High-Entropy Functional Materials

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Applying High-Entropy Concept to Functional Materials

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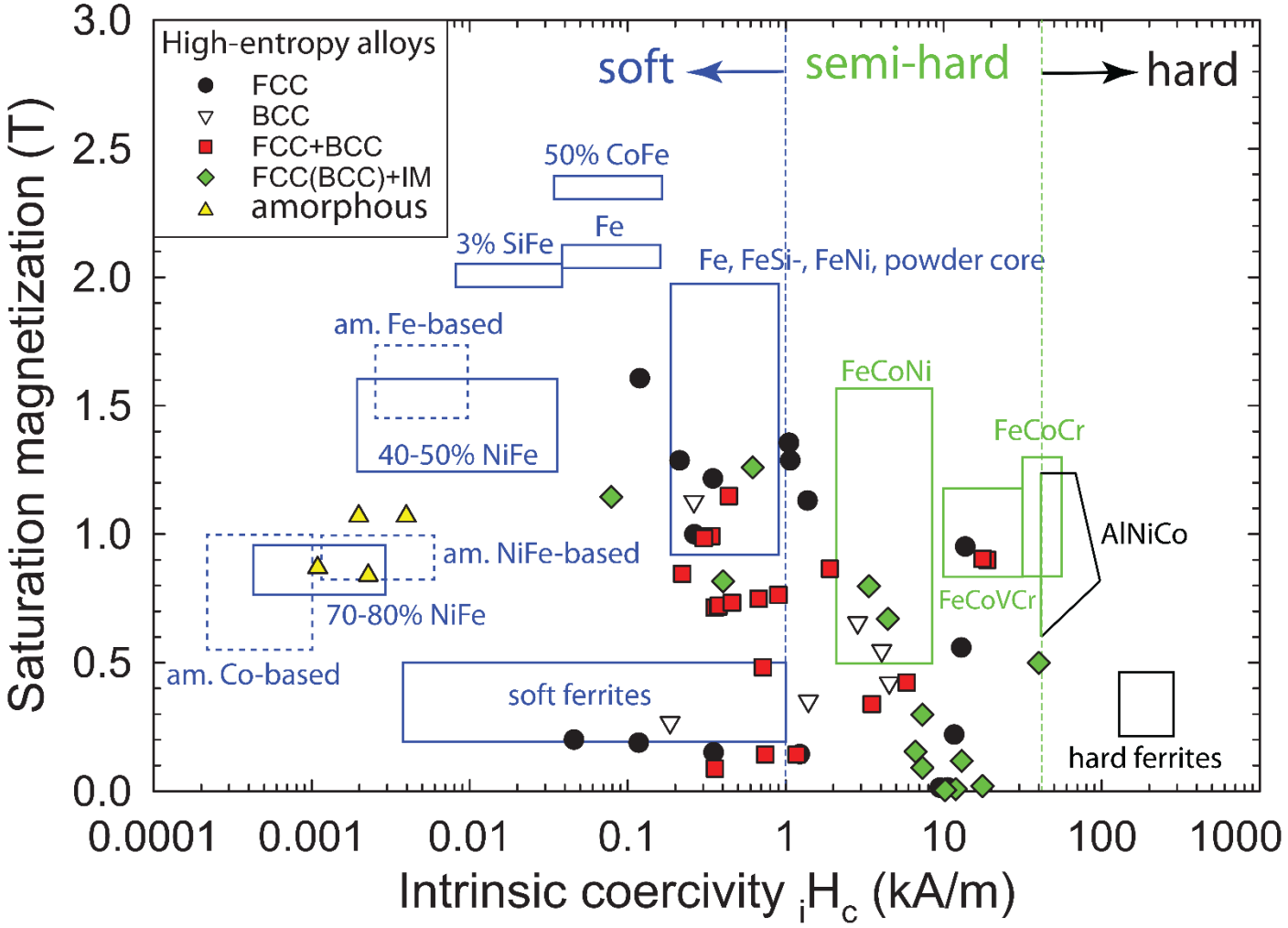
- Conventional alloying strategies used in the functional materials community - preceding the initial high entropy papers in 2004 - have produced a vast literature of functional HEAs and MPEAs, which may be missed by conventional literature searches. Many functional materials have been studied that satisfy HEA definitions or are consistent with the broader concept of MPEAs but they have not been identified with the HEA concept.
- Since conventional efforts to develop functional materials precede the high-entropy concept, and since early work in the high-entropy field focused on structural properties, these two communities appear to be rather disconnected.
- Two general alloying approaches including doping and iso-electronic (also called iso-structure) substitution have been established to improve the balance of functional properties in ordered compounds. Simply stated, the iso-electronic concept mixes two or more chemically or electronically similar elements on a specific sub-lattice of an ordered crystal structure.
- In both doping and iso-electronic approaches, alloying elements are selected based on considerations that include their influence on the electronic structure of the compound or the charge carrier density, atomic size, and the ability to retain the crystal structure of the host compound.
- Important features in both approaches include the concentrations of elemental substitutions, the sub-lattice in the ordered structure targeted by the alloying additions, and the number of candidate alloying elements that satisfy the alloying strategy.

Contents

- **Magnetic properties**
  - Soft magnets
  - Theoretical calculations
  - Magnetocaloric effect (MCE)
- **Physical properties**
- **Thermoelectric properties**
- **Superconducting materials**
- **Hydrogen storage materials**

M.C. Gao, D.B. Miracle, D. Maurice, X.H. Yan, Y. Zhang, and J.A. Hawk, "Functional High-Entropy Materials," J. Mater. Res., 33 (2018) 3138-3155..

