Thermoelectric Properties of Quasicrystalline Approximant in Al–Cu–Ir System*1

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The thermoelectric properties of a cubic quasicrystalline approximant in the Al–Cu–Ir system were investigated experimentally and theoretically. A homogeneous sample with no secondary phase was synthesised by arc melting and spark plasma sintering followed by a heat treatment at 1173 K, and its thermoelectric properties were measured at temperatures between 373 K and 1023 K. Theoretical calculations of the thermoelectric properties were performed under three different approximations, i.e., constant-relaxation-time, constant-mean-free-path and constant-diffusion-coefficient approximations, for the energy dependence of the relaxation time of electrons. The experimental Seebeck coefficient was consistently reproduced, and a physically acceptable lattice thermal conductivity was estimated only under the constant-diffusion-coefficient approximation. The thermoelectric figure of merit $zT$ of the present sample was lower than 0.1, and the maximum value of $zT \approx 0.3$ achievable by electron doping was predicted by theoretical calculation under the rigid-band approximation.


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1. Introduction

Quasicrystals and their approximant crystals that are composed of aluminium and transition-metal elements have been investigated as thermoelectric materials because they often show electrical properties comparable to those of degenerate semiconductors and a low thermal conductivity comparable to that of glass.1−12) The potential of thermoelectric materials is conveniently measured by the figure of merit $zT = T \sigma S^2/k$, where $T$ is the absolute temperature, $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $k \equiv k_\text{el} + k_\text{lat}$ is the (total) thermal conductivity, $k_\text{el}$ is the electron thermal conductivity and $k_\text{lat}$ is the lattice thermal conductivity. The highest $zT$ of $\approx 0.26$ for an Al–Ga–Pd–Mn quasicrystal9) among the quasicrystals and approximant crystals investigated thus far is still too low for practical applications, for which $zT > 1$ is usually required.

Recently, first-principles calculations have been applied to analyse or predict the properties of thermoelectric materials. In the earliest studies, Scheidemantel et al.13) calculated the electronic thermoelectric properties from the first-principles electronic band structure assuming a common relaxation time for all electrons. This approximated method was implemented in BOLTPZTRAP code14) and has been widely used by researchers. For $k_\text{lat}$, a property of phonons, a first-principles method for calculating the lattice thermal conductivity was also implemented,13) although it is still rather difficult for most researchers to apply because of its limited number of implementations and its high computational cost.

In this work, we attempted to estimate the potential of aluminium-based quasicrystals and their approximant crystals as thermoelectric materials by first-principles methods. Since first-principles band calculations are still difficult to apply to quasicrystals, we focused on approximant crystals, to which the periodic boundary condition can be applied. Another difficulty is to construct a perfect crystal model, which is usually required by band calculations, because most of the experimentally determined structural models of approximant crystals show structural or chemical disorder. We have recently studied the electronic band structure of a less disordered approximant crystal in the Al–Cu–Ir system (space group Fm3, Pearson symbol cF244), whose structural model was reported by Dshemuchadse et al.,15) and we found a semimetallic electronic band structure for the approximant crystal.16) In this work, we measured the thermoelectric properties of the Al–Cu–Ir approximant experimentally and analysed the properties by first-principles methods. To analyse the energy dependence of the relaxation time of electrons, we extended the method of Scheidemantel et al. without significantly increasing the computational cost. The extensions of the method are also reported in this paper.

2. Methods

2.1 Experimental methods

Alloy ingots of desired nominal compositions were prepared from powder elements of aluminium (Kojundo Chemical Lab. Co., Ltd., Japan, purity > 99.99%), copper (Kojundo Chemical Lab. Co., Ltd., Japan, 99.9%) and iridium (Kojundo Chemical Lab. Co., Ltd., Japan, 99.9%) by melting in an arc furnace (NEV-ACD-05, NISSIN GIKEN Corporation, Japan) under argon atmosphere. Then, the ingots were crushed into fine powders with a particle diameter of 10 µm order, and the powders were compacted into disk-shaped pellets using a pulsed-current sintering system (SPS-515S, Sumitomo Coal Mining Co., Ltd., Japan).
under a uniaxial pressure of 57 MPa and argon atmosphere. The maximum temperature during sintering was 1226 K, and the temperature was kept above 1173 K for 90 min. After that, the pellets were wrapped in tantalum foil, sealed in a quartz tube under argon atmosphere and annealed in an electric furnace. We used several annealing temperatures between 1073 K and 1223 K, but no significant difference was observed in the products. The samples used for the following analyses were annealed at 1173 K for 108 h.

Phases in the samples were identified using an x-ray diffractometer (SmartLab, Rigaku Corporation, Japan, copper K-\text{L}_{2,3} \text{ radiation}), and the compositions of the samples were analysed using a characteristic x-ray spectrometer (energy-dispersive spectrometer (EDS) equipped in a scanning electron microscope (JSM-6010LA, JEOL Ltd., Japan)). For the analyses, elemental aluminium, copper and iridium (JEOL Ltd., Japan) were used as standard materials in the measurement of the intensities of K-series x-rays of aluminium, K-series x-rays of copper and L-series x-rays of iridium, respectively, and the ratios of the x-ray intensities from samples to those from the standard materials (usually referred to as \(k\)-ratios) were corrected using \textsc{calczaf} code\(^{15}\) with the default Armstrong/Love/Scott model.

