Fermi Surface–Brillouin Zone Interactions in 2/1-2/1-2/1 Bergman-Type Approximant $\text{Na}_{27}\text{Au}_{27}\text{Ga}_{31}$

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The X-ray diffraction studies on a newly synthesized $\text{Na}_{26}\text{Au}_{25}\text{Ga}_{29}$ single crystal revealed the formation of a single phase 2/1-2/1-2/1 Bergman-type approximant and the presence of Au/Ga mixed occupancies in its unit cell containing 680 atoms. The structure model of the 2/1-2/1-2/1 approximant with composition $\text{Na}_{27}\text{Au}_{27}\text{Ga}_{31}$ was constructed by eliminating the chemical disorder with a minimum sacrifice of composition displacement. The full potential linearized augmented plane wave electronic structure calculations with subsequent full potential linearized augmented plane wave-Fourier analysis were performed for the 2/1-2/1-2/1 approximant $\text{Na}_{27}\text{Au}_{27}\text{Ga}_{31}$ with space group $Pa\bar{3}$. The square of the Fermi diameter $(2k_F)^2$, electrons per atom ratio e/a and the critical reciprocal lattice vector $|\mathbf{G}|^2$ are determined. A shallow pseudogap at the Fermi level was interpreted as originating from interference of electrons having $(2k_F)^2 = 109.2 \pm 1.0$ with sets of lattice planes with $|\mathbf{G}|^2$'s centered at 108. The effective e/a value for the compound is found to be 1.76 in good agreement with 1.73 derived from a composition average of $(e/a)_{\text{Na}} = 1.0$, $(e/a)_{\text{Au}} = 1.0$ and $(e/a)_{\text{Ga}} = 3.0$.

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1. Introduction

Through systematic exploration of the Na–Au–Ga system, Lin and his coworkers have discovered a series of structurally complex metallic alloy (CMA) phases including an icosahedral quasicrystal $\text{Na}_{13}\text{Au}_{12}\text{Ga}_{15}$, an orthorhombic approximant $\text{Na}_{32}\text{Au}_{38}\text{Ga}_{30}$, two structurally related Bergman-type 1/1-1/1-1/1 approximants $\text{Na}_{26}\text{Au}_{36}\text{Ga}_{19}$ and $\text{Na}_{26}\text{Au}_{18}\text{Ga}_{36}$ and the Bergman-type 2/1-2/1-2/1 approximant $\text{Na}_{26}\text{Au}_{25}\text{Ga}_{29}$ [1, 2]. By studying the total crystal orbital Hamilton population (COHPs) in the framework of linear muffin-tin (MT) orbital in the atomic sphere approximation (LMTO-ASA) band calculations, they pointed out the presence of strong covalent bonding in both Ga–Au and Na–Au interactions in the model 1/1-1/1-1/1 approximant $\text{Na}_{26}\text{Au}_{24}\text{Ga}_{30}$ and took it as a characteristic feature of the polar intermetallics in spite of the possession of low electrons per atom ratio e/a equal to 1.75. It is, therefore, of great interest to investigate whether the Hume-Rothery stabilization mechanism is effective in such polar CMAs.

Mizutani and coworkers [3–8] employed first-principles full potential linearized augmented plane wave (FLAPW) electronic structure calculations and established a powerful technique to extract Fermi surface-Brillouin zone (FsBz) interactions associated with the interference phe-

nomenon and to determine the e/a value for elements and intermetallic compounds, regardless of whether a transition metal (TM) element is involved or not. They have made full use of its formalism, in which the wave functions outside the MT spheres are expanded into plane waves over allowed reciprocal lattice vectors $\mathbf{G}$.

Prior to the discovery of the Bergman-type 2/1-2/1-2/1 approximant $\text{Na}_{26}\text{Au}_{25}\text{Ga}_{29}$, Lin and Corbett [9] had already identified the $\text{Mg}_{27}\text{Al}_{10.7}\text{Zn}_{47.3}$ compound to be a Bergman-type 2/1-2/1-2/1 approximant with space group $Pa\bar{3}$. Encouraged by their pioneering work, we could refine the crystallographic data for the 2/1-2/1-2/1 approximant $\text{Na}_{26}\text{Au}_{25}\text{Ga}_{29}$ from both powder and single crystal X-ray diffraction studies. After constructing its model structure free from chemical disorder, the FLAPW band calculations with the subsequent FLAPW-Fourier analysis was performed. To the best of our knowledge, first-principles FLAPW band calculations have been carried out for the first time for a 2/1-2/1-2/1 approximant.

