Density functional study of elastic and vibrational properties of the Heusler-type alloys Fe_2VAl and Fe_2VGa

V. Kanchana[1*], G. Vaitheeswaran[1,2], Yanming Ma[3], Yu Xie[3], A. Svane[4] and O. Eriksson[5]

[1]*Applied Materials Physics,*

Department of Materials Science and Engineering,

Royal Institute of Technology,

Brinellvägen 23, 100 44 Stockholm, Sweden

[2]*Advanced Centre of Research in High Energy Materials (ACRHEM),*

University of Hyderabad,

Gachibowli, Hyderabad 500 046,

Andhra Pradesh, India

[3]*National Lab of Superhard Materials,*

Jilin University,

Changchun 130012, P. R. China

[4]*Department of Physics and Astronomy,*

University of Aarhus,

DK-8000 Aarhus C, Denmark

[5]*Department of Physics and Materials Science,*

Uppsala University, Box 590,

SE-751 21, Uppsala, Sweden

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Abstract

The structural and elastic properties as well as phonon-dispersion relations of the Heusler-type alloys Fe_2VAl and Fe_2VGa are computed using density-functional and density-functional perturbation theory within the generalized-gradient approximation. The calculated equilibrium lattice constants agree well with the experimental values. The elastic constants of Fe_2VAl and Fe_2VGa are predicted for the first time. From the elastic constants the shear modulus, Young's modulus, Poisson's ratio, sound velocities and Debye temperatures are obtained. By analyzing the ratio between the bulk and shear modulii, we conclude that both Fe_2VAl and Fe_2VGa are brittle in nature. The computed phonon-dispersion relation shows that both compounds are dynamically stable in the $L1_2$ structure without any imaginary phonon frequencies. The isomer shifts of Fe in the two compounds are discussed in terms of the Fe s partial density of states, which reveal larger ionicity/less hybridization in Fe_2VGa than in Fe_2VAl. For the same reason the Cauchy pressure is negative in Fe_2VAl but positive in Fe_2VGa.

I. INTRODUCTION

The Heusler-type intermetallic compounds Fe_2VAl and Fe_2VGa have recently attracted great attention due to their facinating thermal, electrical, magnetic and transport properties,[1,2,3,4] not only from the basic science prespectives but also from the potential application as thermoelectric materials.[4,5,6] Though Heusler-type intermetallics commonly appear as metals,[7] semiconducting behaviour has been observed in Fe_2VAl and Fe_2VGa, as evidenced by their negative temperature coefficient of resistivity[1]. This feature has been attributed to the appearance of a pseudo gap in the density of states in the vicinity of the Fermi level, and these materials have been characterized as semimetals. Nuclear magnetic resonance experiments and optical conductivity measurements further confirmed the existence of deep pseudo gaps near the Fermi energy (E_F) in both compounds.[8,9] Recently, it has been reported by Lue et al.[10] that the partial substitution of Ga by Ge in Fe_2VGa effectively dopes electrons to the system thereby leading to a dramatic decrease in the electrical resistivity A similar study for Fe_2VAl was carried out by Nishino et al.[11] with the same conclusion. The variation of the Seebeck-coefficient with a sign change from possitive to negative can be understood by means of a rigid band like shifting of the Fermi level across the pseudogap.

Several band structure calculations have been reported providing various insights into Fe_2VAl and Fe_2VGa, all confirming that Fe_2VAl is a non-magnetic semimetal with a pronounced pseudo gap at the Fermi level[12,13,14,15,16,17,18]. The calculated pseudo gap seems however too wide to explain the experimental data. Guo et al.[12] suggested the negative temperature coefficient of resistance to arise from carrier localisation, while Singh and Mazin[13] pointed towards the interaction of carriers with fluctuating magnetic moments, and Weht and Pickett[14] proposed dynamic correlations between holes and electrons to be responsible for the unusual resistivity behavior. The importance of magnetic moment formation in off-stoichiometric compounds have been confirmed experimentally,[19] and recent theoretical studies of the $Fe_{2+x}V_{1-x}Z$ (Z=Al,Ga) compounds[20,21] with a supercell approach predicted that antisite defects or excess atoms in the Heusler lattice may induce a radical change in the electronic and magnetic properties. Similarly, Antonov et al.[22] have studied the electronic structure and X-ray magnetic circular dichroism in $Fe_{2-x}V_{1+x}Al$ for various x using first principles calculations, which confirm the formation of magnetic moment on vanadium

