INTERNATIONAL JOURNAL OF CURRENT ADVANCED RESEARCH
ISSN: O: 2319-6475, ISSN: P: 2319-6505, Impact Factor: 6.614
Available Online at www.journalijcar.org
Volume 12; Issue 07(A); July 2023; Page No. 2210-2213
DOI: http://dx.doi.org/10.24327/ijcar.2023.2213.1483

Research Article

FIRST PRINCIPLE STUDIES ON NOVEL CuCrMnAl QUATERNARY HEUSLER ALLOY FOR THERMOELECTRIC AND SPINTRONIC APPLICATIONS

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A R T I C L E I N F O

Article History:
Received 06th April, 2023
Received in revised form 14th May, 2023
Accepted 23rd June, 2023
Published online 28th July, 2023

Key words:
Quaternary Heusler alloy, thermoelectric materials, dynamical stability, figure of merit.

A B S T R A C T

We report the structural stability, dynamical stability, feasibility of physical synthesis, electronic, magnetic, thermodynamic and thermoelectric properties of novel CuCrMnAl quaternary Heusler alloys using first principle studies based on density functional theory (DFT). CuCrMnAl alloy is found to be stable in cubic phase with equilibrium lattice constant 5.6568Å**,** fitted with Birch-Murnaghan equation of state. When compared to Non-magnetic and Ferromagnetic states, Ferri-magnetic state is stable due to large negative energy. The observed negative formation energy (-3.8066 eV) makes this alloy a physically synthesizable compound. Further non-zero density of states (DOS) in spin-down channels and zero density of states in spin-up channel near to Fermi energy prove its half-metallic character. Absence of imaginary frequencies in phonon dispersion spectrum confirms the dynamical stability of the compound. Integration of DOS indicates the magnetic moment of a compound and estimated magnetic moment is 0.98μB. It is observed that major contribution for magnetic moment is coming from Mn atoms. It can be observed that strong bonding between Mn-Ni atoms are due to stronger Heisenberg's exchange coupling strength. The calculations of different thermodynamic properties such as entropy, free energy and specific heat at constant volume (C_V) of CuCrMnAl alloy are performed by varying the temperature from 0 K to 2000 K. To estimate thermoelectric properties of CuCrMnAl alloy as a function of chemical potential and temperature, we have used the BoltzTrap code based on the Boltzmann model via Boltzmann transport equation. The figure of merit (ZT) is very large of 0.5 at 400K as calculated thermal conductivity is low and Seebeck coefficient is large value and also power factor also reasonably good, shows that our CuCrMnAl alloy can be used for powerful thermoelectric devices. The figure of merit further enhanced by reducing lattice contribution to thermal conductivity, this could be possible by annealing sample under proper conditions leads to adjustment of its crystallographic order. Mn-Ni based samples usually are high entropy heusler alloys can be used as efficient magnetic refrigerant materials.

INTRODUCTION

Heusler materials are ternary or quaternary inter-metallic compounds having two transitions metals and one main group element. Heusler alloys are categorized as Half Heusler alloys [1] (XYZ) and Full Heusler alloys (X_2YZ) where X, Y-Transition elements, Z–Main Block elements. Site preference rule (SPR) is usually employed to determine the possible atomic preference of full-Heusler alloys X_2YZ. The classic full-Heusler alloys X_2YZ have the highly ordered structures, there are four atom sites occupied by the atom are A (0,0,0), B (0.25,0.25,0.25), C (0.5,0.5,0.5), and D (0.75,0.75,0.75). Normal Heusler alloys are attractive with the following properties, such as high spin polarization (P=100%), high magnetization, high Curie temperature, lattice constant compatibility, high thermoelectric power conversion. Properties of heusler compounds are different from their constituent elements [2-4]. Many heusler compounds exhibits half-metallic property in which compounds do not have energy gap in one spin channel and there is an energy gap in another spin channel. For thermoelectric and spintronic applications material should have lattice, mechanical, thermal stabilities and should have high figure of merit. Heusler alloys, which were first found in 1903, are commonly utilized in electronic spin devices, such as magnetoresistive random access memory (MRAM), giant magneto-resistance (GMR) and magnetic sensors. Heusler alloys (HA) were gaining attraction due to their extensive functional properties in electronics, spintronics, magnetism and thermoelectrics among other fields.

