Introduction to Heusler compounds: From the case of Fe$_2$VAI

Chin Shan Lue (呂欽山)

2017-03-28-NTU
Outline

1) Introduction to Heusler compounds
   - Full-Heusler compounds
   - Half-Heusler compounds

2) Case study of Fe$_2$VAl

3) Promising characteristics of Heusler compounds
   - Thermoelectric properties
   - Spintronic applications
   - Topological materials

4) Summary
# Heusler compounds

**Full-Heusler compounds:** $X_2YZ$

**Half-Heusler compounds:** $XYZ$

First full-Heusler $Cu_2MnAl$ in 1903

First half-Heusler $NiMnSb$ in 1951

More than 1000 real Heusler compounds

---

| Period 2 | | Period 3 | | Period 4 | | Period 5 | | Period 6 | | Period 7 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | H | 2 | He | 11 | Na | 12 | Mg | 21 | Sc |
| 3 | Li | 4 | Be | 9 | Al | 10 | Si | 19 | K |
| 5 | B | 6 | C | 7 | N | 8 | O | 13 | Al |
| 7 | C | 8 | N | 9 | O | 10 | F | 14 | Si |
| 9 | F | 10 | Ne | 11 | Na | 12 | Mg | 21 | Ca |
| 12 | Mg | 13 | Al | 14 | Si | 15 | P | 22 | Ti |
| 15 | P | 16 | S | 17 | Cl | 18 | Ar | 23 | V |
| 18 | Ar | 19 | K | 20 | Ca | 21 | Sc | 22 | Ti |
| 20 | Ca | 21 | Sc | 22 | Ti | 23 | V | 24 | Cr |
| 21 | Sc | 22 | Ti | 23 | V | 24 | Cr | 25 | Mn |
| 22 | Ti | 23 | V | 24 | Cr | 25 | Mn | 26 | Fe |
| 23 | V | 24 | Cr | 25 | Mn | 26 | Fe | 27 | Co |
| 24 | Cr | 25 | Mn | 26 | Fe | 27 | Co | 28 | Ni |
| 25 | Mn | 26 | Fe | 27 | Co | 28 | Ni | 29 | Cu |
| 26 | Fe | 27 | Co | 28 | Ni | 29 | Cu | 30 | Zn |
| 27 | Co | 28 | Ni | 29 | Cu | 30 | Zn | 31 | Ga |
| 28 | Ni | 29 | Cu | 30 | Zn | 31 | Ga | 32 | Ge |
| 29 | Cu | 30 | Zn | 31 | Ga | 32 | Ge | 33 | As |
| 30 | Zn | 31 | Ga | 32 | Ge | 33 | As | 34 | Se |
| 31 | Ga | 32 | Ge | 33 | As | 34 | Se | 35 | Br |
| 32 | Ge | 33 | As | 34 | Se | 35 | Br | 36 | Kr |
| 33 | As | 34 | Se | 35 | Br | 36 | Kr | 37 | Rb |
| 34 | Se | 35 | Br | 36 | Kr | 37 | Rb | 38 | Sr |
| 35 | Br | 36 | Kr | 37 | Rb | 38 | Sr | 39 | Y |
| 36 | Kr | 37 | Rb | 38 | Sr | 39 | Y | 40 | Zr |
| 37 | Rb | 38 | Sr | 39 | Y | 40 | Zr | 41 | Nb |
| 38 | Sr | 39 | Y | 40 | Zr | 41 | Nb | 42 | Mo |
| 39 | Y | 40 | Zr | 41 | Nb | 42 | Mo | 43 | Tc |
| 40 | Zr | 41 | Nb | 42 | Mo | 43 | Tc | 44 | Ru |
| 41 | Nb | 42 | Mo | 43 | Tc | 44 | Ru | 45 | Rh |
| 42 | Mo | 43 | Tc | 44 | Ru | 45 | Rh | 46 | Pd |
| 43 | Tc | 44 | Ru | 45 | Rh | 46 | Pd | 47 | Ag |
| 44 | Ru | 45 | Rh | 46 | Pd | 47 | Ag | 48 | Cd |
| 45 | Rh | 46 | Pd | 47 | Ag | 48 | Cd | 49 | In |
| 46 | Pd | 47 | Ag | 48 | Cd | 49 | In | 50 | Sn |
| 47 | Ag | 48 | Cd | 49 | In | 50 | Sn | 51 | Sb |
| 48 | Cd | 49 | In | 50 | Sn | 51 | Sb | 52 | Te |
| 49 | In | 50 | Sn | 51 | Sb | 52 | Te | 53 | I |
| 50 | Sn | 51 | Sb | 52 | Te | 53 | I | 54 | Xe |
| 51 | Sb | 52 | Te | 53 | I | 54 | Xe | 55 | Cs |
| 52 | Te | 53 | I | 54 | Xe | 55 | Cs | 56 | Ba |
| 53 | I | 54 | Xe | 55 | Cs | 56 | Ba | 57 | Fr |
| 54 | Xe | 55 | Cs | 56 | Ba | 57 | Fr | 58 | Ra |
| 55 | Cs | 56 | Ba | 57 | Fr | 58 | Ra | 59 | Ac |
| 56 | Ba | 57 | Fr | 58 | Ra | 59 | Ac | 60 | Th |
| 57 | Fr | 58 | Ra | 59 | Ac | 60 | Th | 61 | Pa |
| 58 | Ra | 59 | Ac | 60 | Th | 61 | Pa | 62 | U |
| 59 | Ac | 60 | Th | 61 | Pa | 62 | U | 63 | Np |
| 60 | Th | 61 | Pa | 62 | U | 63 | Np | 64 | Pu |
| 61 | Pa | 62 | U | 63 | Np | 64 | Pu | 65 | Am |
| 62 | U | 63 | Np | 64 | Pu | 65 | Am | 66 | Cm |
| 63 | Np | 64 | Pu | 65 | Am | 66 | Cm | 67 | Bk |
| 64 | Pu | 65 | Am | 66 | Cm | 67 | Bk | 68 | Cf |
| 65 | Am | 66 | Cm | 67 | Bk | 68 | Cf | 69 | Es |
| 66 | Cm | 67 | Bk | 68 | Cf | 69 | Es | 70 | Fm |
| 67 | Bk | 68 | Cf | 69 | Es | 70 | Fm | 71 | Md |
| 68 | Cf | 69 | Es | 70 | Fm | 71 | Md | 72 | No |
| 69 | Es | 70 | Fm | 71 | Md | 72 | No | 73 | Lr |

