Comparative study of high-temperature specific heat for Al–Pd–Mn icosahedral quasicrystals and crystal approximants

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Abstract
Quasicrystals (QCs) have a peculiar structural order characterized by quasiperiodicity and non-crystallographical point group symmetry. To reveal their characteristic physical property reflecting the peculiar structural order, specific heat measurements were performed for Al–Pd–Mn icosahedral QCs (i-QCs) and a series of crystal approximants (CAs) of 2/1-1/1- and 1/0-cubic types at 400–1200 K. The measured specific heat per atom at constant pressure \( c_V \) was converted to that at constant volume \( c_V \) by using data of the thermal expansion coefficient and bulk modulus. Below \( \sim 700 \) K, the \( c_V \) values of all the specimens of i-QCs and CAs were close to \( 3 R \) (\( R \): Boltzman’s constant), i.e., they obeyed Dulong–Petit’s law. With further increase in temperature, the i-QCs showed a dramatic increase in \( c_V \) with increasing temperature, and reached \( 5 R \) at 1100 K. In contrast, the 2/1 CAs showed a similar but slightly smaller increase in \( c_V \), whereas the 1/1 and 1/0 CAs showed a negligible increase. The systematic behavior of \( c_V \) in the order of CAs and QC demonstrates that a large excessive specific heat is a characteristic feature of QCs, reflecting the peculiarity of their structural order. Its possible physical mechanism was discussed in terms of anharmonic atomic vibrations, electronic excitations, and phason excitations.

1. Introduction

Quasicrystals (QCs) have a peculiar structural order characterized by quasiperiodicity and non-crystallographical point group symmetry [1, 2]. Since their discovery in an Al-Mn alloy in 1984 [3], many efforts have been devoted to revealing the physical properties that reflect truly the peculiar structural order of QC alloys. Unusual behavior in specific heat observed at high temperatures for some QC alloys may be one such property. In the early 2000s, the results of specific heat measurements for an icosahedral (i-) Al–Pd–Mn and a decagonal (d-) Al-Cu-Co QC alloys in a high temperature range were reported [4, 5], in which large upward deviations from the Dulong-Petit value were shown. Here, the values of specific heat per atom at constant volume, \( c_V \), were 4.5–5 \( R \) (\( R \): Boltzman’s constant) at 1100 K, which is substantially larger than the Dulong–Petit value of 3 \( R \). Specific heat measurements for an Al–Cu–Fe i-QC were reported in 2008 [6]; the value of \( c_V \) for the i-Al-Cu-Fe was approximately 3.6 \( R \) at 900 K. Recently, specific heat measurements were reported for Al-Cu-Ru i-QCs [7], where the \( c_V \) ranged within 4–4.5 \( R \) at 1100 K and a peak was observed for the \( c_V \) with the maximum value of about 6.5 \( R \) at about 1200 K.

Although the origin of the large excessive specific heat has been discussed [4–10], it has not yet been clarified. A possible origin could exist in the phason elastic degrees of freedom of QCs [11, 12]. In principle, with increasing temperature, the phason fluctuations could grow, increasing the internal energy of the system. Here, phason fluctuations consist of rearrangements of atoms, and differ from atomic vibrations around the equilibrium position. This indicates that the increase in internal energy through phason fluctuations should be additive to that by phononic atomic vibrations. Therefore, phason fluctuations should result in an excessive...
specific heat, in addition to the Dulong–Petit value. However, the excessive specific heat observed for an Al-Cu-Fe i-QC in a high temperature region has been interpreted as a part of a Schottky-type anomaly with a two-level excitation of the energy increment of 0.25 eV [8, 9]. An electronic excitation is considered to be the most plausible source of this two-level excitation.

By approximating the ratios of the incommensurate length scales in QC structures by rational values, periodic structures that are locally similar to the structure of QCs can be obtained. Phases for which the atomic structure can be interpreted as such periodic structures are called the crystal approximant (CA). Periodic structures that are locally similar to the structure of QCs can be obtained. Phases for which the atomic behavior of the energy increment of 0.25 eV are called the crystal approximant (CA) to the QC [13]. To clarify whether the large excessive specific heat observed for QCs in a high-temperature range truly reflects their peculiar structural order, comparing the behavior of CA and CAs must be crucially important.

