Covalency, semiconductor-like and thermoelectric properties of Al-based quasicrystals: icosahedral cluster solids

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Abstract

A unified picture of icosahedral cluster solids obtained by comparing Al-based icosahedral quasicrystals to boron-based cluster solids, which consist of icosahedral clusters of the same group III element, B, is discussed. Metallic-covalent bonding conversion in icosahedral clusters of Al and B was demonstrated by molecular orbital calculations. According to the electron density distribution obtained using the maximum entropy method and the Rietveld method, the bonding conversion phenomenon occurs even in cluster solids such as some Al- and B-based icosahedral approximant phases (Al\textsubscript{12}Re, \(\alpha\)-AlMnSi, \(\alpha\)-rhombohedral boron). The covalent bonds observed by the electron density analysis give rise to extremely low carrier density and small density of states at \(E\textsubscript{F}\) in \(\alpha\)-AlMnSi and perhaps in icosahedral quasicrystals. In \(\beta\)-rhombohedral boron, the electronic structure and properties depend on slight variation in atomic environment of the icosahedral multiple-shell structure of the crystals. As metallic atoms are doped into specific atomic sites of \(\beta\)-rhombohedral boron, the atomic structure, the electrical conductivity and its temperature dependence approach those of AlLiCu icosahedral quasicrystal and equal those of AlPdRe icosahedral quasicrystal. From the absolute density measurement, it was revealed that the concept of rigid sphere packing, i.e. metallic bonding, is not applicable to AlPdRe icosahedral quasicrystal. Various semiconductor-like behaviors of Al-based icosahedral quasicrystals were demonstrated by means of not only conventional conductivity and Hall coefficient measurements but also modulated photocurrent measurements. In addition, the thermoelectric properties of AlPdRe quasicrystal were estimated. The potential for application of the icosahedral quasicrystals as thermoelectric materials is also discussed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Quasicrystal; icosahedral cluster; molecular orbital calculation; metallic-covalent bonding conversion; MEM/Rietveld method; multiple-shell structure; optical conductivity; atomic density; photodconductivity; thermoelectric conversion material

1. Introduction

Some Al-based icosahedral quasicrystals and approximants exhibit semiconductor-like electron transport, although they consist of almost metallic elements and have a finite electron density of states (DOS) at the Fermi energy, \(E\textsubscript{F}\). They are, therefore, considered to be intermediate substance between semiconductors and metals. Unique electric properties, particularly anomalous high-resistivity, of some Al-based icosahedral quasicrystals have been reported by many researchers since the beginning of the 1990s. The origin of high-resistivity has been explained by the combination of a Hume–Rothery pseudogap in the electron DOS at \(E\textsubscript{F}\) and the localization tendency of electrons near \(E\textsubscript{F}\) [1]. The Hume–Rothery pseudogap reduces the number of relevant carriers and the localization tendency causes minimal carrier mobility. Quantum interference effects such as weak localization and electron–electron interaction, which are applied to Boltzmann’s transport theory, have been supported to be realized experimentally by the temperature and magnetic field dependence of the electrical conductivity. A variable-range hopping (VRH) regime also seems to be acceptable, qualitatively. These interpretations, however, are originally applicable to disordered solids such as amorphous alloys. Thus, there is room for discussion on whether the fundamental nature of the electron localization arises from quasiperiodicity or from structural defects which are randomly distributed in icosahedral quasicrystals.

Approximant crystals have been identified in many alloy systems. Icosahedral approximant crystals consist of a periodic packing of icosahedral clusters which have similar local atomic arrangement to icosahedral quasicrystals. The lattice constant of an approximant crystal corresponds to the order of approximation to quasiperiodicity. The higher the order of approximation is, the larger the lattice constant
is. Both the structure and physical properties of a higherorder approximant crystal are similar to those of quasicrystal. However, Kimura et al. pointed out that in Al-based icosahedral quasicrystals and approximants, the electrical conductivity depends strongly on the difference in alloy systems rather than that in the order of approximation, as shown in Fig. 1 [2]. Thus, it means that the bonding nature of icosahedral clusters play a significant role in electronic transport rather than long-range structural order, such as quasiperiodicity. Considering icosahedral atomic clusters as building blocks or structural units for icosahedral quasicrystals and approximants, it becomes easier to discuss the relationship between atomic structure and physical properties. We have attempted to develop a unified picture of icosahedral cluster solids by comparing Al-based icosahedral quasicrystals to boron (B)-based icosahedral cluster solids, which consist of icosahedral clusters of the same group III element, B [2].

