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Thermoelectric properties of $Al_{82.6-x}Re_{17.4}Si_x$ $(7 \leqslant x \leqslant 12)$ 1/1-cubic approximants

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The thermoelectric power $S(T)$ and thermal conductivity $\kappa(T)$ were systematically studied for a series of $Al_{82.6-x}Re_{17.4}Si_x$ $(7 \leqslant x \leqslant 12)$ 1/1-cubic approximants. We found that $S(T)$ of these approximants is characterized by large magnitude, sign reversal with varying composition, and nonlinear temperature dependence, all of which are also known as characteristics of the corresponding quasicrystals. The calculated $S(T)$ on the basis of the Boltzmann transport formula with accurately determined electronic structure showed extremely good agreement with the measured ones not only in their magnitude but also in the temperature and composition dependence. These results strongly indicate that these characteristic behaviors in $S(T)$ of the approximants and the corresponding quasicrystals are brought about by their characteristic electronic structure, i.e., the presence of a pseudogap across the Fermi level.

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I. INTRODUCTION

The Al-based Mackay-type icosahedral quasicrystal has attracted a great deal of interest as a potential candidate for a new thermoelectric material[1] because it possesses large thermoelectric power (S), more than 50 μV/K,[2–5] and low thermal conductivity (κ),[5] as low as 1 W/K m.[3,5–9] These characteristic properties are often discussed in relation to the quasiperiodicity unique to the quasicrystals. However, the mechanism leading to the large magnitude of $S(T)$ and small thermal conductivity in quasicrystals is not fully understood. One of the most plausible factors other than quasiperiodicity leading to these characteristics in $S(T)$ would be the presence of a pseudogap across the Fermi level (E_F).

$S(T)$ of quasicrystals is characterized not only by large magnitude but also by strong temperature and composition dependence.[2–4] The behavior of $S(T)$ is generally determined by the energy dependence of the electrical conductivity $[\sigma(\varepsilon)]$. Unfortunately, the electronic structure and atomic arrangements, which greatly affect $\sigma(\varepsilon)$, have hardly been analyzed for quasicrystals because quasiperiodicity in quasicrystals prevents us from applying ordinary band calculations or structure analyses well developed for crystalline materials. Here we notice that if the characteristics in $S(T)$ of quasicrystals are brought about by the presence of a pseudogap across E_F, the corresponding approximants having a pseudogap at E_F also possess similar behaviors in their $S(T)$, and that one can gain deep insight into the nature of their $S(T)$ by employing approximants rather than quasicrystals, because their electronic structure and local atomic arrangements can be accurately determined by ordinary band calculations[10–13] and structure analyses.[14–17]

Investigation of the electronic structure and the local atomic arrangements also plays an important role in the proper understanding of the thermal conductivity κ and electrical resistivity ρ, both of which are necessary for estimation of the potential of thermoelectric materials in the dimensionless figure of merit defined as $ZT=S^2T/(\kappa\rho)$. The electrical conduction in the approximants can be well investigated by using the Boltzmann transport equation on the basis of Bloch theory. With the great help of the accurately determined electronic structure of rational approximants, the role of electronic structure including the influence of the pseudogap across E_F on the electrical resistivity should be clearly revealed. Thermal conductivity is generally determined by contributions not only of the conduction electrons but also of the phonons, and the former can be roughly estimated from the electrical conductivity by using the Wiedemann-Franz law. The latter is closely related to the atomic structure and is often discussed in terms of the quasiperiodicity.[3,6–9] By using rational approximants rather than the corresponding quasicrystals, one can clearly reveal the local atomic arrangements and their influence on the thermal conductivity can be unambiguously discussed.

In this study we have systematically measured thermoelectric power and thermal conductivity for a series of $Al_{82.6-x}Re_{17.4}Si_x$ $(7 \leqslant x \leqslant 12)$ 1/1-cubic approximants. The measured thermoelectric power and thermal conductivity together with previously reported electrical resistivity[18] are used to evaluate the performance of the approximant as a thermoelectric material. By comparing the measured $S(T)$, $\kappa(T)$, and $\rho(T)$ of quasicrystals with those of the approximants, the influence of quasiperiodicity upon these thermoelectric properties is also discussed. We also discuss the origin of the characteristic behaviors of the thermoelectric power in the $Al_{82.6-x}Re_{17.4}Si_x$ $(7 \leqslant x \leqslant 12)$ 1/1-cubic approximants in terms of the electronic structure and local atomic arrangements. It will be demonstrated, as a consequence of the present analysis, that the behaviors in the thermoelectric power of these 1/1-cubic approximants are quantitatively simulated from the accurately determined electronic structure, and that the characteristic behavior in $S(T)$ in the approximants and perhaps in the quasicrystals is accounted for by simply considering the presence of a pseudogap across E_F.

II. EXPERIMENTAL PROCEDURE

We employed in this study a series of $Al_{82.6-x}Re_{17.4}Si_x$ $(7 \leqslant x \leqslant 12)$ 1/1-cubic approximants without any precipitation of secondary phases. Ribbon samples were prepared by the single-role melt-quenching technique and used for the measurement of the thermoelectric power. Bulk samples were used for the thermal conductivity measurement. The details of sample preparation and phase determination were reported previously.[18]

The thermoelectric power was measured at temperatures from 90 to 400 K with a Seebeck Coefficient Measurement System (MMR). We also used the Physical Properties Measurement System (Quantum Design) with the thermal transport option to simultaneously measure the thermoelectric power and thermal conductivity for samples of $\sim 1 \times 1 \times 10$ mm^3 in dimension over $5 \leqslant T \leqslant 300$ K.

