Low-Temperature Thermodynamic and Thermal-Transport Properties of Decagonal $Al_{65}Cu_{20}Co_{15}$

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We report measurements of the specific heat $C_p(T)$ and of the thermal conductivities $\lambda^p(T)$ along the periodic direction and $\lambda^q(T)$ along a direction in the quasiperiodic plane for decagonal $Al_{65}Cu_{20}Co_{15}$ at low temperatures. The phonon contribution to $\lambda^p(T)$ shows a maximum at 25 K, typical for periodic crystals. The dominant feature in the phonon contribution to $\lambda^q(T)$ is an extended plateau between 30 and 70 K, in agreement with the concept of generalized umklapp processes in quasicrystals. The coefficient $\gamma = 0.512$ mJ g atom^{-1} K^{-2} of the linear term to $C_p(T)$ indicates a low density of electronic states at E_F. [S0031-9007(96)00832-0]

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Decagonal quasicrystals share structural properties of periodically and quasiperiodically structured matter. They are periodic along the tenfold symmetry axis and quasiperiodic in the plane perpendicular to it. Since the recent discovery of thermodynamically stable decagonal quasicrystals in the Al-Cu-Co and Al-Ni-Co systems [1,2], it has become possible to study properties of both periodically and quasiperiodically structured matter along different directions of one single sample. The growth of fairly large single grains has been reported for Al-Cu-Co and Al-Ni-Co decagonal quasicrystals [2,3], which is of primary importance for reliable investigations of the anisotropic behavior. For decagonal quasicrystals in these systems, strong anisotropies of electrical- [4] and thermal- [5] transport properties, and also of the optical conductivity [6] have experimentally been established.

Below we describe our results of measurements of the specific heat $C_p(T)$ and of the thermal conductivities $\lambda^p(T)$ and $\lambda^q(T)$ along the periodic direction and along a direction in the quasiperiodic plane, respectively, of high-quality single-grained samples of decagonal Al-Cu-Co in varying temperature ranges between 0.06 and 105 K. This set of data contains information on the specific heat, to our knowledge not investigated before for decagonal quasicrystals. It also extends the temperature range of previous investigations of thermal-transport properties in these materials [5] by more than 2 orders of magnitude, thus providing evidence for the conceptually different lattice conduction of heat via $\lambda^p(T)$ and $\lambda^q(T)$, defined above.

The ingot with a nominal composition $Al_{65}Cu_{20}Co_{15}$ was synthesized from 99.999% pure aluminum, 99.9985% pure copper, and 99.997% pure cobalt by arc melting suitable amounts of the constituents to a single piece and remelting it several times. The resulting ingot was remelted again at 1100 °C in an alumina crucible sealed under vacuum inside a silica ampoule, cooled to 920 °C at the rate 2 °C per h, annealed at 920 °C for 24 h, and subsequently cooled to room temperature. Faceted decaprisms up to 1.5 mm in diameter and up to 6 mm in length were cut from the ingot using spark erosion. Two decaprisms with approximate dimensions $2.9 \times 1.5 \times 0.4$ and $2.0 \times 0.6 \times 0.4$ mm^3 have been selected for our experiments. Their naturally formed facets were polished to remove possible surface contaminations. A high degree of quasicrystalline order was confirmed by electron diffraction experiments. Laue photographs taken on both samples have confirmed that they are single grains. The smaller sample has been used for measurements of the thermal conductivity $\lambda^p(T)$ along the tenfold symmetry axis, while the larger grain has been used for measuring $\lambda^q(T)$ along a direction in the quasiperiodic plane and also for the specific heat $C_p(T)$ measurements.

The thermal conductivity $\lambda(T)$ was measured using a standard steady-state heat-flow technique monitoring the temperature gradient along the sample. The specific heat $C_p(T)$ was measured using a conventional relaxation-type method. The temperatures in the range between 0.06 and 1 K were reached using a dilution refrigerator, and we used ^{3}He and ^{4}He cryostats for temperatures between 0.35 and 3 K, and above 1.5 K, respectively.