impurities.

Alloys based on Fe_2VAl are good candidates for thermoelectric materials.[4,5,6] Although they have a high thermoelectric power, because of their high electrical conductivities and high Seebeck coefficients, they have poor figures of merit compared with other state-of-the-art thermoelectric materials due to their high thermal conductivity, κ. Hence reduction of κ is required for practical applications,[6] which may be achieved by sustitution of Al by a heavier element.[5] Large experimental efforts have been devoted to characterization of Fe_2VAl based materials,[23] including x-ray absorption[24] and photoemission[25,26] to reveal their surface and bulk electronic structure and electrical and thermal properties.[27,28,29] Yet, the lattice dynamics and mechanical properties have not been explored, which is taken as the objective of the present work. Here we present results of computations of the elastic constants and phonon-dispersion relations for Fe_2VAl and Fe_2VGa using density functional and density functional pertubation theory within the generalised gradient approximation. From the modulus of elasticity, we predict the mechanical behaviour of these compounds.

II.   COMPUTATIONAL DETAILS

The all-electron linear muffin-tin orbital method[30] in a full-potential (FP-LMTO) implementation[31] is used to calculate the total energies, and basic ground state and elastic properties of Fe_2VAl and Fe_2VGa. In this method, the crystal volume is split into two regions: non-overlapping muffin-tin spheres surrounding each atom and the interstitial region between the spheres. We used a double κ spdf LMTO basis to describe the valence bands, i.e. Hankel-functions characterized by decay constants κ are smoothly augmented with numerical radial functions within the atomic spheres. The calculations included the 4s, 4p, 3p, and 3d basis functions for iron and vanadium, the 3s, 3p and 3d basis for aluminum, and the 4s, 4p and 3d bases from gallium. The exchange correlation potential was calculated within the generalized gradient approximation (GGA) scheme[32]. Inside the muffin-tin spheres, the charge density and potential were expanded in terms of spherical harmonics up to l_{max}=6, while in the interstitial region, they were expanded in plane waves, with 12050 waves (energy up to 171 Ry) included in the calculation. Total energies were calculated as a function of volume for a (28 28 28) k-mesh containing 624 k-points in the irreducible wedge of the Brillouin zone. The energy curves were fitted to a second order Birch equation of state[33] to
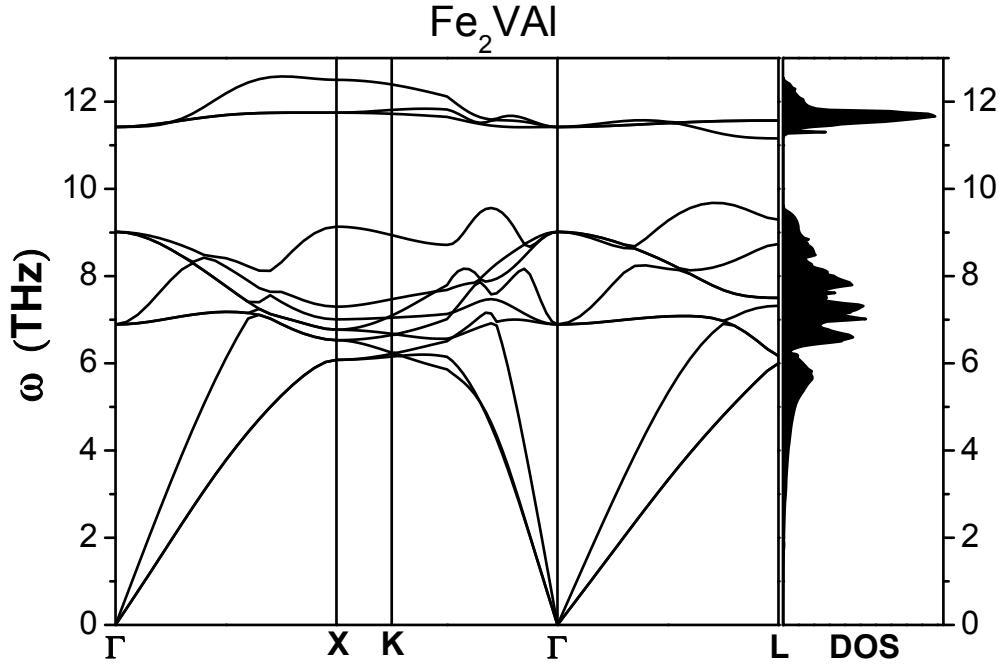
FIG. 1: Calculated phonon dispersion curves and phonon density of states of Fe_2VAl