Thermodynamically stable $Al_{62.5}Cu_{24.5}Fe_{13}$, $Al_{63}Cu_{24}Fe_{13}$, $Al_{62.5}Cu_{25}Fe_{12.5}$, $Al_{63}Cu_{24.5}Fe_{12.5}$, $Al_{62.5}Cu_{25.5}Fe_{12}$, and $Al_{63}Cu_{25}Fe_{12}$ icosahedral quasicrystals and $Al_{74.6}Mn_{17.4}Si_8$ 1/1-cubic approximants were also prepared by the same method as that for the $Al_{82.6-x}Re_{17.4}Si_x$ $(7 \leqslant x \leqslant 12)$ 1/1-cubic approximants. The $S(T)$'s of the Al-Cu-Fe icosahedral quasicrystals and $\kappa(T)$ of the $Al_{74.6}Mn_{17.4}Si_8$ 1/1-cubic approximants were measured and used for comparison with those of the the $Al_{82.6-x}Re_{17.4}Si_x$ $(7 \leqslant x \leqslant 12)$ 1/1-cubic approximants.

For the analysis of $S(T)$ in the $Al_{82.6-x}Re_{17.4}Si_x$ 1/1-cubic approximants, we employed the electronic density of states of the $Al_{73.6}Re_{17.4}Si_9$ 1/1-cubic approximant calculated by the linear muffin-tin orbital LMTO atomic-sphere approximation ASA method with atomic structure determined by a synchrotron radiation Rietveld analysis. Details of the band calculation and the Rietveld analysis were also reported in our previous paper.[18]

III. RESULTS

Figure 1(a) shows the measured $S(T)$ of the $Al_{82.6-x}Re_{17.4}Si_x$ $(7 \leqslant x \leqslant 12)$ 1/1-cubic approximants. The $S(T)$ observed for these $Al_{82.6-x}Re_{17.4}Si_x$ 1/1-cubic approximants is characterized by a large value of $|S|$ exceeding 50 μV/K and a strong composition dependence. The composition dependence of S(100 K), S(200 K), and S(300 K) is plotted in Fig. 1(b). Notably, the compositions at which the maximum and minimum values in $S(T)$ were observed are not at the center of the formation range of these approximants but near the lowest and highest limits of the Si concentrations, respectively.

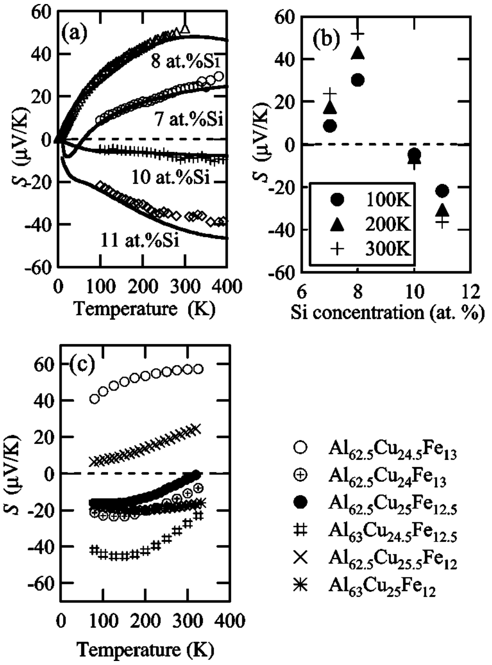

FIG. 1. (a) Thermoelectric power of $Al_{82.6-x}Re_{17.4}Si_x$ 1/1-cubic approximants as a function of temperature. Solid lines represent the calculated $S(T)$ on the basis of accurately determined electronic structure. Details of the calculation are described in Sec. IV. (b) Thermoelectric power measured at 100, 200, and 300 K as a function of Si concentration. (c) Thermoelectric power of the Al-Cu-Fe icosahedral quasicrystals. Strong temperature and composition dependence is observed for the $Al_{82.6-x}Re_{17.4}Si_x$ 1/1-cubic approximants. These behaviors are similar to those in the Al-Cu-Fe icosahedral quasicrystals and other pseudogap systems including Fe_2 VAl (Ref. 21).

$S(T)$ in metallic alloys is often discussed using the well-known formula[19]

$$S(T) = \frac{\pi^3}{3}\frac{k_B^2}{e}T\left[\frac{\partial \ln \sigma(\varepsilon)}{\partial \varepsilon}\right]_{\varepsilon=\mu}, \qquad (1)$$

where $\sigma(\varepsilon)$ and μ represent the electrical conductivity at ε and the chemical potential, respectively. Equation (1) is useful to understand the Si concentration dependence of $S(T)$ in the $Al_{82.6-x}Re_{17.4}Si_x$ 1/1-cubic approximants. Since electrical conductivity in the metallic phase is known to be directly proportional to the electronic density of states $N(\varepsilon)$, Eq. (1) indicates that S becomes positive or negative when the sign of $\partial N(\varepsilon)/\partial\varepsilon$ at μ is negative or positive, respectively. Note here that e is negative in sign and ln x increases with increasing x. If μ is located at an energy lower than that of the bottom of pseudogap (ε_{bottom}), $S(T)$ becomes positive because of the negative value of $\partial N(\varepsilon)/\partial\varepsilon$ at μ, and vice versa.

