Structure-Induced Covalent Bonding in Al-Li Compounds

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Formation mechanism of a deep pseudogap in the electronic density of states of the Al-Li Bergman and Zintl compounds is discussed with an emphasis on the differences among isostructural Al-Mg compounds. Since Li scatters electrons very weakly in comparison with Al and Mg, the potential landscape for electrons in Al-Li compounds is not that of the entire close-packed structure but that of the Al sublattice, which is a rather porous network like the diamond lattice. The porous network structure realized by the chemical decoration of close-packed structures enhances the covalent nature of electronic structures, hence the deep pseudogap in the electronic density of states. A concept of structure-induced covalent bonding in a network realized by the chemical decoration of close-packed structures may provide a novel picture in the electronic structures of complex intermetallic compounds.

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The discovery of quasicrystal (QC) is one of the most prominent discoveries in condensed matter physics in the last century [1]. It disproved the established theory that fivefold symmetry is incompatible with strong Bragg reflections and brought us a new aspect of nature. Quasicrystal has been obtained so far in more than 100 alloys and is recognized as a universal phase of matter [2]. Stable QCs are obtained by controlling the average number of the valence electrons per elements. This suggests that the system is stabilized electronically. Electronic structure calculations based on the density-functional method revealed that a pseudogap appears universally in the electronic density of states (DOS) of QC-related compounds and the Fermi energy is located at the pseudogap. The formation mechanism of the pseudogap is thus considered as a cohesion mechanism of QCs and has been discussed by many authors [3].

As the formation mechanism of the pseudogap, the Brillouin-zone (BZ) Fermi-sphere (FS) interaction [the Hume-Rothery (HR) mechanism] was proposed and widely accepted [4]. In the nearly free-electron model, a strong interference of electronic waves with wave vectors $\mathbf{k}$ and $\mathbf{k}+\mathbf{G}$ leads to splitting of energy bands at the zone boundary, $\mathbf{k}=\mathbf{G}/2$, where $\mathbf{G}$ is a reciprocal-lattice vector giving strong Bragg scattering. Because of the sphericity of distribution of the reciprocal-lattice vectors in QC, the interference effect induces very effectively a pseudogap in the electronic DOS. When the Fermi wave number k_F satisfies $k_F \approx |\mathbf{G}|/2$, the Fermi energy is located at the pseudogap.

The scattering potential for electrons can be expanded in Fourier series as $V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$. The Fourier component is divided into structure and form factors for individual atomic species as

$$V_{\mathbf{G}} = \sum_{\alpha} \rho_{\mathbf{G}}^{(\alpha)} v_{\mathbf{G}}^{(\alpha)}, \tag{1}$$

where α denotes an atomic species. The structure and form factors are defined as

$$\rho_{\mathbf{G}}^{(\alpha)} = \sum_{i} e^{-i\mathbf{G}\cdot\mathbf{R}_i}, \tag{2}$$

$$v_{\mathbf{G}}^{(\alpha)} = \frac{1}{V}\int d\mathbf{r}\, v_{\alpha}(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}}, \tag{3}$$

where $v_{\alpha}(\mathbf{r})$ is a pseudopotential for the atomic species α. Summation is taken over atomic positions for the α atom and integration is carried out over the entire volume V of the system. The structure factors represent geometric effects whereas the form factors represent chemical effects.

In the most naive application of the HR idea, the electronic structure is treated within a rigid-band model where a drastic change in the atomic form factor or pseudopotential is primarily neglected. Effects of alloying are considered only through a change in the number of valence electrons. In this sense, the HR mechanism is interpreted as of geometric origin and depends only on the structure factor. This picture might be justified for Cu-Zn alloys where constituent elements are very similar. However, in alloys of elements with different chemical natures, the atomic form factor plays an essential role. For example, for a cubic Cd_6M alloy, which is an approximant crystal of the Cd-based QCs, a shallow pseudogap appears near the Fermi energy for $M = \mathrm{Yb}$ and Ca whereas a free-electron-like DOS without distinct gap is obtained for $M = \mathrm{Mg}$ [5]. This is due to the difference in the atomic form factors of Yb or Ca and Mg.