Figure 1(a) shows the complete set of our results of the specific heat $C_p(T)$ measured in the temperature range between 1.5 and 17 K, plotted on logarithmic scales. Our $C_p(T)$ data between 1.5 and 4.5 K, shown in Fig. 1(b) as C_p/T vs T^2, are well fitted by

$$C_p(T) = \gamma T + \beta T^3, \qquad (1)$$

indicating that the main contributions are from the common electronic and lattice excitations at low temperatures. The results of the fit are $\gamma = 0.512$ mJ g atom^{-1} K^{-2}, and $\beta = 9.22$ μJ g atom^{-1} K^{-4}. The coefficient γ of decagonal $Al_{65}Cu_{20}Co_{15}$ cannot easily be compared with an estimate of a free-electron value of the electronic specific heat because the number of electrons, donated by the d-transition-element atoms to the conduction band, is not

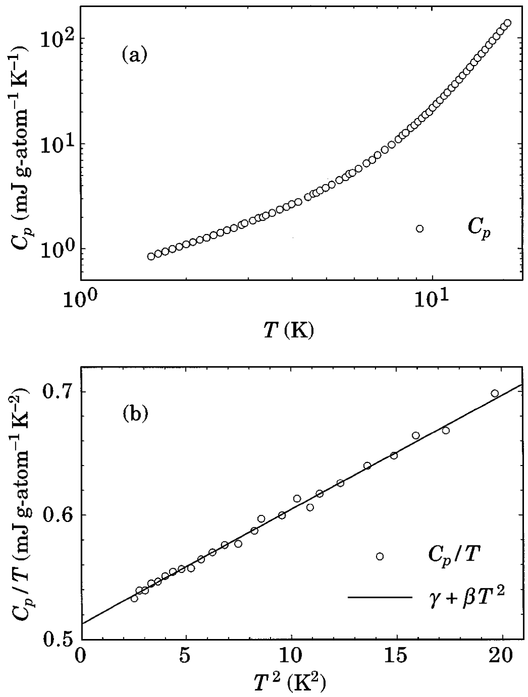

FIG. 1. (a) Specific heat $C_p(T)$ of decagonal $Al_{65}Cu_{20}Co_{15}$ between 1.5 and 17 K. (b) C_p/T vs T^2. The solid line represents the fit (see text).

well defined. In any case, we note a low value of the electronic specific heat, amounting to approximately one-third of that of aluminum, if all of the γT term is ascribed to electronic degrees of freedom. This γ value is comparable to $\gamma = 0.41$ mJ g atom^{-1} K^{-2} previously reported for icosahedral $Al_{70}Mn_9Pd_{21}$ and tentatively attributed to the presence of a pseudogap in the electronic density of states at the Fermi level E_F [7]. Subsequent optical reflectivity measurements using the same sample confirmed this conclusion [8].

It has previously been claimed that a Hume-Rothery mechanism plays a dominant role in the stability of the icosahedral quasicrystals [9,10]. This is mainly because the existence of a pronounced pseudogap in the density of electronic states at E_F has experimentally been indicated for various icosahedral phases [11,12]. In contrast, it is controversial at present as to whether the same mechanism also leads to the stabilization of decagonal quasicrystals. Based on the results of Hall-effect measurements [13], Wang and co-workers have claimed that the Hume-Rothery-type stabilization is essential. A band-structure calculation for a *periodic approximant* of a decagonal structure of Trambly de Laissardière and Fujiwara gave further support by confirming the existence of a well-pronounced pseudogap at the Fermi level for this particular case [14]. On the contrary, recent optical conductivity measurements [6] and photoemission spectroscopy experiments [15] show no evidence for a pseudogap. We expect to address this problem in a forthcoming publication.

Our value of the parameter β is compatible with a Debye temperature Θ_D of 596 K, to our knowledge the highest of all the Θ_D values reported previously for thermodynamically stable quasicrystals.