2. Atomic structure determinations and electronic structure calculations

It was revealed that the $\text{Na}_{26}\text{Au}_{25}\text{Ga}_{29}$ compound crystallizes into a Bergman-type 2/1-2/1-2/1 approximant containing 680 atoms per unit cell with space group $Pa\bar{3}$ and lattice constant of 23.446 Å. A structure refinement led us to conclude that the compound is free from chemical disorder except for Au/Ga mixed site occupancies. To facilitate FLAPW band calculations, we constructed the model structure $\text{Na}_{27}\text{Au}_{27}\text{Ga}_{31}$ by eliminating the Au/Ga chemical disorder from the refined

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crystallographic data, which will be reported elsewhere.

FLAPW band calculations have been performed by employing the commercially available WIEN2k program package [10] with INTEL version Linux personal computers. The WIEN2k was run by using the cut-off parameter $R_{MT}K_{max} = 5.8$ and 6.2 , which determines the number of basis functions or size of the matrices, and the number of meshes, $N_k = 216$ for $Na_{27}Au_{27}Ga_{31}$. Our in-house Fortran90 Program was employed to carry out the FLAPW-Fourier analysis by using the “case.output1” file generated by running WIEN2k [3–8]. Briefly, the FLAPW-Fourier spectrum represents the energy dependence of the square of the Fourier coefficient of the plane wave specified by the square of reciprocal lattice vector $|\mathbf{G}|^2$ in units of $(2\pi/a)^2$ at selected symmetry points of the Brillouin zone. One can extract electronic states dominating at the Fermi level from the energy spectrum. The $|\mathbf{G}|^2$ thus extracted is called *critical*. As another tool, the energy dispersion relation is constructed for electrons outside the MT spheres. We specifically call it the Hume-Rothery plot, since it allows us to determine the square of the effective Fermi diameter $(2k_F)^2$ and e/a values for each intermetallic compound studied [3–8].

3. Results and discussions

The total DOS for $Na_{27}Au_{27}Ga_{31}$ is shown in Fig. 1a and b, where ordinates are shown on linear and logarithmic scales, respectively. As guided by a dotted line in Fig. 1b, a shallow pseudogap becomes noticeable and is found to be widely spread over -2 to $+3$ eV across the Fermi level E_F .

A DOS pseudogap is hardly seen on linear scales. The DOS profile is very similar to that reported for the Bergman-type 1/1-1/1-1/1 model approximant $Na_{26}Au_{24}Ga_{30}$ [1, 2].

Fig. 1. The total DOS for the 2/1-2/1-2/1 approximant $Na_{27}Au_{27}Ga_{31}$ on (a) the linear and (b) logarithmic scale for the ordinate. Dotted lines drawn in (b) are guide to the eye.

Fig. 2. (a) Na-, (b) Au- and (c) Ga-partial DOS of the 2/1-2/1-2/1 approximant $Na_{27}Au_{27}Ga_{31}$.

The Na-, Au- and Ga-partial DOSs in $Na_{27}Au_{27}Ga_{31}$ are shown in Fig. 2–c, respectively. A peak is found across E_F in the Ga-4p partial DOS. This is nothing but the formation of the anti-bonding Ga-4p states as a result of orbital hybridizations with Au-5d states. This explains why the DOS pseudogap minimum at E_F is masked and lends support to the presence of strong covalent Au–Ga bonding [1, 2]. Now the origin of the shallow pseudogap is discussed in terms of FbZ interactions by constructing both FLAPW-Fourier spectrum and the Hume-Rothery plot.

Figure 3 shows the FLAPW-Fourier spectra at symmetry points X , Γ and R over the range $|\mathbf{G}|^2 = 90$ to 129 along with the total DOS for the 2/1-2/1-2/1 approx-

imant $Na_{27}Au_{27}Ga_{31}$. One can immediately find that the center of gravity energy marked with green circles meets the Fermi level for LAPW waves of $|\mathbf{G}|^2 = 108$ at symmetry point Γ . More important is the fact that the Fourier coefficients remain finite at the Fermi level over a wide range of $|\mathbf{G}|^2$ from 96 to 126. This is taken as the evidence for the participation of *multi-zones* in the interference phenomenon and also for the development of spatially localized polar interactions. Among them, $|\mathbf{G}|^2 = 108$ can be selected to be *critical*. It is emphasized that *multi-zone* effects are commonly observed in CMAs with a giant unit cell like the RT-type Al-Mg-Zn 1/1-1/1-1/1 approximant and that only a shallow and widely spread pseudogap is formed [3, 4, 6].

