First Principles Study of Structural, Electronic, Mechanical and Density of State Properties of the Half - Heusler Alloy NaCrGe

Abstract

First Principal Study of Structural, Electronic, Mechanical and Density of State Properties of the Half Heusler alloy NaCrGe. The investigated structural parameters revealed that NaCrGe is stable at beta phase. We obtained that the material is a narrow bandgap semiconductor half-Heusler alloys with measured gap of 1.050 eV. The structure NaCrGe conduction band minimum (CBM) position at gamma(Γ) and the valence band maximum (VBM) located at X-point of the Brillouin zone. This indicates that the alloy NaCrGe has indirect bandgap semiconductors. The material NaCrGe is considered hybrids between metals and semiconductors. Hence, NaCrGe is Half-metallic heusler alloy. The calculated mechanical properties indicate that NaCrGe possesses good mechanical stability, making it suitable for structural applications. B/G ratio for NaCrGe is 2.40. This implies that NaCrGe is "ductile" in nature at ambient condition. Also NaCrGe is confirmed "ductile" in nature at positive value of $C_{11} - C_{44}$ (+48.07). PDOS shows that Na-4p, Cr-4p and Ge- 2p has the highest orbital contribution for Na, Cr and Ge atoms respectively. At fermi energy both spin up and spin down is at zero point in the plot of projected density of state (PDOS) against energy. This revealed that NaCrGe is a half metallic heusler alloy.

Keywords : Half heusler; half-metallic gap; electronic band structure; mechanical properties; density of state; alloys

1.0 Introduction

Half-Heusler alloys are ternary intermetallic compounds with the general formula XYZ, where X and Y are typically transition or rare-earth metals, and Z is usually a main group element. They are known for their versatile electronic, magnetic, and thermoelectric properties, making them of interest for various applications, including spintronics, thermoelectric devices, and topological insulators. (Hirohata, 2006; Anand, 2018)

Half-metallic ferromagnets represent a relatively new class of materials which have recently attracted a lot of interest due to their possible applications in spin electronics (also known as magnetoelectronics). (Aravinda, 2022; Atsufumi, 2022). The two spin bands behave entirely differently in these materials. A typical metallic behavior is displayed by one of them (typically the majority-spin band, also called the spin-up band) with a non-zero density of states (DOS) at the Fermi level EF, while the minority (spin-down) band displays a semiconducting behavior with a gap at EF. As a result, these half-metals can be regarded as semiconductor and metal hybrids. (Babalola, 2022)

Theoretical investigations using first-principles calculations based on Density Functional Theory (DFT) have proven to be invaluable in understanding and predicting the properties of materials with high accuracy. DFT enables the exploration of electronic structures, mechanical behaviors, and thermodynamic properties without the

need for experimental data, providing insights into the fundamental nature of materials and guiding experimental efforts. (Benatmane, 2019; Babalola, 2023 ; Babalola, 2021).

Half-Heusler alloys have garnered significant attention due to their intriguing electronic, magnetic, and mechanical properties, which make them suitable for a wide range of applications, from thermoelectrics to spintronics. (Harrington et al., 2017; Ettah, 2023; De, 2001). The NaCrGe alloy, a member of the half-Heusler family, is of particular interest due to its potential high thermoelectric performance and favorable electronic structure. In this study, we employ first-principles calculations to investigate the structural, electronic, mechanical, and density of state properties of NaCrGe, aiming to elucidate its potential for future technological applications. (Dal, 2016, Casper, 2012).

2.0 Literature Review

Intermetallic Heusler alloys are amongst the most attractive half-metallic systems due to their high Curie temperatures and their structural similarity to binary semiconductors. In this review we present an overview of the basic electronic and magnetic properties of both Heusler families: the so-called half-Heusler alloys like NiMnSb and the full-Heusler alloys like Co2 MnGe. Ab initio results suggest that both the electronic and magnetic properties in these compounds are intrinsically related to the appearance of the minority-spin gap. The total spin magnetic moment Mt scales linearly with the number of the valence electrons Zt , such that Mt = Zt − 24 for the full-Heusler and Mt = Zt − 18 for the half-Heusler alloys, thus opening the way to engineer new half-metallic alloys with the desired magnetic properties. (Galanakis, et al., 2006)

2.1 Murnaghan Equation of State

$$E(V) = E_0 + \frac{B_0 V}{B'_0}\left(\frac{(V_0/V)^{B'_0}}{B_0 - 1} + 1\right) \quad (1)$$

where E(V) is the total energy at volume V, E_0 is the equilibrium energy, V_0 is the equilibrium volume, B_0 is the bulk modulus, and B0′ is the pressure derivative of the bulk modulus.