High-Entropy Magnetic Materials



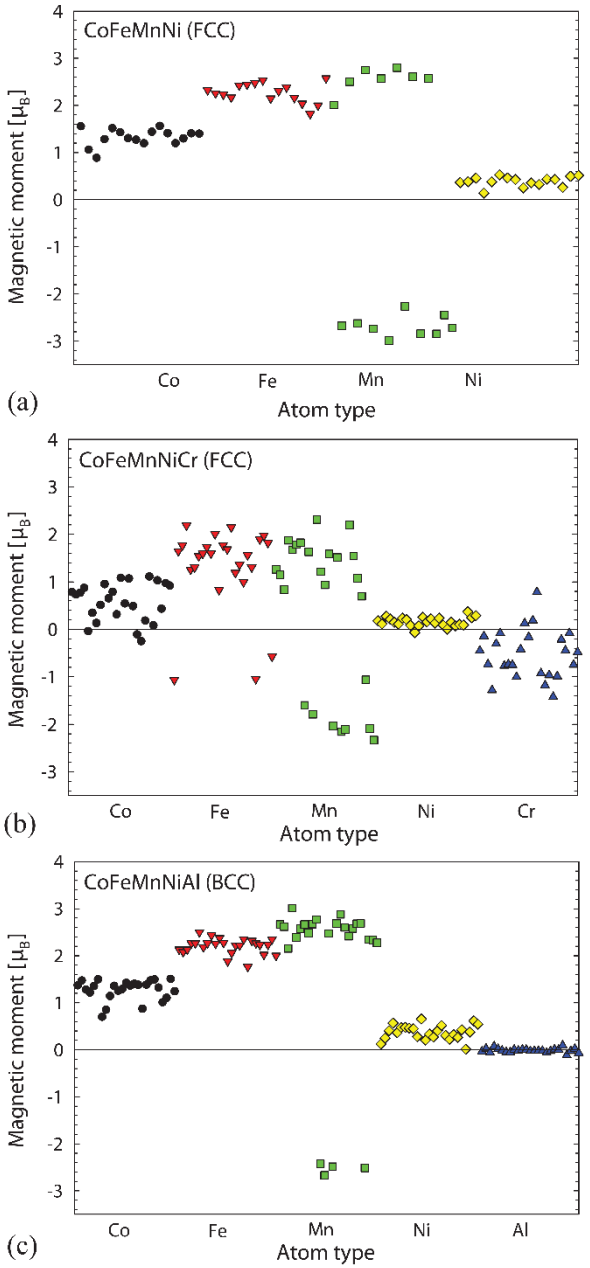
- Magnetic transition metal elements Co, Cr, Fe, Mn and Ni are mainly considered.
- Intrinsic coercivity is around 1 kA/m.
- Saturation magnetization is less than 1.5 T.

High-Entropy Magnetic Materials

Property	Projected Trend (HEA vs conventional)	Rationale for Projection
Saturation Magnetization (M_s)	Lower	Lower content of ferromagnetic elements
Intrinsic Coercivity ($_iH_c$)	Higher	Lattice structures will tend to pin domain walls
Permeability (μ)	Lower	Lower content of high permeability elements
Electrical Resistivity	Higher	Greater lattice distortion; potentially higher content of non-metallic elements
Curie Temperature (T_c)	May be higher or lower	Less compact lattices tend to reduce T_c; smaller particle sizes tend to reduce T_c; changes in crystal structure and in alloying elements can raise or lower T_c.
Corrosion Resistance	Higher	Cocktail effect promotes the formation of various surface oxide films.
Wear Resistance	Higher	Severe lattice distortion tend to improve hardness and strength, high temperature softening resistance tend to facilitate high wear resistance.

M.C. Gao, D.B. Miracle, D. Maurice, X.H. Yan, Y. Zhang, and J.A. Hawk, "Functional High-Entropy Materials," J. Mater. Res., 33 (2018) 3138-3155..

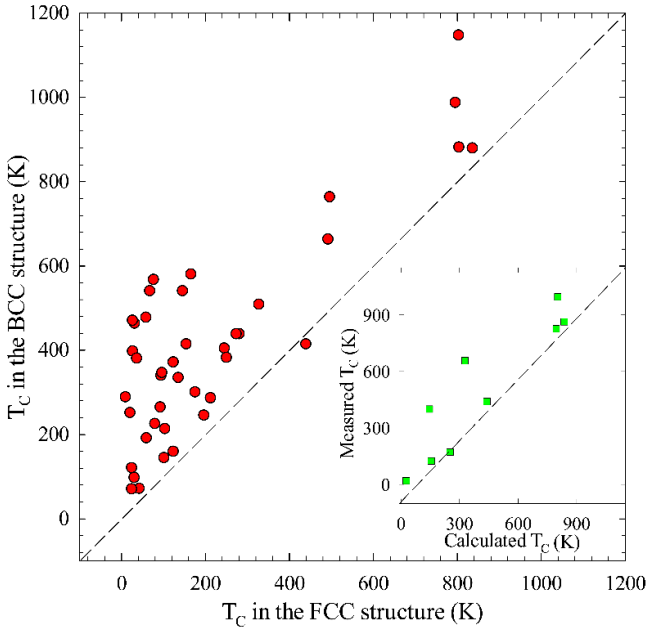
High-entropy Magnetic Materials



Use the mean-field approximation to estimate the Curie temperature:

$$k_B Tc = 2\,(E_{FM} - E_{PM})/3(1-c)$$

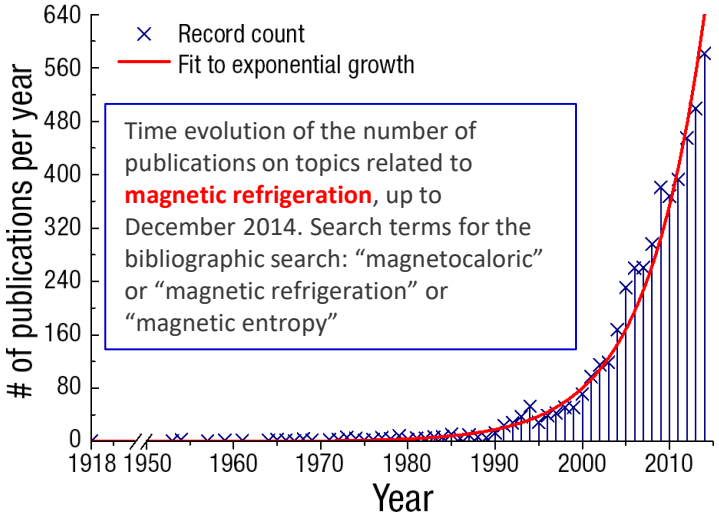
k_B is the Boltzmann constant, c is the mole fraction of the nonmagnetic element, and E_{FM} and E_{PM} are the total energies of the alloy in the ferromagnetic and paramagnetic states, respectively.



DFT calculations can be useful in predicting magnetic properties such as magnetization and critical magnetic ordering temperatures, and thus can be used to accelerate the development of high-entropy magnetic alloys.

M.C. Gao, D.B. Miracle, D. Maurice, X.H. Yan, Y. Zhang, and J.A. Hawk, "Functional High-Entropy Materials," J. Mater. Res., 33 (2018) 3138-3155..