Fig. 3. FLAPW-Fourier spectrum at symmetry points X , Γ , and R for the 2/1-2/1-2/1 approximant $\text{Na}_{27}\text{Au}_{27}\text{Ga}_{31}$. The total DOS is superimposed. The circle indicates the center of gravity energy in each $|\mathbf{G}|^2$ -specified wave. The line connecting circles is drawn as guide to the eye.

Figure 4a shows the energy dependence of $\langle |\sum_{\mathbf{k}+\mathbf{G}} |\mathbf{C}_{\mathbf{k}+\mathbf{G}}|^2 \rangle_E$ or briefly $\langle |\mathbf{C}|_{\text{max}}^2 \rangle_E$, which represents the square of the maximum Fourier coefficient extracted from wave functions outside the MT spheres on a given energy surface $E(\mathbf{k}) = E$ [6]. The summation is taken over all $\mathbf{k}_j$ meshes ($1 \leq k_j \leq N_{\mathbf{k}}$) in the Brillouin zone. Its value at the Fermi level, $\langle |\mathbf{C}|_{\text{max}}^2 \rangle_{E_F}$ may be used as a measure to judge the itinerancy of electrons at the Fermi level. Electrons at the Fermi level are regarded as being itinerant, if $\langle |\mathbf{C}|_{\text{max}}^2 \rangle_{E_F} > 0.1$ [6]. The value for $\text{Na}_{27}\text{Au}_{27}\text{Ga}_{31}$ turns out to be 0.035, indicating that electrons at the Fermi level are highly immobile in spite of the shallow pseudogap.

The Hume-Rothery plot and its non-dimensional standard deviation $F(E)$ [6] for $\text{Na}_{27}\text{Au}_{27}\text{Ga}_{31}$ are shown in Fig. 4b. The data points should fall on a straight line in the free electron model. An anomaly over -6 to -3 eV reflects the localized Au-5d band. Except for the range of the Au-5d band, the data points are found to fall on a straight line, in particular, across E_F , as indicated in Fig. 4b. The square of the Fermi diameter $(2k_F)^2$, in units of $(2\pi/a)^2$, can be read off from the intersection with E_F and deduced to be 109.2 ± 1.0 . The application of the so called tetrahedron method, while taking the center of gravity energy in the energy distribution of the FLAPW-Fourier spectrum, has enabled us to determine the value accurately in the presence of the d-band anomaly in the Hume-Rothery plot [7]. In the present case, it is found to be 109.0 ± 1.0 , a result that is in a

Fig. 4. (a) Energy dependence of $\langle |\mathbf{C}|_{\text{max}}^2 \rangle$ and (b) Hume-Rothery plot for the 2/1-2/1-2/1 approximant $\text{Na}_{27}\text{Au}_{27}\text{Ga}_{31}$. Dots in (b) represent the data points satisfying the condition $\sum |\mathbf{C}_{\mathbf{k}+\mathbf{G}}|^2 > 0.1$ [7]. $F(E)$ in (b) represents non-dimensional standard deviation [6].

good agreement with the local reading value mentioned above.

It is clear that the interference condition $(2k_F)^2 = |\mathbf{G}|^2$, which plays a key role in the formation of a pseudogap at the Fermi level, is well satisfied, since $(2k_F)^2 = 109.2$ agrees well with the critical $|\mathbf{G}|^2 = 108$ mentioned above. We believe that the origin of the pseudogap across the Fermi level can be well explained in terms of FsBz interactions even in such polar intermetallics. As emphasized above, however, zones over $|\mathbf{G}|^2$ from 96 to 126 are all participating in the interference phenomenon with electrons at the Fermi level. We consider *multi-zone* effects to be highly intensified as a result of the polar interactions between Au and Ga atoms and to be responsible for the formation of a widely spread shallow pseudogap in the 2/1-2/1-2/1 approximant $\text{Na}_{27}\text{Au}_{27}\text{Ga}_{31}$. It would be highly interesting to construct the FLAPW-Fourier spectrum for the isostructural but less polar 2/1-2/1-2/1 approximant Al-Mg-Zn in order to study the effect of the polarity on the degree of *multi-zone effects*. As stated in Introduction, its atomic structure information is available in the literature [9].

The effective e/a value can be immediately calculated by inserting $(2k_F)^2$ obtained above into $e/a = \left\{ \pi [(2k_F)^2]^{3/2} \right\} / (3N)$, where N is the number of atoms per unit cell and is equal to 680. It turns out to be 1.76 in good agreement with 1.73 obtained by taking a composition average of the well-established atomic values $(e/a)_{\text{Na}} = (e/a)_{\text{Au}} = 1.0$ and $(e/a)_{\text{Ga}} = 3.0$ [7, 8]. Hence, we can say that the strong polarity in the 2/1-