

## Supplementary Information

### Rigid Band model

The structural stability of simple FCC and BCC phases, and all other complex phases observed in multi-component alloys can be investigated by using the frozen potential approximation (FPA) to density functional theory (DFT). Within the first order approximation the energy difference between any two non-magnetic structures is given by the difference between their band energies at a fixed equilibrium volume,  $V_0$ <sup>35,36,49</sup>:

$$\Delta E_{Non-Mag}^{(1-2)} \approx \Delta E_{Band}^{(1-2)} = \left[ 2 \int_{-\infty}^{\varepsilon_F^{(1)}} \varepsilon D^{(1)}(\varepsilon) d\varepsilon - 2 \int_{-\infty}^{\varepsilon_F^{(2)}} \varepsilon D^{(2)}(\varepsilon) d\varepsilon \right]_{V_0=0} \quad (I)$$

where  $D^{(1)}(\varepsilon)$  and  $D^{(2)}(\varepsilon)$  are the densities of states (DOS) per atom with a factor of 2 for a spin to energy  $\varepsilon$  and  $\varepsilon_F^{(1)}$  and  $\varepsilon_F^{(2)}$  are the Fermi energies for structure 1 and 2, respectively. They are determined from the number of valence electrons per atom:

$$n = 2 \int_{-\infty}^{\varepsilon_F^{(1)}} D^{(1)}(\varepsilon) d\varepsilon = 2 \int_{-\infty}^{\varepsilon_F^{(2)}} D^{(2)}(\varepsilon) d\varepsilon \quad (II)$$

Frozen potentials for the different atomic species are determined from self-consistent calculations, normally for structures with a small unit cell. They are then transferred into other structures with the same alloy composition and the same equilibrium volume. The difference between the band energies  $\Delta E_{Band}^{(1-2)}$  is calculated under the constraint that the potential within the Wigner-Seitz sphere remains unchanged (frozen) when going from one structure type to another. Since the energy difference in the first order frozen potential approximation is computed assuming fixed atomic volumes, this approximation is correct for structures with relatively similar equilibrium atomic volumes like for example FCC and BCC phases, which can be related to each other through the Bain transformation.

Assuming that alloying changes the number of valence electrons per atom but the electronic DOS of different phases remain rigid (the rigid band approximation), the variation of the energy difference as a function of the number of electrons can be evaluated by comparing the band energies, see equation (I)<sup>19,20,50</sup>.

Within the present work, the RBA model has been generalised for the case of magnetic materials like CCFN-based alloys using the Stoner model of magnetism<sup>23-27</sup>. In transition metal alloys the latter one introduces magnetism by introducing local exchange fields within the band energy concept. In particular, electrons with spins up and down have different on-site energies depending on whether their spin is parallel or anti-parallel to the local magnetic moment. The effective on-site energy  $\varepsilon_i^\sigma$  is given by

$$\varepsilon_i^\sigma = \varepsilon_i \pm \frac{1}{2} I_i m_i \quad (III)$$

where  $\varepsilon_i$  is the single-particle non-magnetic on-site energy,  $m_i = n_i^\downarrow - n_i^\uparrow$ , is the difference between electron occupancies of site  $i$  by spin-down and spin-up electrons with a spin index  $\sigma$ . The Stoner exchange parameter  $I_i$  refers to the exchange splitting of on-site energies of electrons with spin up and spin down due to the local magnetic moment  $m_i$ <sup>23,24,26,27,30</sup>.

From equation (III), the energy difference between two magnetic structures, following the Stoner model of magnetism (Stoner Model I), corrected for the double counting contribution, and normalised by the number of atoms,  $N$  in both structures can be given by:

$$\Delta E_{Mag}^{(1-2)} = \Delta E_{Spin-Band}^{(1-2)} + \frac{1}{4N} \left[ \sum_i I_i^{(1)} m_i^{2(1)} - \sum_i I_i^{(2)} m_i^{2(2)} \right] \quad (IV)$$

where the first term is the spin-polarised band energy difference between any two magnetic structures at a fixed equilibrium volume  $V_0$  (defined below in equation (V)), the second term is the double-counting contribution arising from magnetic interactions<sup>23-25</sup>, and  $N$  is the number of atoms in both considered structures.  $\Delta E_{Spin-Band}^{(1-2)}$  is defined as:

$$\Delta E_{Spin-Band}^{(1-2)} = \left[ \int_{-\infty}^{\mathcal{E}_F^{(1)}} (\mathcal{E} D^{(1)\uparrow}(\mathcal{E}) + \mathcal{E} D^{(1)\downarrow}(\mathcal{E})) d\mathcal{E} - \int_{-\infty}^{\mathcal{E}_F^{(2)}} (\mathcal{E} D^{(2)\uparrow}(\mathcal{E}) + \mathcal{E} D^{(2)\downarrow}(\mathcal{E})) d\mathcal{E} \right]_{N_0=0} \quad (V)$$

where  $D^{(1)\uparrow}(\mathcal{E})$  and  $D^{(2)\uparrow}(\mathcal{E})$  are the spin-polarised total DOS per atom for electrons with spin-up and  $D^{(1)\downarrow}(\mathcal{E})$  and  $D^{(2)\downarrow}(\mathcal{E})$  are the spin-polarised total DOS per atom for electrons with spin-down. The Stoner parameters in equation (IV) are assumed to be constant for each type of atoms<sup>51</sup>. However, application of equation (IV) requires knowledge of the magnetic moments of all atoms as a function of  $n$  in the system, of which is difficult to be validated experimentally. Therefore, we use an effective Stoner parameter  $I_{eff}$  which refers to the exchange splitting of the on-site energies of electrons with spin-up and spin-down due to the average atomic magnetic moment  $m_{av}$ , defined as:

$$I_{eff} m_{av} = \mathcal{E}_F^{\downarrow} - \mathcal{E}_F^{\uparrow} \quad (VI)$$

where  $\mathcal{E}_F^{\uparrow}$  and  $\mathcal{E}_F^{\downarrow}$  are the Fermi energies for electrons with spin-up and spin-down, respectively, defined as energies of the non-magnetic total DOS,  $D(\mathcal{E})$ , which are the number of electrons per atom with spin-up and spin-down, obtained from the spin-polarised total DOS. The average magnetic moment of the entire simulation cell from the non-magnetic total DOS is equal to the one obtained from the spin-polarised total DOS and is given by:

$$m_{av} = \int_{-\infty}^{\mathcal{E}_F} D^{\downarrow}(\mathcal{E}) d\mathcal{E} - \int_{-\infty}^{\mathcal{E}_F} D^{\uparrow}(\mathcal{E}) d\mathcal{E} = \int_{\mathcal{E}_F^{\uparrow}}^{\mathcal{E}_F^{\downarrow}} D(\mathcal{E}) d\mathcal{E} \quad (VII)$$

By using the effective Stoner parameter and the average magnetic moment the energy difference between any two magnetic structures in the effective Stoner Model II can now be written as:

$$\Delta E_{Mag}^{(1-2)} = \Delta E_{Spin-Band}^{(1-2)} + \frac{1}{4} \left[ I_{eff}^{(1)} m_{av}^2{}^{(1)} - I_{eff}^{(2)} m_{av}^2{}^{(2)} \right] \quad (VIII)$$

Both Stoner Model I and effective Stoner Model II can be justified by the comparison of energy differences with those obtained using the LMTO code. As shown in Table SI the energy differences between the considered magnetic structures and the BCC structures with the same composition calculated using both equation (IV) and (VIII) are in quantitative agreement with each other and in line with the results calculated using the LMTO code. The only exception is that the C14 structure of  $\text{Co}_9\text{Cr}_{12}\text{Fe}_9\text{Ni}_6$  alloy which is less stable than the BCC phase when equation (VIII) is applied and it is more stable than the BCC phase by using equation (IV) and the LMTO code. However, all the considered methods predict that the FCC phase is the most stable one.

**Supplementary Table SI.** Average magnetic moments obtained using equation (VII) ( $m_{av}$ ) and energy differences ( $\Delta E_{Mag}$ ) between the considered magnetic structures and the BCC structures with the same composition calculated using equations (IV) and (VIII), compared with the results calculated using the LMTO code.  $I_{eff}$  is the effective Stoner parameters calculated using equation (VI). Energies, magnetic moments and effective Stoner parameters are given in  $eV$ ,  $\mu_B$  per atom and  $eV / \mu_B$ , respectively. The valence electron concentration of considered structures is indicated by  $n$ .

