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Theoretical Foundation for the Hume-Rothery Electron Concentration Rule for Structurally Complex Alloys

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An electron concentration parameter, expressed as the number of itinerant electrons per number of atoms N in a structural unit cell of an alloy, e/uc, is a useful parameter that can be used in interpreting the origin of a band structure pseudogap often evident at the Fermi level for structurally complex metallic alloy phases. It can be expressed in terms of the interference condition $e/uc = \frac{\pi}{3}[|\boldsymbol{G}|^2_\mathrm{c}]^{3/2}$, where $|\boldsymbol{G}|^2_\mathrm{c}$ is the square of the *critical* reciprocal lattice vector associated with the specific set of lattice planes interfering with electrons at the Fermi level. This parameter is similar to the well-known Hume-Rothery electron concentration parameter e/a, which represents the number of electrons per atom and is linked with e/uc through the relation $e/uc = N(e/a)$. We have demonstrated that certain complex metallic alloy structures appear to be stable at or near certain values of e/a. We show that the $e/a = 1.60$ rule holds for the sub-group of gamma-brasses with space group $I\bar{4}3m$ and Pearson symbol $cI52$, the $e/a = 4.34$ rule for skutterudite compounds with $Im\bar{3}$ and $cI32$, the $e/a = 2.74$ rule for $\mathrm{Al_6TM}$ (TM = Mn, Tc, Re, Fe, and Ru) compounds with $Cmcm$ and $oC28$, the $e/a = 1.62$ rule for the sub-group of the Heusler compounds with $Fm\bar{3}m$ and $cF16$, and the $e/a = 2.09$ rule for the sub-group of Zintl compounds $\mathrm{MX_1}$ (M = Li and Na, $\mathrm{X_1}$ = Al, Ga, In, and Tl) with $Fd\bar{3}m$ and $cF32$. The e/a rule holds in sub-groups of isostructural compounds, regardless of the degree of orbital hybridizations and the polarity involved.

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1. Introduction

Since the nominal valences for the pure noble metals and some number of polyvalent elements have been known *a priori* already in the 1920s, one can relatively easily assign an average electrons per atom ratio e/a for many noble metal alloy phases simply by taking a composition average of nominal valences of constituent elements across the phase diagram. Thanks to it, Hume-Rothery and his contemporaries could establish the so-called Hume-Rothery electron concentration rule for noble metal alloys in the 1930s [1]. More recently, Tsai et al. [2–4] could successfully synthesize a series of the Mackey icosahedral MI-type quasicrystals in Al–Cu–TM (TM = Fe, Ru, and Os) and Al–Pd–TM (TM = Mn and Re) alloy systems by using the Hume-Rothery electron concentration rule as a guide. They claimed that they are stabilized at e/a nearly equal to 1.8, provided that the negative e/a values which Raynor proposed in 1949 [5] are assigned to the transition metal (TM) elements. However, the assignment of negative e/a values for TM elements has remained controversial. Indeed, it has become a central issue in metal physics why the e/a-dependent phase stabilization mechanism or the Hume-Rothery stabilization mechanism works even for TM containing compounds, where orbital hybridizations are significant. The effectiveness of the Hume-Rothery stabilization mechanism for a number of TM-bearing compounds including MI-type approximants to quasicrystals as well as the determination of reliable e/a values for 3d-, 4d- and 5d-TM elements has been recently established by making full use of the full-potential linearized augmented plane wave (FLAPW) Fourier method, as described below [6–11].

