Electronic States of Al–Mg–Zn Quasicrystal and Its Approximant Based on First-Principles Calculations

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First-principles calculations are performed to investigate the electronic states of 1/1 and 2/1 approximants with the composition Al_{14.5}Zn_{41.0}Mg_{44.1}, which is close to the quasicrystal (QC) Al_{14.0}Zn_{41.0}Mg_{44.1}, in which the superconductivity recently has been discovered. The density of states for the 1/1 approximant shows a wide pseudogap structure near the Fermi level as commonly observed in various approximants of the QCs, whereas those for the 2/1 approximant do not show such a wide pseudogap. Instead of the wide pseudogap, the 2/1 approximant shows a remarkable narrow pseudogap at the Fermi level in contrast to the 1/1 approximant, which shows a shallow hump at the Fermi level within the wide pseudogap. This seems to be consistent with the experimental observation of the electrical resistivity, which increases with decreasing temperature from room temperature down to around the superconducting transition temperature for the 2/1 approximant together with the QC, whereas it monotonically decreases for the 1/1 approximant.

1. Introduction

In the classical crystallography, solids are conventionally divided into two classes: crystal and amorphous. The crystal has translational symmetry with twofold (or three-, four-, and sixfold) rotational symmetry, whereas the amorphous has no such symmetry. In contrast to the classical crystallography, quasicrystals (QCs), first discovered by Schechtman et al. in 1984 in Al–Mn alloy,[1] have specific structures, which are not periodic but have kinds of translational orders with the fivefold (or eight-, ten-, and twelvefold) rotational symmetry and, then, are classified as the third class of solids. Because of the specific structures, QCs are expected to show unique physical properties and have been extensively investigated.[2]

Recently, superconductivity in the Al_{14.5}Zn_{41.0}Mg_{44.1} QC at a transition temperature $T_c \approx 0.05$ K has been discovered by Kamiya et al.[3] and has attracted much attention for its symmetry and pairing mechanism. They have also found the superconductivity in its approximant crystals (ACs), which are periodic in contrast to QCs but have the local structures similar to the QC, with the two types of 1/1 and 2/1 ACs.[3]

In the 2/1 AC whose local structure is very close to the QC, the temperature dependence of the electrical resistivity $\rho$ almost coincides with that in the QC, where $\rho$ increases with decreasing temperature from the room temperature down to around $T_c$. On the other hand, in the 1/1 AC whose local structure is less similar to the QC than the 2/1 AC, $\rho$ monotonically decreases with decreasing temperature. Therefore, it is important to clarify the difference in the electronic states between the 1/1 and 2/1 ACs with the composition corresponding to the superconducting QC to discuss transport properties not only for the ACs but also for the QC.

Theoretically, Sakai et al.[4] have recently investigated the superconductivity in the attractive Hubbard model on the twodimensional Penrose lattice simulating a QC using the real-space dynamical mean-field theory and have found that spatially extended Cooper pairs appear due to the aperiodicity of the lattice. As for the electronic states, the 1/1 AC with the composition Al_{14.5}Zn_{41.0}Mg_{44.1} was previously studied on the basis of the first-principles calculation, and its density of states (DOS) was found to show a wide pseudogap structure at the Fermi level as commonly observed in various ACs.[5] However, the electronic states with the composition corresponding to the superconducting QC in addition to the 2/1 AC were not discussed there. The purpose of this article is to investigate the electronic states of the both 1/1 and 2/1 ACs with the composition Al_{14.5}Zn_{41.0}Mg_{44.1} close to the superconducting Al_{14.0}Zn_{41.0}Mg_{44.1} QC and to clarify the difference between the 1/1 and 2/1 ACs.

2. Calculation Method

We perform the first-principles calculations for the 1/1 and 2/1 ACs with the composition Al_{14.5}Zn_{41.0}Mg_{44.1} using OpenMX code,[6] which is a fully linear-scaling density functional theory (DFT) method both in the building of the DFT Hamiltonian and in its solution. We use norm-conserved pseudopotentials,[7] with an energy cutoff of 200 Ry for charge density and pseudopotomic localized functions,[8] which are set as Al7.0–s3p3d2, Zn6.0–s3p3d3f1, and Mg7.0–s3p3d2.[9] We also set k-space sampling points of $7 \times 7 \times 7$ for reciprocal lattice vectors.