The pseudogap across E_F in the present 1/1-cubic approximants, as well as that in other quasicrystals and approximants,[10–12,20] was already confirmed experimentally and reported previously.[18] At low Si concentrations less than 8 at. % Si, the sign of the thermoelectric power of these approximants stays positive over a whole temperature range of the present measurement, while it turns out to be negative at higher Si concentrations larger than 10 at. % Si. By considering that an increase of Si increases electron concentration in the system, one may naturally notice that the composition dependence of $S(100\ \mathrm{K})$, $S(200\ \mathrm{K})$, and $S(300\ \mathrm{K})$ can be qualitatively accounted for by the presence of a pseudogap and μ moving across it from the lower to the higher energy side with increasing carrier concentration. Similar behavior in $S(T)$ was reported for $(\mathrm{Fe}_{2/3}\mathrm{V}_{1/3})_y\mathrm{Al}_{1-y}$, which is known as one of the well-known pseudogap systems.[21]

The $S(T)$ of these 1/1-cubic approximants is also characterized by a nonlinear temperature dependence, in sharp contrast to the T-linear dependence expected from Eq. (1). The Nonlinear temperature dependence in $S(T)$ suggests that Eq. (1) is not appropriate for the quantitative evaluation of the temperature dependence of $S(T)$ for the present 1/1-cubic approximants. We noticed that this inconsistency between Eq. (1) and the measured $S(T)$ is caused by an inappropriate assumption used when Eq. (1) is deduced. We shall return to this point later and discuss it in more detail (see Sec. IV).

We described above the characteristic behaviors in $S(T)$, which are (a) large magnitude, (b) strong composition dependence, and (c) nonlinear temperature dependence, for the $\mathrm{Al}_{82.6-x}\mathrm{Re}_{17.4}\mathrm{Si}_x$ 1/1-cubic approximants. It is particularly important to stress here that the corresponding icosahedral quasicrystals show similar behaviors in their thermoelectric power.[2–4] For example, $S(T)$ of Al-Cu-Fe icosahedral quasicrystals of six different compositions is shown in Fig. 1(c). Obviously (a) large magnitude, (b) strong composition dependence, and (c) nonlinear temperature dependence can be confirmed in the $S(T)$ of the Al-Cu-Fe icosahedral quasicrystals. It is, thus, strongly argued that the dominant factors leading to the large magnitude and strong composition dependence in $S(T)$ should be essentially the same in quasicrystals and approximants, and that the quasiperiodicity existing only in the quasicrystals has a less important role in causing the large magnitude of $S(T)$. Precise analyses of the $S(T)$ of the approximants, therefore, would provide us proper understanding of $S(T)$ not only in the approximants but also in their corresponding quasicrystals.

The thermal conductivity at room temperature $[\kappa(300\ \mathrm{K})]$ of the $\mathrm{Al}_{82.6-x}\mathrm{Re}_{17.4}\mathrm{Si}_x$ 1/1-cubic approximants is plotted as a function of Si concentration x in Fig. 2(a). Surprisingly, the $\kappa(300\ \mathrm{K})$ of the $\mathrm{Al}_{82.6-x}\mathrm{Re}_{17.4}\mathrm{Si}_x$ 1/1-cubic approximants is always kept below 1.6 W/K m regardless of the Si concentration. The temperature dependence of κ for the $\mathrm{Al}_{74.6}\mathrm{Re}_{17.4}\mathrm{Si}_8$ 1/1-cubic approximant is also depicted in Fig. 2(b) together with that of $\mathrm{Al}_{74.6}\mathrm{Mn}_{17.4}\mathrm{Si}_8$ which is prepared by substituting Mn for Re in the $\mathrm{Al}_{74.6}\mathrm{Re}_{17.4}\mathrm{Si}_8$ 1/1-cubic approximant. The lower κ in $\mathrm{Al}_{74.6}\mathrm{Re}_{17.4}\mathrm{Si}_8$ than that of $\mathrm{Al}_{74.6}\mathrm{Mn}_{17.4}\mathrm{Si}_8$ indicates the strong effect of heavy Re in reducing the thermal conductivity of the approximants as it is well known that heavy atoms in an array of light elements greatly contribute to reducing the thermal conductivity, most likely due to their role as a strong scatterer for the phonons and to the localization of phonons about the heavy atoms.