Magnetocaloric Effect (MCE)



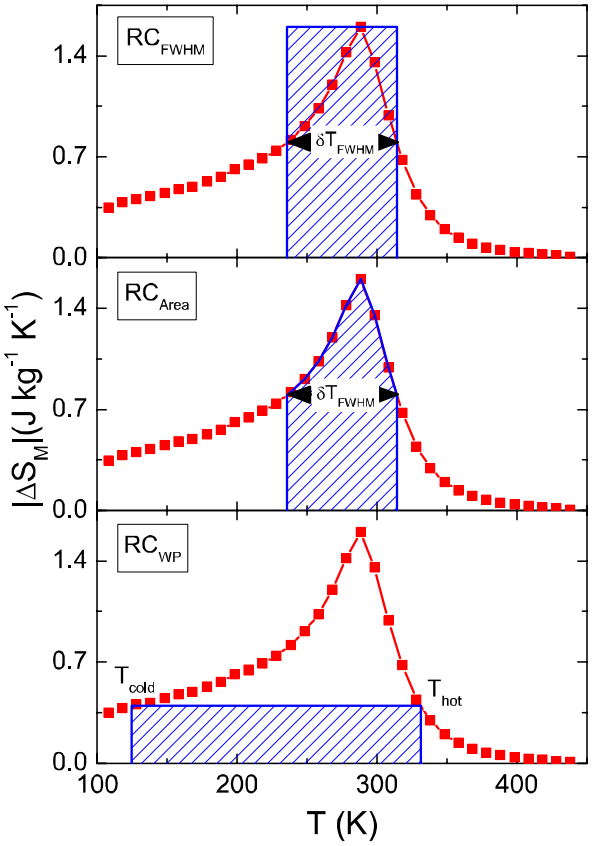
Time evolution of the number of publications on topics related to **magnetic refrigeration**, up to December 2014. Search terms for the bibliographic search: "magnetocaloric" or "magnetic refrigeration" or "magnetic entropy"

- Thermodynamic Maxwell relation: $\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H$
- Under adiabatic conditions, ΔS_m must be compensated by an equal but opposite change of the entropy associated with the lattice, resulting in a change in temperature of the material, and vice versa.

To get high RC values, we need:

- High $|\Delta S_M|$ values
- High ΔT_{FWHM} values

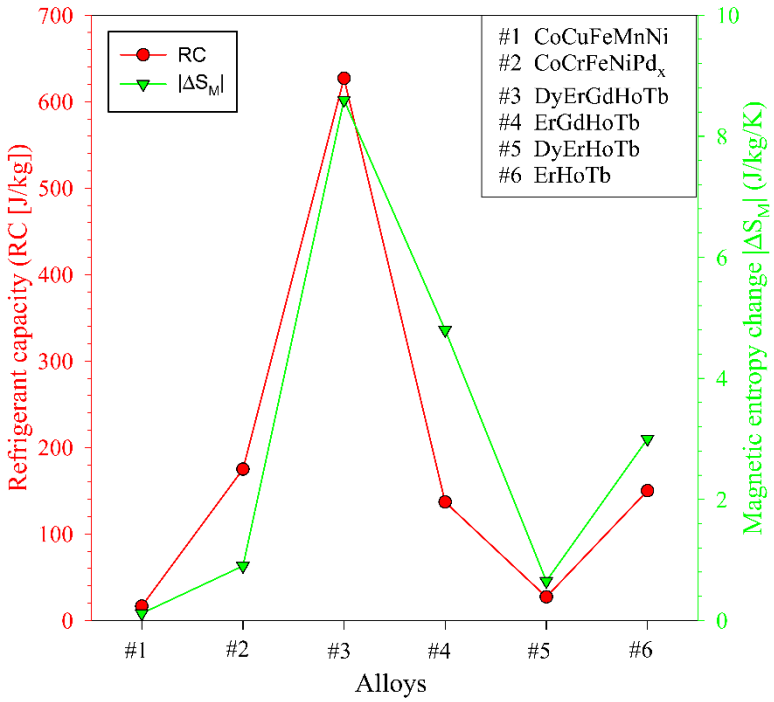
- $\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH$
- $RC = |\Delta S_M \Delta T_{FWHM}|$



There are mainly three ways to calculate **refrigerant capacity (RC)**. The first one is commonly used.