In the first-principles FLAPW electronic structure calculation method, the wave functions outside the muffin-tin (MT) spheres are expanded into plane waves over allowed reciprocal lattice vectors $\boldsymbol{G}$. By making full use of its formalism, Mizutani and coworkers [1, 6–11] have devised the FLAPW-Fourier method to extract FsBz (Fermi surface–Brillouin zone) interactions and to determine the e/a value for elemental solids as well as intermetallic compounds, regardless of whether a TM element is involved, or not. It was emphasized that the number of electrons per unit cell, e/uc, in place of e/a, plays a key role in justifying the interference condition $(2k_\mathrm{F})^2 = |\boldsymbol{G}|^2_\mathrm{c}$ or equivalently, $e/uc = \frac{\pi}{3}[|\boldsymbol{G}|^2_\mathrm{c}]^{3/2}$, where $(2k_\mathrm{F})^2$ is the square of the Fermi diameter and $|\boldsymbol{G}|^2_\mathrm{c}$ is the square of *critical* reciprocal lattice vector, which is defined such that the center of gravity energy in the energy dependence of the $|\boldsymbol{G}|^2$-wave at symmetry points of the Brillouin zone coincides with the Fermi level E_F. Indeed, the e/uc versus $|\boldsymbol{G}|^2_\mathrm{c}$ data for structurally complex metallic alloy (CMA) phases having a prominent pseudogap in

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*corresponding author; e-mail: uichiro@xa3.so-net.ne.jp the density of states (DOS) at E_F fall on a straight line with a slope of 3/2 on a log–log scale diagram [10]. This is taken as the validation of the Hume-Rothery stabilization mechanism, in which the pseudogap at E_F originates from the interference phenomenon mentioned above.

What about the role of e/a? The present work reports the FLAPW-Fourier analysis for a number of pseudogap CMAs to demonstrate that the e/a = constant rule for many CMAs *does* hold not only for noble metal alloys but also for TM-bearing compounds. We thus provide a consistent theoretical basis towards a comprehensive understanding of the Hume-Rothery e/a-rule.

2. Electronic structure calculations

FLAPW band calculations have been performed by employing the WIEN2k program package [12]. Our in-house Fortran90 Program has been devised to carry out the FLAPW-Fourier analysis by using the "case.output1" file generated by running WIEN2k [1, 6–11]. Briefly, the FLAPW-Fourier spectrum was constructed by plotting the energy dependence of the plane wave specified by the square of reciprocal lattice vector $|\boldsymbol{G}|^2$ in units of $(2\pi/a)^2$ for cubic systems or the sum of the Miller indices at selected symmetry points of the Brillouin zone. The $|\boldsymbol{G}|^2$-specified *critical* electronic state, i.e. $|\boldsymbol{G}|^2_c$, can be extracted as the one, in which the center of gravity of its energy spectrum coincides with E_F. The energy dispersion relation is also constructed for electrons outside the MT spheres. It is specifically called the Hume-Rothery plot, since it allows us to determine the square of the effective Fermi diameter $(2k_F)^2$ and the e/a value for each intermetallic compound studied [1, 6–11].

3. Results and discussions

The family of gamma-brasses with space group $I\bar{4}3m$ (or $P\bar{4}3m$) (or) and the Pearson symbol $cI52$ (or $cP52$) has been divided into three subgroups, depending on the combination of atomic species of constituent elements: (1) noble metals and polyvalent elements, (2) TM elements and polyvalent elements, and (3) monovalent Ag and Li [1, 11]. To begin with, we direct our attention to the Cu_5Zn_8 and Al_4Cu_9 gamma-brasses in the subgroup 1. They are characterized by a pseudogap at E_F and have already been proved to obey the Hume-Rothery stabilization mechanism with *critical* $|\boldsymbol{G}|^2 = 18$ and $e/a = 1.60$ [1]. We confirmed that the $e/a = 1.60$ rule is also justified for Ag_5Zn_8 and In_4Ag_9 gamma-brasses. In the case of the isostructural Al_8V_5 gamma-brass in the subgroup 2, however, we revealed that a *critical* $|\boldsymbol{G}|^2$ is increased to 22, appearing next to $|\boldsymbol{G}|^2 = 18$ at symmetry points N of the bcc Brillouin zone, and that $e/a = 2.19$ [11]. The pseudogap is masked by the V $3d$ states and is no longer found at E_F in its total DOS. Thus, the $e/a = 1.60 \pm 0.02$ rule holds in the subgroup 1 but not in the subgroups 2 and 3 [1, 11]. The data for the subgroup 1 gamma-brasses obeying the $e/a = 1.60$ rule are listed in Table.

TABLE

Numerical data relevant to the e/a = constant rule for different families of CMAs.