obtain the ground state properties. The elastic constants were obtained from the variation of the total energy under volume-conserving strains, as outlined in Refs. 35.

In order to calculate the vibrational properties of the Heusler alloys we used the density functional perturbation theory as implemented in the plane-wave pseudopotential method, through the Quantum-ESPRESSO package[36]. We have used the Troullier-Martins non-conserving pseudopotentials[37]. Convergence tests lead to the choice of kinetic energy cutoffs of 80 Ry, and a (8 8 8) Monkhorst-Pack[34] grid of k-points for the Brillouin zone integration.

III. PHONONS

The calculated phonon dispersion curves of Fe_2VAl and Fe_2VGa are presented in figures 1 and 2, respectively. We do not find any imaginary phonon frequency in the whole Brillouin zone for the two compounds. This supports the dynamical stability of both compounds in the Heusler structure, which is not *a-priori* evident in view of instabilities found in similar alloys, *e. g.* Ni_2MnAl and Ni_2MnGa.[38,39] It is interesting to note that the optical phonons for Fe_2VGa are coupled, falling in a broad frequency range between 5.2 and 9.1 THz. This

is in contrast to Fe$_2$VAl, where three optical phonon branches are separated from the lower frequency phonons. Inspection of the atomic masses of Fe, V, Ga and Al allows us to understand this difference between the two compounds. The similar atomic masses of Fe, V and Ga lead to the coupled phonon dispersions, while the significantly lower atomic mass of Al results in the phonon seperation. The three highest optical phonon modes of Fe$_2$VAl have their major amplitude contribution on Al atoms.

The lattice thermal conductivity is inversely proportional to the sound velocity,[40] so assuming similar phonon scattering properties (relaxation times) for Fe$_2$VAl and Fe$_2$VGa, the former compound thus should have the smaller thermal conductivity, which might be an observation of relevance in efforts of minimization of thermal conductivity for good thermoelectric figures of merits. Note that in the study of Ge substitution for Al in Fe$_2$VAl in Ref. 5 the opposite trend was found, i.e. κ is reduced when the heavier Ge substitutes for Al, but this was attributed to the change in phonon relaxation time due to the incorporation of impurities with a large mass difference.