We measured the lattice constant (\(a\)), density (\(\rho\)), longitudinal and transverse speeds of sound (\(v_l\) and \(v_t\), respectively), thermal diffusivity (\(\alpha\)), specific heat capacity at a constant pressure (\(C_p\)), and \(\sigma\) and \(S\) for a single-phase sample. For the measurement of \(a\), silicon powder (SRM 640d, National Institute of Standard and Technology, USA) was mixed with a powdered sample as an internal line-position standard, and an x-ray diffraction profile was measured from 2\(\theta = 70^\circ\) to 2\(\theta = 150^\circ\) using the same equipment as for the phase identification. Then, the measured profile was fitted using \textsc{rieten-fp} code\(^{20}\). \(\rho\) was evaluated from the volume and mass of a bulk specimen (bulk density) and from those of a powdered sample (true density). To measure the volume of the powdered sample, we used a helium pycnometer (Accupyc 1330, Micromeritics Instrument Corp., USA). \(v_l\) and \(v_t\) were measured using an echometer (ECHOMETER 1061, KARL DEUTSCH Prüf-und Messgerätebau GmbH + Co, ultrasonic pulse-echo method). \(\alpha\) was evaluated by fitting the transient temperature profiles measured by the laser flash method (TC-7000, ULVAC-RIKO, Inc., Japan), where CFP32 code\(^{21}\) was used for the fitting. \(C_p\) was measured using a differential scanning calorimeter (DSC7020, SII NanoTechnology Inc., Japan). Alumina powder (SII NanoTechnology Inc., Japan) was used as a standard material in the measurement of \(C_p\), and aluminium containers were used for such measurement. \(\sigma\) and \(S\) were measured by the four-terminal method and temperature gradient method, respectively (ZEM-1, ULVAC-RIKO, Inc., Japan).

### 2.2 Calculational methods

The electronic band structure was calculated within the density functional theory by an all-electron full-potential linearised augmented plane-wave method implemented in a code based on \textsc{elk} code.\(^{22}\) The ground-state electron density of a perfect crystalline model of the Al–Cu–Ir approximant (\(\text{Al}_{0.629}\text{Cu}_{0.129}\text{Ir}_{0.242}\)) was previously calculated by self-consistently solving the Kohn–Sham equation using a 4 \(\times\) 4 \(\times\) 4 regular wave-number grid in the Brillouin zone and has already been reported elsewhere.\(^{18}\) In this work, Kohn–Sham orbitals (\(\phi_{nk}\), where \(n\) is the band index and \(k\) is the wave-number vector) were calculated on an 8 \(\times\) 8 \(\times\) 8 regular wave-number grid using the previously calculated ground-state electron density and used for the following calculations. To calculate the thermoelectric properties at a temperature \(T\), we used the orbital energy (\(\epsilon_{nk}\)), group velocity (\(v_{nk}\)) and relaxation time at \(T\) \([\tau_{nk}(T)]\) of the Kohn–Sham orbitals. Approximations for \(\tau_{nk}\) used in this study are explained later.

Our method used to calculate the thermoelectric properties is the same as that of Scheidemann et al.\(^{13}\) except for the treatment of \(\tau_{nk}(T)\). The method is briefly summarised below. In this paper, the thermoelectric properties are treated as scalars because the material studied in this work was cubic. The transport spectrum is defined as \(\xi(\epsilon; T) = \tau_{el}(\epsilon; T) v_{el}^2(\epsilon) N_{el}(\epsilon)/3\), where

\[
\tau_{el}(\epsilon; T) = \frac{\int_{BZ} \sum_{n,k} \delta(\epsilon_{nk} - \epsilon) v_{nk}^2 \tau_{nk}(T) \, dk}{\int_{BZ} \sum_{n,k} \delta(\epsilon_{nk} - \epsilon) v_{nk}^2 \, dk} \tag{1}
\]

is the averaged relaxation-time spectrum of electrons,

\[
v_{el}(\epsilon) = \left[ \int_{BZ} \sum_{n,k} \delta(\epsilon_{nk} - \epsilon) v_{nk}^2 \, dk \right]^{1/2} \tag{2}
\]

is the speed-of-electron spectrum, \(v_{nk} = \sqrt{v_{nk} \cdot v_{nk}}\) is the Dirac delta function, \(\int_{BZ} \sum_{n,k} \delta(\epsilon_{nk} - \epsilon) \, dk\) is the volume integral over the first Brillouin zone and

\[
N_{el}(\epsilon) = \frac{1}{(2\pi)^3} \int_{BZ} \sum_{n,k} \delta(\epsilon_{nk} - \epsilon) \, dk \tag{3}
\]

is the electronic density of states. An auxiliary function \(w_m(\epsilon; \mu, T) = (\epsilon - \mu)/T\)\([\{-\partial f(\epsilon; \mu, T)/\partial \epsilon\}]\) is also defined, where \(\mu\) is the chemical potential of electrons, \(f(\epsilon; \mu, T) = 1/(\exp[(\epsilon - \mu)/k_bT] + 1)\) is the Fermi–Dirac distribution and \(k_b\) is the Boltzmann constant. The integral of the product of a function \(A(\epsilon)\) and the auxiliary function is denoted by

\[
\langle A(\epsilon) \rangle_{m}(\mu, T) = \int_{-\infty}^{\infty} w_m(\epsilon; \mu, T) A(\epsilon) \, d\epsilon \tag{4}
\]