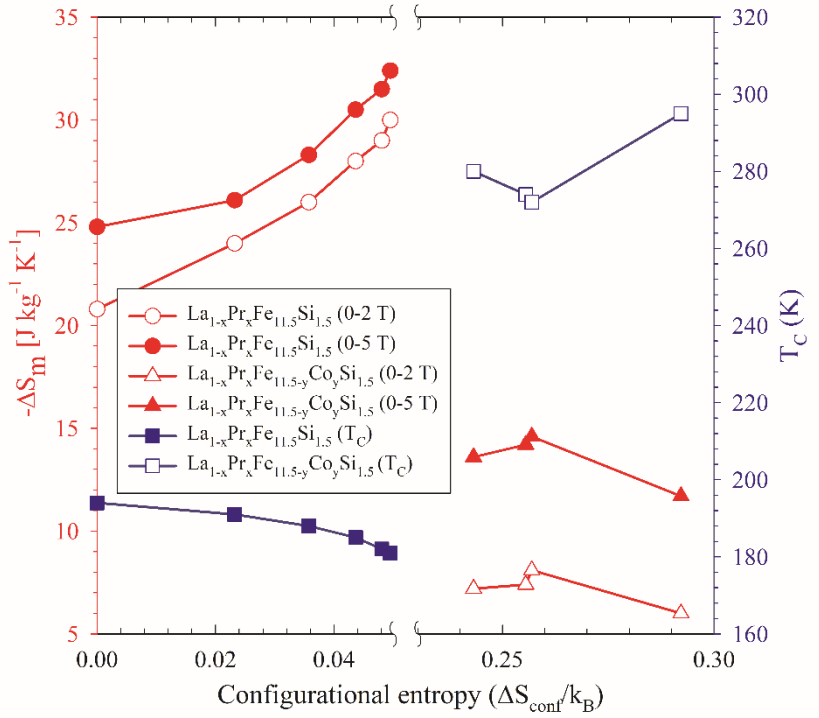
High-Entropy MCE Materials

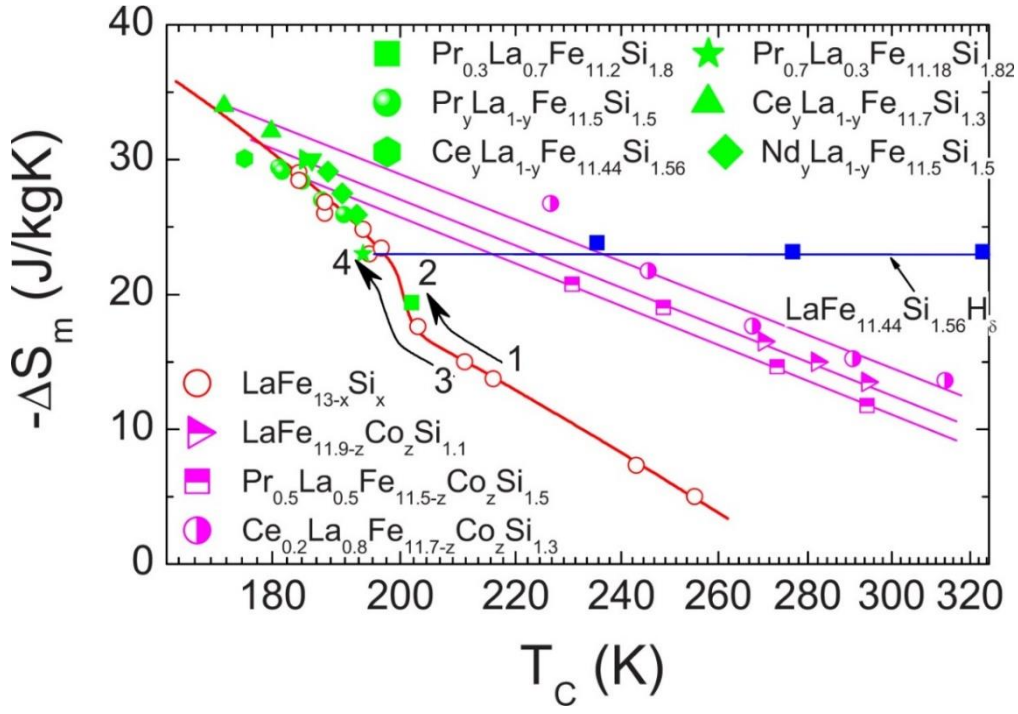
Composition	Applied field (T)	$\|\Delta S_M\|$ (J/kg/K)	RC (J/kg)	Ref.
CoCuFeMnNi	1.5	0.115	16.5	12
$CoCu_{0.975}FeMn_{1.025}Ni$	1.5	0.094	15.3	12
$CoCu_{0.95}FeMn_{1.05}Ni$	1.5	0.10	13.5	12
$CoCu_{0.925}FeMn_{1.075}Ni$	1.5	0.084	12.2	12
$CoCu_{0.9}FeMn_{1.1}Ni$	1.5	0.081	9.6	12
$CoCuFe_{0.975}Mn_{1.025}Ni$	1.5	0.105	14	12
$CoCuFe_{0.95}Mn_{1.05}Ni$	1.5	0.071	10	12
$CoCrFeNiPd_x$	5	<0.9	<175	59
DyErGdHoTb	5	8.6	627	13
ErGdHoTb	3	4.8	137	13
DyErHoTb	3	0.65	27.3	13
ErHoTb	3	3	150	13



Reported high entropy alloys for example DyErGdHoTb do show extraordinary refrigerant capacity (RC), and the RC values increase with increasing the configurational entropy of the alloys but Gd seems to be critically important.

Traditional MCE Materials



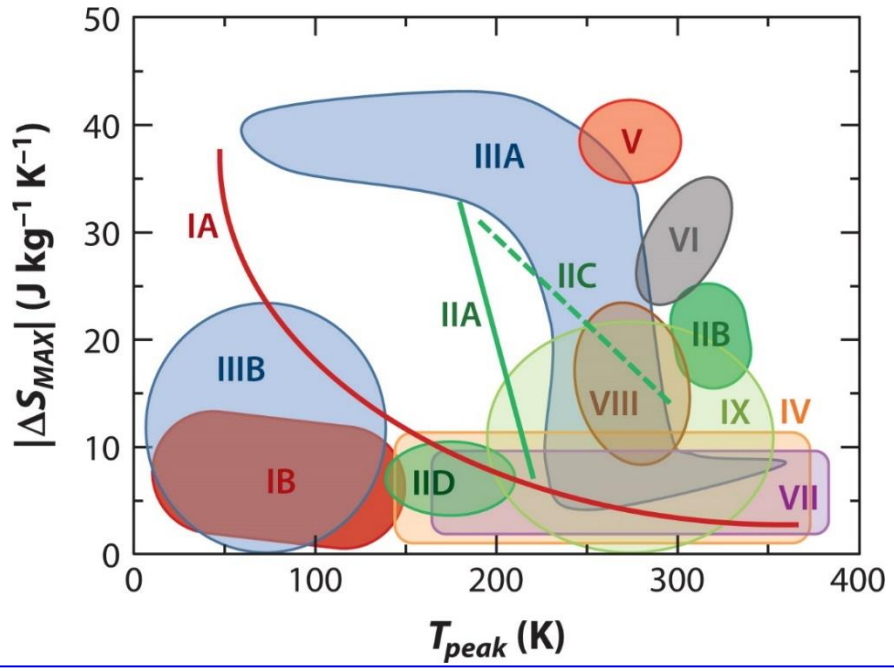


- Magnetic entropy change does **NOT** always increase with increasing the configurational entropy of the alloys.
- For $LaFe_{11.5}Si_{1.5}$, substituting Pr for La increases ΔS_m but decreases T_C, while substituting Co for Fe lowers ΔS_m but increases T_C.
- To balance ΔS_m and T_C, Substituting in both La and Fe sites are required.

$\Delta S_m - T_C$ relations of magnetic rare-earth element doped and transition metal-doped $LaFe_{13-x}Si_x$ family compounds

Jia et al. "Magnetocaloric effects in the La„Fe,Si13 intermetallics doped by different elements", J. Appl. Phys. 2009. 07A924. M.C. Gao, D.B. Miracle, D. Maurice, X.H. Yan, Y. Zhang, and J.A. Hawk, "Functional High-Entropy Materials," J. Mater. Res., 33 (2018) 3138-3155..