	Structure	$\Delta E_{Mag}$ (equation (IV))	$\Delta E_{Mag}$ (equation (VIII))	$\Delta E_{Mag}$ (LMTO)	$m_{av}$ (equation (VII))	$m_{av}$ (LMTO)	$I_{eff}$ (equation (VI))
<b>CCFN</b> <b>Co<sub>8</sub>Cr<sub>8</sub>Fe<sub>9</sub>Ni<sub>8</sub></b> <b>(n = 8.25)</b>	FCC	-0.136	-0.099	-0.083	0.372	0.372	1.295
	BCC				0.421	0.421	1.302
<b>CCFN-Al</b> <b>Co<sub>8</sub>Fe<sub>8</sub>Ni<sub>8</sub>Al<sub>8</sub></b> <b>(n = 7.5)</b>	FCC	-0.043	-0.020	-0.001	0.939	0.930	3.940
	BCC				1.011	0.990	4.392
	B2	-0.065	-0.102	-0.072	0.948	0.948	4.124
<b>CCFN-Pd</b> <b>Co<sub>6</sub>Cr<sub>7</sub>Fe<sub>7</sub>Ni<sub>6</sub>Pd<sub>6</sub></b> <b>(n = 8.5)</b>	FCC	-0.139	-0.070	-0.064	0.881	0.864	3.631
	BCC				0.913	0.915	3.746
<b>CCFN-V</b> <b>Co<sub>9</sub>Cr<sub>12</sub>Fe<sub>9</sub>Ni<sub>6</sub></b> <b>(n = 8.133)</b>	FCC	-0.147	-0.123	-0.073	0.350	0.344	1.228
	BCC				0.415	0.422	1.205
	Sigma	-0.151	-0.120	-0.069	0.312	0.317	0.993
<b>CCFN-Ti</b> <b>Co<sub>9</sub>Cr<sub>12</sub>Fe<sub>9</sub>Ni<sub>6</sub></b> <b>(n = 7.917)</b>	FCC	-0.063	-0.027	-0.021	0.687	0.171	0.987
	BCC				0.691	0.172	0.831
	C14	-0.018	0.022	-0.013	0.817	0.819	0.909

## References

1. Pettifor, D. G. Pressure-cell boundary relation and application to transition-metal equation of state. *Commun. Theor. Phys.* **1**, (1977).
2. Andersen, O. K., Skriver, H. L., Nohl, H. & Johansson, B. J. Electronic structure of transition metal compounds; ground-state properties of the 3d-monoxides in the atomic sphere approximation. *Pure Appl. Chem.* **52**, 93 (1980).
3. Pettifor, D. G. Individual orbital contributions to the SCF virial in homonuclear diatomic molecules. *J. Chem. Phys.* **69**, 2930 (1978).
4. Nguyen-Manh, D., Paxton, A., Pettifor, D. G. & Pasturel, A. On the phase stability of transition metal trialuminide compounds. *Intermetallics* **3**, 9–14 (1995).
5. Paxton, A., Methfessel, M. & Pettifor, D. G. A bandstructure view of the Hume-Rothery electron phases. *Proc. R. Soc. A* **453**, 1493 (1997).
6. Jones, H. J. Concentrated solid solutions of normal metals. **23**, *Journal de Physique et le Radium* (1962).
7. Liu, G., Nguyen-Manh, D., Liu, B. G. & Pettifor, D. G. Magnetic properties of point defects in iron within the tight-binding-bond Stoner model. *Phys. Rev. B* **71**, 174115 (2005).
8. Nguyen-Manh, D. & Dudarev, S. L. Model many-body Stoner Hamiltonian for binary FeCr alloys. *Phys. Rev. B* **80**, 104440 (2009).
9. Dudarev, S. L. & Derlet, P. M. Interatomic potentials for materials with interacting electrons. *J. Comput.-Aided Mater. Des.* **14**, 129 (2008).
10. Derlet, P. & Dudarev, S. Million-atom molecular dynamics simulations of magnetic iron. *Prog. Mater. Sci.* **52**, 299–318 (2007).
11. Kübler, J. K. *Theory of itinerant electron magnetism*. (Oxford University Press, 2009).
12. Lucas, M. S. *et al.* Magnetic and vibrational properties of high-entropy alloys. *J. Appl. Phys.* **109**, 7 (2011).

13. Christensen, N., Gunnarsson, O., Jepsen, O. & Andersen, O. J. Local spin density theory for ferro- and antiferromagnetic materials. *J. Phys. C* **8**, (1988).