In Section 2, we report metallic-covalent bonding conversion in icosahedral clusters of Al and B demonstrated by molecular orbital calculations. The bonding nature of Al- and B-based icosahedral approximants is estimated in Section 3, using the experimentally obtained electron density distribution. In Section 4, the possibility of the metallic-covalent bonding conversion phenomenon in icosahedral cluster solids is discussed in view of the multiple-shell structure of icosahedral clusters. Details of semiconductor-like properties of Al-based icosahedral quasicrystals are reported in Section 5. We also mention our study on the application of icosahedral quasicrystals as thermoelectric materials in Section 6.

2. Metallic-covalent bonding conversion in icosahedral clusters of group III element

Fujimori and Kimura clarified the bonding nature of isolated icosahedral clusters by semiempirical molecular orbital calculation [3]. Geometry optimization of the cluster by total energy calculations and the successive search for the stationary point of an atom added to the cluster were performed, and the results are shown in Fig. 2 and Table 1. In the case of B clusters, the stationary point of an external atom added to 12-atom icosahedron B_{12} (without a center atom) is the vertex sticking along fivefold axes of the icosahedron (Fig. 2c). This indicates that the B_{12} icosahedron have a covalent bonding nature with strongly oriented bonds. On the other hand, the stationary point of an external atom added to 13-atom icosahedron B_{13} (with a center atom) has more tendency to be a point on the triangular face of the icosahedron (Fig. 2a). This means that no directional bond is formed in the B_{13} icosahedron with the external atoms. The B_{13} icosahedron reveals the nature of the close-packed structure, in other words, the metallic bonding nature. In the case of Al, contracted Al icosahedron should be used for the calculation since for Al icosahedra in Al-based icosahedral quasicrystals, it was found that the interatomic distance between Al atoms is 0.24 nm, approximately 10% shorter than that of fcc-type Al crystal (0.286 nm). According to the same calculation for the Al_{12} icosahedron whose cluster radii were contracted 10% (0.243 nm → 0.219 nm), it was revealed that the contracted Al_{12} icosahedra have covalent bonds. These results coincide with the global tendency that the bond length is shorter and the packing fraction is smaller in solids with covalent bonds than in those with metallic bonds. In clusters of group III elements, atomic occupation...
of the center of the icosahedra and changing the interatomic distance appear to induce the metallic-covalent bonding conversion phenomenon. The tendency of the bonding conversion was also ensured by the different electron density distribution obtained by ab initio molecular orbital calculations. On the other hand, the results for the atomic clusters of group II elements (Be and Mg), which are arranged in hcp-type crystals, consistently showed the metallic bonding nature of the clusters, independent of the atomic occupation of the center or the change in the interatomic distance. Murakami and Kanayama determined the stable structure of the clusters of Si (group IV element), which consist of up to 10 Si atoms [4]. According to their study, it was found that the Si clusters, whose dangling bonds are terminated by hydrogen atoms, takes the sp$^3$ covalent clusters, parts of the typical diamond structure, while the Si clusters without hydrogen atom termination take the metallic, more close-packed structures. The difference in the bonding nature of these Si clusters corresponds to drastic changes in the atomic arrangement. As mentioned above, small changes in cluster structure can induce the metallic-covalent bonding conversion in Al and B clusters. The bonding conversion phenomenon in Al and B clusters, therefore, shows the unique nature of group III elements.

For the 1/1 cubic approximant phase of Al-based icosahedral quasicrystals, Yamada et al. reported that the electrical conductivity at 300 K decreases 10 times as the cluster radii of Al$_{13}$ icosahedra are contracted 10% [5]. The covalent bonds calculated for the 10% contracted Al$_{13}$ icosahedra as discussed above may be related to their results.