The basic structure in the Al–Zn–Mg QC and AC systems is the Bergman-type cluster[10] consisting of four shells, as shown in Figure 1a–e. The first and third shells are icosahedrons.
indicate that the space group 2 using the relation

\[ \gamma = \frac{2\pi^2 k_B^2}{3} D(E_F) \]  

The obtained values of \( \gamma \) are 0.778 mJ K\(^{-2}\) mol\(^{-1}\) for the 1/1 AC and 0.793 mJ K\(^{-2}\) mol\(^{-1}\) for the 2/1 AC. Those are comparable to the experimental values of \( \gamma \), which are 0.813 mJ K\(^{-2}\) mol\(^{-1}\) for the 1/1 Al\(_{14.9}\)Zn\(_{41.0}\)Mg\(_{44.1}\) AC and 0.726 mJ K\(^{-2}\) mol\(^{-1}\) for the 2/1 Al\(_{14.9}\)Zn\(_{42.1}\)Mg\(_{43.0}\) AC\(^{(3)}\), although the compositions are slightly different from Al\(_{14.9}\)Zn\(_{40}\)Mg\(_{45}\) for the both 1/1 and 2/1 ACs in the present calculations. The calculated value of \( \gamma \) for the 1/1 AC is slightly smaller than that for the 2/1 AC, in contrast to the experimental observation where \( \gamma \) for the 1/1 AC is larger than that for the 2/1 AC. This discrepancy will be discussed later.

4. Summary and Discussions

In summary, we have investigated the electronic states of 1/1 and 2/1 ACs with the composition Al\(_{13}\)Zn\(_{40}\)Mg\(_{45}\), which is close to

Figure 2a–d shows the energy band dispersions and the densities of states for the 1/1 and 2/1 ACs with the composition Al\(_{13}\)Zn\(_{40}\)Mg\(_{45}\). In the case with the 2/1 AC, we observe a wide pseudogap structure with the width of O (1 eV) in the DOS near the Fermi level (see Figure 2b) as previously observed in the 1/1 AC with the different composition Al\(_{13}\)Zn\(_{40}\)Mg\(_{45}\). As is well known, the pseudogap structures have been commonly observed in various ACs and have frequently discussed in relation to the stability of QCs. On the other hand, the 2/1 AC does not show such a wide pseudogap but shows a remarkable narrow pseudogap with the width of O (0.1 eV) at the Fermi level (see Figure 2d). This is a striking contrast to the 1/1 AC, which shows a shallow hump with the width of O (0.1 eV) at the Fermi level within the wide pseudogap (see Figure 2b). These results seem to be consistent with the experimental observation of the electrical resistivity, which increases with decreasing temperature from the room temperature down to around \( T_c \) for the 2/1 AC, whereas it monotonically decreases for the 1/1 AC as mentioned before.

Due to the complex structure of the Bergman-type cluster composed of many atoms (see Figure 1), the energy bands are complexly intertwined, and then, many energy bands cross the Fermi level, as shown in Figure 3a,b. In the case with the 1/1 AC, the Fermi level sits in around the middles of the relatively wide energy bands across the Fermi level, resulting in the shallow hump in the DOS, as shown in Figure 2b and 3a. On the other hand, in the case with the 2/1 AC, the Fermi level sits in around the edges of the relatively narrow energy bands across the Fermi level, resulting in a semiconducting behavior with the narrow pseudogap together with the relatively large DOS around the Fermi level, as shown in Figure 2d and 3b.

We also estimate the specific heat coefficient \( \gamma \) from the DOS per spin at the Fermi level \( D(E_F) \) using the relation

\[ \gamma = \frac{2\pi^2 k_B^2}{3} D(E_F) \]  

AC and the 2/1 Al\(_{14.9}\)Zn\(_{42.1}\)Mg\(_{43.0}\) AC mentioned before for calculations of the 1/1 and 2/1 Al\(_{13}\)Zn\(_{40}\)Mg\(_{45}\) ACs, respectively.