In the present study, specific heat measurements were performed for Al–Pd–Mn i-QCs and a series of crystal approximants (CAs) of 2/1 in 1/1- and 1/0-cubic types in a high-temperature range. This is the first comparative study of high-temperature specific heat between QCs and a complete series of CAs available. A systematic behavior of CA in the order of CAs and QC was observed, demonstrating that the large excessive specific heat is a characteristic feature of QCs, reflecting the peculiarity of their structural order. Its possible physical mechanism was discussed in terms of anharmonic atomic vibrations, electronic excitations, and phasonic excitations.

### 2. Experimental procedures

We produced samples of four phases: i-QC and CAs of the cubic 2/1, 1/1, and 1/0 types. Here, \( p/q \) indicates a rational approximant to the golden means \( \tau = (1 + \sqrt{5})/2 \) that are the ratios of incommensurate length scales along three mutually orthogonal twofold directions in the i-QC structure. We can construct a series of the rational approximants, \( \{ F_n/n = 1, 2, \ldots \} \) defined by \( F_{n+2} = F_{n+1} + F_n \), where \( F_1 = 0 \) and \( F_2 = 1 \). Here, \( n \) in \( F_{n+1}/F_n \) corresponds to the order of CA, which are 3, 2, and 1 for \( p/q = 2/1, 1/1, \) and 1/0, respectively; the larger the value of \( n \), the closer the CA is to the QC.

We prepared the alloys listed in table 1 from the elemental constituents through arc melting under an argon atmosphere, where the compositions of the phases were selected based on [14–19]. As shown in table 1, several alloys were prepared for each phase, including those with different compositions. The alloys were annealed typically at 1073 K for 24 h, followed by water-quenching. Powder x-ray diffraction measurements were performed using Cu Kα radiation to identify the phases that were formed. From the annealed ingots, we cut out specimens with a circular column shape \((5 \text{ mm} \times 1 \text{ mm})\) and performed specific heat measurements through differential scanning calorimetry (DSC; NETZSCH STA404F3 instrument) with a heating rate of 20 K min\(^{-1}\). The temperature ranges in the measurements were from 400 K to 1100 K for i-QCs, to 1040 K for 2/1-CAs, to 1050 K for 1/1-CAs, to 1170 K for Al-Pd-Fe 1/0-CAs, and to 1400 K for Al-Pd-Ru 1/0-CAs. The upper limit temperatures were determined in view of the melting temperatures \( T_m \) of the respective phases: they are approximately 50 K below \( T_m \). The DSC apparatus was equipped with an oxygen trap system, using which the oxygen concentration at the sample could be reduced to below 1 ppm. High-temperature x-ray diffraction experiments were conducted using Cu Kα radiation to evaluate the thermal expansion coefficients of the i-QC in the temperature range of 373–1023 K. By using the evaluated thermal expansion coefficients and the bulk elastic

| Sample | Alloy composition | Phase |
|--------|------------------|-------|
| APM-1  | Al\(_{71.3}\)Pd\(_{20.3}\)Mn\(_{2}\) | i-QC  |
| APM-2  | Al\(_{71.3}\)Pd\(_{20.3}\)Mn\(_{2}\) | i-QC  |
| APM-3  | Al\(_{71.3}\)Pd\(_{20.3}\)Mn\(_{2}\) | i-QC  |
| APM-4  | Al\(_{71.3}\)Pd\(_{20.3}\)Mn\(_{2}\) | i-QC  |
| APM-5  | Al\(_{71.3}\)Pd\(_{20.3}\)Mn\(_{2}\) | i-QC  |
| APMS-1 | Al\(_{69.5}\)Pd\(_{23}\)Mn\(_{6.2}\)Si\(_{1.3}\) | 2/1  |
| APMS-2 | Al\(_{69.5}\)Pd\(_{23}\)Mn\(_{6.2}\)Si\(_{1.3}\) | 2/1  |
| APMS-3 | Al\(_{69.7}\)Pd\(_{11}\)Mn\(_{14.4}\)Si\(_{1.3}\) | 2/1  |
| APMS-4 | Al\(_{69.7}\)Pd\(_{11}\)Mn\(_{14.4}\)Si\(_{1.3}\) | 2/1  |
| APF-1  | Al\(_{65}\)Pd\(_{30}\)Fe\(_{5}\) | 1/0  |
| APF-2  | Al\(_{65}\)Pd\(_{30}\)Fe\(_{5}\) | 1/0  |
| APR-1  | Al\(_{68}\)Pd\(_{20}\)Ru\(_{11.5}\) | 1/0  |
| APR-2  | Al\(_{68}\)Pd\(_{20}\)Ru\(_{11.5}\) | 1/0  |
| APR-3  | Al\(_{68}\)Pd\(_{20}\)Ru\(_{11.5}\) | 1/0  |
moduli previously reported [20], the measured specific heats at constant pressure were converted to those at constant volume.