IV.   GROUND STATE AND ELASTIC PROPERTIES

The calculated equilibrium lattice constant and the bulk modulus along with the experimental and other theory work is given Table. 1. The lattice constant obtained from the present calculation is underestimated by 0.8% for Fe$_2$VAl and 0.7% for Fe$_2$VGa when compared with the experimental value. The present results on lattice constant and bulk modulus agree quite well with the recent FLAPW calculations.[24] The calculated elastic constants of Fe$_2$VAl and Fe$_2$VGa are presented in Table II. This is the first theoretical prediction of the elastic constants, which still awaits experimental confirmation. It is noticeable that the Cauchy pressure, $C_P \equiv C_{12} - C_{44}$ is negative for Fe$_2$VAl ($C_P = -45$ GPa) but positive for Fe$_2$VGa ($C_P = +9$ GPa). According to Pettifor[41] this reflects a more covalent character of bonding in Fe$_2$VAl. A simple relationship, empirically linking the plastic properties of materials with their elastic moduli has been proposed by Pugh.[42] The shear modulus G represents the resistance to plastic deformation, while the bulk modulus B represents the resistance to fracture. A high B/G ratio may then be associated with ductility, whereas a low value would correspond to a more brittle nature. The critical value separating ductile and brittle materials is around 1.75 according to Ref. 42. In the case of Fe$_2$VAl the value

of B/G is 1.37 and for Fe_2VGa the value is 1.73 from our calculated values in Table II, and therefore Fe_2VAl can be classified as a brittle material, while Fe_2VGa resides on the borderline between brittle and ductile. Frantsevich[43] has a similar criterion based on the Poisson ratio, namely $\nu < 1/3$ ($\nu > 1/3$) for brittle (ductile) character, hence categorizing both compounds as brittle (see Table II). The difference merely reflects the imprecise nature of the concept.[44]

The sound velocities of Fe_2VAl and Fe_2VGa may be derived from the calculated elastic constants,[35] see Table III. The properties of the two compounds are quite similar apart from the heavier mass of Ga compared to Al, which is the dominating factor leading to smaller sound velocities in Fe_2VGa compared to Fe_2VAl. The Debye temperature may be estimated from the simple isotropic approximations, $k_B\Theta_D = \hbar v_m k_D$, where k_B and k_D are the Boltzmann constant and the Debye vector, respectively, and v_m the average sound velocity. Hence, the smaller sound velocity in Fe_2VGa directly leads to a smaller Debye temperature. The sound velocities may also be read from the acoustic phonon branches in figures 1 and 2. They are listed in the Table as well. One notices quite some anisotropy, the sound velocities along [110] being ~ 30 % larger than along the [100] and [111] directions.

The isomer shift of Fe in Fe_2VAl and Fe_2VGa have been measured by Ref. 45. The isomer shift is proportional to the difference in electron contact density, $\rho(0)$, between the sample and reference materials,