3. Electron density distribution of icosahedral cluster solids

In order to experimentally estimate the bonding nature of Al- and B-based icosahedral cluster solids, analysis of the electron density distributions using structure factors is useful. Fujimori et al. determined the electron density distribution of the α-rhombohedral boron crystal (α-B) using the maximum entropy method along with the Rietveld method (MEM/Rietveld method) [6]. These methods were developed by Takata et al. [7] and Sakata and Sato [8]. The MEM electron density distribution maps are consistent with the observed structure factors, leaving the uncertainties maximum, that is, least biased with respect to the unobserved structure factors. Using an accurate and reliable data set obtained by synchrotron radiation, the MEM could provide physically meaningful electron density distribution. α-B crystal consists of a rhombohedral arrangement of B$_{12}$ icosahedra without a center atom. Fig. 3(a) shows the electron equidensity surface of a B$_{12}$ icosahedron. Using MEM/Rietveld analysis, multicenter covalent bonds in the B$_{12}$ cluster are clearly observed. The other unique covalent bonding nature, i.e. a bent inter-B$_{12}$ cluster bond and interacting dangling bonds of three B$_{12}$ clusters, are also reported [6].

As mentioned in the introduction, higher-order approximant phases possess quasicrystalline-like, i.e. nonmetallic, properties. Among such approximant phases, most can be described as a periodic arrangement of the icosahedral cluster, e.g. the Mackay icosahedral (MI) cluster [9] or the Bergman cluster [10], considered to be the basic space-filling unit of icosahedral quasicrystals. In Al-transition metal (TM) icosahedral approximants, properties of the 1/1-approximant phases with a lattice constant, $a$, of approximately 1.2 nm are important because such a lattice constant plays a critical role in determining nonmetallic and metallic behavior. For instance, the α-AlMnSi phase [11] ($a = 1.266$ nm) and the AlCuFeSi phase [12] ($a = 1.233$ nm) exhibit the former behavior, while the AlCuRu phase [13] ($a = 1.24$ nm), the latter. In addition, the properties of 1/0-approximant phases whose lattice constants are $\tau$ times shorter than 1.2 nm, e.g. AlCuRu [13] and Al$_{13}$Re [14], are metallic; where $\tau = (1 + \sqrt{5})/2$ is the golden mean number. Kirihara et al. analyzed the electron density distribution of nonmetallic α-AlMnSi and metallic Al$_{13}$Re using a similar MEM/Rietveld method [14,15]. The α-AlMnSi crystal has a bcc packing structure of the MI cluster, whose first shell is an Al(or Si) icosahedron without a center.

| Clusters | Al$_{12}$ | Al$_{13}$ |
|----------|-----------|-----------|
| Equilibrium | Face | Face | Face |
| Contracted | Face | Edge | Face |

Fig. 3. Equidensity surfaces of electron density for icosahedral clusters in (a) α-rhombohedral boron and (b) Al$_{13}$Re. Electron density at surfaces is indicated in each figure.
atom. On the other hand, Al$_{12}$Re crystal has a bcc packing structure of 13-atom icosahedral cluster, which is an Al$_{12}$ icosahedron with a central Re atom. Fig. 3(b) shows the electron equidensity surface of the 13-atom icosahedron in Al$_{12}$Re. In contrast with the multicenter covalent bonds in the B$_{12}$ cluster, no covalent bond exists for inter-Al atoms of the 13-atom icosahedral cluster. Fig. 4(a) and (b) shows section contour maps of the electron density distribution for Al$_{12}$Re in the (200) plane and for α-AlMnSi in the (100) plane, respectively. In contrast with the charge density of Al$_{12}$Re, the α-AlMnSi crystal has a strong directional Mn-Al covalent bond (Mn−A$_1$) in the second shell of the MI cluster, with similar covalent bonds (Mn−G$_1$) existing between the Mn atom in the second shell and the Al atom at G$_1$ sites; both representing the crystal’s strongest bonds. Interatomic Al(or Si)−Al(or Si) covalent bonds for the first shell and Al(or Si)−Mn covalent bonds (A$_1$−Mn) connecting the first and second shells were observed as well. Although such a weak covalent bond is also observed between Al and Re atoms for the 13-atom icosahedron in Al$_{12}$Re, the bonding nature of this cluster is considered to be more metallic than that of the 12-atom icosahedron in α-AlMnSi. Variation in the bonding nature of the icosahedral cluster could well depend on the center occupany of the icosahedral cluster, i.e. the 12-atom icosahedron in α-B and α-AlMnSi has more covalent bonds whereas the 13-atom icosahedron in Al$_{12}$Re has more metallic bonds. This result experimentally supports the idea of metallic-covalent bonding conversion in the icosahedral cluster, as revealed by the molecular orbital calculation.