3. Results

Figures 1(a)–(f) show x-ray diffraction spectra for some of the samples in table 1. Here, the Cu Kα₂ component was removed from the raw data through data treatment. In figures 1(a) and (b), all the peaks in APM-1 and APM-4 correspond to the i-QC, respectively. Furthermore, all the peaks in figures 1(c) and (d) for APMS-1 and APMS-4 can be assigned as 2/1- and 1/1-CAs, respectively. Finally, all the peaks in figures 1(e) and (f) for APF-1 and APR-2 correspond to the 1/0-CA, respectively. All the x-ray diffraction peaks in figures 1(a)–(f) are sharp, and the peak widths are close to the instrumental resolution limit, indicating the high structural quality of the samples. The other samples in table 1 were also examined through x-ray diffraction and are confirmed to be of a single respective phase with high quality.

Figure 2(a) presents the 664004 peaks in the x-ray diffraction spectra of i-QC measured at different temperatures for APM-4, where we follow the indexing scheme of Elser [21]. Here, the Cu Kα₂ component has been removed from the raw data through data treatment. As observed, the peak position shifts toward a low angle with increasing temperature, and this is attributable to thermal expansion. The peak position was determined by fitting the data with a Voigt function. Based on the determined peak position, we evaluated the value of $d = \lambda/(2 \sin \theta)$ ($\lambda$: x-ray wavelength). These values were normalized to that at 373K, and plotted against temperature, as shown in the inset of figure 2(a). Curve fitting was performed for the $d/d_{373}$ data, and the linear thermal expansion coefficient, $\alpha$, was calculated by differentiating the function fitted to the data, as presented in figure 2(b). The temperature dependence of the bulk modulus $B$ previously reported by Tanaka et al [20] for an Al–Pd–Mn i-QC is also plotted in figure 2(b). The data are fitted to the function $B = B_0 - AT \exp(-T_0/T)$ [22] with $B_0 = 126$ GPa, $A = 0.045$ GPa/K and $T_0 = 530$ K (broken line). The $\alpha$ and $B$ curves thus obtained were used in converting the specific heats at constant pressure, $c_p$, to those at constant volume, $c_v$, as explained in the following text.

Figure 3(a) presents the data of $c_p$ measured for the samples listed in table 1. We converted the measured $c_p$ to $c_v$, by using the following thermodynamic relation:

$$c_v = c_p - 9VB\alpha^2T,$$  (1)