Elastic Moduli

$$B = \frac{C_{11} + 2C_{12}}{3} \quad (2)$$

Shear Modulus

$$G = \frac{C_{11} - C_{12} + 3C_{44}}{5} \quad (3)$$

Young's Modulus

$$E = \frac{9GB}{3B + G} \quad (4)$$

Mechanical Stability Criteria (Born Criteria for cubic crystals)

$$C_{11} > 0, C_{44} > 0, C_{11} > IC_{12}I, (C_{11} + 2C_{12}) > 0 \quad (5)$$

3.0 Methodology

We performed first-principles calculations using the density functional theory (DFT) as implemented in the Vienna Ab-initio Simulation Package (VASP). The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) was used for the exchange-correlation potential. The projector augmented-wave (PAW) method was employed to describe the core electrons. A plane-wave cutoff energy of 400 eV was set for the basis set expansion, and a k-point mesh of 8x8x8 was used for Brillouin zone integration.

Optimized input file used for simulation¶

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 Ý   outdir='./',      Ý    Ý    Ý    Ý    Ý    Ý    Ý!.Directory for temporary files¶
Ý/¶
Ý    &system¶
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Ý    celldm(1)=11.857,          Ý    Ý    Ý    Ý    Ý!.lattice parameter a¶
 Ý   nat=3,                     Ý    Ý    Ý    Ý    Ý    Ý!.Number of atoms in the unit cell¶
 Ý   ntyp=3,  Ý    Ý    Ý    Ý    Ý    Ý    Ý!.Number of atom types¶
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Ý    ecutwfc= 65,    Ý    Ý    Ý    Ý    Ý    Ý    Ý!.Planewave kinetic energy cutoff¶
Ý/¶
Ý    &electrons¶
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 Ý   diagonalization='david'          Ý    Ý    Ý    Ý    Ý!.Diagonalization¶
 Ý   electron_maxstep = 400    Ý    Ý    Ý    Ý    Ý!.Electron maximum step¶
Ý/¶
Ý    ATOMIC_SPECIES Ý    Ý    Ý    Ý!.Type of atom used, atomic mass, and pseudopotential¶
Ý    Na  22.98976928  Na.pbe-spn-kjpaw_psl.0.2.UPF¶
Ý    Cr  51.9961  Cr.pbe-spn-kjpaw_psl.0.2.3.UPF¶
Ý    Ge  72.64  Ge.pbe-dn-kjpaw_psl.0.3.1.UPF¶
Ý¶
Ý    ATOMIC_POSITIONS    Ý    Ý    Ý    Ý    Ý    Ý!.Position of atom with respect to the crystal¶
Ý    Na  0.500  0.500  0.500¶
Ý    Cr  0.250  0.250  0.250¶
Ý    Ge  0.000  0.000  0.000¶
Ý¶
Ý    K_POINTS (automatic)    Ý    Ý    Ý!.Points in the reciprocal space used to sample the Brillouin zone¶
Ý    8 8 8 0 0 0¶
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This Quantum ESPRESSO input file sets up a self-consistent field (SCF) calculation for a spin-polarized system within a face-centered cubic (fcc) lattice structure. The control section specifies the type of calculation,

file prefixes, and directories for pseudopotentials and temporary files. The system section defines key parameters such as the Bravais lattice index (ibrav=2), lattice parameter (celldm(1)), and the number of atoms (nat) and types (ntyp) in the unit cell. Additionally, it handles electronic state occupations using Marzari-Vanderbilt smearing and sets initial magnetizations for each atomic type, with a specified plane-wave kinetic energy cutoff (ecutwfc) to ensure the accuracy of the wavefunctions. (Giannozzi, 2020; Giannozzi, 2009; Giannozzi, 2017 ; Ležaić et al., 2005)