Let \(K_m(\mu, T) = \langle \xi(\epsilon; T) \rangle_{m}(\mu, T)\), \(\sigma, S\) and the Lorentz number \((L = \sigma_0/T\sigma)\) are represented as

\[
\sigma(\mu, T) = e^2 K_0(\mu, T), \tag{5}
\]

\[
S(\mu, T) = -\frac{K_1(\mu, T)}{eK_0(\mu, T)} \tag{6}
\]

and

\[
L(\mu, T) = \frac{K_2(\mu, T)}{e^2 K_0(\mu, T)} - \left[ \frac{K_1(\mu, T)}{eK_0(\mu, T)} \right]^2, \tag{7}
\]

respectively, where \(e\) is the elementary charge.
We used three different approximations for $\tau_{sd}(\varepsilon; T)$, which is the average of $\tau_{sd}(T)$ on a constant-energy surface with the energy $\varepsilon = \varepsilon$. One is the constant-relaxation-time approximation (CRA) $\tau_{sd}(\varepsilon; T) \approx \tau_{sd}(T)$, where the $\tau_{sd}(T)$ is a parameter that corresponds to the averaged relaxation time. Another is the constant-mean-free-path approximation (CFP) $\tau_{sd}(\varepsilon; T) \approx l_{e}(T)/v_{sd}(\varepsilon)$, where $l_{e}(T)$ is a parameter that corresponds to the averaged mean free path. The other is the constant-diffusion-coefficient approximation $\tau_{sd}(\varepsilon; T) \approx 3D_{\text{CDA}}(T)/v_{d}(\varepsilon)$, where $D_{\text{CDA}}(T)$ is a parameter that corresponds to the averaged diffusion coefficient. In these approximations, the parameters $l_{e}(T), D_{\text{CDA}}(T)$ and $D_{\text{CDA}}(T)$ can be moved outside the integral in $K_{0}(\mu, T)$; therefore, $\sigma$ is proportional to the parameters, whereas $S$ and $L$ are independent of the parameters.

2.3 Model for the specific heat capacity at constant pressure

We used the following theoretical model to extrapolate $C_{P}$ to high temperatures.

By assuming the Debye model for the dispersion relation of phonons, the lattice specific heat capacity at a constant volume was calculated as

$$C_{V}^{(0)} = \frac{3R}{M} \sum_{i=1}^{3} \left( \frac{T}{T_{D,i}} \right)^{3} \int_{0}^{\infty} \frac{x^{4}e^{x}}{(e^{x} - 1)^{4}} dx,$$

where $R$ is the gas constant, the index $i = 1$ denotes the longitudinal branch, $i = 2, 3$ denote the two transverse branches, $M$ is the molar mass (averaged atomic weight multiplied by 1 g/mol), $T_{D,i} = h\nu_{i}/(2\pi^{2}N_{\text{atom}})^{1/3}/k_{B}$ is the Debye temperature for the $i$th branch ($T_{D,1} = T_{D,2} = T_{D,3} = T_{D}$), $h$ is the Dirac constant, $\pi$ is the ratio of a circle’s circumference to its diameter, $v_{i}$ is the speed of sound for the $i$th branch ($v_{1} = v_{1}, v_{2} = v_{3} = v_{t}$) and $\rho_{\text{atom}}$ is the number density of the atoms. We used experimental values for $v_{1}$ and $v_{t}$, $M$ was calculated from the experimentally analysed composition. $\rho_{\text{atom}}$ was calculated from the composition and the experimental value of $\rho$.

Letting $K_{0}(\mu, T) = \langle N_{\text{el}}(\varepsilon) \rangle_{\mu}(\mu, T)$, the electron specific heat capacity at a constant volume was calculated from the electronic density of states calculated by the band calculation and the experimental value of $\rho$ as

$$C_{V}^{(0)}(\mu, T) = \frac{T}{\rho} \left[ K_{2}(\mu, T) - \frac{K_{1}(\mu, T)}{K_{0}(\mu, T)} \right],$$

$C_{P}$ was calculated using the thermodynamic relation

$$C_{P} = C_{V} + \left[ 1 - \frac{\alpha_{\nu}^{2}B_{3}(T)}{\rho C_{V}} - \frac{1}{2} \right] C_{V},$$

where $C_{V} = C_{V}^{(0)} + C_{V}^{(0)}$, $B_{3}$ is the isentropic bulk modulus and $\alpha_{\nu}$ is the volumetric thermal expansion coefficient. By assuming isotropic elasticity, the room-temperature value of $B_{3}$ was calculated from the experimental values of $\rho$ and $v_{t}$ as $B_{3}(300 \text{ K}) = (\rho v_{t}^{3} - 4v_{t}^{3})/3$. Tanaka et al.\(^{25}\) found a universal relation of the form $B_{3}(T)/B_{3}(0 \text{ K}) = g(T/T_{M})$ between the $T$ dependence of $B_{3}$ and the melting temperature ($T_{M}$) for some classes of metals and semiconductors including aluminium–transition-metal quasicrystals. The Al–Cu–Ir quasicrystalline approximant, the target of this study, is expected to obey this relation similarly to quasicrystals. The relation can be approximated as $g(T/T_{M}) = 1 - [0.11(T/T_{M} + 0.17(T/T_{M})^{2})]$. If we assume a relative standard uncertainty of 20% for the second term, which represents the variation of the ratio from that at 0 K, this formula reasonably reproduces the dispersion of the data reported by Tanaka et al. By changing the base temperature from 0 K to 300 K, the formula is modified to