where $V$ is the average atomic volume, which we calculated from the density of an Al–Pd–Mn i-QC [20]. The values of $V$, $\alpha$, and $B$ in figure 2(b) were used not only for i-QCs but also for the CAs under the assumption that they are similar for the i-QC and the CAs. The values obtained for $c_v$ are presented in figure 3(b), which shows that the difference between $c_p$ and $c_v$ is not significant, i.e., $\approx 0.2$ $k_B$ at 1100 K. Note that Dulong–Petit’s law, i.e., $c_v = c_{2p} = 3$ $k_B$ holds satisfactorily for all the samples below 700 K. Above 700 K, upward deviations of $c_v$ from
were observed, where the degree of deviation depends systematically on the order of CAs and QC. The QC samples show the largest deviation, i.e., the $c_V$ values reach $5k_B$ at 1100 K. The 2/1 CAs show a similar but slightly smaller deviation whereas the 1/1 and 1/0 CAs show a much smaller deviation. For Al-Pd-Ru 1/0-CAs, the measurements were done up to 1400 K. No appreciable increase in $c_V$ was observed up to this temperature. The QC samples of APM-1, 2, 3, and 5 show a peak at about 1000 K, which is attributable to melting of the crystalline phase of Al$_6$Mn at its melting temperature [23]. The peak areas correspond to 0.20, 0.17, 0.17, and 0.096 kJ/mol for APM-1, 2, 3, and 5, respectively. On the other hand, heats of fusion have been evaluated for Al-Co and Al-Fe intermetallic compounds [24]: 18 kJ mol$^{-1}$ (Al$_{13}$Co$_4$), 17 kJ mol$^{-1}$ (Al$_{13}$Co$_{26}$), 19 kJ mol$^{-1}$ (Al$_{13}$Fe$_4$), and 20 kJ mol$^{-1}$ (Al$_3$Fe$_2$). Assuming that the heat of fusion for Al$_6$Mn is comparable to these values, the amount of Al$_6$Mn in the samples should be 0.5%–1%. This indicates that the $c_V$ curves for these samples in figure 3(b) come almost entirely from i-QC except the peak. The inclusion of the phase could not be detected by x-ray diffraction.

For i-QC, the measurements were performed for the samples with various compositions; however, no noticeable composition dependence was observed. The results for the samples with the same compositions showed that the data scatter is not large except for APM-1, which shows fairly larger $c_V$ values than other QC samples; we were unable to discern the reason for this phenomenon.

**Figure 2.** (a) The 664004 peaks in the x-ray diffraction spectra of i-QC measured at different temperatures for APM-4, where the Cu K$_{α1}$ component was removed from the raw data through data treatment. The measurements were first conducted when heating from 373 to 1023 K and then cooling from 1023 to 373 K. The peaks measured during the heating and cooling are represented by the solid and broken lines, respectively. Temperature dependence of $d/d_{373K}$ ($d = \lambda/(2 \sin \theta)$) deduced from the peak positions is shown in inset. (b) Temperature dependences of linear thermal expansion coefficient, $\alpha$, and bulk modulus $B$. The former was deduced by differentiating the function fitted to the $d/d_{373K}$ data in (a), whereas the latter was deduced from the data previously reported for an Al-Pd-Mn i-QC by Tanaka et al [20] The broken line indicates a function fitted to the data.
4. Discussion

In principle, we potentially have several origins for the excessive specific heat observed for the QCs. Theoretically, the Dulong–Petit value of \( c_{DP} = 3k_B \) is due to harmonic atomic vibrations; anharmonic atomic vibrations generally give rise to an excessive specific heat \( c_{ah} \). However, the temperature dependence of \( c_{ah} \) is theoretically formulated as \( c_{ah} = c_A T \) (where \( A \) is a constant) at high temperatures [25, 26], which is not in agreement with those observed for the QCs in figure 3(b), that is, \( \Delta c_V = c_V - c_{DP} \approx 0 \) below 700 K and a rapid increase in \( \Delta c_V \) is observed above 700 K. In addition, not only high-order CAs but also low-order ones such as \( 1/1 \) and \( 1/0 \) CAs generally have similar local structures to those of QCs, suggesting that the degree of anharmonicity in such CAs should be similar to that in QCs. Because the large \( \Delta c_V \) was not observed for the low-order CAs, the large \( \Delta c_V \) for the QCs in figure 3(b) was likely not caused by anharmonic atomic vibrations.

Next, we examined an electronic specific heat \( c_e = \gamma \cdot T \), where \( \gamma \) is the Sommerfeld coefficient. In general, this contribution is negligible, except at very high temperatures for metals with very high melting point, such as W and Mo. Such a small electronic specific heat is generated because the number of thermally excited electrons, which is \( \approx ZN (T/T_F) \) (\( Z \): valence, \( N \): number of atoms, \( T_F \): Fermi temperature), is much smaller than that of thermally excited phonon modes (3\( N \)), as long as the temperature is not extremely high. More specifically, the electronic specific heat per atom is given as \( c_e = (1/2)\pi^2k_B^2Z (T/T_F) \) in the free electron approximation, which is \( c_e \approx 0.1k_B \approx 0.03c_{DP} \) at \( T = 1000 \) K, assuming \( Z = 2 \). The \( c_e \) values for QC alloys must be even smaller (\( c_e \ll 0.01c_{DP} \)), because the Fermi level is located within a pseudogap of the electronic density of states [27].