The electrons section focuses on convergence settings for the SCF procedure, specifying the mixing factor (mixing_beta) and the diagonalization algorithm (Davidson). It also sets the maximum number of iterations (electron_maxstep) to ensure the calculation converges properly. These parameters are crucial for achieving a reliable and efficient solution to the electronic structure problem, especially for complex systems involving multiple atom types and spin polarization. (Giannozzi, 2020; Giannozzi, 2009 ; Katubi, 2023 ; Pask, 2003)

The atomic species and atomic positions sections detail the types of atoms present, their masses, and the corresponding pseudopotentials. This includes sodium (Na), chromiun (Cr) , and germanium(Ge) each with specific pseudopotential files. The k-points section defines the mesh for sampling the Brillouin zone, using an 8x8x8 grid with no shift, which is essential for accurately capturing the electronic properties of the material. This comprehensive setup ensures a thorough and precise simulation of the material's electronic and magnetic properties. (Mouhat, 2014)

4.0 Results and Discussion

4.1. Structural Properties

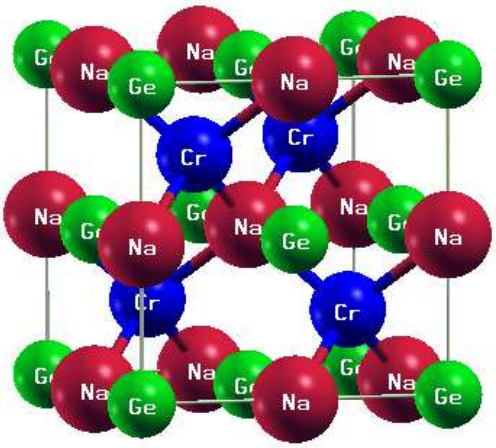

Fig. 1: Crystal structure of β - phase of NaCrGe material

Table 1: Structural Parameters for NaCrGe compound

Compound	a_0 (a.u)	B(Gpa)	$B^{/}$	E_g(eV)
NaCrGe	11.5174	60.1	4.77	-672.79

Fig.1. Shows that crystal structure of NaCrGe compoud for beta(β) – phase. The structure is a face centre cubic system with it atomic position. While table 1 contained calculated structural parameter of NaCrGe material. The lattice constant (a_o) for non magnetic calculation is 11.5174a.u. bulk modulus(B) is 60.1Gpa, pressures derivative $B^{/}$ is 4.77 and minimum energy Eg is -672.79eV. Fig. 2 is a plot of energy against lattice parameter which shows that the compound NaCrGe is stable at beta phase .