$$\frac{B_{3}(T)}{B_{3}(300 \text{ K})} = 1 + \frac{g(T/T_{M}) - g(300 \text{ K}/T_{M})}{g(300 \text{ K}/T_{M})},$$

and, again, a relative standard uncertainty of 20% is assumed for the second term. We used this formula to estimate the $T$ dependence of $B_{3}$. Although $T_{M}$ for the Al–Cu–Ir approximant phase was not determined, its possible range is from 1673 K\(^{24,25}\) to 1773 K.\(^{17}\) Thus, we estimated $T_{M}$ to be 1.73(3) kK. $\alpha_{\nu}$ for cubic crystalline materials can be calculated from the linear expansion coefficient ($\alpha_{l}$) as $\alpha_{\nu} = 3\alpha_{l}$. We used $\alpha_{l} = 13$ MK\(^{-1}\), which was reported for an Al–Fe–Pd quasicrystalline approximant by Edagawa et al.,\(^{26}\) and estimated a relative standard uncertainty of 10%.

2.4 Estimation of unknown parameters

To compare the calculated thermoelectric properties with experimental data, we need to estimate $\mu$ corresponding to the actual sample. If we know the number of valence electrons per primitive unit cell ($n_{el}$) and use the rigid-band approximation, i.e., the dispersion relation is assumed to be independent of $T$ and $n_{el}, \mu$ can be determined from the relation

$$n_{el} = V \int_{-\infty}^{\infty} N_{\text{el}}(\varepsilon; \mu, T) d\varepsilon,$$

where $V$ is the volume of a primitive unit cell. $n_{el}$ can be calculated from the numbers of aluminium atoms ($n_{Al}$), copper atoms ($n_{Cu}$) and iridium atoms ($n_{Ir}$) per primitive unit cell as $n_{el} = 3n_{Al} + 11n_{Cu} + 9n_{Ir}$, and thus, we can calculate $\mu$ under the rigid-band approximation. However, from the results and discussion of a previous study on the electronic structure of the Al–Cu–Ir approximant,\(^{18}\) the number of valence states per primitive unit cell ($n_{V}$) is considered to be variable, and a general formula used to evaluate $n_{V}$ was suggested. In the case of the Al–Cu–Ir approximant, the formula is expressed as $n_{V} = 116 + 10n_{T}$, where $n_{T} = n_{Cu} + n_{Ir}$ is the number of transition-metal atoms per primitive unit cell. Using this specific formula, the number of valence states in $\text{Al}_{11}\text{Ir}_{11}$ (space group $\text{Pnma}$, Pearson symbol $\text{oP60}$),\(^{27}\) another approximant with a similar crystal structure, has also been exactly evaluated.\(^{19}\) Recently, the general formula has successfully applied to estimate the number of valence states in aluminium–transition-metal quasicrystals.\(^{28}\) Now, the formula is understood as a general variant of the well-known $18 - n$ rule,\(^{29}\) which predicts and explains the number of valence states in many main-group–transition-metal intermetallic compounds,\(^{10}\) and thus, the wide applicability of the formula has been well proved. Taking into account the variability of $n_{V}$ with respect to the composition, we adopted the rigid-band approximation with the assumption that the change in $n_{V}$ did not significantly
affect the dispersion relation near the Fermi energy. In this approximation, the relative number of valence electrons, $n_d^* = n_v - n_{el}$, can be directly compared among different compositions. The sign of $n_d^*$ is chosen so as to be positive in the case of electron deficiency compared with $n_v$.

In experiments, we evaluated $n_d^*$ from the composition, $a$ and $\mu$. However, the standard uncertainty of $n_d^*$ evaluated by this method was rather large. Therefore, we estimated $n_d^*$ complementarily by another method. Because the calculation of $S$ does not involve the parameters for the relaxation time, i.e., $\tau_{CFA}(T)$, $l_{CFA}(T)$ or $D_{CDA}(T)$, we can apply the least-squares method to estimate $n_d^*$. Let $T_i, S_i$ and $u(S_i)$ be the temperature, Seebeck coefficient and standard uncertainty of $S_i$, respectively, for the $i$th measurement point. The weighted sum of squared residuals is then defined as $J = \sum_i [(S_i - S(\mu_i, T_i))/u(S_i)]^2$, where $\mu$ depends on $n_d^*$. $n_d^*$ was estimated by minimising $J$.