Prekul et al [7, 8] interpreted the excessive specific heat observed for an Al–Cu–Fe i-QC in a high temperature region as a part of a Schottky-type anomaly with a two-level excitation with the energy increment of 0.25 eV. We attempted to fit our \( \Delta c_V \) data of Al–Pd–Mn i-QCs to the function form of the Schottky-type heat anomaly:

\[
\Delta c_V = A \cdot \exp\left(-\frac{E}{k_B T}\right)
\]
where \( N_0 \) is the number of the two-level sites, \( N \) is the number of atoms, and \( \varepsilon \) is the energy difference between the two levels. Figure 4 shows that the \( \Delta c_V \) data satisfactorily fit to equation (2), where we obtained \( N_0/N = 15 \) and \( \varepsilon = 0.5 \) eV. Though Prekul et al. attributed the two-level excitation identified for the i-Al–Cu–Fe QC to the electronic excitation between two spiky states on either side of the Fermi level in the electronic density of states [8], such an interpretation should not apply to the present case. The number of electrons involved in such an excitation should be much smaller than the number of atoms, namely, \( N_0/N \ll 1 \), similar to the case of the conventional electronic specific heat described in the preceding paragraph.

Lastly, we examined the possibility of the specific heat originating in the phason degrees of freedom in QCs [10, 11]. Figure 3(b) shows that the magnitude of \( \Delta c_V = c_V - 3 k_B \) depends systematically on the order of CAs and QC; QCs show the largest \( \Delta c_V \) and 2/1 CAs show a similar but slightly smaller \( \Delta c_V \), whereas 1/1 and 1/0 CAs only show an insignificant value of \( \Delta c_V \). These results demonstrate that a large \( \Delta c_V \) value is the characteristic feature of QCs, reflecting the peculiarity of their structural order, which is most likely the existence of phason degrees of freedom. In general, phasons are activated only at high temperatures. Coddens et al. performed inelastic neutron scattering experiments to investigate phason dynamics in Al–Pd–Mn quasicrystals [28]. In the experiments, quasielastic scattering caused by correlated phason atomic jumps was observed above 700 K, in good agreement with the temperature range where the upward deviation of \( c_V \) is seen for i-QCs in figure 3(b). This also suggests that a large \( \Delta c_V \) observed for the QCs is of phasonic origin.

The elasticity of QCs can be described in terms of the phonon (conventional) elastic field, \( \mathbf{u}(\mathbf{r}) \), and the phason elastic field, \( \mathbf{w}(\mathbf{r}) \). Within linear elasticity, the elastic energy, \( E_{el} \), of QCs can be expressed as [10, 11]:

\[
E_{el} = E_u + E_w + \text{(coupling term)}
\]

\[
= \frac{1}{2} \int K_{ijkl}^{uu} u_i \dot{u}_j \dot{u}_l \dot{u}_k d\mathbf{r} + \frac{1}{2} \int K_{ijkl}^{ww} w_i \dot{w}_j \dot{w}_l \dot{w}_k d\mathbf{r} + \text{(coupling term)},
\]

(3)

where \( E_u \) and \( E_w \) are the conventional and phason elastic energies, \( u_i = \frac{1}{2} \left( \frac{\partial \mathbf{u}}{\partial r_i} + \frac{\partial \mathbf{u}}{\partial r_i} \right) \) and \( w_i = \frac{\partial \mathbf{w}}{\partial r_i} \) are the conventional and phason strains, respectively, and \( K_{ijkl}^{uu} \) and \( K_{ijkl}^{ww} \) are corresponding elastic constant tensors. Note that for conventional crystals, \( E_{el} \) has only the term \( E_u \), i.e., \( E_{el} = E_u \) and \( E_w = 0 \) in equation (3) can be rewritten as