	System	N	$\|\boldsymbol{G}\|^2$	$(2k_F)^2$	e/a
gamma-brasses $I\bar{4}3m$, $cI52$ $P\bar{4}3m$, $cP52$ in subgroup 1	Cu_5Zn_8	52	18	18.5 ± 0.1	1.60 ± 0.02
	Ag_5Zn_8	52	18	18.5 ± 0.1	
	Al_4Cu_9	52	18	18.5 ± 0.1	
	In_4Ag_9	52	18	18.5 ± 0.1	
skutterudites $Im\bar{3}$, $cI32$	$CoAs_3$	32	26	25.2 ± 0.2	4.34 ± 0.20
	$RhAs_3$	32	26	26.3 ± 0.2	
	$IrAs_3$	32	26	26.7 ± 0.2	
	$CoSb_3$	32	26	26.5 ± 0.2	
	$RhSb_3$	32	26	27.3 ± 0.2	
	$IrSb_3$	32	26	27.8 ± 0.2	
	NiP_3	32	26	25.1 ± 0.2	
	CoP_3	32	26	25.0 ± 0.2	
	RhP_3	32	26	25.9 ± 0.2	
	IrP_3	32	26	26.7 ± 0.2	
Al_6TM $Cmcm$, $oC28$	Al_6Mn	28	17.4	17.3 ± 0.3	2.74 ± 0.05
	Al_6Tc	28	17.5	17.5 ± 0.3	
	Al_6Re	28	17.5	17.6 ± 0.3	
	Al_6Fe	28	17.5	17.5 ± 0.3	
	Al_6Ru	28	17.5	17.5 ± 0.3	
Heusler $Fm\bar{3}m$, $cF16$ in subgroup 1	Fe_2VAl	16	8	8.1 ± 0.3	1.62 ± 0.20
	Na_3As	16	8	8.8 ± 0.3	
	Li_3Sb	16	8	8.7 ± 0.2	
in subgroup 2	$AlTiAu_2$	16	11	11.5 ± 0.3	2.55 ± 0.10
Zintl $Fd\bar{3}m$, $cF32$ in subgroup 1	LiAl	32	16	16.3 ± 0.2	2.09 ± 0.06
	LiGa	32	16	16.0 ± 0.2	
	LiIn	32	16	15.8 ± 0.2	
	NaIn	32	16	16.0 ± 0.2	
	NaTl	32	16	16.0 ± 0.2	

We have extended our studies to the following families of compounds to examine whether the e/a = constant rule holds: ten skutterudite compounds with space group $Im\bar{3}$ and the Pearson symbol $cI32$, five Al_6TM (TM = Mn, Tc, Re, Fe, and Ru) compounds with $Cmcm$ and $oC28$, four Heusler compounds with $Fm\bar{3}m$ and $cF16$ and seven Zintl compounds MX_1 (M = Li, Na and X_1 = Al, Ga, In, and Tl) and MX_2 (M = Li and X_2 = Zn and Cd) with $Fd\bar{3}m$ and $cF32$. All structural information is available from the literature [13].

As the representative for the skutterudite compounds, the FLAPW-Fourier spectra at symmetry points N along with the total DOS and the Hume-Rothery plot for the $CoAs_3$ compound are depicted in Fig. 1a and b, respectively. A DOS pseudogap is clearly seen at the Fermi level. This is true for all skutterudite compounds studied. The Fourier coefficient $\sum |C_{\boldsymbol{k}+\boldsymbol{G}}|^2$ in each $|\boldsymbol{G}|^2$-specified wave remains finite at E_F over the range of $|\boldsymbol{G}|^2$ from 18 to 34 in $CoAs_3$ (see the definition of the Fourier coefficient in Refs. [1, 6–11]). Nevertheless, we find that the center of gravity energy coincides with E_F at $|\boldsymbol{G}|^2 = 26$, as highlighted with red color. From the Hume-Rothery plot shown in Fig. 1b, we can determine both $(2k_F)^2$ and e/a to be 25.2 ± 0.2 and 4.14 for $CoAs_3$, respectively. All the relevant data for skutterudite compounds are summarized in Table. We see that all of them are characterized by a common *critical* $|\boldsymbol{G}|^2_{\mathrm{c}} = 26$. Moreover, the values of $(2k_{\mathrm{F}})^2$ are distributed in the neighborhood of 26, satisfying the common interference condition. Therefore, we conclude that the $e/a = 4.34 \pm 0.20$ rule holds for all skutterudite compounds.