The half-metallic (HM) character of these materials makes them particularly well-suited for use in magnetoelectronic

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devices. A metallic-type band structure can be found in any of the two spin states of HM materials and a semiconducting-type band structure can be found in the other spin state as can be found in many HA. Quaternary Heusler Alloys (QHA) have attracted a lot of attention as a result of their special physical characteristics, which include a higher Curie temperature, strong magnetism, and a large energy gap. However, there hasn't been much research done on Fe-based QHA. Many Heusler alloys have recently been discovered to offer TE qualities comparable to traditional Bi_2Te_3 and PbTe-based TE materials. Fe-based Heusler alloys have recently been identified with thermoelectric and spintronic applications [5-8]. The computed total magnetic moment of FeRhCrZ (Z = Si and Ge) is 3.00μ_B per formula unit confirms that the alloys are half-metallic ferromagnets and reported maximum *ZT* of 0.45 at high temperature. p-Type FeTaSb and n-type FeMnTiSb show high *ZT* values of 0.72 and 0.46 at 1100 K respectively. The total spin magnetic moment of FeCr-based QHA is found to be 1.00 to 4.00μ_B per formula unit confirms that the alloys are half-metallic ferromagnets in nature. In recent years, half metallic, thermoelectric and optical properties in Heusler alloys and perovskite have received a lot of attention from researcher.

Computational Details

Properties like structural, magnetic, electronic, thermodynamic and thermoelectric properties are calculated with quantum espresso within DFT formalism. PAW potential is taken to express the electron interactions [9]. Kohn-sham plane wave basis is developed with the kinetic energy cut-off of 500 eV and 20x20x20 k-point grid is taken for calculating Brillouin zone parameters. Generalized gradient approximation (GGA) is taken for explaining exchange interaction and correlations in a compound. PHONOPHY [10] package is taken for explain the Phonon density of states. Full potential spin polarized relativistic Hamiltonian with l_{max} =3 is used for Brillouin zone calculations. we have used the Boltz Trap code which is based on the Boltzmann model via Boltzmann transport equation for calculating the thermoelectric properties of a sample. Thermodynamic properties are acquired by the quasi-harmonic model of Debye model as implemented in Gibbs program.

RESULTS AND DISCUSSION

Lattice constant Optimization

Equilibrium lattice constant for studied compound was obtained by using Birch-Murnaghan equation of state to fit the total energies. In continuum mechanics, an equation of state suitable for modelling solids is naturally rather different from the ideal gas law. A solid has a certain equilibrium volume V_0, and the energy increases quadratically as volume is increased or decreased a small amount from that value. The simplest plausible dependence of energy on volume would be a harmonic solid, with next simplest reasonable model would be with a constant bulk modulus. Birch-Murnaghan equations give us relationship between Energy and lattice constant [10,11]. c/a ratio has taken starting from 0.70, 0.71, 0.72 … 1.50 with spacing of 0.01 calculations are performed with a = 5.7722 Å. Birch- Murnaghan equation of state is used to fit the energy as a function of volume, modulus of compressibility and derivative of modulus of compressibility. At c/a ratio of 0.98 we got global minima of energy. As our crystal system is cubic so, its equilibrium lattice constant is a= 5.6568 Å. At equilibrium lattice constant no external strain will act upon the crystal so that compound would be in its lowest energy state.

