# Role of electron concentration parameter e/a in energy-gap formation mechanism through interference phenomenon

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Dr.E.Belin-Ferré and I met for the first time at LAM8 conference in Vienna in 1992. We learned that both of us share a common interest in the electronic structure and electron concentration parameter **e/a** of complex compounds and could produce successive joint papers over 1994 to 2000. After the retirement from Nagoya University in 2005, I have been engaged in studying long-standing **e/a** issues for transition metal (TM) compounds in collaboration with my co-worker Prof.H.Sato, with the aim at deepening a theoretical insight into the Hume-Rothery electron concentration rule for TM compounds.

Mizutani and Sato have developed the *FLAPW-Fourier theory*, which is capable of making *ab initio* determination of the number of itinerant electrons per atom, **e/a**, for elements and compounds, almost regardless of the degree of metallicity, covalency and ionicity involved in the van Arkel-Ketelaar triangle diagram [1-3]. This certainly promises us to pave the way to establish the theoretical basis of the electron theory for any compounds involving TM and/or rare earth elements.

The theory makes a full use of the formalism of the FLAPW (Full-potential Linearized Augmented Plane Wave) electronic structure calculations based on the density functional theory: the *j*-th wave function in the interstitial region with the energy eigenvalue $E^j$ at the wave vector $\mathbf{k}_i$ obtained by partitioning the first Brillouin zone into $N_{\mathbf{k}}$ meshes, is expanded into a Fourier series:

$$y^j(\mathbf{r}, \mathbf{k}_i) = \frac{1}{\sqrt{V}} \sum_p C^j_{\mathbf{k}_i+\mathbf{G}_p} \exp\{i(\mathbf{k}_i+\mathbf{G}_p)\cdot\mathbf{r}\}, \quad (1)$$

where V is the volume of the unit cell and $\mathbf{G}_p$ is the reciprocal lattice vector of a given system. The square of the Fourier coefficient $\left|C^j_{\mathbf{k}_i+\mathbf{G}_p}\right|^2$ forms a matrix with the electronic state $\left|2(\mathbf{k}_i+\mathbf{G}_p)\right|^2$ in row and energy eigenvalue $E^j$ in column. The Fourier coefficients are plotted on the diagram with $\left|2(\mathbf{k}_i+\mathbf{G}_p)\right|^2$ as ordinates and $E^j$ as abscissa with the choice of $\mathbf{k}_i$ in two ways: one all $\mathbf{k}_i$'s in the Brillouin zone and the other $\mathbf{k}_i$'s only on its high-symmetry points. The center of gravity energy $E^{cg}_{\mathbf{k}_i+\mathbf{G}_p}$ is calculated for each electronic state $\left|2(\mathbf{k}_i+\mathbf{G}_p)\right|^2$ by using the relation:

$$E^{cg}_{\mathbf{k}_i+\mathbf{G}_p} = \frac{\sum_j E^j(\mathbf{k}_i)\left|C^j_{\mathbf{k}_i+\mathbf{G}_p}\right|^2}{\sum_j \left|C^j_{\mathbf{k}_i+\mathbf{G}_p}\right|^2}, \quad (2)$$

where the sum is taken in the state $|\mathbf{k}_i+\mathbf{G}_p|$ over first $L$ Fourier coefficients in the descending order in the $j$-th wave function.

The set of $\left\{2\left(\mathbf{k}_i+\mathbf{G}_p\right)\right|^2, E^{cg}_{\mathbf{k}_i+\mathbf{G}_p}\}$ represents the *NFE* dispersion relation of itinerant electrons for any crystals including TM elements and their compounds. The **e/a** and **e/uc**, the product of **e/a** and the number of atoms per unit cell, can be calculated from $\left(2k_F\right)^2$ read off from the intercept of the *NFE* line with the Fermi level. The *critical* reciprocal lattice vector $|\mathbf{G}|^2_c \circ \left|2\left(\mathbf{k}_i+\mathbf{G}_p\right)\right|^2_{ZSPs}$ responsible for yielding a gap through the interference phenomenon can be extracted from $E^{cg}_{\mathbf{k}_i+\mathbf{G}_p}$ closest to the Fermi level.