High-Performance MCE Materials

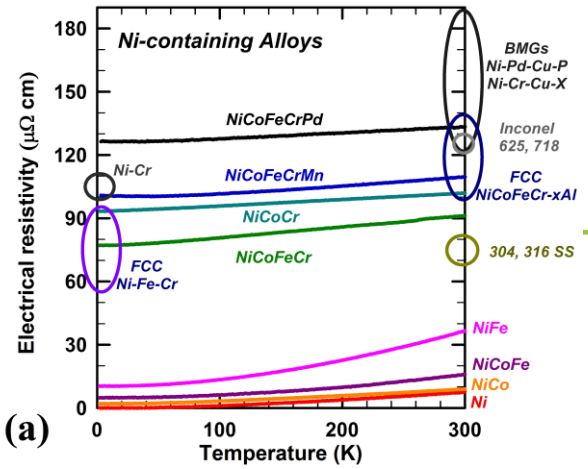


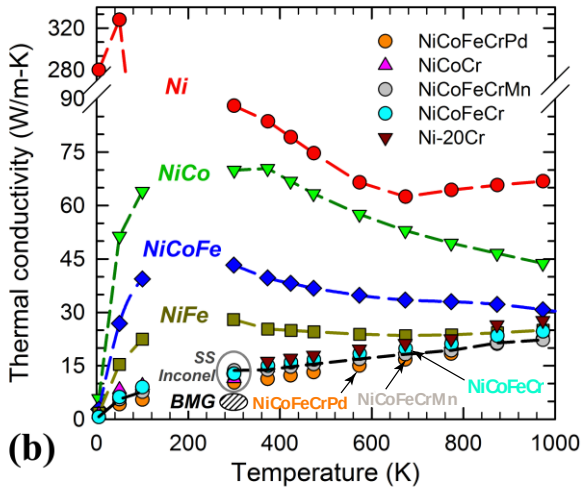
- IA Laves phases
- IB Low T SOMT Laves phases
- IIA $La(FeSi)_{13}$
- IIB $La(FeSi)_{13}$-H
- IIC $La(FeCoSi)_{13}$
- IID $La(FeAl)_{13}$
- IIIA $Gd_5(SiGe)_4$
- IIIB $RE_5(SiGe)_4$
- IV Ln-manganites
- V MnFe(AsP)
- VI MnAs
- VII Other Mn-based
- VIII FeRh
- IX Heusler alloys

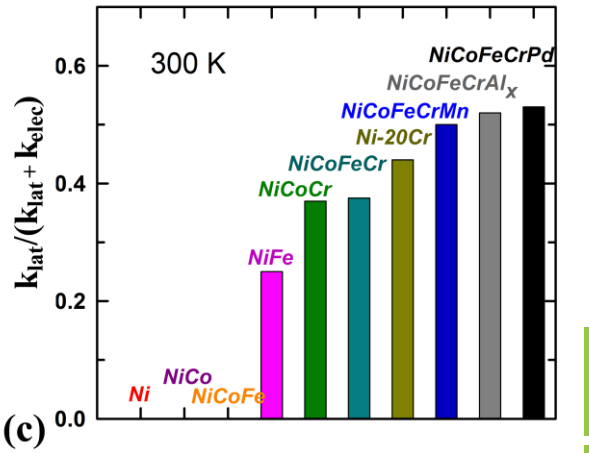
Reported maximum magnetic entropy change for H = 5 T versus peak temperature for different families of magnetocaloric materials

- Magnetic refrigeration requires MCE materials with high refrigerant capacity (RC) to be operated at room temperature.
- Maximum magnetic entropy change $|\Delta S_M|$ usually occurs around the magnetic critical temperature, e.g., Curie temperature.
- Most reported MCE materials that have high $|\Delta S_M|$ tend to have too low T_C temperatures.
- Many MCE materials that have high T_C temperatures tend to have low $|\Delta S_M|$ values.
- It is important to design high-performance MCE materials that have high RC values with T_C around room temperature.