* Lanthanide series
* # Actinide series
Common crystal structures of Heusler compounds

First determination of crystal structure for Cu$_2$MnAl by Otto Heusler in 1934

**L$_2$1 structure**

Cu$_2$MnAl-type
16 atoms per unit cell
Fe$_2$VAl, Ru$_2$NbGa, Ni$_2$MnGa (HT), …

**Anti-site disorder**

**B2 structure**

CsCl-type
2 atoms per unit cell
Co$_2$MnAl, Ru$_2$NbAl, Ru$_2$VAl, …
**DO$_3$ structure**

BiF$_3$-type
16 atoms per unit cell
Fe$_3$Al; Fe$_3$Ga; Fe$_3$Si, ...

**Half-Heusler XYZ**

C$_{1b}$ structure

MgAgAs-type
12 atoms per unit cell
NiMnSb, NiZrSn, CoTiSb, ...
Various properties of Heusler compounds

**Ferromagnetism:** $\text{Co}_2\text{MnZ}$, $\text{Pd}_2\text{Mn(In,Sn)}$, …

**Superconductivity:** $\text{Pd}_2\text{YSn}$ ($T_C = 4.9$ K), $\text{Ni}_2\text{NbSn}$, $\text{Pd}_2\text{ErSn}$, …

**Shape memory behavior:** $\text{Ni}_2\text{MnGa}$ (Martensitic transformation $T_M = 220$ K), …

**Semiconducting:** $\text{Fe}_2\text{VAL}$, $\text{Ru}_2\text{TaAl}$, $\text{IrNbSb}$, $\text{NiHfSn}$, $\text{CoTiSb}$, …