We roughly estimated the contribution of conduction electrons (κ_{el}) using the Wiedemann-Franz law and superimposed the resulting κ_{el} in Figs. 2(a) and 2(b). Since κ_{el} is directly proportional to the electrical conductivity, it shows a minimum at $x \approx 9-10$ where electrical resistivity possesses a maximum. The lattice contribution of thermal conductivity deduced as $\kappa_{lat} = \kappa - \kappa_{el}$ at room temperature obviously shows a maximum value at $x=9$ where the disordering in the structure was reported to disappear,[18] and drastically decreases with both increasing and decreasing Si concentration from $x \approx 9$. By considering similar composition dependence between $\kappa(300\ \mathrm{K})$ and $\kappa_{lat}(300\ \mathrm{K})$, we can safely argue that the composition dependence of $\kappa(300\ \mathrm{K})$ is dominantly brought about by the Si concentration dependence of disordering in the structure. Note here that the magnitude of $\kappa(300\ \mathrm{K})$ observed for the $\mathrm{Al}_{82.6-x}\mathrm{Re}_{17.4}\mathrm{Si}_x$ 1/1-cubic approximants is comparable with that of the corresponding icosahedral quasicrystals.[6–9] This experimental fact strongly indicates that the quasiperiodicity has a less important contribution to the reduction in the thermal conductivity, and that short-range atomic arrangements have a much stronger influence on it.

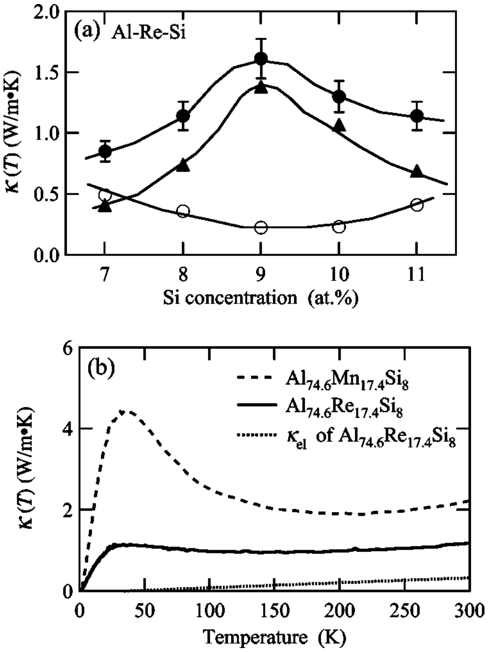

FIG. 2. (a) Thermal conductivity κ of $\mathrm{Al}_{82.6-x}\mathrm{Re}_{17.4}\mathrm{Si}_x$ 1/1-cubic approximants measured at room temperature (solid circles) as a function of Si concentration. Contribution of the conduction electrons κ_{el} deduced from the electrical resistivity by using the Wiedemann-Franz law and that of the lattice defined as $\kappa_{lat} = \kappa - \kappa_{el}$ are also plotted as open circles and solid triangles, respectively. The magnitude of the thermal conductivity of the $\mathrm{Al}_{82.6-x}\mathrm{Re}_{17.4}\mathrm{Si}_x$ 1/1-cubic approximants is surprisingly small regardless of their composition. Obviously, the composition dependence of κ is dominantly determined by κ_{lat}. (b) Temperature dependence of thermal conductivity observed for $\mathrm{Al}_{74.6}\mathrm{Mn}_{17.4}\mathrm{Si}_8$ and $\mathrm{Al}_{74.6}\mathrm{Re}_{17.4}\mathrm{Si}_8$ 1/1-cubic approximants. Although the structures of these two compounds are essentially the same, the magnitude of the thermoelectric power is fairly different. The important role of the heavy Re atoms in reducing their thermal conductivity is strongly suggested.

Although we mentioned above that the magnitude of κ in the present approximants is strongly influenced by the presence of disordering in the structure, the most dominant factors providing such a very small $\kappa \leqslant 1.6$ W/K m, are not

TABLE I. Thermoelectric properties of the $\mathrm{Al}_{82.6-x}\mathrm{Re}_{17.4}\mathrm{Si}_x$ 1/1-1/1-1/1 approximant.

Composition	ρ(300 K) (Ref. 18) ($\mu\Omega$ cm)	γ (Ref. 18) (mJ/mol K)	S(100 K) (μV/K)	S(200 K) (μV/K)	S(300 K) (μV/K)	κ(300 K) (W/m K)	κ_{el}(300 K) (W/m K)	κ_{lat}(300 K) (W/m K)	$ZT_{300\ \mathrm{K}}$
$\mathrm{Al}_{75.6}\mathrm{Re}_{17.4}\mathrm{Si}_7$	1500	0.6	8.7±0.9	18±2	24±3	0.9±0.1	0.49	0.41	0.013
$\mathrm{Al}_{74.6}\mathrm{Re}_{17.4}\mathrm{Si}_8$	1800	0.45	30±3	43±5	52±6	1.1±0.1	0.36	0.74	0.04
$\mathrm{Al}_{73.6}\mathrm{Re}_{17.4}\mathrm{Si}_9$	3500	0.3				1.6±0.2	0.22	1.38	
$\mathrm{Al}_{72.6}\mathrm{Re}_{17.4}\mathrm{Si}_{10}$	3300	0.28	−4.6±0.5	−5.9±0.6	−9±1	1.3±0.1	0.23	1.07	0.001
$\mathrm{Al}_{71.6}\mathrm{Re}_{17.4}\mathrm{Si}_{11}$	1800	0.31	−22±3	−9±1	−36±5	1.1±0.1	0.41	0.69	0.02
$\mathrm{Al}_{70.6}\mathrm{Re}_{17.4}\mathrm{Si}_{12}$	1400	0.42					0.53		