3. Result

Figure 1. Bergman-type cluster in the Al–Zn–Mg systems consists of four shells with a,c) the first and third icosahedral shells composed of 12 Zn/Al atoms, b) the second dodecahedral shell composed of 20 Mg atoms, and d) the fourth truncated icosahedral shell composed of 60 atoms of Mg and Zn/Al. e) The four stacked shells composed by all the atoms.
the superconducting QC $\text{Al}_{14.9}\text{Zn}_{41.0}\text{Mg}_{44.1}$ on the basis of the first-principles calculation. What we have found are: 1) The DOS for the 1/1 AC shows a wide pseudogap structure with the width of $O\,(1\text{ eV})$ near the Fermi level as commonly observed in various ACs, whereas those for the 2/1 AC do not show such a wide pseudogap. 2) Instead of the wide pseudogap, the 2/1 AC shows a remarkable narrow pseudogap with the width of $O\,(0.1\text{ eV})$ at the Fermi level in contrast to the 1/1 AC, which shows a shallow hump at the Fermi level within the wide pseudogap. 3) The calculated values of $\gamma$, 0.778 mJ K$^{-2}$ mol$^{-1}$ for the 1/1 AC and 0.793 mJ K$^{-2}$ mol$^{-1}$ for the 2/1 AC, are comparable to the experimental values of $\gamma$, 0.813 mJ K$^{-2}$ mol$^{-1}$ for the 1/1 $\text{Al}_{14.9}\text{Zn}_{41.0}\text{Mg}_{44.1}$ AC and 0.726 mJ K$^{-2}$ mol$^{-1}$ for the 2/1 $\text{Al}_{14.9}\text{Zn}_{42.1}\text{Mg}_{43.0}$ AC.

The narrow pseudogap in the 2/1 AC seems to be consistent with the experimental observation of the electrical resistivity, which increases with decreasing temperature from the room temperature down to around $T_c$, whereas it monotonically decreases for the 1/1 AC.$^{[3]}$ To be more conclusive, we need an explicit calculation of the electrical conductivity using the Boltzmann equation where we may use the energy band dispersions obtained from the present calculations. In addition to the electrical conductivity, it is interesting to calculate the other transport coefficients, such as the Hall coefficient and the Seebeck coefficient, using the same approach and to compare the results between the 1/1 and 2/1 ACs.

There are about 5% discrepancies between the calculated and experimental values of $\gamma$ for the both 1/1 and 2/1 ACs. This may be due to the slight difference in the composition between the calculated and experimental systems. In addition, the effects of the chemical disorder in Zn/Al atoms are considered to occur in the real materials but are not considered in the present calculations. The virtual crystal approximation is an available approach to consider such effects on the basis of the first-principles calculation and will be an important future work.

As the local structure of the 2/1 AC is very close to the QC, the electronic states of the 2/1 AC are expected to be a good starting point to discuss the QC. In fact, the temperature dependence of the electrical resistivity and the value of $T_c$ in the 2/1 AC almost coincide with those in the QC. Therefore, it is important to calculate the transport properties and the superconductivity in the 2/1 AC on the basis of the first-principles calculation to also discuss those in the QC. Explicit calculations are now under way and will be reported elsewhere.

Figure 2. The energy band dispersions and the DOS for a,b) the 1/1 AC and c,d) the 2/1 AC, respectively, with the composition $\text{Al}_{14.9}\text{Zn}_{44.1}\text{Mg}_{44.1}$ obtained from first-principles calculations (OpenMX), where $E_F=0$ is the Fermi level and the two-way arrows show the wide and the narrow pseudogaps for the 1/1 AC in (b) and for the 2/1 AC in (d), respectively.
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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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[1] D. Schechtman, I. Blech, D. Gratias, J. W. Chan, Phys. Rev. Lett. 1984, 53, 1951.
[2] Physical Properties of Quasicrystals (Ed: Z. M. Stadnik), Springer, Berlin 1999.
[3] K. Kamiya, T. Takeuchi, N. Kabeya, N. Wada, T. Ishimasa, A. Ochiai, K. Deguchi, K. Imura, N. K. Sato, Nat. Commun. 2018, 9, 154.
[4] S. Sakai, N. Takemori, A. Koga, R. Arita, Phys. Rev. B 2017, 95, 024509.
[5] H. Sato, T. Takeuchi, U. Mizutani, Phys. Rev. B 2001, 64, 094207.
[6] OpenMX code, http://www.openmx-square.org (accessed: February 2020).
[7] N. Troullier, J. L. Martine, Phys. Rev. B 1991, 43, 1993.
[8] T. Ozaki, H. Kino, Phys. Rev. B 2004, 69, 195113.
[9] For example, Zn6.0–s3p3d3f1 indicates a pseudo-atomic function for Zn consists of three s-orbitals, three p-orbitals, three d-orbitals and one f-orbital with a cutoff radius of 6.0 Bohr.
[10] G. Bergman, J. Waugh, L. Pauling, Acta Crystallogr. 1957, 10, 254.