Soft X-ray emission spectroscopic studies by Belin et al. [16] and Takeuchi et al. [17] showed that hybridization between the Al p band and the Mn d or Re d band is responsible for the opening in the pseudogap near $E_F$. In this work, we have observed the real-space image of the strong Mn−Al covalent bonds in α-AlMnSi which were discussed in such spectroscopic study. The value of the minimum electron density of Al$_{12}$Re is 0.118e/Å$^3$, being approximately 100 times larger than that of α-AlMnSi (0.001e/Å$^3$). This significant feature of the electron density background of Al$_{12}$Re may virtually correspond to that of a free electron model; thus, this large value is apparently related to the metallic behavior of electrical resistivity and its temperature coefficient. The origin of the pseudogap in Al-based icosahedral quasicrystals is considered to be a Fermi surface–Jones zone (FS–JZ) interaction such as that exhibited in Hume–Rothery alloys. The Hume–Rothery picture, however, applies to a nearly free electron system in which the potential of the valence electron is rather weak. For icosahedral Al–TM phases that possess high-resistivity, the origin of the pseudogap is considered to be the covalent bonds rather than the Hume–Rothery mechanism. The covalency of the Al icosahedron and that between Al and TM give rise to an extremely low carrier density and a small DOS at $E_F$ in α-AlMnSi and perhaps in icosahedral quasicrystals.

4. Multiple-shell structure and electronic properties of icosahedral cluster solids

Kimura et al. proposed a unified picture in icosahedral cluster solids about a relationship of the structure and the bonding nature of clusters to the electronic properties, by paying attention to the similarity of multiple-shell structures between Al-based icosahedral approximant crystals and β-rhombohedral boron (β-B) crystal [2]. Fig. 5 shows the atomic structures for α-AlMnSi and AlLiCu approximants and β-B. The details of the multiple-shell structures can be.
described by illustrating the atomic arrangement from the first to the third shell. Considering the concentric sphere positioned at the vertex of a unit cell, the structural similarity up to the third shell between the AILiCu approximant and β-B is clearly seen although the unit cell shapes of AILiCu and β-B are cubic and rhombohedral, respectively. The shell structure of AlMnSi differs slightly from those of AILiCu and β-B except for the first shell icosahedra. The significant feature in these structures is that some atomic sites in the second shell cluster, which are occupied in the case of α-AlMnSi and AILiCu approximants, are vacant in β-rhombohedral boron (β-B). This atomic site is called ‘A-site’ for β-B. The β-B is a semiconductor whose electrical resistivity is \( \sim 10^5 \) Ω cm at room temperature. As metallic atoms are doped into the A-site, the electrical resistivity and its temperature dependence approach those of the AILiCu icosahedral quasicrystal and equal those of the AlPdRe icosahedral quasicrystal, as shown in Fig. 4. The coordination number of A-site is 12 and the arrangement of the nearest-neighbor atoms of the A-site resembles that of the icosahedron. It is supposed that by atom occupation at the A-site, the bonding nature of the icosahedral cluster surrounding the A-site is considered to convert from covalent to metallic. Transition of the electrical properties of β-B to those of metals may occur when the ratio of the number of icosahedral clusters that converted to a metallic bonding nature exceeds a percolation threshold. For V-doped β-B, in which 1 at.% of vanadium (V) atom is doped to the A-site, not only dc electrical conductivity but also optical conductivity would be the same as those of the AlPdRe icosahedral quasicrystal, as shown in Fig. 7. Enhancement of the DOS at \( E_F \) as observed by photoemission spectroscopy.
Fig. 6. Temperature dependence of DC conductivity for some icosahedral Al-based quasicrystals and metal-doped β-rhombohedral boron crystals.