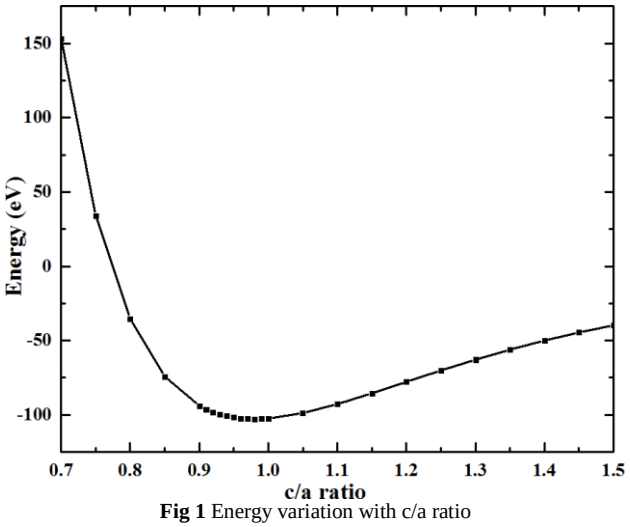

Fig 1 Energy variation with c/a ratio

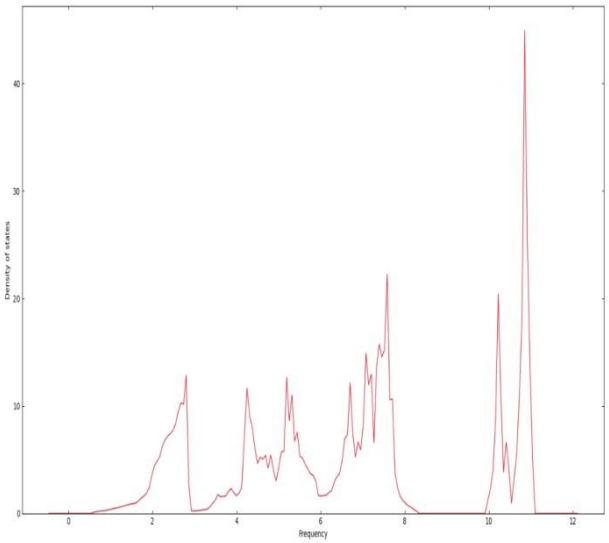

Fig 2 Phonon density of states with highsymmetry points

K-Mesh Point Optimization

Consider the K-mesh point as n x n x n format with

Table 1

K-mesh	Energy (eV)
4x4x4	-102.863645
8x8x8	-102.841490
12x12x12	-102.851479
16x16x16	-102.852137
20x20x20	-102.857132

Table 2

$E_{CuCrMnAl}$	**-25.619710 eV**
E_{Cr}	-09.475636 eV
E_{Al}	-03.681934 eV
E_{Cu}	-03.659029 eV
E_{Mn}	-04.996467 eV
$E_{Formation} = E_{CuCrMnAl} - \{(E_{Cu}) + (E_{Mn}) + (E_{Cr}) + (E_{Al})\}$	-25.61971 - {-3.659029+(-4.996467) + (-9.475636)+ (-3.681934)} = -3.221859 eV

More the number of points more will be the accuracy in obtaining the results. Though it is getting slightly higher values at high mesh point grid but for obtaining better results we should have simulations with high mesh point grid.

Calculation of Formation Energy

The estimated formation energy of a compound as shown in Table.2 is negative suggests that studied compound can be synthesized physically.

Phonon Density of States

Phonon dispersion curves are plotted along the Brillouin zone of high symmetry points. In dispersion spectrum upper portion indicates optical modes and lower portion indicates the acoustic modes of a compound. Absence of imaginary frequencies in phonon dispersion spectrum confirms the dynamical stability of the compound.