---

**New Class of Materials:** Half-Metallic Ferromagnets

R. A. de Groot and F. M. Mueller
Unusual physical behavior in Fe$_2$VAI

Paramagnetic behavior in Fe$_2$VAI by Webster & Ziebeck in 1983

Semiconductor-like behavior of electrical resistivity in Heusler-type Fe$_2$VAI compound

Y. Nishino, M. Kato, and S. Asano
Department of Materials Science and Engineering, Nagoya Institute of Technology, Showa-ku, Nagoya 466, Japan

K. Soda, M. Hayasaki, and U. Mizutani
Department of Crystalline Materials Science, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan
(Received 7 March 1997)

Fe$_3$Al $T_c = 790$ K

(Fe$_{1-x}$V$_x$)$_3$Al

x = 0.33 Fe$_2$VAI $T_c = 0$ K

Semiconductor-like in $\rho$

Semimetal
Possible 3d heavy fermion for Fe$_2$VAI

\[ \gamma = 14 \text{ mJ/mol K}^2 \]

Low-T \[ C = C_e + C_{ph} = \gamma T + \beta T^3 \]

\[ C/T = \gamma + \beta T^2 \]

Sommerfeld coefficient based on free electron model

\[ \gamma_{th} = \frac{\pi^2 k_B^2}{3} N(E_F) \propto m_e \]

\[ \frac{\gamma_{exp}}{\gamma_{th}} \approx 50-100 \]

for Fe$_2$VAI

Expected behavior for ordinary semimetals (low Fermi-level DOS)

\[ \gamma = 1.07 \text{ mJ/mol K}^2 \]

Semimetallic Ru$_2$TaAl

\[ \frac{\gamma_{exp}}{\gamma_{th}} \approx 3 \]

from C. M. Wei et al.
Simple concept for heavy fermions

*f*-electron heavy fermions

\[ \text{CeAl}_3 \gamma = 1620 \text{ mJ/mol K}^2 \]
\[ \text{CeCu}_6 \gamma = 1300 \text{ mJ/mol K}^2 \]
\[ \text{UBe}_13 \gamma = 1100 \text{ mJ/mol K}^2 \]
\[ \text{U}_2\text{Zn}_{17} \gamma = 500 \text{ mJ/mol K}^2 \]

......

It is less likely to observe heavy fermion behavior in *d*-electron systems since the corresponding wave-functions of *d*-orbitals are more dispersive.

*d*-electron heavy fermion???

Spinel LiV\(_2\)O\(_4\) \(\gamma = 420 \text{ mJ/mol K}^2\)

PRL 78, 3729 (1997); PRL 85, 1052 (2000)
PRL 89, 267201 (2002); PRL 99, 167402 (2007)
Nat. Comm. 3, 981 (2012); PRL 113, 236402 (2014);
Band structure calculations for Fe$_2$VAI


Electronic structure and magnetism of Fe$_3$-xV$_x$X (X=Si, Ga, and Al) alloys by the KKR-CPA method, A. Bansil, et al., Phys. Rev. B 60, 13396 (1999)
NMR evidence for semimetallic behavior in Fe$_2$VAI

Semimetallic behavior in Fe$_2$VAI: NMR evidence

Chin-Shan Lue* and Joseph H. Ross, Jr.†
Department of Physics, Texas A&M University, College Station, Texas 77843-4242
(Received 3 June 1998)

Thermally excited carriers across electronic bands near $E_F$

Activation energy $E_A \sim 0.27$ eV

Korringa relation $1/T_1 T \sim C[N(E_F)]^2$

Low $V$-3$d$ $N(E_F) = 0.11$ states/eV atom
Field-dependent specific heat in Fe$_2$VAl and the question of possible 3$d$ heavy fermion behavior