The other parameters to be estimated are $\tau_{CRA}(T)$, $l_{CFA}(T)$ and $D_{CDA}(T)$. For the convenience of comparison, we defined a common parameter related to these three parameters. The new parameter is the effective relaxation time $\tau_{el}^*(\mu, T) = (\tau_{el}(\mu, T) + \tau_{el}^*(\mu, T))$, which is related to $\sigma(\mu, T) = \epsilon^2 \tau_{el}(\mu, T)\Phi^2\tau_{el}(\mu, T)N_{el}(\mu, T)/3$, where $N_{el}(\mu, T) = (N_{el}(\mu))/\mu(T)$ is the effective density of states and $\Phi(\mu, T) = \sqrt{(\tau_{el}(\mu, T)/\mu(T))(N_{el}(\mu))/\mu(T)}$ is the effective speed of electrons. From the condition $\sigma(\mu, T) = e^2 \tau_{el}(\mu, T) = 3\tau_{el}(\mu, T)/\Phi^2\tau_{el}(\mu, T)$, follows, where $\mu$ is fixed at the value estimated as explained above. The original parameters can be evaluated using the relations $\gamma_{el}^*(\mu, T) = \tau_{CRA}(T)$ for CRA, $\gamma_{el}^*(\mu, T) = l_{CFA}(T)/\Phi(\mu, T)$ for CFA and $\gamma_{el}^*(\mu, T) = 3D_{CDA}(T)/\Phi^2(\mu, T)$ for CDA.

### 3. Results and Discussion

In this paper, the number in parentheses following the value of any data is the standard uncertainty referred to the last digit of the quoted value. In the graphs, the uncertainty is represented by error bars (for discrete data) or filled regions (for continuous data). The uncertainty is omitted if it is negligible compared with the reported data. For the names of phases, we follow the convention of Kapush et al.25 The name of the Al–Cu–Ir approximant phase is C$_2$ (space group Fm$\bar{3}$).

#### 3.1 Identification of the samples

X-ray diffraction profiles for the samples with the nominal compositions of Al$_{0.660}$Cu$_{0.110}$Ir$_{0.230}$ (sample A), Al$_{0.650}$Cu$_{0.120}$Ir$_{0.230}$ (sample B) and Al$_{0.652}$Cu$_{0.129}$Ir$_{0.242}$ (sample C) are shown in Fig. 1. Sample A was identified as a mixture of C$_2$ (or possibly C), Al$_3$Ir and D$_1$ phases. Sample B was identified as a single C$_2$ phase. Sample C was identified as a mixture of C$_2$, $\beta$ and Al$_3$CuIr phases.

The compositions of the samples analysed by using an EDS are plotted in Fig. 2. The composition of sample B lies near the boundary of the tie triangle of the phases in sample A, and therefore, it is near the aluminium-rich limit of the C$_2$ phase. The mole fraction of aluminium is 1% higher than that at the phase boundary at 1173 K reported by Kapush et al. This may be due to the different correction model used in the quantitative analyses. Although sample C was identified as a mixture of C$_2$, $\beta$ and Al$_3$CuIr phases by x-ray diffraction, we could not find grains of the Al$_3$CuIr phase with an analysable size. In Fig. 2, the stoichiometric composition of Al$_3$CuIr is plotted as a guide for the readers.

The results of the phase identification and composition analyses are summarised in Table 1. Sample B was successfully synthesised as a single C$_2$ phase. Therefore, we measured the properties of sample B. $a$ for sample B was 1.5390(2) nm, which lies within the range of the reported values (from 1.5384 nm to 1.5395 nm$^{17,25,31}$). The bulk density was 7.82(4) Mg m$^{-3}$ and the true density was 7.8(2) Mg m$^{-3}$; hence, the relative density was 101(2)%. In the following analyses, we used the weighted average of the bulk and true densities of 7.82(3) Mg m$^{-3}$ as the value of $\rho$. $v_1$ was 5.64(2) km s$^{-1}$ and $v_2$ was 2.99(1) km s$^{-1}$. $M = 69.5(5)$ g mol$^{-1}$ was evaluated from the composition. $\rho_{\text{atom}} = 68.5(5)$
value of 165 GPa.\(^{18}\) This is probably due to the local density approximations for \(n=\) 0.3 Mm s\(^{-1}\). The value of \(B_\parallel\) was evaluated from the composition, \(C\) and \(F\) are chosen as the origin for convenience in comparison. The value of \(B_\parallel\) was higher than that of CRA in these ranges for the same reason.

### Table 1 Phases in the samples and their compositions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Analysed composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>C(_2) (or C)</td>
<td>(Al_0.665(3)Cu_0.118(1)Ir_0.227(3))</td>
</tr>
<tr>
<td></td>
<td>Al(_3)Ir</td>
<td>(Al_0.656(3)Cu_0.068(1)Ir_0.235(3))</td>
</tr>
<tr>
<td></td>
<td>D(_1)</td>
<td>(Al_0.617(3)Cu_0.215(3)Ir_0.168(3))</td>
</tr>
<tr>
<td>B</td>
<td>C(_2)</td>
<td>(Al_0.649(3)Cu_0.121(2)Ir_0.239(3))</td>
</tr>
<tr>
<td>C</td>
<td>(\beta)</td>
<td>(Al_0.623(3)Cu_0.122(2)Ir_0.255(3))</td>
</tr>
<tr>
<td></td>
<td>(Al_2CuIr)</td>
<td>(Al_0.542(3)Cu_0.131(2)Ir_0.327(4))</td>
</tr>
</tbody>
</table>

* We could not find grains of this phase with an analysable size, although we confirmed their existence by x-ray diffraction measurement.

nm\(^{-3}\) was evaluated from the composition and \(\rho\). \(T_{D1} = 688(5)\) K and \(T_{D2} = 365(3)\) K were evaluated from \(v_0\), \(v_1\) and \(\rho_{\text{com}}\). \(B_\parallel(300\) K\) = 156(2) GPa was evaluated from \(v_0\), \(v_1\) and \(\rho\). The value of \(B_\parallel(0\) K\) = 159(2) GPa extrapolated using eq. (11) was 4\% smaller than the theoretically calculated value of 165 GPa.\(^{18}\) This is probably due to the local density approximation, which tends to overestimate \(B_\parallel(0\) K\).\(^{32}\)

\(n_{Al} = 40.1(5), n_{Cu} = 7.5(1), n_{Ir} = 14.2(1)\) and \(n_{el}^* = 3(2)\) were evaluated from the composition, \(a\) and \(\rho\).