obvious now because the disorder-free $\mathrm{Al}_{73.6}\mathrm{Re}_{17.4}\mathrm{Si}_9$ also possesses very small κ.[18] The disordering in the present approximants occurs only in the glue sites which are connecting the Mackay clusters existing at the body center and vertices of the cubic lattice. If the Mackay clusters behave as an extremely heavy hypothetical atom most likely due to the strong bonds between atoms inside the cluster,[22] and if these heavy hypothetical atoms are connected with weak links of the glue atoms, the group velocity of the acoustic phonon will be greatly reduced. This will cause a small magnitude in the thermal conductivity. Moreover, one may easily consider from this scenario that the disordering in the glue sites strongly scatters the acoustic phonons. This mechanism would be equally applicable to the corresponding quasicrystals. This consideration, however, is no more than a speculation because we have only limited information about the relation between structure and thermal conductivity in the approximant. To gain real insight into the origin for the small thermal conductivity in the quasicrystals and approximants, investigation of the relation between the atomic arrangements and thermal conductivity should be performed not only for the present approximants but also for other approximants. Thus we decided to leave this problem still open.

Electrical resistivity, as well as the thermoelectric power and thermal conductivity, is one of the factors that determines the performance of thermoelectric materials. We should comment here on our previous data for room temperature electrical resistivity $[\rho(300\ \mathrm{K})]$ of the $\mathrm{Al}_{82.6-x}\mathrm{Re}_{17.4}\mathrm{Si}_x$ 1/1-cubic approximants.[18] We reported in our previous paper[18] that $\rho(300\ \mathrm{K})$ of the $\mathrm{Al}_{82.6-x}\mathrm{Re}_{17.4}\mathrm{Si}_x$ 1/1-cubic approximants possesses a maximum value at $x=9-10$, where the electronic specific heat coefficient (γ value) takes its minimum. This unique Si concentration dependence of the γ value and $\rho(300\ \mathrm{K})$ definitely indicates that the Si concentration dependence of $\rho(300\ \mathrm{K})$ is dominated by the shape of the pseudogap existing across μ. A smaller $\rho(300\ \mathrm{K})$, which is preferable for thermoelectric materials, is obtained when μ is located not at ε_{bottom} but at rather lower or higher energies, where large $|S(T)|$ is also observed.

By using the measured thermoelectric power, electrical resistivity, and thermal conductivity, we calculated the dimensionless figure of merit $[ZT=S/(\rho\kappa)]$ for the present 1/1-cubic approximants. The resulting ZT are summarized in Table I. A large magnitude of thermoelectric power is not obtained when μ is located at the bottom of the pseudogap but rather at lower or higher energies, where the electrical resistivity fortunately shows lower magnitude because of the relatively large electrical density of states. As a consequence of the simultaneous achievement of large thermoelectric power, low electrical resistivity, and small thermal conductivity, ZT of the 1/1-cubic approximants is enhanced up to 0.04 at room temperature. The largest ZT values with a positive S (p type) and negative S (n type) at room temperature are 0.04 in $\mathrm{Al}_{74.6}\mathrm{Re}_{17.4}\mathrm{Si}_8$ and 0.02 in $\mathrm{Al}_{71.6}\mathrm{Mn}_{17.4}\mathrm{Si}_{11}$, respectively. These values are slightly smaller than the maximum ZT reported for icosahedral quasicrystals.[23,24] However, since $S(T)$ increases and $\rho(T)$ decreases with increasing temperature, we may observe much larger ZT at high temperatures above 300 K. In addition, we already confirmed that a partial substitution of Re for Mn in the $\mathrm{Al}_{82.6-x}\mathrm{Re}_{17.4}\mathrm{Si}_x$ 1/1-cubic approximants enhances ZT. Thermoelectrical properties of quaternary Al-Mn-Re-Si 1/1-cubic approximants will be reported elsewhere in the near future.

IV. DISCUSSION

In this section, we concentrate on discussing the mechanism leading to the nonlinear temperature dependence, large magnitude, and strong concentration dependence of $S(T)$ observed for the present $\mathrm{Al}_{82.6-x}\mathrm{Re}_{17.4}\mathrm{Si}_x$ 1/1-cubic approximants in terms of the electronic structure near E_{F}.

Maciá[25,26] reported an analytical calculation of the temperature dependence of thermoelectric power for icosahedral quasicrystals. He used a hypothetical $\sigma(\varepsilon)$ consisting of two Lorenzian-type pseudogaps, which was originally proposed by Landauro and Solbrig.[27] They had to employ this hypothetical $\sigma(\varepsilon)$ because information about a realistic $\sigma(\varepsilon)$ is, at this moment, neither experimentally nor theoretically available for icosahedral quasicrystals due to their lack of periodicity. We emphasize here that if we employ the rational approximants instead of their corresponding quasicrystals, $S(T)$ can be quantitatively evaluated without using a hypothetical $\sigma(\varepsilon)$, because information about $\sigma(\varepsilon)$ is obtained using the accurately determined electronic structure and local atomic arrangements. Since $S(T)$ observed for icosahedral quasicrystals shows essentially the same behaviors as those of the corresponding approximants, the present analysis of $S(T)$ of the approximants might reveal the mechanism leading to the unusual behaviors of $S(T)$ not only in approximants but also in quasicrystals.