C. S. Lue* and Joseph H. Ross, Jr.†
Department of Physics, Texas A&M University, College Station, Texas 77843-4242

C. F. Chang and H. D. Yang
Department of Physics, National Sun Yat-Sen University, Kaohsiung, Taiwan
(Received 19 August 1999)

Small $\gamma = 1.5$ mJ/mol K$^2$
False heavy fermion behavior in Fe$_2$VAl

For non-interacting magnetic clusters with spin $J > 1/2$, the magnetic specific heat can be generated by the so-called multi-level Schottky function as

$$C_m = N k_B \left[ \frac{x^2 e^x}{(e^x - 1)^2} - \frac{(2J + 1)^2}{(e^{(2J+1)x} - 1)^2} \right]$$

$$x = \frac{g \mu_B H}{k_B T}$$

$$J = \frac{3}{2} \rightarrow \mu = g \mu_B \sqrt{J(J+1)} = 3.7 \mu_B$$

$$f = 0.36\% \text{ population per formula unit}$$

The low-T upturn in $C$ is not intrinsic; It is reasonably associated with magnetic clusters due to anti-site disorder in real samples.
Effects of magnetic clusters in Fe$_2$VAI, Fe$_2$VGa and Fe$_2$TiSn

“Weak ferromagnetism induced by atomic disorder in Fe$_2$TiSn”,

“Kondo-type behavior in Fe$_{2-x}$M$_x$TiSn(M=Co,Ni)”,

“Fe–3s core-level splitting and local magnetism in Fe$_2$VAI”,

“Superparamagnetism and magnetic defects in Fe$_2$VAI and Fe$_2$VGa”,

“Structure and magnetic order in Fe$_{2+x}$V$_{1-x}$Al”,

“NMR and Mössbauer study of spin dynamics and electronic structure of Fe$_{2+x}$V$_{1-x}$Al and Fe$_2$VGa”,

“Transport and magnetic properties of the Heusler-type Fe$_{2-x}$V$_{1+x}$Al system (−0.01⩽x⩽0.08)”,

“Evidence for cluster glass behavior in Fe$_2$VAI Heusler alloys”,
Band structure calculations for Fe$_2$VAl


LETTER TO THE EDITOR

Electronic structure of possible 3d ‘heavy-fermion’ compound Fe$_2$VAl

郭光宇, G Y Guo‡, G A Botton‡ and Y Nishino∥

Electronic structure, local moments, and transport in Fe$_2$VAl,

Excitonic correlations in the intermetallic Fe$_2$VAl,

Hybridization-induced band gaps in transition-metal aluminides,

Electronic structure and magnetism of Fe$_{3-x}$V$_x$X (X=Si, Ga, and Al) alloys by the KKR-CPA method, A. Bansil, et al., Phys. Rev. B 60, 13396 (1999)
More first-principles calculations on Fe$_2$VAI

“Electronic structure and x-ray magnetic circular dichroism in Heusler-type Fe$_{2-x}$V$_{1+x}$Al: First-principles calculations”,

“Density functional study of elastic and vibrational properties of the Heusler-type alloys Fe$_2$VAI and Fe$_2$VGa”,

“Electronic and thermoelectric properties of Fe$_2$VAI: The role of defects and disorder”,

“Effect of onsite Coulomb repulsion on thermoelectric properties of full-Heusler compounds with pseudogaps”,

“Low-Dimensional transport and large thermoelectric power factors in bulk semiconductors by band engineering of highly directional electronic states”,

“Quantum many-body intermetallics: Phase stability of Fe$_3$Al and small-gap formation in Fe$_2$VAI”,

……
Thermoelectric materials

RSC Advances 5, 52 (2015)