### 3.2 Calculation of the transport spectrum

Figure 3(a) shows the calculated \(\xi(\varepsilon; T)\) near the Fermi energy of the \(Al_3CuIr\) model (\(\varepsilon_F\)) under the three approximations for \(\tau_0(\varepsilon; T)\), where \(\varepsilon_F\) is chosen as the origin of the energy, i.e., \(\varepsilon_F = 0.0\) aJ (0.0 eV), 1 aJ \(\approx 6.2415\) eV. In this figure, the values of the parameters in \(\tau_0(\varepsilon; T)\) are chosen so that the three \(\xi(\varepsilon; T)\) curves have the same magnitude within the energy range between 0.0 aJ (0.0 eV) and 0.2 aJ (1.2 eV) for convenience in comparison. There is a valley-like structure in every spectrum between 0.0 aJ (0.0 eV, 1 aJ) and 0.2 aJ (1.2 eV). It originates from the so-called pseudogap; a similar structure is observed in \(N_{el}(\varepsilon)\) [Fig. 3(b)]. As shown in Fig. 3(c), \(\nu_{el}(\varepsilon)\) is approximately 0.3 Mms\(^{-1}\) and does not vary significantly in the same range. As a result, \(\xi(\varepsilon; T)\) curves are similar in shape in the same range. In the energy ranges below 0.0 aJ (0.0 eV) and above 0.2 aJ (1.2 eV), the \(\xi(\varepsilon; T)\) curves are different from one another because the energy dependence of \(\nu_{el}(\varepsilon)\) is significant in these ranges. The \(\xi(\varepsilon; T)\) of CFA is higher than that of CRA in these ranges because the \(\xi(\varepsilon; T)\) of CFA is proportional to that of CRA divided by \(\nu_{el}(\varepsilon)\). The \(\xi(\varepsilon; T)\) of CDA is higher than that of CFA in these ranges for the same reason.

Figure 3(d) shows \(\mu(0\) K\) as a function of \(n_{el}^*\); \(n_{el}^* = 0\) near the bottom of the pseudogap.

### 3.3 Comparison of experimental and calculated Seebeck coefficients

Figure 4 shows the experimentally measured \(S\) for sample B and its best-fitting curves calculated under CRA, CFA and CDA. The experimental \(S\) increases with \(T\) from 12(1)\(\mu V\) K\(^{-1}\) at 379(1) K to 45(2)\(\mu V\) K\(^{-1}\) at 1020(4) K. Under CRA and CFA, the experimental \(S\) could not be fitted well with any value of \(n_{el}^*\). Under CDA, the experimental \(S\) was fitted within the standard uncertainty except for temperatures around 1000 K. The values of \(J\) for the best-fitting curves under CRA, CFA and CDA are 127, 65 and 9, respectively. This quantitatively confirms the goodness of the fitting under CDA. The values of \(n_{el}^*\), 2.2(1) for CRA, 2.4(1) for CFA and 2.79(6) for CDA were estimated from the fitting.
These values are comparable to the value of \( n^*_{el} = 3(2) \) estimated from the composition, \( \alpha \) and \( \rho \).

Hereafter, we consider three models, the fitted CRA (FCRA), fitted CFA (FCFA) and fitted CDA (FCDA) models, for which the values of \( n^*_{el} \) are fixed at the estimated values. For the best-fitting FCDA model, \( n^*_{el} = 2.79(6) \) and the corresponding visible in the vicinity of \( \mu(0\,\text{K}) \) was 0.04 aJ \((0.25 \text{ eV}) \) [Fig. 3(d)]. Figure 3(e) shows the \( T \) dependence of \( \mu \) for the three models. \( \mu \) increases with \( T \) for these models. In this figure, the energy ranges \( \mu(T) \pm 5\epsilon_B T \), which affect the thermoelectric properties significantly, are also shown. The conduction bands can affect the properties approximately above 800 K.

### 3.4 Comparison of experimental and calculated electromagnetic conductivities

Figure 5(a) shows the experimentally measured \( \sigma \) for sample B. \( \sigma \) decreases with increasing \( T \) from 0.43(4) MS m\(^{-1}\) at 379(1) K to 0.26(2) MS m\(^{-1}\) at 1020(4) K.