\[
E_u = \frac{1}{2} \int \frac{1}{(2\pi)^3} \mathbf{\tilde{K}}^{uu}_{ij}(\mathbf{q}) \mathbf{\tilde{u}}_i(\mathbf{q}) \mathbf{\tilde{u}}_j(\mathbf{q}) d\mathbf{q}
\]

and

\[
E_w = \frac{1}{2} \int \frac{1}{(2\pi)^3} \mathbf{\tilde{K}}^{ww}_{ij}(\mathbf{q}) \mathbf{\tilde{w}}_i(\mathbf{q}) \mathbf{\tilde{w}}_j(\mathbf{q}) d\mathbf{q},
\]

(4)
in terms of the Fourier transforms,

\[ \tilde{u}(q) = \int u(r) e^{-iqr}dr \quad \text{and} \quad \tilde{w}(q) = \int w(r) e^{-iqr}dr. \]

(5)

Here, \( \tilde{K}_{ij}^{\rho}(q) \) and \( \tilde{K}_{ij}^{\omega}(q) \) are given as

\[ \tilde{K}_{ij}^{\rho}(q) = K_{ijkl}^{\rho} q_k q_l \quad \text{and} \quad \tilde{K}_{ij}^{\omega}(q) = K_{ijkl}^{\omega} q_k q_l, \]

(6)

respectively. For simple crystals with an atom per unit cell, \( E_u \) has the following form:

\[ E_u = \frac{1}{2} \sum_{l=1}^{N} \frac{\Delta q}{(2\pi)^3} \tilde{K}_{ij}(q_k) \tilde{u}_i(q) \tilde{u}_j(q), \]

(7)

where \( N \) is the number of allowed \( q \), and it is equal to the total number of atoms. \( E_u \) in equation (7) corresponds to the total potential energy of atoms, \( E_{pot} \). Then, the law of equipartition of energy implies that the expected value of \( E_{pot} \) and its contribution to the specific heat per atom, \( c_{pot} \), should be

\[ \langle E_{pot} \rangle = \langle E_u \rangle = (3N) \cdot \frac{1}{2} k_B T \]

and

\[ c_{pot} = \frac{1}{N} \frac{\partial \langle E_{pot} \rangle}{\partial T} = \frac{3}{2} k_B, \]

(8)

respectively. On the other hand, the expected value of the total kinetic energy of atoms, \( E_{kin} \), and its contribution to the specific heat per atom is given in a similar form:

\[ \langle E_{kin} \rangle = (3N) \cdot \frac{1}{2} k_B T \]

and

\[ c_{kin} = \frac{1}{N} \frac{\partial \langle E_{kin} \rangle}{\partial T} = \frac{3}{2} k_B, \]

(9)

Thus, we obtain \( c_{QP} = c_{pot} + c_{kin} = 3k_B \).

For crystals with multiple atoms per unit cell, \( E_{pot} \) cannot be expressed as the simple form of \( E_u \) in equation (7). However, it can still be written as the sum of \( 3N \) quadratic terms, and therefore, equation (8) should hold. Moreover, this should be true also for QCs. On the other hand, equation (9) is always true for any system, resulting in \( c_{QP} = 3k_B \) for every crystal and quasicrystal. In addition, \( E_u \) must contribute to the specific heat for QCs. If we assume that \( E_u \) in equation (4) can also be written in the form of \( E_u \) in equation (7), it should contribute \( (3/2)k_B \) to the specific heat. Then, by neglecting the phonon–phason coupling effect, which is usually small, we obtain the total specific heat of QC \( c_v = c_{QP} + (3/2)k_B = (9/2)k_B \) for QCs. This additional \( c_v \) should be observable only at high temperatures where phonons are activated, and it may correspond to what is observed in figure 3(b). In general, the higher the degree of approximation of an CA, the closer its structure is to that of a QC. Then, while in low-order CAs such as the 1/1- and 1/0-CAs only local phason flips are allowed, correlated phason flips or long-ranged phason fluctuations expected in the QC should partially occur in high-order CAs such as the 2/1-CA. This explains the systematic trend in the magnitude of \( \Delta c_v \) in figure 3(b).