We introduce here a rigorous equation to calculate $S(T)$:[19]

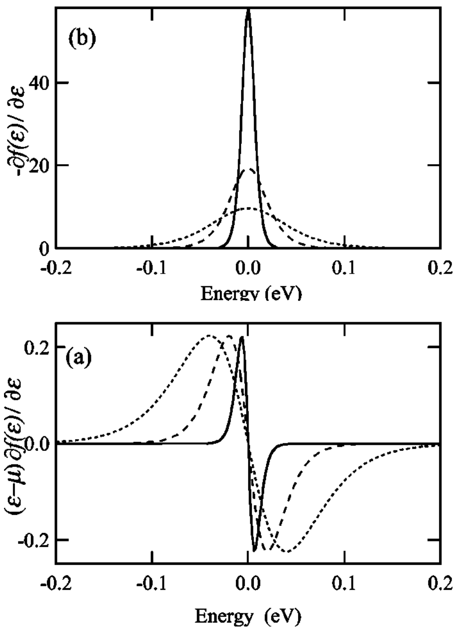

FIG. 3. Functions in the integrands in Eq. (2). The solid line, dashed line, and dotted line indicate those calculated with $T=50$, 150, and 300 K, respectively.

$$S(T) = \frac{1}{eT}\frac{\displaystyle\int_{-\infty}^{\infty}\sigma(\varepsilon)(\varepsilon-\mu)[\partial f(\varepsilon)/\partial\varepsilon]d\varepsilon}{\displaystyle\int_{-\infty}^{\infty}\sigma(\varepsilon)[\partial f(\varepsilon)/\partial\varepsilon]d\varepsilon}. \tag{2}$$

Equation (1) is deduced from Eq. (2) by using techniques used in the Sommerfeld expansion, in which some factors in the integrands in both the numerator and denominator vanish at $\varepsilon\approx\mu$. The approximation employed to deduce Eq. (1) causes essentially the same result as that caused by an assumption of a linearly varying electrical conductivity with energy. One may naturally realize that this is unsatisfactory especially at high temperatures, because the energy width of a few k_BT centered at $\varepsilon=\mu$, where $\partial f(\varepsilon)/\partial\varepsilon$ has meaningful magnitudes, increases with increasing temperature and the nonlinear energy dependence of $\sigma(\varepsilon)$ is no longer trivial.

In order to calculate $S(T)$ of the present 1/1-approximants with Eq. (2), we employed a numerical integration rather than an analytical treatment. McIntosh and Kaiser[28] reported a method in which the integrands in Eq. (2) were divided into three functions $\sigma(\varepsilon)$, $-\partial f(\varepsilon)/\partial\varepsilon$, and $(\varepsilon-\mu)\partial f(\varepsilon)/\partial\varepsilon$, and separately treated. Two of these functions, $-\partial f(\varepsilon)/\partial\varepsilon$ and $(\varepsilon-\mu)\partial f(\varepsilon)/\partial\varepsilon$, can be easily calculated at a given temperature and are shown in Figs. 3(a) and 3(b) for three different temperatures, respectively. Both functions serve as windows that define the energy range of integration as a result of a negligibly small contribution outside the energy range of a few k_BT in width centered at μ. Since the electrical conductivity $\sigma(\varepsilon)$ exists in the integrals with these two window-functions, one has to take $\sigma(\varepsilon)$ into account only in a narrow energy range of a few k_BT centered at μ.

The function $-\partial f(\varepsilon)/\partial\varepsilon$ is an even function about μ and its integrated intensity $-\int_{-\infty}^{\infty}(\partial f/\partial\varepsilon)d\varepsilon$ gives rise to unity regardless of the temperature. Thus, $-\int_{-\infty}^{\infty}(\partial f/\partial\varepsilon)\sigma(\varepsilon)d\varepsilon$ results simply in a mean value of $\sigma(\varepsilon)$ averaged over the energy range of a few k_BT centered at μ. On the other hand, $(\varepsilon-\mu)\partial f(\varepsilon)/\partial\varepsilon$ is an odd function and its maximum and minimum, both of which are temperature independent, occur at $\varepsilon\approx-1.3k_BT$ and at $\varepsilon\approx1.3k_BT$, respectively. The values deduced from $\int_{-\infty}^{\mu}(\varepsilon-\mu)(\partial f/\partial\varepsilon)d\varepsilon$ and $\int_{\mu}^{\infty}(\varepsilon-\mu)(\partial f/\partial\varepsilon)d\varepsilon$ are positive and negative with the same magnitude. Thus $\int_{-\infty}^{\infty}(\varepsilon-\mu)(\partial f/\partial\varepsilon)\sigma(\varepsilon)d\varepsilon$ possesses a positive value when the intensity of $\sigma(\varepsilon)$ at about $\varepsilon=-1.3k_BT$ is larger than that at about $\varepsilon=1.3k_BT$, and vice versa. These considerations on $-\partial f(\varepsilon)/\partial\varepsilon$ and $(\varepsilon-\mu)\partial f(\varepsilon)/\partial\varepsilon$ encourage us to argue that a large thermoelectric power is obtained if $\sigma(\varepsilon)$ averaged over a few k_BT in width about μ is kept small and if the magnitude of $\sigma(\varepsilon)$ at $\varepsilon\approx1.3k_BT$ is much smaller or much larger than that at $\varepsilon\approx-1.3k_BT$.