$$I.S. = \alpha(\rho(0) - \rho_{ref}(0)).$$

We calculated the electron contact density of Fe in the Fe_2VAl and Fe_2VGa compounds and compared to that of α-Fe. Using the calibration constant $\alpha = -0.22a_0^3$ mm/s (Ref. 46), this leads to the isomer shifts listed in Table IV. The difference in contact density is quite small, being larger in Fe_2VAl than in Fe_2VGa by 0.45 a_0^{-3}. Thus the isomer shift of the latter compound is larger by 0.10 mm/s, in excellent agreement with the experimental finding. However, the calculated isomer shifts relative to α-Fe are about 0.04 mm/s smaller than measured, which could be a temperature related effect, since the experiments are conducted at room temperature, while our theory pertains to 0 K. The origin of the different value for the isomer shift in Fe_2VAl and Fe_2VGa is the difference in electronegativity of Al and Ga. Although the electronic structures of these compounds are very similar,[16] the greater electronegativity of Ga compared to Al transcripts into a deeper position of the Ga-dominated deepest s-band in Fe_2VGa compared to the position of the equivalent Al
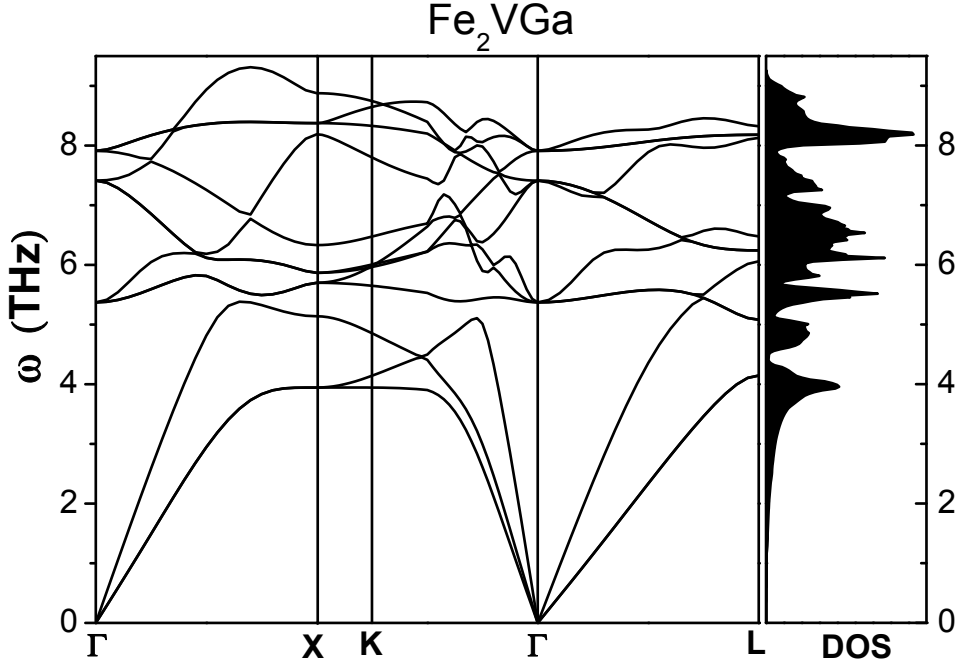
FIG. 2: Calculated phonon dispersion curves and phonon density of states of Fe_2VGa

s-band in Fe_2VAl. This leads to reduced hybridization of Fe s into this band in Fe_2VGa compared to Fe_2VAl. To illustrate this, we plot in figure 3 the partial density of states of Fe s-character for the two compounds. This is the relevant quantity to consider, since the dominant contribution to the electron contact density *variations* in solids stems from the valence s-electrons (only s-states - and relativistic $p_{1/2}$-states extend their amplitude into the nuclear region). Thus, in figure 3 the relevant s-band is the the lower part of the density of states (between -10.3 eV and -7.5 eV in Fe_2VGa, between -9.3 eV and -6 eV in Fe_2VAl, relative to the Fermi level). The reduced hybridization of Fe s into this band leads to the smaller band width in Fe_2VGa compared to Fe_2VAl, as well as the fewer integrated number of Fe s electrons for this band (Table IV), which almost exactly reflects the difference in isomer shifts. In contrast, the upper part of the Fe s partial density of states in figure 3, which describes the hybridization of Fe s into the Fe and V d-bands, is much more similar in the two cases, and also integrates to almost the same number of Fe s charge. The larger hybridization in Fe_2VAl compared to Fe_2VGa also explains the difference in sign of the Poisson ratio, discussed above.
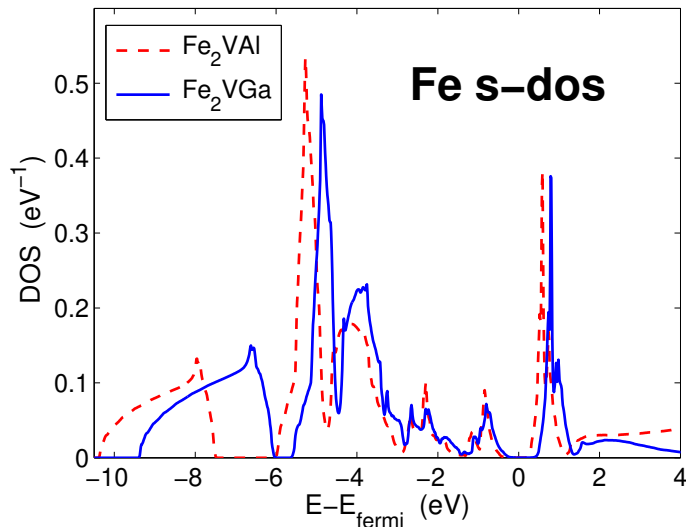
FIG. 3: Calculated Fe s partial density of states (in units of electrons per eV and per Fe atom) in Fe_2VAl (red) and Fe_2VGa (blue). The zero of energy is placed at the Fermi level, which falls in the pseudo gap within the Fe and V d-bands.