(PES) and a decrease of the lowest edge of the conduction band observed by electron energy loss spectroscopy (EELS) were also reported for the V-doped β-B. The decrease of the lowest edge of the conduction band is about 1 eV and it reveals a major part of the band gap, 1.5 eV, of nondoped β-B. In the case of Li doping, the Li atoms do not occupy the A-site and the decrease of the lowest edge of the conduction band does not occur even at a doping level of 8 at.%. The results of V-doped β-B obtained by PES and EELS lead us to an interpretation that the alloying of V and B is induced by strong hybridization between the electronic states of V and B. The creation of isolated V impurity levels in the band gap such as V in Si is not applicable to understanding these results. These experimental results may provide evidence of the conversion to the metallic bonds for the icosahedral cluster surrounding the A-site atom.

In icosahedral quasicrystals, it is not easy to determine the atomic positions and the bonding nature because of the difficulty of structural analysis. The analysis of electron density distributions performed for the approximant phases could not be applied to the case of quasicrystals. The AlPdRe icosahedral quasicrystal appears to have a stronger covalent bonding nature than the other quasicrystals since it possesses the highest value of the electrical resistivity [18] among the quasicrystals. Sawada et al. reported that both the quasilattice constant (QLC) and the electrical conductivity increase with increasing concentration of TM (Pd or Re) in AlPdRe icosahedral quasicrystals [19]. QLC indicates the length of the edge of the rhombohedra that serve as the building blocks of the icosahedral quasilattice structure. If the metallic bonds are dominant in the bonding nature of the icosahedral quasicrystal, the atomic packing can be described as being rigid sphere packing. Since the atomic radius (Goldschmidt radius) of Pd and Re, 0.137 nm, is smaller than that of Al, 0.143 nm, QLC should decrease with increasing TM concentration in this case. The quasilattice expansion reported by Sawada et al. indicates that atom packing of AlPdRe icosahedral quasicrystals could not be described by the rigid sphere packing. In order to discuss the bonding nature of AlPdRe quasicrystals, Kirihara et al. determined the average atomic packing [20] from the atomic density that is obtained from the absolute density measurement and the composition analysis of the phase. Since Pd and Re have smaller atomic radii than Al, the average atomic radius decreases with increasing concentrations of Pd and Re. Despite this, it was revealed that QLC keeps a constant value or increases slightly with increasing TM concentration. Fig. 8 shows the relationship between the atomic density and QLC. The atomic density is represented by number of atoms per cube whose side is 1 nm long. The expansion of the quasilattice also causes a decrease in atomic density. The solid line in Fig. 8 shows the variation of the atomic density by the expansion of the quasilattice. The atomic density decreases more rapidly than the quasilattice expansion as QLC and the concentration of TMs increase. It reveals that the concept of rigid sphere packing is not acceptable in the AlPdRe system. The quasilattice expansion and the atomic density decrease are considered to originate from the increase in the covalent bonding nature, i.e. stronger bonding direction and smaller coordination number.

Because of the difficulty of structural analysis, as discussed...
above, we assumed that the local atomic structure model in the AlPdRe icosahedral quasicrystal is a MI. Under this assumption, we estimated the decrease in the number of atoms per unit cell of a 1/1 cubic approximant, in which MI clusters have bcc packing. The unit cell size of the 1/1 cubic approximant was calculated using the QLC of AlPdRe samples. The decrease in the number of atoms, where TM concentration increases from 27 to 32 at.%, is approximately 10.6 in a 1/1 cubic unit cell [21]. This reveals that the occupancies of specific atom sites in the icosahedral quasicrystal should be taken into account, although it is difficult to distinguish its contribution from the decrease in the average coordination number in the present study. We could consider some candidates for the specific atomic sites from the atomic structure shown in Fig. 3. For α-AlMnSi, reduction of the occupancy of Al atom sites in the second shell of the MI that corresponds to vacant A-sites in β-B and the center of the icosahedral cluster may enhance the covalent bonding nature in the icosahedral clusters. The bonding conversion from metallic to covalent may occur near the atomic sites whose occupancy are reduced, contrary to the previous case of conversion from covalent to metallic for V-doping in the A-site of β-B.