Physical Properties

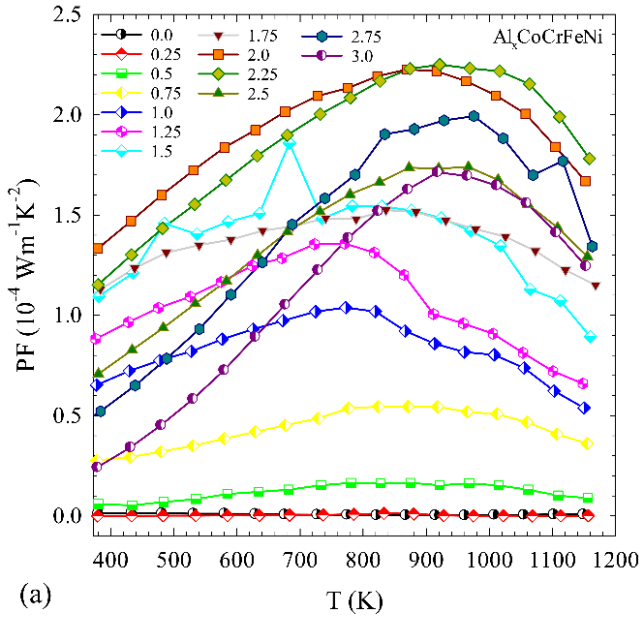


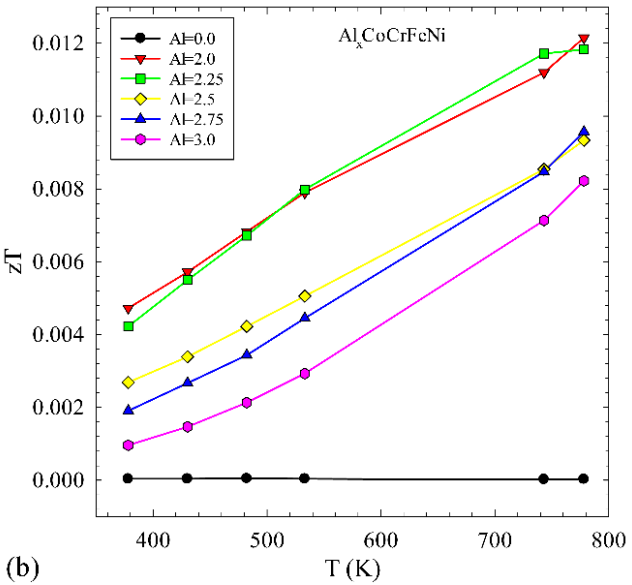


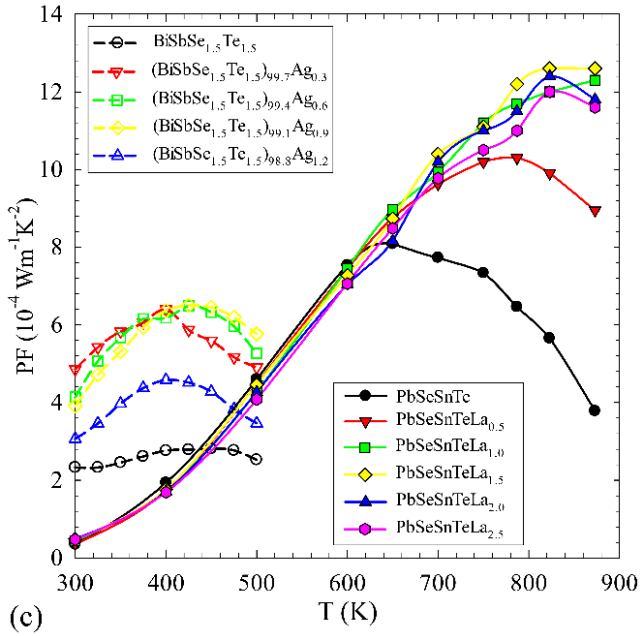


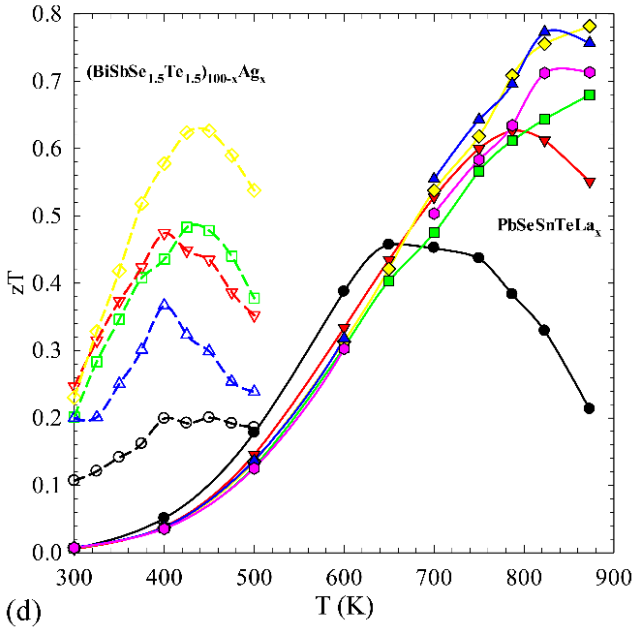
- The overall trend for FCC Ni-alloys is that increasing entropy results in increased electrical resistivity, but not always.
- However, Cr-containing HEAs have significantly higher resistivity than those without Cr by about one order of magnitude.
- Electronic structure calculations reveal that alloying with Cr promotes d-band smearing in both minority and majority spin channels, resulting in a much reduced electron mean free path and hence high electrical resistivity.
- For those Ni alloys that do not contain Cr, the majority spin channel has a large (or infinite) electron mean free path, providing a short circuit and hence an overall low resistivity.
- Overall, alloying reduces the thermal conductivity of Ni, but thermal conductivity is sensitive to both configurational entropy and alloying elements.
- Thermal conductivity is comprised of electronic and lattice contributions. Contrasted to pure metals for which the electronic contribution is dominant, HEAs have significantly enhanced lattice contribution compared to electronic contribution.

K. Jin and H. Bei: Single-phase concentrated solid-solution alloys: bridging intrinsic transport properties and irradiation resistance Front. Mater. 5, 1 (2018)









High-Entropy Thermoelectric Materials

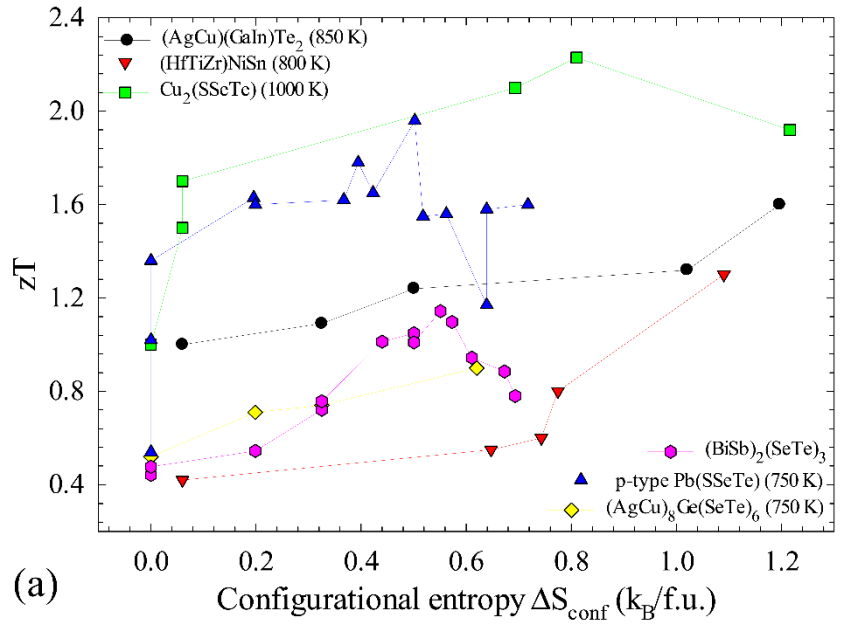
$$zT = \frac{\sigma S^2 T}{\kappa}$$

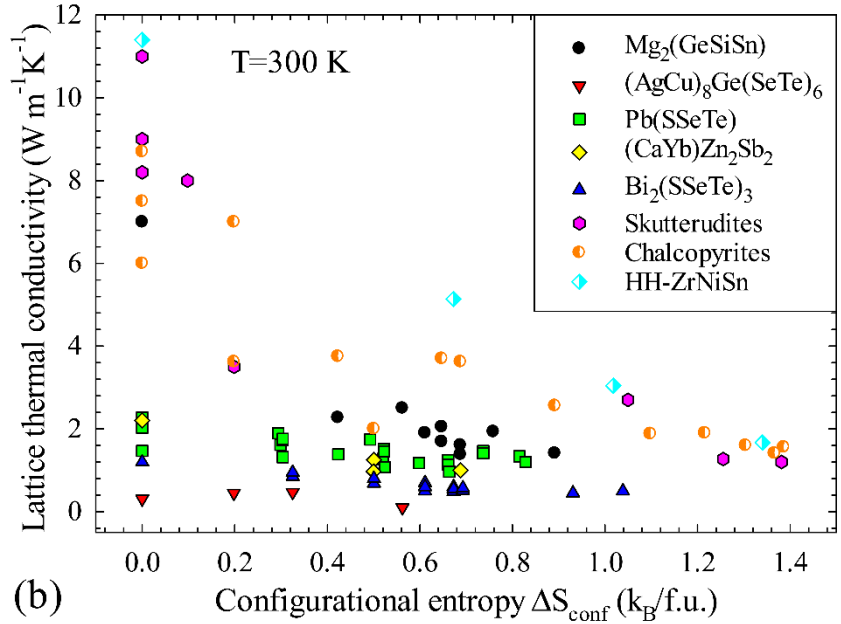
S is the Seebeck coefficient, κ is thermal conductivity, σ is electrical conductivity, and T is temperature. The product σS^2 is also called the "power factor" (PF).