Absolute values of $\int_{-\infty}^{\mu}(\varepsilon-\mu)(\partial f/\partial\varepsilon)d\varepsilon$ and $\int_{\mu}^{\infty}(\varepsilon-\mu)\times(\partial f/\partial\varepsilon)d\varepsilon$ always linearly increase with increasing temperature. If we assume an electrical conductivity $\sigma(\varepsilon)$ to vary linearly with energy across μ, one may naturally realize that $\int_{-\infty}^{\infty}(\varepsilon-\mu)(\partial f/\partial\varepsilon)\sigma(\varepsilon)d\varepsilon$ possesses T^2 dependence. Since $\int_{-\infty}^{\infty}(\partial f/\partial\varepsilon)\sigma(\varepsilon)d\varepsilon$ is constant and equal to $\sigma(\mu)$ in the case of the ε-linear $\sigma(\varepsilon)$, Eq. (2) involving T in its denominator possesses T-linear temperature dependence as it is suggested by Eq. (1). The thermoelectric power, therefore, is more enhanced if the slope of the linearly varying $\sigma(\varepsilon)$ is larger and $\sigma(\mu)$ is smaller under the assumption of a linearly varying $\sigma(\varepsilon)$ with energy. These conditions for a large S are exactly the same as those discussed on the basis of Eq. (1).

Analytical treatment of Eq. (2) is far from being straightforward. However, we showed above that, if we separately treat the three functions $\sigma(\varepsilon)$, $-\partial f(\varepsilon)/\partial\varepsilon$, and $(\varepsilon-\mu)\partial f(\varepsilon)/\partial\varepsilon$, the temperature dependence of the thermoelectric power can be calculated numerically from Eq. (2) even though $\sigma(\varepsilon)$ has a nonlinear energy dependence, provided that information about $\sigma(\varepsilon)$ is precisely determined. Therefore, we consider it most important to gain precise information about $\sigma(\varepsilon)$ for the determination of $S(T)$.

Here we employ the Boltzmann-type electron conduction mechanism to evaluate $\sigma(\varepsilon)$ of the approximants. This must be appropriate because the temperature range we consider is not very low but rather high, where the weak localization and the electron-electron correlation effects would be less important and the Boltzmann-type equation can be used to interpret the temperature dependence of the electrical conductivity as was suggested by the Mott-Kaveh formula.[18,29] The Boltzmann-type electrical conductivity in an isotropic system is described as

$$\sigma(\varepsilon) = \frac{e^2}{3}N(\varepsilon)v(\varepsilon)\ell(\varepsilon), \tag{3}$$

where $N(\varepsilon)$, $v(\varepsilon)$, and $\ell(\varepsilon)$ represent the electron density of states, group velocity, and mean free path, respectively. We assume here an isotropic electronic structure because icosahedral quasicrystals and their rational cubic approximants are

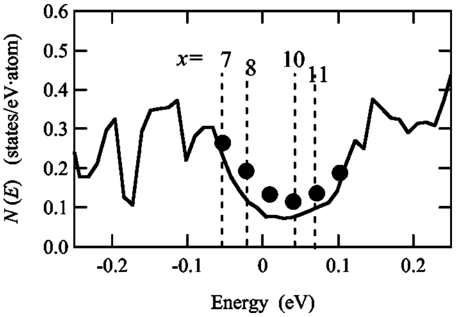

FIG. 4. The electronic density of states for the $Al_{73.6}Re_{17.4}Si_9$ 1/1-cubic approximants calculated by the LMTO ASA method (Ref. 18). Those calculated from the electronic specific heat coefficient are superimposed. The μ for each Si concentration x used to calculate $S(T)$ is shown with dashed lines with x.

nearly isotropic. If we additionally assume energy independent v and ℓ, these energy independent terms can be pulled out of the integrals in both denominator and numerator and cancel out. As a consequence, $\sigma(\varepsilon)$ in Eq. (2) is simply replaced by $N(\varepsilon)$. The resulting equation we used in our analysis is

$$S(T) = \frac{1}{eT}\frac{\int_{-\infty}^{\infty} N(\varepsilon)(\varepsilon-\mu)[\partial f(\varepsilon)/\partial\varepsilon]d\varepsilon}{\int_{-\infty}^{\infty} N(\varepsilon)[\partial f(\varepsilon)/\partial\varepsilon]d\varepsilon}. \tag{4}$$

We introduce here the density of states $N(\varepsilon)$ of the $Al_{73.6}Re_{17.4}Si_9$ 1/1-cubic approximant calculated on the basis of the LMTO ASA method using the reliable crystal structure determined by synchrotron radiation Rietveld analysis.[15] The details of the LMTO ASA calculation and of the Rietveld analysis were reported elsewhere.[15,18] The LMTO ASA density of states of the $Al_{73.6}Re_{17.4}Si_9$ 1/1-cubic approximant is depicted in Fig. 4, and that deduced from electronic specific heat coefficients is superimposed on it. The carrier concentration dependence of the density of states deduced from the electronic specific heat coefficients for these two series of 1/1-approximants showed extremely good agreement with the theoretically calculated density of states. This means that the substitution of Si for Al does not significantly affect the shape of $N(\varepsilon)$ but simply increases the number of valence electrons in the system. Thus we calculated $S(T)$ for different Si concentrations using Eq. (4) and $N(\varepsilon)$ of the 1/1-cubic approximants with a proper choice of E_F, which is shown in Fig. 4(b) with dashed lines.