However, the aforementioned arguments on the specific heat originating in phasons may encounter certain problems. First, the small \( q \) components of \( w(r) \), i.e., phasons with long wavelength may be substantially frozen, and therefore, not contribute to specific heat. Actually, the phason modes are diffusive, and the relaxation time is given as \( \tau = \lambda^2/(4\pi^2D) \) (\( \lambda \): phason wavelength, \( D \): phason diffusion constant) [29]. Francouel et al. [30, 31] measured \( \tau \) for an i-QC of Al–Pd–Mn through coherent x-ray scattering, and demonstrated the relation of \( \tau = \lambda^2/(4\pi^2D) \) with \( D = 2.2 \times 10^{-18} \text{ m}^2 \cdot \text{s}^{-1} \) at 923 K. If we require \( \tau < 1 \text{ s} \) for the phason modes to contribute to the specific heat, \( \lambda < \lambda_0 \approx 9 \text{ nm} \). The ratio of the number of phason modes that do not contribute to specific heat to the total number of phason modes is of the order of \((a_0/\lambda_0)^3\), where \( a_0 \) is the nearest neighbor interatomic distance. With \( a_0 \approx 0.2 \text{ nm} \), \((a_0/\lambda_0)^3 \approx 10^{-7}\), which is negligible.

Further, the large \( q \) components of \( w(r) \) with a short wavelength would encounter the following major drawback: equation (1) would not be valid for phason fluctuations with such a short wavelength. The energy cost for such phason fluctuations and the corresponding specific heat must be evaluated by inspecting individual phason defects (chemical species swaps and tile flips), instead of using equation (1). If we assume that the threshold value of \( \lambda = 5a_0 \), above which equation (1) is valid, only about 1/5 th phason modes are supported by equation (1). Then, to estimate the phason contribution to the specific heat, we may need to perform computational simulations using a realistic model. Recently, Mihalkovic and Widom [32] performed molecular
dynamic simulations, supplemented with Monte Carlo moves, by using interatomic potentials based on the density functional theory (DFT) to investigate the stability of an Al–Cu–Fe i-QC. They calculated temperature dependence of the free energy of the i-QC, including the contributions by harmonic and anharmonic vibrations, phason–related chemical species swaps and tile flips, and electronic excitations. This type of simulation would significantly aid in clarifying the origin of excessive specific heat observed in the experiments.

5. Conclusions

Specific heat measurements were performed for Al–Pd–Mn icosahedral quasicrystals (i-QCs) and a series of crystal approximants (CAs) of 2/1–1/1–1, and 1/0-cubic types in the temperature range of 400–1200 K. The measured specific heat per atom at constant pressure \( c_P \) was converted to that at constant volume \( c_V \) by using the data of thermal expansion coefficient measured for an Al–Pd–Mn i-QC and the data of bulk modulus reported in [20]. Below \( \sim 700 \) K, \( c_V \) values of all the specimens of i-QCs and CAs were close to \( 3k_B \), i.e., they obeyed Dulong–Petit’s law. Then, the i-QCs showed a dramatic increase in \( c_V \) with increasing temperature, and reached \( 5k_B \) at 1100 K. The 2/1 CAs showed a slightly smaller increase in \( c_V \), whereas the 1/1 and 1/0 CAs showed a negligible increase. The systematic behavior of \( c_V \) of the order of CAs and QC demonstrates that the large excessive specific heat is a characteristic feature of QCs, reflecting the peculiarity of their structural order.

A possible physical mechanism for the large excessive specific heat, \( \Delta c_V \), was discussed in terms of anharmonic atomic vibrations, electronic excitations, and phasonic excitations. Anharmonic atomic vibrations are not likely the cause of the large \( \Delta c_V \) because its temperature dependence is not in accordance with theoretical expectation and the degree of anharmonicity is expected to be similar for the CAs and QCs. The magnitude of the observed \( \Delta c_V \) is too large to be attributed to electronic excitations. Phasonic excitations could be the likely cause of the large \( \Delta c_V \), because they are characteristic of QCs. In reality, phason excitations can increase the internal energy of the system, which should contribute to \( \Delta c_V \). However, quantitative evaluation of this effect requires further research including computational simulations using a realistic model.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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