From positron annihilation study, vacancy sites that correspond to the center of an icosahedron or the second shell atomic sites as mentioned above have been observed. Recently, Sato et al. determined the vacancy concentration of icosahedral quasicrystals from positron lifetime measurements and the S-parameter obtained by monochromatic energy spectroscopy of a positron beam [22]. It was found that highly resistive AlPdRe icosahedral quasicrystals have higher vacancy concentration than the AlPdMn icosahedral quasicrystal. This result also supports the discussion mentioned above.

5. Semiconductor-like properties of AlCuRu and AlPdRe icosahedral quasicrystals

Poon pointed out that the highly resistive icosahedral quasicrystal is a semimetal since its Fermi level is positioned in a deep pseudogap and the coefficient of the electronic specific heat is a finite value [23]. However, experimental observations, which demonstrate not typical semimetallic, but semiconductor-like properties, have also been reported.

Haberkern et al. [24] and Tamura et al. [25] reported that according to the temperature dependence of the Hall coefficient, carrier concentration increases with increasing temperature in icosahedral quasicrystals. Fig. 9 shows such behaviors along with the temperature dependence of the mobility obtained by one-band analysis. These behaviors differ evidently from that of semimetals. Qualitatively speaking, the behaviors of the carrier concentration and the mobility are similar to those of semiconductors. Recently, it was found by Haberkern et al. that the carrier concentration of AlPdRe thin films obtained from the Hall coefficients increases rapidly up to a high temperature of about 1000 K [26]. These results have been described by the enhancement of semimetallic band overlapping. It also differs from the behavior of typical semimetals. On the other hand, Delahaye et al. demonstrated VRH transport for AlPdRe quasicrystal in low-temperature conductivity measurement in the temperature range down to 20 mK [27]. The VRH transport behavior is typical for semiconductors, i.e. it is observed in amorphous semiconductors, doped semiconductors, and dirty metals in the nonmetallic side.

Photocurrent was observed for the first time by Takeda et al. for the highly resistive AlPdRe quasicrystal using the modulated photocurrent method [28]. In conventional metals or semimetals, photoconductivity could not be
measured even by the high-resolution method because of the large concentration and mobility of dark current carriers and the short lifetime of photoexcited carriers. However, photocurrent, whose magnitude is 1% of the dark current, was observed, as shown in Fig. 10. Sakairi et al. improved the accuracy of the measurement and then clarified that the lifetime of photoexcited carriers (recombination time) is approximately $10^{-2}$ s, which is approximately six orders of magnitude longer than those of typical semiconductors and that the mobility of the photoexcited carriers is almost the same as that of the dark current carrier (several cm$^2$/Vs) [29,30]. The long lifetime of the photoexcited carriers has been interpreted by a unique model of carrier recombination. In the model, it is assumed that a dense set of quasilocalized states distributes in the pseudogap and mobility is sufficiently low and energy-independent in the DOS. In this case, photoexcited carriers repeat relaxation and thermal excitation between the narrow bands of the quasilocalized states and then recombine after falling to $E_F$. Recently, it was found that the temperature coefficient of the magnitude of photocurrent changes from a positive value for nondoped $\beta$-B to a negative value for V-doped $\beta$-B [31]. The behavior of V-doped $\beta$-B resembles that of the AlPdRe quasicrystal. This provides new experimental evidence that reveals that the properties of V-doped $\beta$-B approaches those of Al-based quasicrystals.

In addition to photocurrent measurement, we succeeded recently in observing the electron spin resonance spectra for AlCuRu and AlPdRe quasicrystals. We will attempt to characterize highly resistive quasicrystals as semiconductors with a peculiarly high density of localized states in the pseudogap rather than a metal with extremely low DOS at $E_F$.