V. CONCLUSIONS

Ab initio electronic structure and phonon frequency calculations based on the density fucntional theory have been presented for the Heusler alloys Fe_2VAl and Fe_2VGa. The elastic constants have been obtained, while no experiments exist for comparison. The differences in phonon dispersions for the two compounds can be explained by the heavier mass of Ga compared to Al, while the difference in Fe isomer shift is attributed to the higher electronegativity of Ga compared to Al, the ensuing reduced covalency in Fe_2VGa compared to Fe_2VAl also explaining the difference in Cauchy pressure.

TABLE I: Calculated lattice constants in Å, bulk modulus in GPa, and its pressure derivative B' of Fe_2VAl and Fe_2VGa at the theoretical equilibrium volume.

Compound		Lattice Constant	Bulk Modulus	B'
Fe_2VAl	Expt.	5.76	-	-
	Theory, this work	5.712	220.8	5.3
	Other theory	5.712^a	212^a	-
Fe_2VGa	Expt.	5.77	-	-
	Theory, this work	5.727	228.5	4.9
	Other theory	5.726^a	214^a	-

^{a}: Ref.24;

TABLE II: Calculated elastic constants, shear modulus (G), and Young's modulus (E) all expressed in GPa, and Poisson's ratio ν for Fe_2VAl and Fe_2VGa at the theoretical equilibrium volume

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	C_{11}	C_{12}	C_{44}	G	E	ν
Fe_2VAl	415.7	125.3	170.7	160.5	387.6	0.208
Fe_2VGa	363.1	161.0	152.3	131.8	331.7	0.258

TABLE III: Calculated longitudinal, shear, and average wave velocity (v_l, v_s, and v_m, respectively) in km/s, and the Debye temperature, θ_D, in Kelvin from the average elastic wave velocity for Fe_2VAl and Fe_2VGa at the theoretical equilibrium volume. Also listed are the directional sound velocities read from the acoustic phonon branches along directions [100], [111] and [110].

Compound		v_l	v_s	v_m	θ_D
Fe_2VAl	isotropic	8.13	4.93	5.45	447
	[100]	7.49	4.44		
	[111]	7.72	4.46		
	[110]	10.23	6.41		
Fe_2VGa	isotropic	7.09	4.05	4.50	369
	[100]	6.29	3.52		
	[111]	6.26	3.13		
	[110]	8.15	4.52,4.19		

TABLE IV: Calculated and measured isomer shifts of Fe_2VAl and Fe_2VGa, in mm/s relative to α-Fe. Also listed are the partial charges inside the Fe muffin-tin sphere (radius $R = 2.305$ a.u.). The Fe s-charge within the lowest s-like band is listed quoted in paranthesis (see text).

	Fe_2VAl	Fe_2VGa
I.S. theo	+0.021	+0.121
I.S. expt[a]	+0.058(5)	+0.161(5)
Fe n_s	0.394(0.140)	0.370(0.111)
n_p	0.437	0.419
n_d	6.112	6.121
n_f	0.015	0.023

[a]: Ref. 45

* Author for Correspondence, E-mail: kanch@kth.se

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