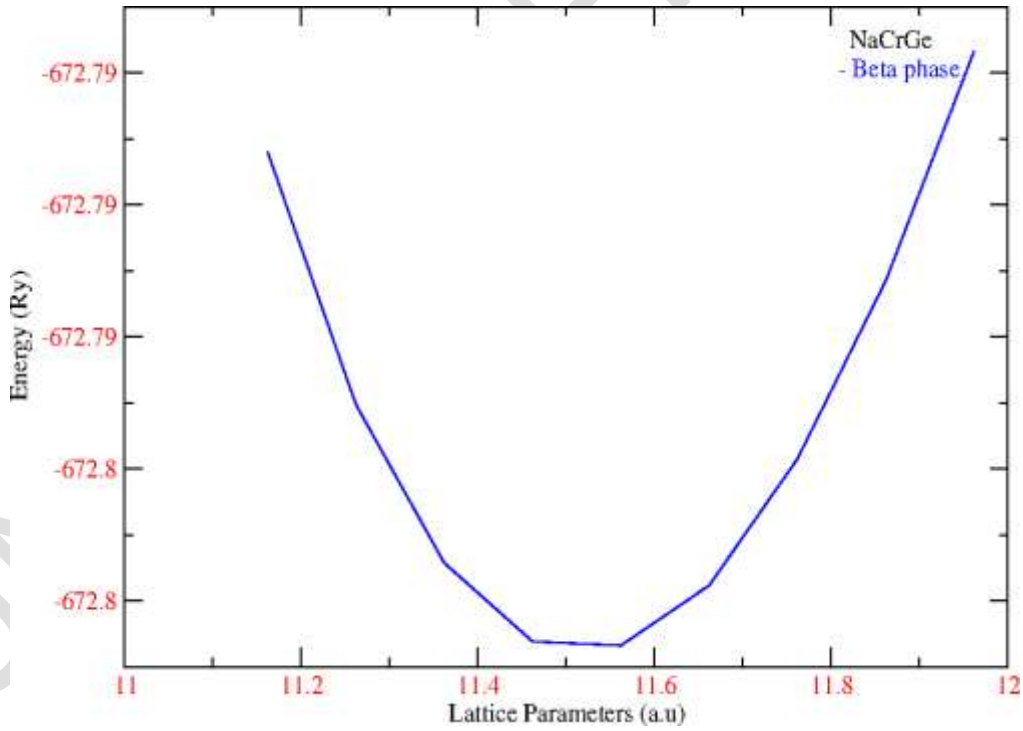

Fig. 2: Enery(Ry) versus Lattice parameter (a.u) for NaCrGe compound

4.2. Electronic Band Structure

The electronic band gap structural properties of NaCrGe alloys has been calculated using the optimized latticed constants in high symmetry directions of the first Brillouin zone M – Γ – R – W – k – Γ as presented in Fig. 3.