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

n is the carrier concentration, and m* is the effective mass of the carrier.

M.C. Gao, D.B. Miracle, D. Maurice, X.H. Yan, Y. Zhang, and J.A. Hawk, "Functional High-Entropy Materials," J. Mater. Res., 33 (2018) 3138-3155..

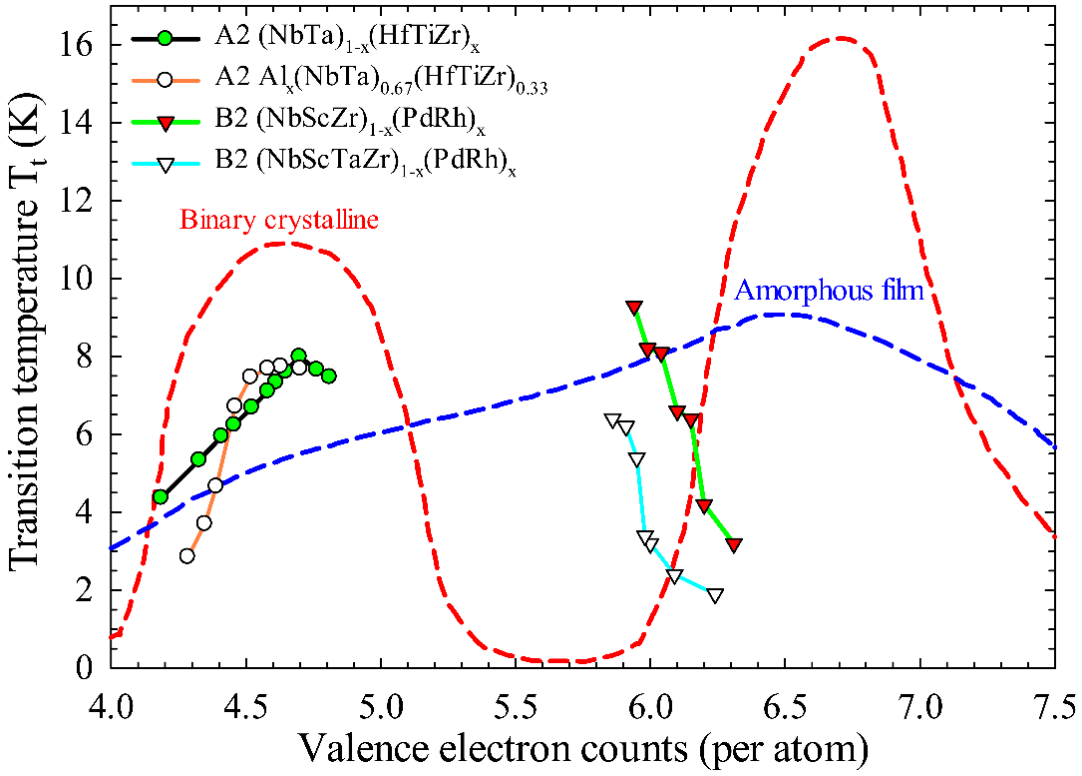




Traditional Thermoelectric Materials

- Configurational entropy has substantial impact on lattice thermal conductivity.
- For HEAs, the thermal conductivity of HEAs is reduced tremendously.
- Computational prediction: balance electrical conductivity, Seebeck coefficient, and thermal conductivity to maximize zT values.
- Doping known thermoelectric materials to promote solid solutions can be a good starting point.
- Apply reduced dimension and band engineering.