The calculated $S(T)$ on the basis of the LMTO ASA density of states were superimposed on Fig. 1(a) with solid lines. The calculated $S(T)$ is in surprisingly good agreement with the measured ones not only in its sign reversal with increasing Si concentration but also the nonlinear temperature dependence. We have to stress here that we did not use any parameter fitting to calculate $S(T)$, but just employed a precisely determined $N(\varepsilon)$ and properly selected μ.

We noticed that the magnitude of $S(T)$ monotonically increases with increasing temperature when the bottom of the pseudogap (ε_{bottom}) remains outside the narrow energy range of a few k_BT in width centered at μ, but it starts to decrease when the temperature is increased high enough at which the energy range covers ε_{bottom}. It is argued, in other words, that the peak temperature where $dS(T)/dT$ becomes zero is roughly determined by the energy difference between μ and ε_{bottom}. This is closely related to the fact that the highest $S(T)$ is obtained not at the condition of $\mu=\varepsilon_{bottom}$ but when μ is located at an energy below or above ε_{bottom}. These features must be characteristic not only of the present approximants but also of all pseudogap systems that include icosahedral quasicrystals. The present analysis of the $S(T)$ of the $Al_{73.6}Re_{17.4}Si_9$ 1/1-cubic approximants lets us conclude that the characteristic behavior of $S(T)$ in these approximants and perhaps that in the corresponding quasicrystals is brought about simply by the presence of a pseudogap of a few hundreds of meV in width.

We discuss next the reliability of the assumptions, the energy independent ℓ and energy independent v, that we employed to calculate $S(T)$ in this study. A weak temperature dependence of the electrical resistivity of the $Al_{82.6-x}Re_{17.4}Si_x$ 1/1-cubic approximants allows us to believe that the mean free path of the conduction electron ℓ is fairly shortened nearly to interatomic distances.[18] In such a case, ℓ can be safely assumed to be energy independent.

On the other hand, it is very difficult to judge if the assumption of energy independent group velocity is appropriate or not for the present $Al_{82.6-x}Re_{17.4}Si_x$ 1/1-cubic approximants. It is confirmed in our analysis that $S(T)$ in the $Al_{82.6-x}Re_{17.4}Si_x$ 1/1-cubic approximants can be quantitatively reproduced from Eq. (4) with the assumption of an energy independent velocity. Perhaps information about the wave number and the group velocity has already been lost in these approximants, most likely because the mean free path ℓ is so shortened as to satisfy the condition of $\ell \approx \lambda_F$ (the Fermi wavelength) known as the Mott limit, where the wave packet is no longer well defined. One may think that this consideration is inconsistent with the use of the Boltzmann formula [Eq. (3)]. However, we believe that the Boltzmann formula is still useful even under the Mott limit, because Mott and Davis[30] gave a proof that the Kubo-Greenwood formula, which is used to interpret the electrical conductivity in nonperiodic materials, reduced to the Boltzmann formula, and because the Boltzmann conductivity σ_B is used as one of the factors in the Mott-Kaveh formula[29] which interprets the temperature dependence of electrical conductivity under the weak-localization effect. It is also very important to note before going on that the group velocity in σ_B is replaced by the energy-independent Mott g factor in Mott's formulation for the electrical conductivity in disordered materials.[31]

It is easily seen that the $S(T)$ calculation we employed in this paper cannot be directly applied to quasicrystals because the electronic structure in quasicrystals is hard to evaluate by the ordinary band calculation developed for crystalline materials. However, we have already developed a method to calculate $S(T)$ on the basis of the experimentally determined electronic structure by using high-resolution photoemission spectroscopy.[32] We are now in progress to experimentally reveal the mechanism leading to the characteristic behavior of $S(T)$ in icosahedral quasicrystals by applying the present method to photoemission spectra of high energy resolution.

In summary, the temperature dependence of $S(T)$ in these phases was quantitatively reproduced by using precisely determined electronic structure. We conclude that the large thermoelectric power in $Al_{82.6-x}Re_{17.4}Si_x$ 1/1-cubic approximants and the corresponding quasicrystals is simply brought about by the presence of a pseudogap across E_F.

V. CONCLUSION

In this study, the temperature dependence of the thermal conductivity and thermoelectric power of $Al_{82.6-x}Re_{17.4}Si_x$ 1/1-cubic approximants was systematically investigated and the dimensionless figure of merit ZT for the thermoelectric materials is evaluated using the measured electron transport properties. These approximants possess large thermoelectric power ranging from −40 to 50 μV/K and small thermal conductivity less than 1.6 W/K m. In combination with the relatively low electrical resistivity, the dimensionless figure of merit reaches 0.04 at $Al_{74.6}Re_{17.4}Si_8$ and 0.02 at $Al_{71.6}Re_{17.4}Si_{11}$ with positive and negative sign of S, respectively. $S(T)$ of these approximants was analyzed on the basis of the Boltzmann transport equation. We found that the large magnitude and the characteristic temperature dependence of $S(T)$ in the approximants and the corresponding quasicrystals are caused by the presence of a pseudogap across the Fermi level.

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