Spin Density of states

Total and partial spin density of states provides a better picture of electronic structure. If density of states is zero for one of the spin channels at Fermi energy level, then it would be a half metallic. The major contribution near Fermi level is coming from d-states of magnetic atoms Mn and Cr. Integration of density of states gives us the magnetic moment of a compound. S and P orbital contribution to Density of states is negligible. Discrepancy in experimental values of magnetic moment from theoretical Slater-Pauling rule is might be due to B2 type and DO3 type disorders in the system. In experimentally synthesized compounds B2 type disorder may be present always. As our proposed compound have energy gap in one spin channel and do not have any energy gap in another spin channel near to Fermi energy so it should be a half -metallic compound. Half metallic nature at Fermi energy leads to a 100% spin polarisation of the compound, which is very much needed for spintronic applications.

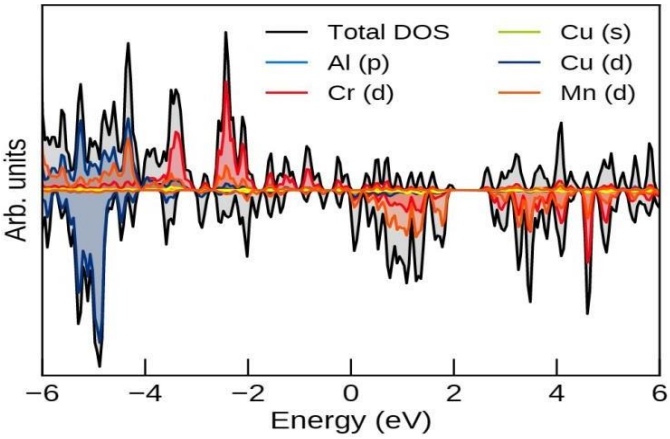

Fig 3 Density of states without taking spin-orbit interaction into account.

Thermodynamic Properties

The thermodynamic properties of CuCrMnAl alloy such as volume variation (V), compressibility modulus (B), Debye temperature, thermal expansion (α), specific capacity (Cp), and thermal capacity (Cv) are acquired by the quasi-harmonic model of Debye model. The calculations of different thermodynamic properties [8] of CuCrMnAl alloy are performed by varying the temperature (T) from 0 K to 2000 K. Specific heat at constant volume reaches to a maximum value as said by Dulong-Petits law. Entropy it is a measure of disorder which increases with temperature. Free energy attains more negative values as temperature increases. By calculating specific heat values at different temperatures and if we found any anomaly then one can get an idea about phase transition [12]. Using value of specific heat one can estimate the Debye temperature Θ_D which in turn gives us the idea of maximum strength of the crystal against the vibration and hence knows about vibrational cut-off frequency of crystal. No hysteresis in expansion coefficient (α) vs temperature (T) graph indicates the first order transition of the compound. The electrical conductivity rises as the temperature rises and peaks at 900 K the high electrical conductivity is induced by the high density of charge carriers, which is a common trend in semiconductor materials. Thus, it is logical to expect thermal conductivity to behave similarly to electrical conductivity. High thermoelectric efficiency suggests that κ is dominated by electrons within a band [13]. Thermal conductivity rises as temperature rises and reaches its peak at 900 K. The S and σ/τ were used to determine the PF of a material which measures a material's efficiency. The study reveals that the PF rises as temperature rises, maximum at 900 K.

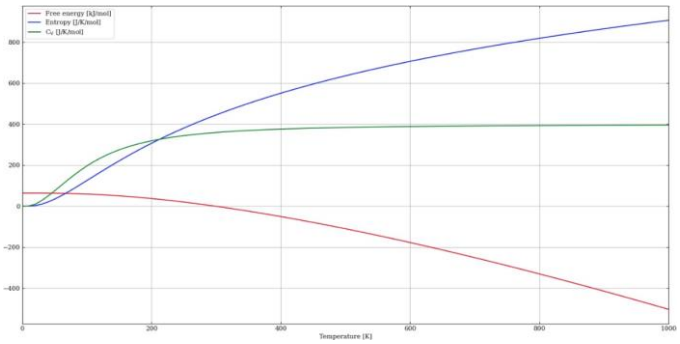

Fig 4 Thermodynamic properties such as free energy, Entropy and specific heat are plotted with temperature

Thermoelectric properties

Heusler alloys have globally demonstrated high thermoelectric performance and have drawn considerable attention to the evolution of thermoelectric materials. For our calculation of thermoelectric properties of CuCrMnAl alloy as a function of chemical potential, we have used the Boltz Trap code which is based on the Boltzmann model via Boltzmann transport equation.