Figure 1 shows the *FLAPW-Fourier spectra* for α-Fe (cI2) in non-magnetic states, Si (cF8) and the half-Heusler compound NiSnZr (cF12): yellow dots represent the distribution of finite Fourier coefficients at $E^j$ with all possible combinations of $\mathbf{k}_i$ and $\mathbf{G}_p$. The coloured vertical line segments represent the maximum Fourier coefficients on high-symmetry points and are drawn in proportion to their magnitudes. The coloured circles indicate $E^{cg}_{\mathbf{k}_i+\mathbf{G}_p}$ on the high-symmetry points. From the intersection of the *NFE* line with the Fermi level, we obtain $\left(2k_F\right)^2$=1.59±0.16, **e/a**=1.05, **e/uc**=2.1 and $|\mathbf{G}|^2_c$=2 for α-Fe. The data for both Si and NiSnZr are incorporated in Figure 1. The possession of common **e/uc**=32 and $|\mathbf{G}|^2_c$=8, 11 and 12 for both Si and NiSnZr is consistent with the fulfilment of the interference condition $\left(2k_F\right)^2=|\mathbf{G}|^2_c$ or $\mathbf{e/uc}=\frac{p}{3}\left\{|\mathbf{G}|^2_c\right\}^{3/2}$ and explains the origin of the energy gap in terms of the *common* interference phenomena of itinerant electrons with set of zone planes associated with $|\mathbf{G}|^2_c$ =8, 11 and 12 [3].

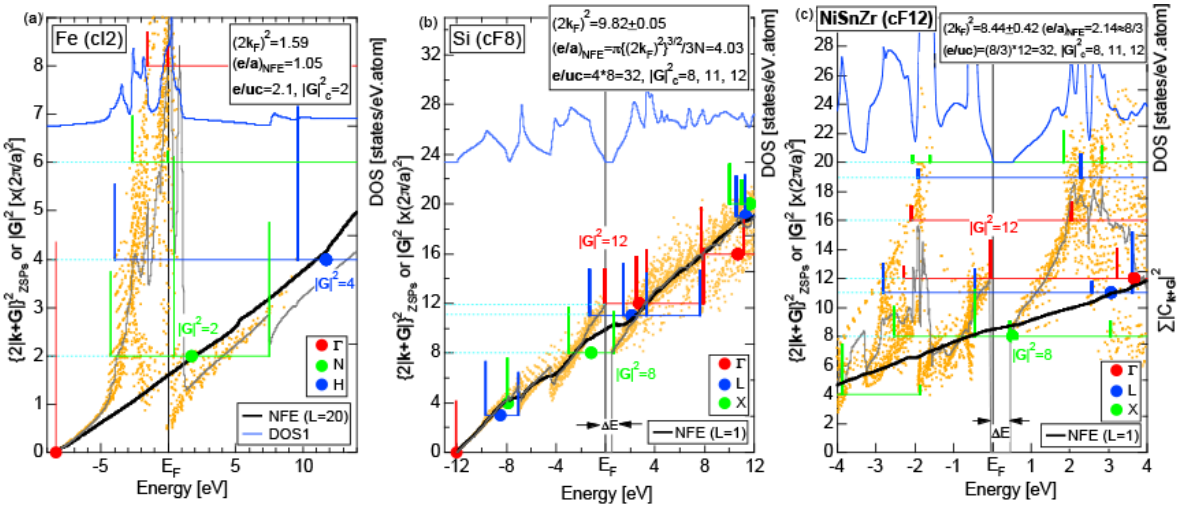


**Figure1.** FLAPW-Fourier spectra of (a) α-Fe (cI2), (b) Si (cF8) and (c) NiSnZr (cF12) [3].


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3. U.Mizutani and H.Sato, *Philos.Mag.*, (2018), **98**, 1307.



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