The HR idea, as the unique general theory predicting phase stability of intermetallic compounds, has been applied widely to various systems, even to QC and QC-

TABLE I. Atomic positions and site occupation of Bergman alloys. Atomic positions are those given for Al-Cu-Li [10].

Site	Wyckoff symbol	x	y	z	Al-Cu-Li [10]	Al-Zn-Mg [11]
	$2a$	0	0	0		(Al)
Al(1)	$24g$	0	0.0944	0.1544	Al/Cu	Al/Zn
Li(1)	$16f$	0.1874	0.1874	0.1874	Li	Mg
Li(2)	$24g$	0	0.3047	0.1171	Li	Mg
Al(2)	$24g$	0	0.1802	0.3150	Al/Cu	Al/Zn
Al(3)	$48h$	0.1574	0.1896	0.4059	Al/Cu	Al/Zn
Al(4)	$12e$	0.4037	0	0.5	Al	Mg
Li(3)	$12e$	0.1985	0	0.5	Li	Mg

related compounds, for which the covalent nature of electronic states is considered to be very essential [6–8]. However, as mentioned above, naive application of the HR idea is not appropriate for some families of QC-related compounds. It would be desirable to check applicability of the HR idea and to develop an alternative concept which is more relevant to the systems with a strong covalent nature. In this Letter, we shall discuss an interplay of the chemical effect (the atomic form factor) and the geometric effect (the structure factor) in the pseudogap formation in Al-based compounds. We shall compare the electronic structures of isostructural compounds, where the atomic form factors are different. Most of the results shown in this Letter are obtained by using the tight-binding linear muffin-tin orbitals (TBLMTO) method in the atomic sphere approximation [9].

A cubic approximant of Al-Cu-Li QC is known as R phase [10] and is isostructural to $(\mathrm{Al},\mathrm{Zn})_{49}\mathrm{Mg}_{32}$ Bergman phase [11], which is a typical Frank-Kasper alloy with tetrahedrally close-packed structure. The structure of the R or Bergman phase is interpreted as a body-centered packing of an atomic cluster with an icosahedral shape (Bergman cluster). The space group is $Im\bar{3}$ and a lattice constant is 13.91 and 14.16 Å for Al-Cu-Li [10] and Al-Zn-Mg [11], respectively. Structural data are given in Table I. The electronic structure of the R phase of Al-Cu-Li was investigated by Fujiwara and Yokokawa [12]. They found that a deep pseudogap appears near the Fermi energy and the substitution of Al or Cu controls the number of valence electrons to adjust the Fermi energy at the minimum of the DOS. It is reasonable to consider that fractional occupation denoted as Al/Zn in Table I for Al-Zn-Mg also contributes to controlling the valence electron number.

We calculate the electronic DOS for hypothetical binary models $\mathrm{Al}_{108}M_{52}$ ($M = \mathrm{Li}$, Mg) by the TBLMTO method. A model structure is constructed by placing Al atoms at all the Al and Al/Cu sites and Li/Mg atoms at the Li sites in Al-Cu-Li. In the Bergman Al-Zn-Mg, the Al(3) sites are occupied by Mg, but we place Al atoms here. The 2a site is assumed to be empty. The lattice constants are taken as 13.91 Å for Al-Li and 14.16 Å for Al-Mg. Note that the hypothetical binary alloys are isostructural except for the lattice constants and the structure factors are absolutely the same.

