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Anomalous effects of Cu-doping on structural and thermoelectric properties of the Al-Ir cubic quasicrystalline approximant

Yutaka Iwasaki [a], [*], Koichi Kitahara [a], [b], Kaoru Kimura [a], [b]

[a] *Department of Advanced Materials Science, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan*
[b] *OPERANDO-OIL, AIST, 148 City Block 4, Kashiwanoha Campus, 178-4 Wakashiba, Kashiwa, Chiba 277-0871, Japan*

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ABSTRACT

The effects of Cu doping on thermoelectric properties and structural properties, such as lattice constant and density, were investigated for the 1/0-cubic quasicrystalline approximant $Al_{73.3-x}Cu_xIr_{26.7}$ ($x = 0–7$). We found that the lattice constant increased as the Cu concentration increased although the atomic radius of Cu is smaller than that of Al. This finding suggested that doped Cu atoms are not only substituted for Al but also added to interstitial sites in the Ir icosahedral cluster to expand the cluster volume. These suggestions are also supported by the fact that the number of atoms per unit cell determined from the density, lattice constant, and analyzed composition increased as Cu content was increased. The Seebeck coefficient (S) of all the samples exhibited metallic behavior with a positive value. The Cu concentration dependence of S showed a maximum value for the $x = 3$-doping sample. This result indicates that substitutional Cu atoms contribute to hole doping and interstitial Cu atoms contribute to electron doping, which stabilizes the system electronically. The present work may contribute to an understanding of the mechanism of electronic stabilization in quasicrystals and related materials over a wide composition range.

1. Introduction

Quasicrystalline approximants have attracted attention because they can contribute to understanding of the unique physical properties of quasicrystals. In particular, the Al-based 1/0-quasicrystalline approximants, so called C-, C_1-, and C_2-phases in fifteen ternary systems, have been reported by Grushko and Velikanova [1] and are well known phase. The crystal structure [2–6], and thermal [7] and electrical properties [8–11] of these systems have been intensively investigated. Although the C-phase possesses a primitive cubic lattice, the C_1- and C_2-phase are double superlattice structures of the C-phase and possess body-centered and face-centered cubic lattices, respectively.

A C-phase system, $Al_{2.75}Ir$ ($Al_{73.3}Ir_{26.7}$), has been reported to possess the $P23$ space group with a lattice constant of 7.674(1) Å [3]. As shown in Fig. 1 (a) (visualized by VESTA 3 [12]), the crystal structure of $Al_{2.75}Ir$ is composed of pseudo Mackay clusters, which contain edge-sharing Ir_{12} icosahedral cluster, including $Ir@Al_{9-10}$ endohedral clusters. Namely, a central Ir atom is surrounded by an average of 9–10 disordered Al atoms. Note that the accurate number and configuration of the inner cluster Al atoms have been the subject of some debate because some differences between the superlattice structures have been observed by X-ray diffraction (XRD) and transmission electron microscope (TEM) imaging, as previously reported [6,10,13]. According to a theoretical study by Mihalkovič et al. [14], some types of realistic configurations of inner Al with superstructures were predicted using pair potentials [15] and fitted to an *ab initio* database [16], combined with replica-exchange simulated annealing [17–19]. Furthermore, if the appropriate composition and configuration is satisfied, a phase known as the 10-phase is predicted to have an insulating electronic structure. In the ternary Al-Cu-Ir system phase diagram [20], the C-phase has a relatively wide composition range and is adjacent to the C_2-phase, which exists in the vicinity of the $Al_{63.3}Cu_{12.3}Ir_{24.4}$ region. As shown in Fig. 1 (b), The Al-Cu-Ir C_2-phase features the $Fm\overline{3}$ space group with a lattice constant of 15.3844 Å owing to the alternatively ordered Cu and Ir sites at the center of edge-sharing Ir_{12} icosahedral cluster [4]. For the electronic structure of the Al-Cu-Ir C_2-phase, our recent study revealed that a semiempirical model of $Al_{39}Cu_8Ir_{15}$ ($Al_{62.9}Cu_{12.9}Ir_{24.2}$) with the space group $Fm\overline{3}$

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[*] Corresponding author. 502, Kiban-toh, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan.
E-mail address: iwasaki@phys.mm.t.u-tokyo.ac.jp (Y. Iwasaki).