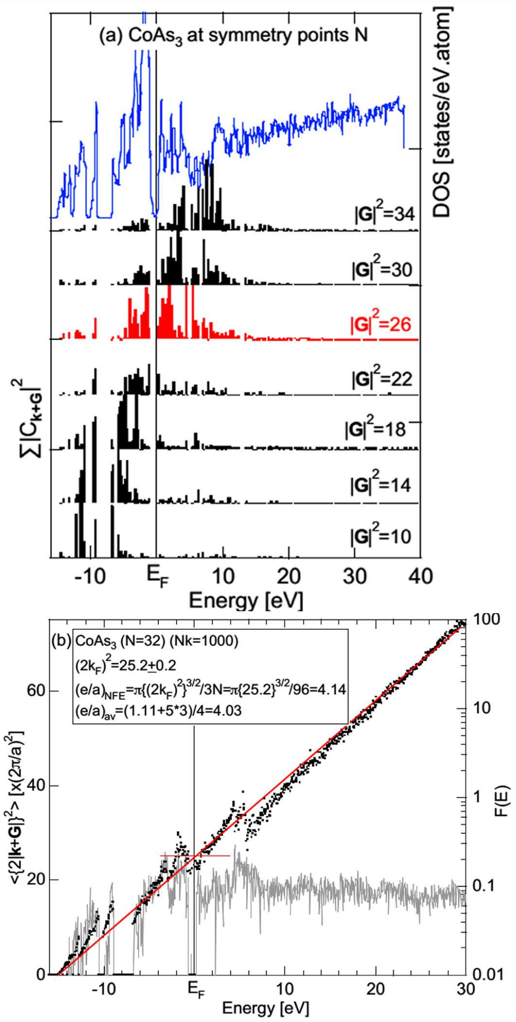

Fig. 1. FLAPW-Fourier spectra (a) at symmetry points N for skutterudite compound $\mathrm{CoAs_3}$ along with its total DOS. The *critical* states are drawn in red. (b) Hume-Rothery plot for $\mathrm{CoAs_3}$. $(e/a)_{\mathrm{av}} = 4.03$ is obtained by taking a composition average of $(e/a)_{\mathrm{Co}} = 1.11$ [5] and $(e/a)_{\mathrm{As}} = 5.0$.

The FLAPW-Fourier spectra and Hume-Rothery plot for the $\mathrm{Al_6Mn}$ and $\mathrm{Al_6Re}$ compounds were already reported elsewhere [11]. As listed in Table for a series of $\mathrm{Al_6TM}$ compounds, the *critical* $|\boldsymbol{G}|^2$ is distributed in the vicinity of 17.5 and the $e/a = 2.74 \pm 0.05$ rule holds well.[†] It is emphasized that the e/a value deduced for the respective compounds can be well reproduced by taking a composition average of e/a values of constituent elements Al and TM [9, 10].