The results are shown in Fig. 1. A distinct pseudogap appears near the Fermi energy for Al-Li whereas there is only a shallow dip in Al-Mg. The position of the pseudogap seems consistent with an assumption that the interference of electronic waves with $\mathbf{k}$ and $\mathbf{k} + \mathbf{G}$ causes splitting of the energy bands at zone boundaries where $\mathbf{G}$ is the reciprocal-lattice vector giving strong Bragg scattering. In Table II, we show values of the structure factors with $1.6\ \mathrm{a.u.}^{-1} < |\mathbf{G}| < 1.75\ \mathrm{a.u.}^{-1}$ for the binary model where values of $|\mathbf{G}|$ are calculated with the lattice constant of Al-Cu-Li. One can see that the large structure factor is obtained for the reciprocal vectors indexed as (631), (354)/(710) and (460), which may lead to a pseudogap at 10 eV above the valence band bottom. However, the pseudogap is not caused entirely by the strong structure factor because the electronic structures are considerably different for the isostructural Al-Li and Al-Mg. Thus, we conclude that the

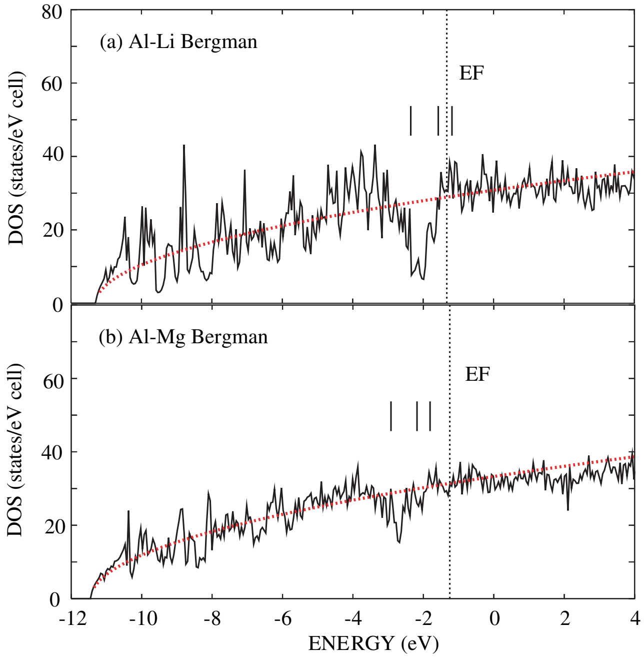

FIG. 1 (color online). The DOS for binary Bergman Al-Li (a) and Al-Mg (b) compounds together with the free-electron DOS (red dotted curve). Bars indicate positions of $\frac{\hbar^2}{2m}(\frac{\mathbf{G}}{2})^2$ with $\mathbf{G} =$ (631), (354)/(710) and (460).

TABLE II. Structure factors for binary Bergman alloy $Al_{108}Li_{52}$.

(LMN)	$\lvert\mathbf{G}\rvert$[a.u.$^{-1}$]	$\frac{\hbar^2}{2m}(\frac{\mathbf{G}}{2})^2$ [eV]	$\rho_{\mathbf{G}}^{(\mathrm{Al})}$	$\rho_{\mathbf{G}}^{(\mathrm{Li})}$
(361)	1.62	8.95	−0.697	0.743
(631)	1.62	8.95	25.0	−3.21
(444)	1.66	9.34	2.63	−0.654
(534)	1.69	9.73	10.7	1.44
(354)	1.69	9.73	18.4	−3.71
(550)	1.69	9.73	1.86	0.817
(170)	1.69	9.73	−8.70	4.09
(710)	1.69	9.73	17.0	−3.00
(460)	1.72	10.1	−17.1	0.993
(640)	1.72	10.1	6.01	1.01

atomic form factor plays an essential role in the pseudogap formation in this system.

A family of intermetallic compounds of alkali-metal (or sometimes alkaline-earth-metal) and post-transition elements is known as the Zintl phase [13]. The Al-Li Zintl compound has the NaTl (B32) structure, which is described as two interpenetrating diamond sublattices with a lattice constant 6.38 Å [14]. In Fig. 2(a), we show the electronic DOS for the Al-Li Zintl phase. One can see very similar band structure to that of the Si diamond. If one assumes that an electron is transferred from electropositive Li to electronegative Al [13,15], Al has four valence electrons per atom and then a tetrahedrally bonded diamond network of Al atoms gives the electronic bands, which are very similar to the Si diamond. The first-principles calculations, however, proved that such charge transfer is not realized in Al-Li [16,17].