Thermoelectric generator module
Thermoelectric efficiency

$$\eta : \text{Generated electrical energy/Absorbed heat energy}$$

$$\eta_{\text{max}} = \left(\frac{T_h - T_c}{T_h}\right) \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_c}{T_h}}$$

with

$$Z = \frac{S^2}{\rho \kappa}, \quad \bar{T} = \frac{T_c + T_h}{2}.$$
Thermoelectric performance

\[ ZT = S^2 T / \rho (\kappa_e + \kappa_l) \]

S: Seebeck coefficient
\( \rho \): electrical resistivity
\( \kappa_e \): electronic thermal conductivity
\( \kappa_l \): lattice thermal conductivity

Physical approach based on Mott equation,

\[ S_e \propto \frac{1}{e} \left( \frac{1}{N(E)} \frac{\partial N(E)}{\partial E} \right)_{E=E_F} \]

Chemical approach by partially substituting heavy elements and/or vacancies to enhance the phonons scattering and thus reduce the contribution of \( \kappa_l \).

Naive expectation:
S = 200 \( \mu \)V/K
\( \rho \) = 1000 \( \mu \)\( \Omega \)-cm
\( \kappa \) = 2 W/m-K
ZT = 1 at 500 K
A simple rule with number of valence electrons

Full-Heusler compounds with $L_21$-type structure
Total number of valence electrons per formula unit $\text{VEC} = Z_t = 24$
In principles $\rightarrow$ Semiconductors
**In reality $\rightarrow$ Semimetals**
Fe$_2$VAI, Fe$_2$VGa, Fe$_2$TiSn, Ru$_2$NbGa, Ru$_2$TaAl, Ru$_2$TiSi, ….

Half-Heusler compounds with $C_b1$-type structure
Total number of valence electrons per formula unit $\text{VEC} = Z_t = 18$
In principles $\rightarrow$ Semiconductors
**In reality $\rightarrow$ Semimetals**
NiTiSn, NiZrSn, NiHfSn, CoTiSb, FeVSb…. 
Thermoelectric studies of Fe$_2$VAl and related compounds

Effect of off-stoichiometry on the transport properties of the Heusler-type Fe$_2$VAl compound


Nishino’s group

……..

Other groups

……..

Thermoelectric properties of the semimetallic Heusler compounds Fe$_{2-x}$V$_{1+x}$M ($M = \text{Al, Ga}$)


……..

High $\kappa$
Thermoelectric studies of Fe$_2$VAl-based compounds

Thermoelectric properties of the Heusler-type Fe$_2$VTa$_x$Al$_{1-x}$ alloys

Optimized $ZT \sim 0.2$

“Narrow band in the intermetallic compounds $M\text{NiSn} \ (M=\text{Ti,Zr,Hf})$”, Z. Phys. B 80, 353 (1990).


“Electronic structure and thermoelectric properties of half-Heusler $\text{Zr}_{0.5}\text{Hf}_{0.5}\text{NiSn}$ by first-principles calculations”, Appl. Phys. Lett. 113, 193705 (2013).

Lattice thermal conductivity of $\text{Ti}_x\text{Zr}_y\text{Hf}_{1-x-y}\text{NiSn}$ half-Heusler alloys calculated from first principles: Key role of nature of phonon modes.
Uncovering high thermoelectric figure of merit in (Hf,Zr)NiSn half-Heusler alloys

Thermoelectric materials based on half-Heusler compounds

**Half-metallic Heusler compounds**

**New Class of Materials: Half-Metallic Ferromagnets**

R. A. de Groot and F. M. Mueller

*Research Institute for Materials, Faculty of Science, Toernooiveld, 6525 ED Nijmegen, The Netherlands*