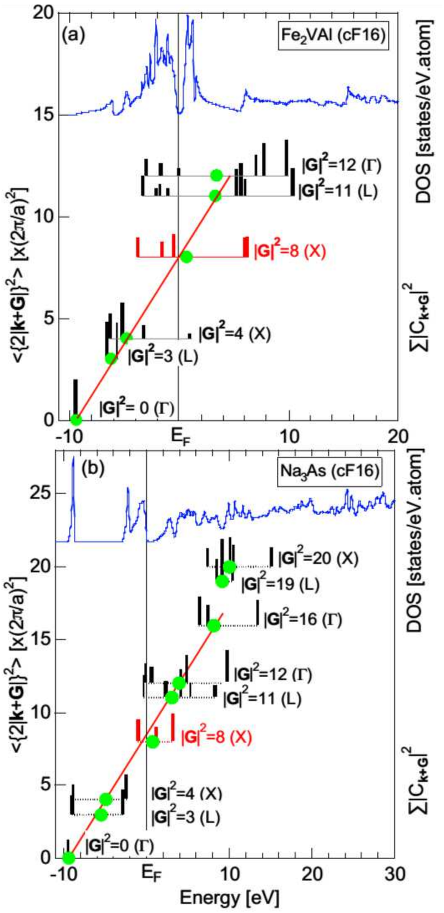

Fig. 2. FLAPW-Fourier spectra at symmetry points N along with its total DOS for the Heusler-type compounds (a) $\mathrm{Fe_2VAl}$ and (b) $\mathrm{Na_3As}$. The center of gravity energy in each $|\boldsymbol{G}|^2$-specified wave is marked with green solid circles. The red line is drawn to pass through the center of gravity energy. The *critical* $|\boldsymbol{G}|^2$ state is highlighted with red color. Its value is commonly deduced to be 8 for both compounds.

Let us now turn our attention to the e/a-rule for the Heusler-type compounds with space group $Fm\bar{3}m$ and Pearson symbol $cF16$. According to Pearson's handbook [13], there are more than 350 compounds belonging to this family. Some of them possess either a true gap or a pseudogap at the Fermi level, while others do not, indicating the existence of diversified stabilization mechanisms in this family. In the present work, we focus only

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[†] In an orthorhombic crystal with lattice constants a, b, and c, $|\boldsymbol{G}|^2$ is expressed as $\left[\left(\frac{bc}{a^2}\right)^{2/3} h^2 + \left(\frac{ca}{b^2}\right)^{2/3} k^2 + \left(\frac{ab}{c^2}\right)^{2/3} l^2\right]$ in units of $\left(\frac{2\pi}{V_o^{1/3}}\right)^2$, where $V_0 = abc$ is the volume of the unit cell and (hkl) is the set of the Miller indices. Hence, the value of $|\boldsymbol{G}|^2$ becomes dependent on lattice constants.

on the gap systems, since its origin can be discussed in terms of the interference condition or Hume-Rothery stabilization mechanism.

Figure 2a and b shows the FLAPW-Fourier spectra at symmetry points Γ, L, and X along with the total DOS for the compounds Fe_2VAl and Na_3As, respectively. The center of gravity energy for each $|\boldsymbol{G}|^2$-specified wave is marked with green solid circles. It is clear that $|\boldsymbol{G}|^2 = 8$ can be commonly extracted as being *critical* in both compounds. As is listed in Table, Fe_2VAl, Na_3As, and Li_3Sb compounds are proved to possess common electronic parameters: *critical* $|\boldsymbol{G}|^2 = 8$ and $e/a = 1.62 \pm 0.20$. The pseudogap compound $AlTiAu_2$ belongs to this family having the next higher *critical* $|\boldsymbol{G}|^2$, that is, 11. Its e/a value is stepwise increased to 2.55 ± 0.10. Thus, we can say that Fe_2VAl, Na_3As, and Li_3Sb compounds belong to the subgroup 1 and that $AlTiAu_2$ to the subgroup 2 in the family of the Heusler-type compounds.

Finally, we focus on the Zintl compounds MX_1 (M = Li and Na, X_1 = Al, Ga, In, and Tl) and MX_2 (M = Li and X_2 = Zn and Cd) with space group $Fd\bar{3}m$ and Pearson symbol $cF32$. All of them are known to exhibit a strong ionic bonding tendency among constituent elements. For example, a complete charge transfer occurs from Na to Tl in NaTl and results in ionic bonding Na^+Tl^-. As a result, $[Tl^-]$ behaves as if it has 4 valence electrons and forms a covalent diamond structure together with Na^+ cations stuffing the lattice. It is highly interesting to study whether the e/a rule holds in such polar compounds.