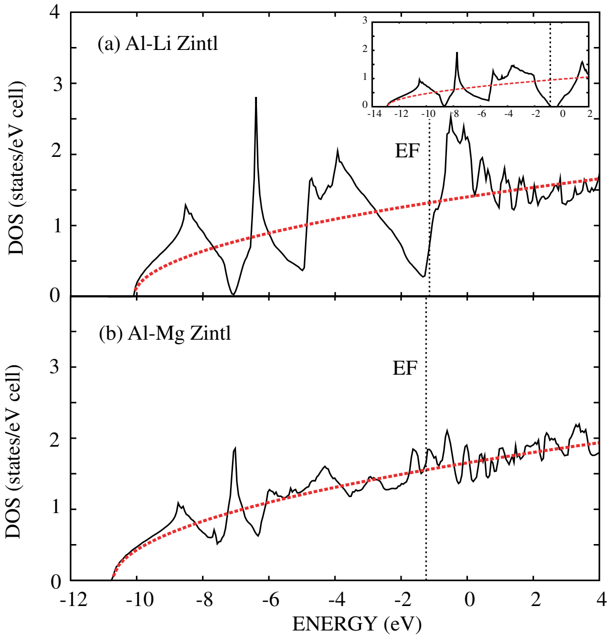

FIG. 2 (color online). The DOS for Zintl Al-Li (a) and Al-Mg (b) compounds together with the free-electron band (red dotted curve). An inset shows the DOS for diamond Si.

It is interesting to compare the Zintl Al-Li with a hypothetical Al-Mg compound with the same structure. The optimal lattice constant for Al-Mg is determined as 6.66 Å. We show the electronic DOS for the hypothetical Al-Mg in Fig. 2(b) together with those for the free-electron model. The DOS of the Al-Mg are very similar to that of the free electrons and no distinct pseudogap appears at all. Again the Al-Li Zintl compound and the present hypothetical Al-Mg are completely isostructural and the different electronic structures come from the difference in the atomic form factors.

In Fig. 3, the atomic form factors for Al, Li, and Mg are shown. Here we estimate the Fourier transform of pseudopotentials as a matrix element $\langle \mathbf{k} + \mathbf{G} | V_{\mathrm{TM}} | \mathbf{k} \rangle$ with $\mathbf{k} = \mathbf{0}$ and V_{TM} being Troullier-Martins nonlocal pseudopotential [18]. A diverging component at $\mathbf{G} \to \mathbf{0}$ comes from a long-range attractive Coulomb potential due to a core ion but is suppressed by screening [19]. For the shorter wavelength components at $G > 0.5$ a.u.$^{-1}$, one can see that the atomic form factor of Mg is very similar to that of Al whereas that of Li is considerably weaker. This suggests the Li is a weak scatterer of electrons and behaves like a vacant site but Mg scatters electrons similarly to Al. Thus, in the Al-Li Zintl compound, electrons are scattered mainly by the Al sublattice with the diamond structure and the electronic structure similar to that in the Si diamond is obtained. In the isostructural Al-Mg compound, electrons are scattered by both of the Al and Mg sublattices, which form a body-centered cubic (bcc) lattice altogether, and the electronic structure similar to that in the bcc lattice is obtained. In other words, the potential landscape for electrons is that which is in the diamond lattice for the Al-Li case but it is that which is in the close-packed bcc structure for the Al-Mg case. These different potential landscapes come from the difference in the atomic form factors.