\( N^*_v \) and \( v^*_v \) calculated for the FCRA, FCFA and FCDA models are shown in Fig. 5(b) and Fig. 5(e), respectively, and \( \tau^*_v \) estimated by comparing the experimental and calculated \( \sigma \) values is shown in Fig. 5(d). \( N^*_v \) and \( v^*_v \) are significantly different among the four models. On the other hand, the differences in \( \tau^*_v \) among the models are small compared with the associated standard uncertainty, which was mainly propagated from that of the experimental \( \sigma \); therefore, the choice of the approximation applied to \( \tau^*_v \) was not important for estimating \( \tau^*_v \) in this case. The \( T \) dependence of \( \sigma \) originates mainly from those of \( N^*_v \) and \( v^*_v \).

### 3.5 Total, electronic and lattice thermal conductivities

Figure 6(a) shows the experimentally measured \( C_p \) for sample B. \( C_p \) increases with \( T \) from 1.78(5) mm\(^2\)s\(^{-1}\) at 373 K to 2.11(6) mm\(^2\)s\(^{-1}\) at 973 K.

Figure 6(b) shows the experimentally measured \( C_p \) for sample B and that calculated using eq. (10) with \( C^\text{lat}_V \) for the Debye model and \( C^\text{FCDA}_V \) for the FCDA model. The calculated \( C_p \) coincides with the experimental \( C_p \) within the standard uncertainty. We used the calculated value to evaluate \( \kappa \).

Figure 6(c) shows \( \kappa \) evaluated from the relation \( \kappa = \alpha C_p \). \( \kappa \) increases with \( T \) from 4.7(2) W m\(^{-1}\)K at 373 K to 6.3(2) W m\(^{-1}\)K at 973 K.

Figure 6(d) shows \( L \) calculated for the FCRA, FCFA and FCDA models, and that based on the Wiedemann–Franz law, i.e., \( L = L_0 = \pi^2 k^2_B/(3e^2) \). The calculated values of \( L \) are approximately 80% of \( L_0 \) or even lower. Both terms in eq. (7) can cause \( L \) to be lower than \( L_0 \). The first term in eq. (7) can be lower than \( L_0 \) if the average curvature of the \( \xi(\epsilon; T) \) curve is negative in the vicinity of \( \epsilon = \mu \), e.g., \( \pm 5\epsilon_B T \). As is obvious from Fig. 3(a) and Fig. 3(c), the average curvature of the \( \xi(\epsilon; T) \) curve is negative for three models. The difference in \( L \) among the three models above 600 K can be attributed to the difference in the shape of the \( \xi(\epsilon; T) \) curve below 0.04 aJ \((0.25 \text{ eV}) \). \( L \) for the FCRA model is the lowest among the three models because the curvature of the \( \xi(\epsilon; T) \) curve is the largest. The second term in eq. (7) is equal to \( -S^2 \); therefore, \( L \) can be low if \( |S| \) is large.

Figure 6(e) shows \( \kappa_\text{lat} \) evaluated from the relation \( \kappa_\text{lat} = L_0 T \); and Fig. 6(f) shows \( \kappa_\text{lat} \) evaluated from the relation \( \kappa_\text{lat} = \kappa - \kappa_\text{el} \). \( \kappa_\text{lat} \) is different among the models because of the difference in \( L \), and hence, \( \kappa_\text{lat} \) is different among the models. If \( L = L_0 \) is assumed, \( \kappa_\text{lat} \) is negative at 973 K. In the cases of the FCRA and FCDA models, \( \kappa_\text{lat} \) unexpectedly increases, but the tendencies are similar to those for the FCDA model.
Fig. 6 Temperature (T) dependence of (a) the thermal diffusivity (α), (b) the specific heat capacity at constant (atmospheric) pressure (Cp) and (c) the thermal conductivity (κ) of sample B (open circles). In (b), the Cp values evaluated using the Debye and FCDA models are shown as a solid line. T dependence of (d) the Lorenz number (L), (e) the electronic thermal conductivity (κel) and (f) the lattice thermal conductivity (κlat) of sample B based on the FCRA (dotted line or open triangles), FCFA (dashed line or open squares) and FCDA (solid line or open circles) models and those based on the Wiedemann–Franz law (dash-dotted line or filled circles). In (f), the minimum thermal conductivity (κmin) for sample B is shown as a solid line. In (e) and (f), the standard uncertainties for the FCRA and FCFA models are not shown to improve visibility. The magnitudes of the standard uncertainties are similar to those for the FCDA model.

with T even at high temperatures. This increasing behavior might be due to the radiative contribution to the thermal conductivity (κrad). According to Murashov and White,\(^1,2\)

\[ \kappa_{\text{rad}} = 16\eta^2\sigma_{\text{SB}}T^3/3k_r, \]

where \( \eta \) is the refractive index, \( \sigma_{\text{SB}} \) is the Stefan–Boltzmann constant and \( k_r \) is the Rosseland mean absorption coefficient. \( \kappa_{\text{rad}} \) can be significant if the material is infrared-transparent. The material studied in this work is opaque to visible light, and it is also probably opaque to infrared light. A sample of an opaque material can be partly transparent if it has pores, but this is not the case for the sample studied in this work as its relative density is 101(2)\%. Furthermore, the curvature of \( \kappa_{\text{lat}} \) curves is negative, whereas it should be positive owing to the \( T^3 \) factor if \( \kappa_{\text{rad}} \) is significant. For these reasons, the increasing behavior of \( \kappa_{\text{lat}} \) for the FCRA and FCFA models cannot be attributed to \( \kappa_{\text{rad}} \).