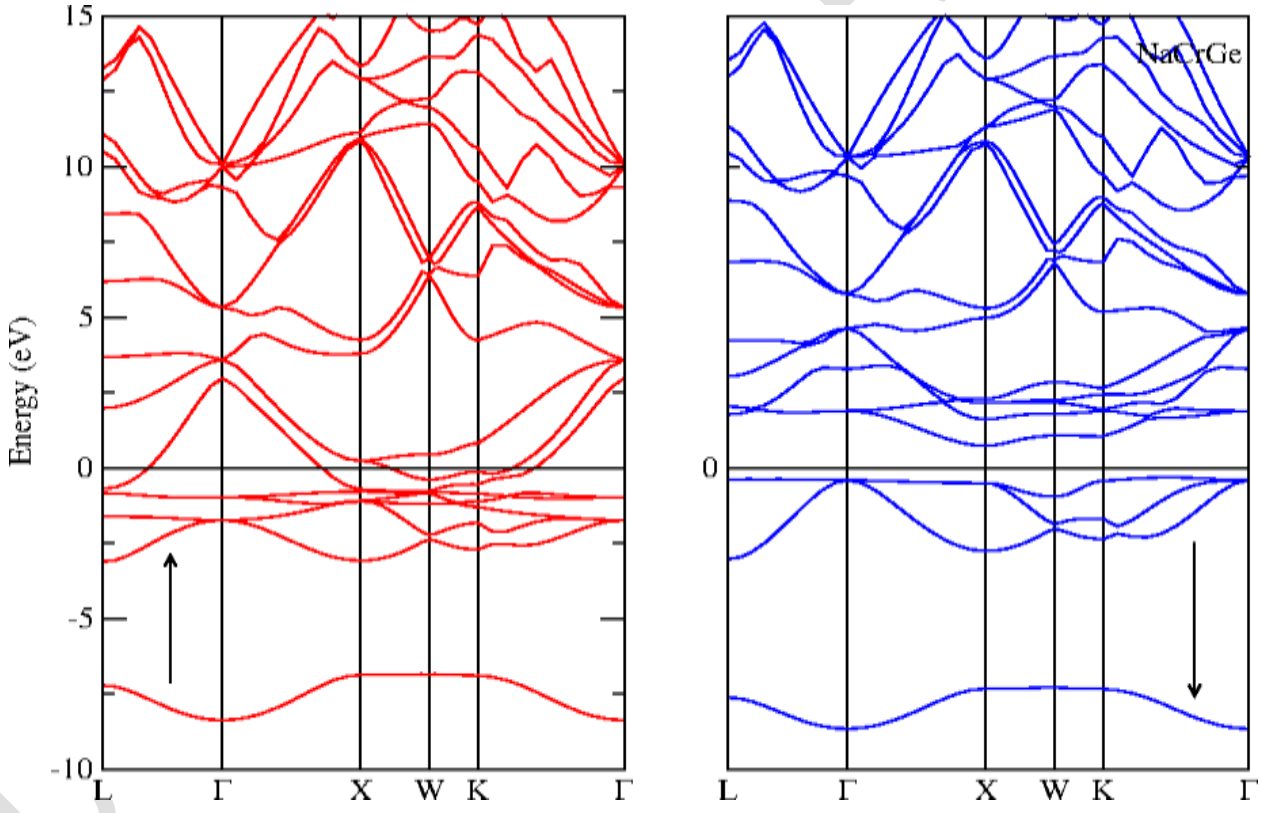

Fig.3. Calculated Electronic Band Structure For NaCrGe

The measured band gap is 1.050eV was obtained for NaCrGe. Hence, the material is a narrow bandgap semiconductor half-Heusler alloys. We observed that the structure NaCrGe conduction band minimum (CBM) at

gamma(Γ) and the valence band maximum (VBM) located at X-point of the Brillouin zone. This indicates that the alloy NaCrGe has indirect bandgap semiconductors. In these materials the two spin bands show a completely different behaviour. While one of them (usually the majority-spin band, henceforth also referred to as spin-up band in red color) shows a typical metallic behaviour at the Fermi level E_F line. Meanwhile, the minority (spin-down, blue color) band exhibits a semiconducting behaviour with a gap at E_F line. The material NaCrGe is considered hybrids between metals and semiconductors. Hence, NaCrGe is Half-metallic heusler alloy.

4.3. Mechanical Properties

Table 2: Calculated Elastic Constants (C_{11}, C_{12} and C_{44}) Bulk modulus(B), shear modulus (G), B/G Ratio, Cauthy's pressure (C_p), young modulus(Y), Poisson ratio(u), Zener Anisotropy factor(A) and Hardness (H) of Half-Heusler Alloy NaCrGe.

Compounds	C_{11}	C_{12}	C_{44}	B (Gpa)	G (Gpa)	B/G (Gpa)	C_p (Gpa)	Y (Gpa)	u
NaCrGe	64.26	64.26	16.19	101.41	16.85	2.40		44.59	0.32

The calculated mechanical properties indicate that NaCrGe possesses good mechanical stability, making it suitable for structural applications. The empirical relationship between bulk and shear moduli B/G is proposed by (Pugh, 2009) could be used to describe the mechanical strength of materials. He suggested that if the B/G ratio is less than 1.75, the material is "britle" in nature otherwise its "ductile". Relaying on this assumptions, we found that B/G ratio for NaCrGe is 2.40. This implies that NaCrGe is "ductile" in nature at ambient condition. It also aggreed with the fact that if $C_{11} - C_{44}$ is negative the material is brittle, when positive the material is ductile. $C_{11} - C_{44}$ (64.26 − 16.19) is +48.07. Hence NaCrGe is "ductile" in nature at positive value of $C_{11} - C_{44}$.