Very different electronic structures of the binary Bergman alloys $Al_{108}M_{52}$ ($M =$ Li, Mg) are understood in the same way. In the Al-Mg compound, the potential landscape for electrons reflects the close-packed structure consisting of both Al and Mg sites. But, in the Al-Li

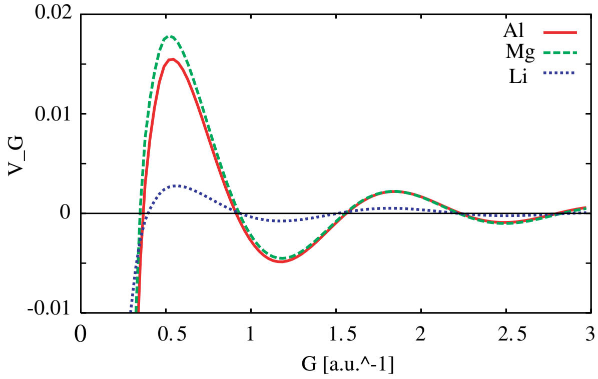

FIG. 3 (color online). The atomic form factors for Al (red full curve), Li (blue dotted curve), and Mg (green dashed curve).

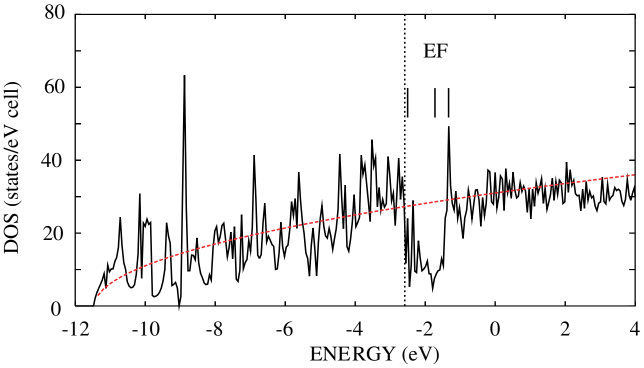

FIG. 4 (color online). The DOS for binary Bergman compound where Li/Mg sites are replaced by vacancies.

compound, electrons are scattered by a rather porous network consisting of only Al sites. To check that such a porous network leads to a deep pseudogap in the electronic DOS, we calculate the electronic structure of the binary Bergman alloy where all the M sites are replaced with vacancies. In Fig. 4, we show the electronic DOS. One can see an even more distinct pseudogap in the DOS than the $M = \mathrm{Li}$ case. Thus we conclude that the deep pseudogap in the Al-Li Bergman compound is a consequence of the porous network structure, which is obtained by chemical decoration of close-packed structures.

In general, directional covalent bonding stabilizes porous network structures. On the other hand, metallic bonding is favored by close-packed structures. For example, crystalline Si with the diamond structure is covalent whereas liquid Si near the melting point with densely packed structure is metallic. This trend is realized also in QC-related systems: Fujimori and Kimura [20] carried out semiempirical molecular orbitals calculations for icosahedral Al clusters with and without Al at the cluster center. They concluded that metallic bonding is realized for the cluster with the center, whereas covalent bonding is realized in the cage cluster without the center. A similar trend is confirmed experimentally by Kirihara *et al.* in the electron density distribution in α-Al(Mn, Re)Si and $\mathrm{Al}_{12}\mathrm{Re}$ [6]. Therefore, as a general statement for Al-based compounds, we conclude that the covalent nature of electrons is enhanced in more vacant structures. Here, the vacant structure is not necessarily realized by cagelike atomic arrangements but obtained by chemical decoration of close-packed structures.

We have discussed the pseudogaps in the DOS of the Al-Li Bergman and Zintl compounds. Since Li scatters electrons very weakly in comparison with Al, the potential landscape for electrons is not that of the entire close-packed structure but that of the Al sublattice, which is a rather porous network like the diamond lattice. The porous network structure realized by the chemical decoration of close-packed structures enhances the covalent nature of electronic structures, hence the deep pseudogap in the electronic DOS. It has been pointed out that the covalent bonding is important to stabilize QC-related compounds. Although the hybridization with d states is often indispensable in many QC-related compounds, the chemical decoration realizing the structure which favors the covalent bonding is another important aspect. A concept of structure-induced covalent bonding in a network realized by the chemical decoration of close-packed structures may provide a novel picture in the electronic structures of complex intermetallic compounds.

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