernzerhof, Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**(18), 3865 (1996). DOI: [10.1103/PhysRevLett.77.3865](https://doi.org/10.1103/PhysRevLett.77.3865).
- [22] H. J. Monkhorst, and J. D. Pack, Special points for Brillouin-zone integrations. *Phys. Rev. B.* **13**(12), 5188 (1976). DOI: [10.1103/PhysRevB.13.5188](https://doi.org/10.1103/PhysRevB.13.5188).
- [23] M. Yamaguchi, T. Furuta, and M. Ishikawa, Calorimetric study of several cuprates with restricted dimensionality. *J. Phys. Soc. Jpn.* **65**(9), 2998 (1996). DOI: [10.1143/JPSJ.65.2998](https://doi.org/10.1143/JPSJ.65.2998).
- [24] Y. Le Page, and P. Saxe, Symmetry-general least-squares extraction of elastic coefficients from ab initio total energy. *Phys. Rev. B.* **63**, 174103 (2001).
- [25] O. Beckstein, *et al.*, First-principles elastic constants and electronic structure of α -Pt₂Si and PtSi. *Phys. Rev. B.* **63**, 134112.1 (2001).
- [26] D. C. Wallace, *Thermodynamics of Crystals* (New York: Wiley, 1972).
- [27] W. Voigt, *Lehrbuch Der Kristallphysik* (Leipzig: Teubner, 1928), 962
- [28] A. Reuss, Berechnung der fließgrenze von mischkristallen auf grund der plastizitätsbedingung für einkristalle. *Z Angew. Math. Mech.* **9**(1), 49 (1929). DOI: [10.1002/zamm.19290090104](https://doi.org/10.1002/zamm.19290090104).
- [29] R. Hill, The elastic behavior of crystalline aggregate. *Proc. Phys. Soc. A.* **65**(5), 349 (1952). DOI: [10.1088/0370-1298/65/5/307](https://doi.org/10.1088/0370-1298/65/5/307).
- [30] V. V. Bannikov, I. R. Shein, and A. L. Ivanovskii, Electronic structure, chemical bonding and elastic properties of the first thorium-containing nitride perovskite TaThN₃. *Phys. Stat. Sol. (Rrl)*. **1**(3), 89 (2007). DOI: [10.1002/pssr.200600116](https://doi.org/10.1002/pssr.200600116).
- [31] H. Koc *et al.*, Ab initio calculation of the structural, elastic, electronic, and linear optical properties of ZrPtSi and TiPtSi ternary compounds. *Comput. Mater. Sci.* **62**, 235 (2012). DOI: [10.1016/j.commatsci.2012.05.052](https://doi.org/10.1016/j.commatsci.2012.05.052).
- [32] H. Koc *et al.*, First principles prediction of the elastic, electronic, and optical properties of Sb₂S₃ and Sb₂Se₃ compounds. *Solid State Sci.* **14**(8), 1211 (2012). DOI: [10.1016/j.solidstatesciences.2012.06.003](https://doi.org/10.1016/j.solidstatesciences.2012.06.003).
- [33] I. R. Shein, and A. L. Ivanovskii, Elastic properties of mono- and polycrystalline hexagonal AlB₂-like diborides of s, p and d metals from first-principles calculations. *J. Phys: Condens. Matter.* **20**, 415218.1 (2008). DOI: [10.1088/0953-8984/20/41/415218](https://doi.org/10.1088/0953-8984/20/41/415218).
- [34] F. Pogh, Relations between the elastic moduli and the plastic properties of polycrystalline pure metals. *Philos. Mag.* **45**, 823 (1954).
- [35] D. H. Chung, and W. R. Buessem, In: *Anisotropy in Single Crystal Refractory Compounds*. Edited by Vahldiek FW, Mersol SA (New York: Plenum, 1968), 217.
- [36] I. Johnston, *et al.*, *Solids State Physics Simulations, the Consortium for Upper Level Physics Software*. (New York: Wiley, 1996).

- [37] O. L. Anderson, A simplified method for calculating the Debye temperature from elastic constants. *J. Phys. Chem. Solids.* **24**(7), 909 (1963). DOI: [10.1016/0022-3697\(63\)90067-2](https://doi.org/10.1016/0022-3697(63)90067-2).
- [38] E. Schreiber, O. L. Anderson, and N. Soga, *Elastic Constants and Their Measurements* (New York: McGraw-Hill, 1973).