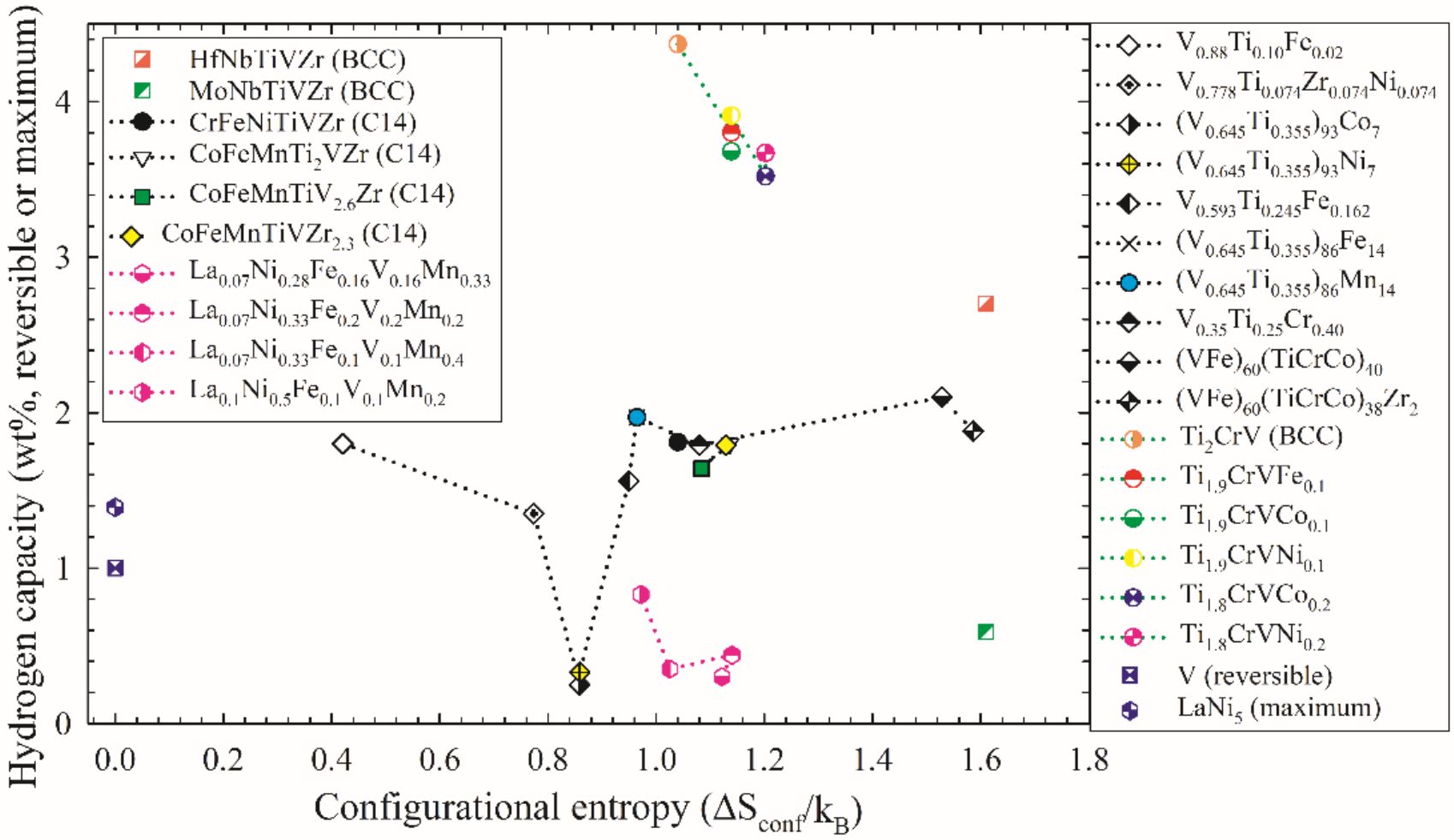
High-Entropy Superconducting Materials



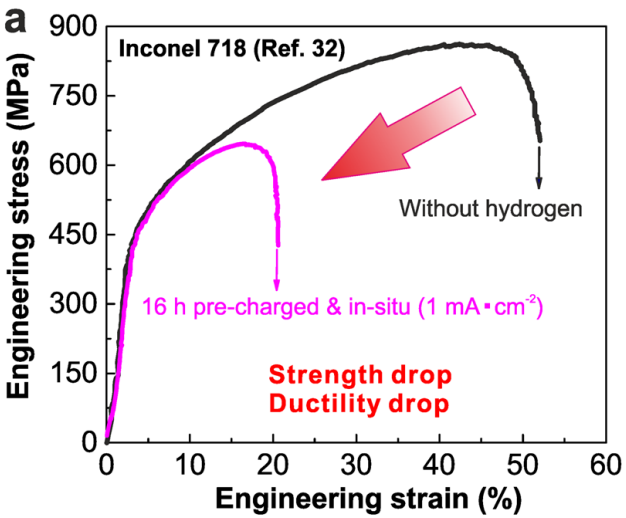
Some commonalities to guide designing high-entropy superconductors:

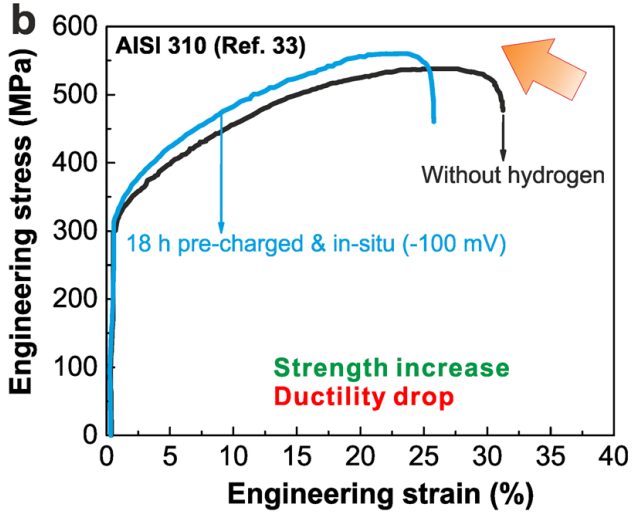
(1) magnetism,
(2) layered crystal structures,
(3) the incorporation of transition metals, and
(4) valence electron/carrier densities within a certain range.

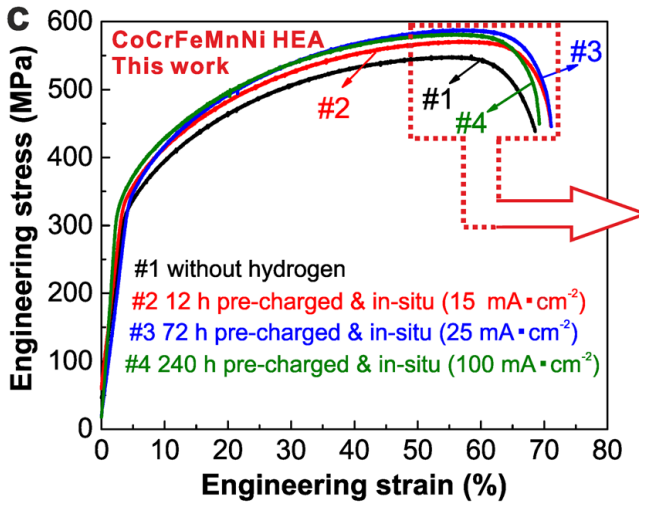
Hydrogen Storage

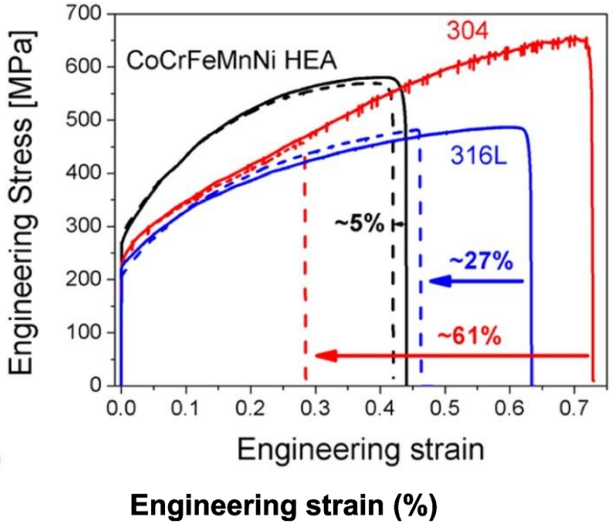


Resistance Against Hydrogen Embrittlement (CoCrFeMnNi)









FCC high entropy alloys can be next-generation strong, ductile, and hydrogen tolerant materials.

Luo et al. 2017
Zhao et al. 2017

H. Luo, Z.M. Li and D. Raabe: Hydrogen enhances strength and ductility of an equiatomic high-entropy alloy Sci. Rep. 7, 9892 (2017). Y. Zhao, D.H. Lee, M.Y. Seok, J.A. Lee, M.P. Phaniraj, J.Y. Suh, H.Y. Ha, J.Y. Kim, U. Ramamurty and J.I. Jang: Resistance of CoCrFeMnNi high-entropy alloy to gaseous hydrogen embrittlement Scripta Mater. 135, 54 (2017)

Summaries

- Doping and iso-electronic (also called iso-structure) substitution have been established to improve the balance of traditional functional properties in ordered compounds.
- Some unique feature of HEAs such as tremendously reduced thermal conductivity makes them promising thermoelectric materials.
- Applying high-entropy concept to known compounds that show excellent functional properties can be a good starting point.
- Extending HEA concept to high-entropy materials and multi-principal element materials can be a transformative approach to design next-generation functional materials.