In the case of the FCDA model, \( \kappa_{\text{lat}} \) decreases with increasing \( T \) at high temperatures, asymptotically approaching the minimum thermal conductivity (\( \kappa_{\text{min}} \)) calculated on the basis of the model of Cahill et al.\(^{24} \) as shown in Fig. 6(f ). In summary, only the FCDA model resulted in a physically acceptable \( \kappa_{\text{lat}} \) for the present sample.

3.6 Energy dependence of the relaxation time of electrons

In this work, we considered three approximations for \( \tau_0(\varepsilon; T) \), i.e., CRA, CFA and CDA. The experimental S was almost completely reproduced by the FCDA model, and a physically acceptable \( \kappa_{\text{lat}} \) was derived only using the FCDA model. This indicates that CDA is a good approximation for the \( \tau_0(\varepsilon; T) \) of the Al–Cu–Ir approximant phase for sample B.

Takeuchi et al.\(^6 \) reported that S for the Al–Re–Si approximant phase was quantitatively reproduced under the assumption that both \( \tau_0(\varepsilon; T) \) and \( \nu_0(\varepsilon) \) were independent of energy. Since this assumption is equivalent to CDA in regard to the calculation of S, CDA can be a good approximation for both the Al–Cu–Ir and Al–Re–Si approximant phases. One may further expect that CDA will be a good approximation for the \( \tau_0(\varepsilon; T) \) of approximant phases in general. To validate this, the physical origin of CDA must be identified. In the case of the Al–Re–Si approximant phase, the origin of CDA was attributed to the Mott limit, where the mean free path of electrons approaches the Fermi wavelength, without examining the value of the mean free path.\(^6 \) In our method, the averaged mean free path can be evaluated as \( l_{\text{eff}}(\mu, T) = \tau_0(\mu, T)\nu_0(\mu, T) \).

Figure 7 shows \( l_{\text{eff}} \) evaluated for sample B using the FCDA model. \( l_{\text{eff}} \) decreases with increasing \( T \) from 1.7(2) nm at 379(1) K to 1.3(1) nm at 1020(4) K. Because \( l_{\text{eff}} \) changes with \( T \), it has not yet reached the Mott limit in this temperature range. This problem may be solved by studying \( \tau_0(\varepsilon; T) \) for these approximant phases in more detail by a first-principles method.
3.7 Thermoelectric figure of merit

Figure 8 shows $zT$ evaluated from $\sigma$, $S$ and $\kappa$ for sample B. $zT$ increases with $T$ from 0.005(1) at 376(3) K to 0.08(1) at 973(2) K.

To estimate the upper limit of $zT$ for the approximant phase, $zT$ was rewritten as

$$zT = \left[ \frac{L}{S^2} + \frac{3(k_{lat}/\rho_{el})}{Te^2\nu_{el}N_{el}^2S^2} \right]^{-1}. \quad (13)$$

Figure 9 shows $k_{lat}/\rho_{el}$ evaluated for sample B. $k_{lat}/\rho_{el}$ is approximately equal to 1.2 GW m$^{-2}$K$^{-1}$ and can be regarded as a constant within the standard uncertainty. Using this value with CDA, $zT$ was calculated as a function of $n_{el}^*$ and $T$ as shown in Fig. 10. The maximum $zT$ was estimated to be 0.3 for $n_{el}^* = 0.5$. Since $n_{el}^* = 2.79(6)$ for sample B, $zT$ may be improved by electron doping.

Another strategy for improving $zT$ is to lower $k_{lat}$, for example, by nanostructuring. However, in the case of the Al–Cu–Ir approximant phase, $k_{lat}$ was estimated to be near $k_{min}$ at high temperatures, and therefore $k_{lat}$ may be lowered only at low temperatures.

A major reason for the low maximum $zT$ is that the band structure of the Al–Cu–Ir approximant (C$_2$ phase) is not semiconducting but semimetallic, i.e., there is no bandgap near the Fermi energy. Our prediction of $zT$ can fail because it is based on the rigid-band approximation. On the other hand, non-rigid-band effects are introduced by elemental substitutions in real systems. If all the copper atoms in the Al–Cu–Ir approximant are substituted by aluminium or iridium atoms, we can obtain an Al–Ir approximant phase (C phase). For the Al–Ir approximant phase, the formation of a semiconducting band structure is theoretically predicted if an appropriate local atomic order is realised.\(^{(27)}\)

4. Conclusion

The thermoelectric properties of a less disordered approximant crystal in the Al–Cu–Ir system (C$_2$ phase) were investigated experimentally and theoretically, and the potential of the approximants as thermoelectric materials was estimated. $zT$ for the experimentally synthesised sample was lower than 0.1. In the calculations, we examined three approximations for $\tau_{el}(e; T)$, i.e., CRA, CFA and CDA. The experimental $S$ was almost completely reproduced under CDA, and a physically acceptable $k_{lat}$ was derived only under CDA. Although the physical origin of CDA is still under discussion, CDA should be considered as an approximation of $\tau_{el}(e; T)$ for approximant crystals. The maximum $zT$ of 0.3 was estimated for the Al–Cu–Ir approximant under the rigid-band model. $zT$ higher than 1 may not be achieved for approximant phases unless semiconducting phases are realised.

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REFERENCES