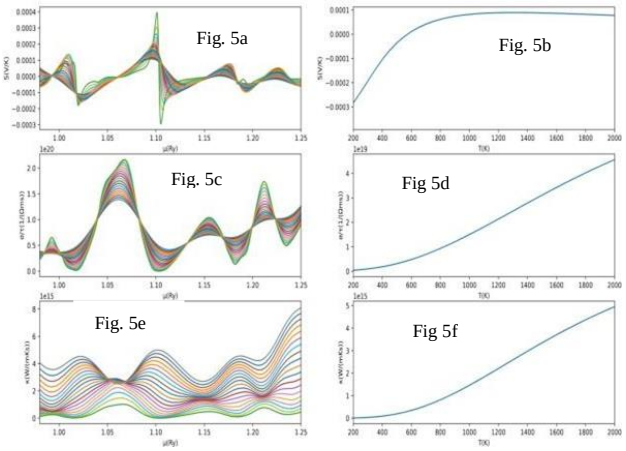

Fig 5 (**a**) Variation of seebeck co-efficient with chemical potential (**b**) Variation of seebeck co-efficient with temperature (**c**) Variation of electrical conductivity with chemical potential(**d**) Variation of electrical conductivity with temperature. (**e**)Variation of thermal conductivity with chemical potential(**f**) Variation of thermal conductivity with temperature.

The Seebeck coefficient (**S**), power factor, and the figure of merit ZT are calculated. Knowing that the figure of merit is written in the form

$$ZT = [S^2 \sigma/(\kappa_e+\kappa_l)]\ T,$$

Where S represents the Seebeck coefficient, σ is the electrical conductivity, T is the temperature, k_e and k_l are the electronic

and lattice thermal conductivities respectively. At temperature 400K, figure of merit is 0.5and at 1000K, figure of merit is 0.1. The figure of merit (ZT) would be very large because calculated thermal conductivity is low because at high temperatures due to phonon scattering phonon contribution decreases and seebeck coefficient is having high value, which shows that our CuCrMnAl alloy can be used for powerful thermoelectric devices [14,15].

CONCLUSION

Our compound has good spintronic and thermoelectric behaviours that may be used in spin injection applications. Thermoelectric materials have low lattice thermal conductivity and high Seebeck coefficient value. Optical spectra reveal that absorption occurs in the visible and near ultraviolet ranges of the spectra. According to current research, a narrow band gap, spin polarization, and high ZT values are all excellent candidates for spintronics and thermoelectric applications. We believe that our findings, indicating the potential of novel alloy as promising spintronics, thermoelectric and optoelectronics material, will motivate and promote experimenters to investigate these materials. Finally figure of merit of 0.5 at 400K made it useful for thermoelectric applications.

Acknowledgement

One of the authors (K. Venkanna) is grateful to NIT Andhra Pradesh for computational facilities, and the author expresses their sincere thanks to the principal SGA GDC-Yelamanchili, Anakapalli (Dt). Also, very much thankful to the Principal GDC-Nakkapalli, Anakapalle (Dt).

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How to cite this article:

Venkanna K, Atchyutha Rao Ch and Jagga Rao P. S (2023) 'First Principle Studies on Novel Cucrmnal Quaternary Heusler Alloy For Thermoelectric And Spintronic Applications', *International Journal of Current Advanced Research*, 12(07), pp. 2210-2213. DOI: http://dx.doi.org/10.24327/ijcar.2023.2213.1483

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