4.4. Density of State

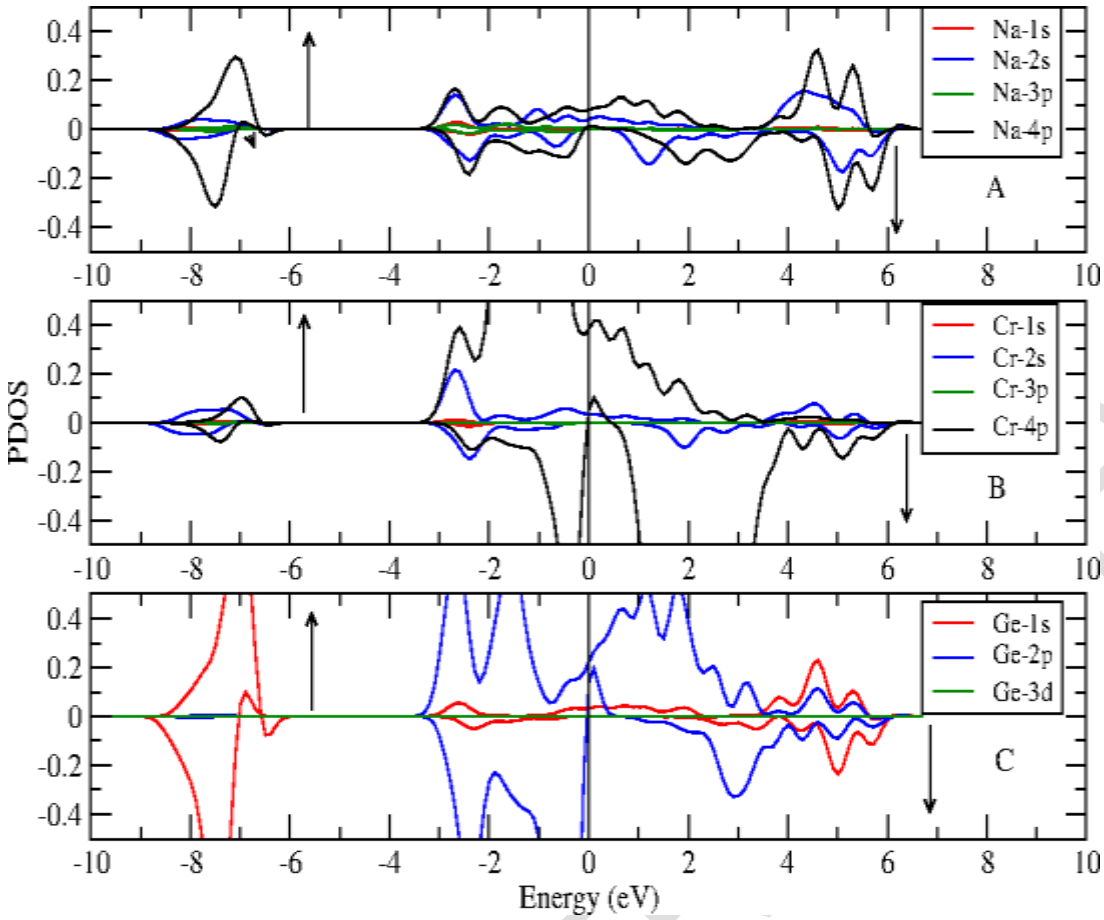

Fig. 4. Plot of PDOS against energy for NaCrGe. Atom projected DOS calculated for the

(a). Na -1s, Na- 2s, Na- 3p, and Na- 4p (b). Cr-1s, Cr-2s, Cr-3p and Cr- 4p and (c). Ge-1s, Ge- 2p, and Ge- 3d.

Fig. 4a shows that Na-4p has the hightest orbital contribution for the Na-atoms. While in Fig. 4b Cr-4p has the hightest orbital present for Cr-atoms. Also Fig.4c. Ge-2p has more orbital donation for the Ge-atoms. At fermi energy both the spin up and spin down is at zero point in plot of partial density of state(PDOS) against energy. This revealed that NaCrGe is a half metallic heusler alloy.

5. Conclusion

In conclusion, the research on the structural, electronic, mechanical and density of state properties of NaCrGr half- heusler alloy was studied using density functional theory provides valuable insights into this intriguing material. The comprehensive understanding of its electronic band structure and potential applications contributes to the ongoing exploration of advanced materials and opens up exciting opportunities for the development of innovative electronic devices. The investigated strutural parameters revealed that NaCrGe is stable at beta phase.We obtained that the material is a narrow bandgap semiconductor half-Heusler alloys with measured gap of 1.050eV. The structure NaCrGe conduction band minimum (CBM) at gamma(Γ) and the valence band

maximum (VBM) located at X-point of the Brillouin zone. This indicates that the alloy NaCrGe has indirect bandgap semiconductors. The material NaCrGe is considered hybrids between metals and semiconductors. Hence, NaCrGe is Half-metallic heusler alloy. The calculated mechanical properties indicate that NaCrGe possesses good mechanical stability, making it suitable for structural applications. B/G ratio for NaCrGe is 2.40. This implies that NaCrGe is "ductile" in nature at ambient condition. Also NaCrGe is confirmed "ductile" in nature at positive value of $C_{11} - C_{44}$ (+48.07). PDOS shows that Na-4p, Cr-4p and Ge- 2p has the highest orbital contribution for Na, Cr and Ge atoms repectively. At fermi energy both the spin up and spin down is at zero point in the plot of projected density of state(PDOS) against energy. This revealed that NaCrGe is a half metallic heusler alloy.

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