<table>
<thead>
<tr>
<th>Compound</th>
<th>$N(E)^\uparrow$</th>
<th>$N(E)^\downarrow$</th>
<th>$n_{3d}^{\text{Mn}}^\uparrow$</th>
<th>$n_{3d}^{\text{Mn}}^\downarrow$</th>
<th>$\mu_{\text{tot}}^{\text{calc}}$</th>
<th>$\mu_{\text{tot}}^{\text{exp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMnSb</td>
<td>9.90</td>
<td>0</td>
<td>4.51</td>
<td>0.87</td>
<td>4.00</td>
<td>3.85</td>
</tr>
<tr>
<td>PtMnSb</td>
<td>10.05</td>
<td>0</td>
<td>4.57</td>
<td>0.79</td>
<td>4.00</td>
<td>3.97</td>
</tr>
<tr>
<td>PdMnSb</td>
<td>9.04</td>
<td>2.97</td>
<td>4.58</td>
<td>0.71</td>
<td>4.05</td>
<td>3.95</td>
</tr>
<tr>
<td>PtMnSn</td>
<td>9.78</td>
<td>19.31</td>
<td>4.40</td>
<td>0.78</td>
<td>3.60</td>
<td>3.42</td>
</tr>
</tbody>
</table>

**Half-Heusler**

**Half-metals**

**100% polarization**
A semi-empirical general rule: Slater-Pauling curve

Half-Heusler compounds

Hybridization between Ni and Mn in minority bands in NiMnSb

Slater-Pauling curve for full-Heusler compounds

More first-principles calculations


Recent advances in the Heusler-based spin gapless semiconductors

- HM
- SGS

21-electrons

Majority | Minority
--- | ---
3t_{2g} | 3t_{2g}
2e_{g} | 2e_{g}
2e_{u} | 2e_{u}
3t_{1u} | 3t_{1u}

HgCu_{2}Ti-type

L2_{1} structure

Cu_{2}MnAl-type

Inverse Heusler
Generalized Slater-Pauling rule for inverse Heusler compounds

Possible SGSs: Theoretical studies

\[ E(k) \text{ [eV]} \]

\[ \Gamma \quad X \quad W \quad K \]

\[ \Gamma \quad X \quad W \quad U \quad K \]

\[ E(k) \text{ [eV]} \]

\[ \text{(a) Majority-Mn}_2\text{CoAl} \]

\[ \text{(b) Minority-Mn}_2\text{CoAl} \]

\[ \text{Phys. Rev. B} \ 77 \ 014427 \ (2008) \]

\[ \text{Total} \]

\[ \text{V1-3d} \]

\[ \text{V2-3d} \]

\[ \text{Total and LDOS (states/eV/atom or cell/spin)} \]

\[ E - E_F \text{ (eV)} \]

\[ -8 \quad 0 \quad 8 \]

\[ -8 \quad 0 \quad 8 \]

\[ \text{Phys. Rev. B} \ 91 \ 094409 \ (2015) \]

\textit{Appl. Phys. Lett.} \textbf{102} \ 022402 \ (2013)
Possible SGSs: Experimental studies

Polycrystalline Mn$_2$CoAl

Polycrystalline V$_3$Al

Polycrystalline CrVTiAl

Thin film Ti$_2$MnAl

Claudia Felser’s group

Topological materials in half-Heusler compounds


Claudia Felser’s group

Topological materials in half-Heusler compounds


Cava’s group
Evidence for topological behavior in half-Heusler compounds

“Observation of a topologically non-trivial surface state in half-Heusler PtLuSb (001) thin films”
J. A. Logan et al., *Nature Communications* 9, 11993 (2016)

“Observation of unusual topological surface states in half-Heusler compounds LnPtBi (Ln=Lu, Y)”

“Large anomalous Hall effect in a half-Heusler antiferromagnet”
Topological materials in full-Heusler compounds

“Room-temperature magnetic topological Weyl fermion and nodal line semimetal states in half metallic Heusler Co$_2$TiX (X=Si, Ge, or Sn)”
Guoqing Chang et al., Scientific Reports 6, 38839 (2016).

“Time-reversal-breaking Weyl fermions in magnetic Heusler alloys”

Single crystalline Co$_2$ZrSn

Cava’s group

Our group
Summary

Theoretical people continue paying attention to Heusler compounds, focusing on their thermoelectric, half-metallic, and topological properties.

Experimental people continue synthesizing novel Heusler compounds and investigating their promising properties for further applications.
Thanks for your attention!