As summarized in Table, a *critical* $|\boldsymbol{G}|^2$ is commonly deduced to be 16 and values of $(2k_F)^2$ are distributed in the vicinity of 16 for the MX_1 compounds. The $e/a = 2.09 \pm 0.06$ rule is revealed in the subgroup 1 of the Zintl compounds consisting of alkali metals and trivalent elements. The nominal e/a value calculated from a composition average of valences of constituent elements is obviously two. A *critical* $|\boldsymbol{G}|^2$ is stepwise decreased to 12 but a pseudogap is no longer present at the Fermi level in the subgroup 2 of the Zintl compounds MX_2. Thus, we can say that the $e/a = 2.09 \pm 0.06$ rule holds in the subgroup 1 of the Zintl compounds. It is more important to emphasize that the e/a = constant rule is justified, regardless of the degree of ionicity and polarity.

4. Summary

We could lay down a theoretical foundation for the e/a rule in the family of isostructural compounds using the following conditions as a guide. First, the isostructural compounds are defined as those belonging to a given space group and the Pearson symbol. The number of atoms per unit cell is thus the same. In the case of I-type compounds with bcc lattice, for example, successively appearing $|\boldsymbol{G}|^2$ s at symmetry points N of its Brillouin zone are common: 2, 6, 10, 14, 18, 22, 26, 30, 34 ... corresponding to {110}, {211}, {310}, {321}, {330}+{411} etc. Hence, *critical* $|\boldsymbol{G}|^2_c$ must be selected from such discrete sets of $|\boldsymbol{G}|^2$ series. Moreover, the interference condition $(2k_F)^2 = |\boldsymbol{G}|^2_c$ is imposed for a pseudogap system. As a result, compounds obeying the e/a rule can be extracted as a subgroup of isostructural compounds, where a common *critical* $|\boldsymbol{G}|^2_c$ is assigned in the presence of the interference condition, thereby guaranteeing the possession of identical $(2k_F)^2$ and e/a value. It may be worthwhile noting that the common e/a does not exist between the Na–Au–Ga and Al–Mg–Zn isostructural compounds [14] but that their respective e/a values are determined through *different critical* $|\boldsymbol{G}|^2_c$ selected from the same series of allowed $|\boldsymbol{G}|^2$ s. Thus, they belong to different subgroups in the family of isostructural compounds, as has been emphasized in the present article.

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References

[1] U. Mizutani, *Hume-Rothery Rules for Structurally Complex Alloy Phases*, CRC Press Taylor &Francis Group, Boca Raton 2010.

[2] A.P. Tsai, A. Inoue, T. Masumoto, *Jpn. J. Appl. Phys.* **27**, L1587 (1988).

[3] A.P. Tsai, A. Inoue, Y. Yokoyama, T. Masumoto, *Mater. Trans. Jpn. Inst. Met.* **31**, 98 (1990).

[4] Y. Yokoyama, A.P. Tsai, A. Inoue, T. Masumoto, H.S. Chen, *Mater. Trans. Jpn. Inst. Met.* **32**, 421 (1991).

[5] G.V. Raynor, *Prog. Met. Phys.* **1**, 1 (1949).

[6] M. Inukai, E.S. Zijlstra, H. Sato, U. Mizutani, *Philos. Mag.* **91**, 4247 (2011).

[7] U. Mizutani, M. Inukai, H. Sato, E.S. Zijlstra, *Philos. Mag.* **92**, 1691 (2012).

[8] U. Mizutani, M. Inukai, H. Sato, E.S. Zijlstra, *Chem. Soc. Rev.* **41**, 6799 (2012).

[9] H. Sato, M. Inukai, E.S. Zijlstra, U. Mizutani, *Philos. Mag.* **93**, 3029 (2013).

[10] U. Mizutani, H. Sato, M. Inukai, E.S. Zijlstra, *Philos. Mag.* **93**, 3353 (2013).

[11] U. Mizutani, M. Inukai, H. Sato, E.S. Zijlstra, in: *Physical Metallurgy* 5th ed., Eds. K. Hono, D. Laughlin, Elsevier, Amsterdam 2013, p. 1.02.

[12] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, J. Luitz, *WIEN2k*, (last accessed on August 30, 2013).

[13] P. Villars, *Pearson's Handbook, Crystallographic Data*, ASM, Materials Park, OH 1997.

[14] U. Mizutani, H. Sato, M. Inukai, E.S. Zijlstra, Q. Lin, J.D. Corbett, G.J. Miller, *Acta Phys. Pol. A* **126**, 535 (2014).