### 6. Potential of icosahedral cluster solids for use as thermoelectric materials

The potential for using quasicrystals as new materials, has attracted much interest in recent years. Some studies have been performed for high-specific-strength Al-based alloys and hydrogen storage in Ti-based quasicrystals. There are, however, a few studies on quasicrystalline materials, which are focused on their unique electrical properties. Recently, Cyrot-Lackmann pointed out that quasicrystals may possess large Seebeck coefficients, which are due to the combination of a rapid change of DOS near $E_F$ and a large phonon drag effect [32]. The potential for use as thermoelectric materials has been discussed for some Al-based icosahedral quasicrystals [33]. The performance of thermoelectric materials is estimated by a figure of merit, $Z = S^2/\sigma\kappa$, where $S$ is the Seebeck coefficient, $\sigma$, the electrical conductivity, and $\kappa$, the thermal conductivity. A large Seebeck coefficient that is typical for semiconductors, large electrical conductivity that is typical for metals, and low thermal conductivity are required to obtain a high figure of merit. Therefore, materials that possess intermediate electrical properties between semiconductors and metals can be optimized for use as thermoelectric materials. As shown in previous sections, we have focused on such intermediate electrical properties of Al- or B-based icosahedral cluster solids. Our purpose in thermoelectric materials development is to control the electronic properties of cluster solids by changing the bonding nature for intra- or interclusters between covalent bonds and metallic bonds. We discuss the thermoelectric properties of B-based cluster solids and AlPdRe icosahedral quasicrystals.

In B-based icosahedral cluster solids, phonon-assisted hopping transport, which differs from the conduction of conventional semiconductors, was reported. Accordingly, the phonon-assisted hopping conduction, both Seebeck coefficient and electrical conductivity, increase with increasing temperature. Thus, an improvement of the thermoelectric figure of merit for these solids could be expected in the temperature range higher than room temperature. Nakayama et al. reported that not only control of electrical properties but also sign change of the Seebeck coefficient could be realized for $\beta$-B by doping TMs into the A-site [34].

For highly resistive AlPdRe icosahedral quasicrystals, their thermoelectric performance is expected to be the best among quasicrystals since they have a stronger covalent bonding nature than other quasicrystals, as mentioned previously. The electrical conductivities of AlPdRe icosahedral quasicrystals monotonically increase with increasing temperature. This temperature dependence is typical for Al-based icosahedral quasicrystals since a few researchers have reported a similar tendency at high temperatures [35,36]. Seebeck coefficients of the samples slightly increase with increasing temperature until they reach a broad maximum centering at 500 K. The peak value of the Seebeck coefficient of the Al$_{71}$Pd$_{29}$Re$_9$ sample is +89 $\mu$V/K. These values
7. Conclusions

Al-based icosahedral quasicrystals are classified as one of the icosahedral cluster solids, which provides a unified picture of icosahedral cluster solids to explain their physical properties, along with the case of B-based ones. Small changes in the cluster structure can induce metallic-covalent bonding conversion in Al and B icosahedral clusters. The bonding conversion phenomenon in Al and B icosahedral clusters also occurs in cluster solids. Furthermore, atomic occupations of specific sites in the multiple-shell structure may also induce the bonding conversion and vary the physical properties of the cluster solids from semiconductor-like to metallic. These characteristics may be due to the location of Al and B elements in the periodic table. Although both Al and B belong to the same group III, Al is classified at the edge of metallic bonding elements whereas B is at the edge of covalent bonding elements. This gives a unique nature to group III elements. Semiconductor-like behavior was observed for highly resistive Al-based icosahedral quasicrystals by various experiments such as electronic transport, photoconductivity and ESR. The highly resistive quasicrystals may be characterized as a semiconductor with a high density of quasilocalized states in the pseudogap rather than as a metal with extremely low DOS at $E_F$. We expect an improvement in the performance of icosahedral quasicrystals by controlling the bonding nature of icosahedral clusters.

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