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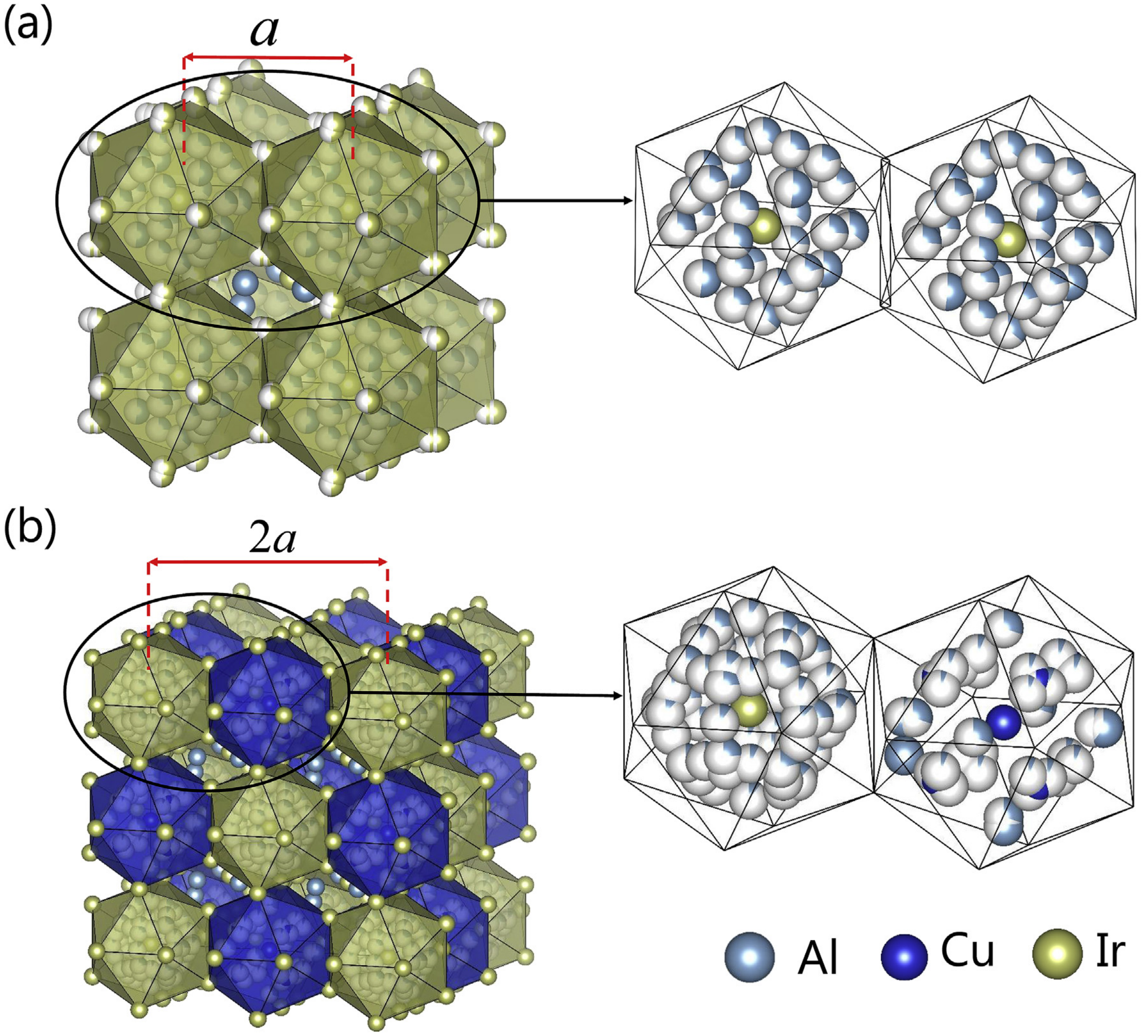

Fig. 1. Crystal structure of (a) $Al_{2.75}Ir$ C-phase [3]; Al sites inside the Ir icosahedral cluster are partially occupied and (b) $Al_{39.22}Cu_{7.56}Ir_{15}$ C_2-phase [4]; central Cu sites are ordered and the other Cu sites are partially occupied. (visualized by VESTA 3 [12]).

possesses a relatively large semimetallic band gap, leading to a deep pseudo gap [21]. Such a pseudo gap is a characteristic feature of quasicrystals and related materials, and the existence of pseudo gap can be confirmed from the thermoelectric properties, which are sensitive to the electronic structure [22–24].

In the present work, we have systematically investigated the relationship between the structural and electronic structure of the Al-Cu-Ir ternary C-phase, based on the lattice constant, density, chemical composition, and thermoelectric properties, to provide a phenomenological understanding of superlattice phase transitions and electronic states in this system. Furthermore, we performed first principles calculations to characterize the electronic structure and thermoelectric properties of the Al-Ir binary C-phase and compared these with the experimental results.

2. Material and methods

2.1. Sample preparation

The synthesis of the Al-Cu-Ir C-phase sample was performed from commercial element powders; Al and Cu (3 N purity; Kojundo Chemical Laboratory Co., Ltd., Japan) and Ir (3 N purity; Rare Metallic Co., Ltd., Japan) with a nominal composition of $Al_{73.3-x}Cu_xIr_{26.7}$ ($x = 0$–7). The mixed powders were pressed under 200 MPa into disc-shaped pellets. Each pellet was melted by an arc-melting method under an argon atmosphere. The yield of all the sample was more than 97%. The ingots were wrapped in a tantalum foil and sealed in a quartz tube filled with argon gas, followed by annealing at 1423 K for 72 h and water quenching. The annealed ingots were reground into powder with a particle size of approximately 10 μm and then sintered by spark plasma sintering (SPS) (SPS-515 S; Sumiseki Materials Co. Ltd., Japan). The temperature of the specimens was increased from room temperature to 1373 K, and then held for 20 min at a uniaxial pressure of 50 MPa under an argon atmosphere. The relative densities of each sintered bulk sample were greater than 90%.

2.2. Characterization

The phase identification of the sample was performed by XRD measurements with CuK-$L_{2,3}$ radiation (Smart Lab; Rigaku Co., Japan). The lattice constants of each sample were refined by Le Bail analysis [25] using RIETAN-FP [26] and silicon powder as a line position standard (SRM640d; NIST, USA). The compositional analyses were performed by conventional scanning electron microprobe–energy dispersive X-ray spectroscopy (SEM–EDX)