

**Local Energies and Energy Fluctuations –  
applied to the High Entropy Alloy CrFeCoNi**

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Supercell calculations with efficient ( $N$ -scaling) codes allow to perform calculations for very large systems. For instance, for disordered magnetic alloys we can calculate the charge density and the magnetisation, in particular the local moments, of all atoms, such that the sum of the local moments gives the total moment of the considered system. However this is not possible for the energy: if we have 1, 10 or 1000 atoms in the supercell, a conventional calculation yields only one energy, i.e. the total energy of the whole system. However, this is not correct, i.e. we can indeed calculate the local energies of all atoms, and show that the sum of these local energies gives the total energy. While this has already been shown in 1982 by M. Weinert et al.[1], it was to our knowledge not discussed in any detail and application. Thus, when one makes a Voronoi construction of the space around each atom  $n$ , the total energy  $E_{\text{tot}}$  can be written as the sum of the local energies  $E_n$  of all  $N$  atoms:  $E_{\text{tot}} = \sum_n^N E_n$ . While this is trivial for the single particle energies, it can also be shown for the double counting energies. We will use this in the following for the calculation of disordered magnetic alloys with many components.

High entropy alloys show a variety of fascinating properties like high hardness, wear resistance, corrosion resistance, etc. They are random solid solutions of many components with rather high concentrations. We perform *ab-initio* calculations for the high entropy alloy CrFeCoNi, with equal concentration of 25 % for each element. By the KKRnano program package, which is based on an order- $N$  screened Korringa-Kohn-Rostoker Green's function method, we consider a face-centred cubic (FCC) supercell with 1372 randomly distributed elements, and in addition also smaller supercells with 500 and 256 atoms.

In parallel to these exact calculations for large supercells, we perform also calculations using the coherent potential approximation (CPA) which is the working horse for electronic structure calculations for disordered alloys [2]. The multiple scattering in the disordered alloy is replaced by embedding a representative atom in a suitable chosen effective medium. Therefore the CPA method can decrease the computational cost considerably. From the present point of view, in the CPA only the local energy on the considered site has to be calculated. The difference compared to the supercell method is that in the latter method the Green's function of the total supercell is calculated exactly, while in the CPA only the Green's function at a local site embedded in an effective medium is needed, which has however to be determined selfconsistently. As we will show, both methods give very similar results.

The supercell method allows not only to calculate the average local energies, but also the energy fluctuations of the different atoms, reflecting the embedding into the different local environments. As an example we show in the figure the energy fluctuation  $E^{\text{Cr}}$  of a Cr atom away from the average value  $\bar{E}^{\text{Cr}}$ , when one varies the number of Cr atoms  $n_{\text{Cr}}^{\text{1st}}$  in the first shell. For the 25% alloy there are on average 3 Cr atoms in the first shell. If one averages over environments with a given  $n_{\text{Cr}}^{\text{1st}}$  number,

one sees a clear trend: the local energy of the Cr atom is lowered, if there is no or 1 or 2 Cr-atoms in the first shell while a larger number of neighbouring Cr atoms is unfavourable. The opposite trend is found, when we look for Cr-atoms in the second shell. Here the energy is considerable lowered for a large number  $n_{\text{Cr}}^{2\text{nd}}$  of Cr atoms in the second shell. This points to an  $L1_2$ -like configuration as shown in the inset of Fig.1(b), where the Cr atoms occupy the corner positions and the Fe, Co and Ni atoms randomly the face-centered positions. This trend is confirmed when one performs supercell calculations for the partially ordered (for the Cr-atoms) and partially disordered (for the Fe, Co and Ni atoms)  $L1_2$  structure. Similar useful energetic information could also be obtained by the calculation of local energies at e.g. surfaces and interfaces as well as for by the interaction of impurities in the bulk.

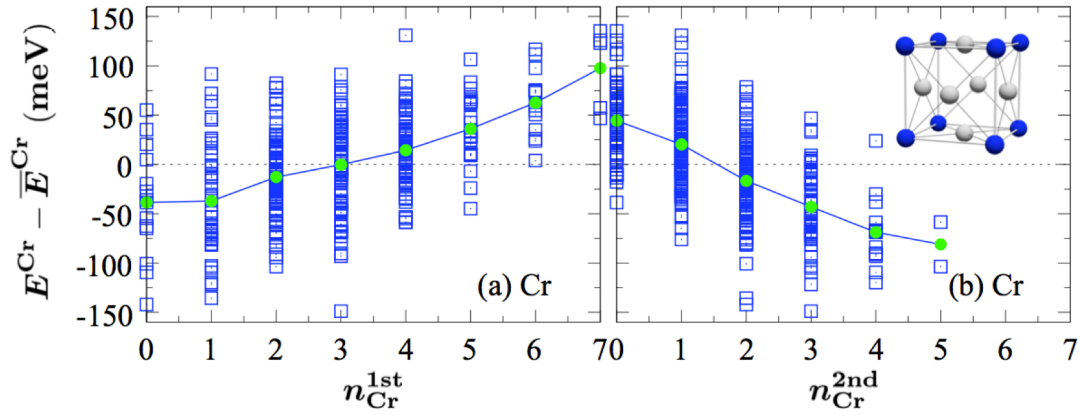


Fig. 1: Local energy fluctuations of Cr atoms ( $E^{\text{Cr}} - \bar{E}^{\text{Cr}}$ ) as a function of number of (a) first nearest neighbor Cr atoms ( $n_{\text{Cr}}^{1\text{st}}$ ) and (b) second nearest neighbor Cr atoms ( $n_{\text{Cr}}^{2\text{nd}}$ ). Green points show the average values. The inset in (b) shows the  $L1_2$  crystal structure.

#### References

- [1] M. Weinert, E. Wimmer, and A. J. Freeman, Phys. Rev. B **26**, 4571 (1982).
- [2] P. Soven, Phys. Rev. B **2**, 4715 (1970); H. Shiba, Prog. Theor. Phys. **46**, 77 (1971).