In Fig. 2(a), we show the total thermal conductivity λ_{tot}^p measured along the periodic direction in the temperature range between 0.45 and 105 K, plotted on logarithmic scales. The phonon contribution λ_{ph}^p to the total thermal conductivity may be obtained by subtracting off an estimate of the electronic contribution λ_{el}^p. The latter was calculated by assuming the validity of the Wiedemann-Franz law and using the electrical conductivity data obtained from this same sample. In Fig. 2(a), the calculated electronic contribution λ_{el}^p is shown as the solid line. The phonon contribution λ_{ph}^p obtained in this manner is shown on a double logarithmic plot in Fig. 2(b). The overall λ_{ph}^p behavior is similar to that of periodic crystals; there is a distinct maximum at an intermediate temperature. In periodic crystals, in the temperature region just above that maximum, the phonon thermal conductivity is dominated by the onset of umklapp processes, and hence the phonon thermal conductivity is expected to decrease exponentially with increasing temperature due to an exponential increase in the number of occupied high-frequency phonon states that allow the occurrence of umklapp processes [16]. In

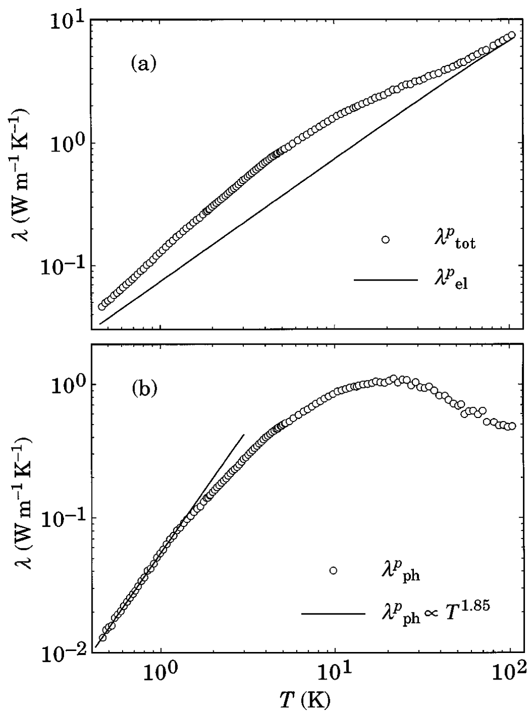

FIG. 2. (a) Temperature dependence of the total thermal conductivity λ_{tot}^p along the periodic direction of decagonal $Al_{65}Cu_{20}Co_{15}$ between 0.45 and 105 K. The solid line is an estimate of the electronic contribution λ_{el}^p, as explained in the text. (b) Phonon contribution λ_{ph}^p as a function of temperature. The solid line indicates a power-law approximation to the λ_{ph}^p data between 0.45 and 1.2 K.

Fig. 2(b), we may see a distinct decrease of $\lambda_{\rm ph}^{p}$ with increasing temperature above the maximum, although we cannot claim that the exponential dependence is actually verified. In general, this exponential dependence is most often masked by isotope or impurity scattering effects [17]. Much below the maximum temperature, the phonon mean free path in periodic crystals is limited by sample-boundary scattering or, in metallic crystals, by phonon-electron scattering. Both these processes result in a positive slope of the $\lambda_{\rm ph}$ curve, and a crossover from high to low temperatures necessarily yields a maximum in the phonon thermal conductivity curve.

Between 0.45 and 1.2 K, the slope of $\lambda_{\rm ph}^{p}(T)$ of our sample is almost constant, and it may be seen that $\lambda_{\rm ph}^{p}(T)$ can adequately be approximated as $\lambda_{\rm ph}^{p} = AT^{n}$ with $n = 1.85$ [see solid line in Fig. 2(b)]. There are two mechanisms of phonon scattering that yield an approximately quadratic temperature dependence of the phonon thermal conductivity, i.e., the scattering of the phonons which involves either conduction electrons or tunneling states. The relatively low resistivity $\rho^{p}(T)$ of our sample suggests that a substantial part of the phonon thermal resistance $(\lambda_{\rm ph}^{p})^{-1}$ might be attributed to phonon-electron interactions.

At the lowest and at the highest temperatures of this experiment, i.e., where the phonon contribution $\lambda_{\rm ph}^{p}$ is expected to be small, $\lambda_{\rm tot}^{p}$ is close in magnitude to $\lambda_{\rm el}^{p}$. This observation corroborates our conjecture that the law of Wiedemann and Franz is approximately valid for the periodic direction of decagonal $Al_{65}Cu_{20}Co_{15}$.

Figure 3(a) shows the total thermal conductivity $\lambda_{\rm tot}^{q}$ along a direction in the quasiperiodic plane, together with the electronic thermal conductivity $\lambda_{\rm el}^{q}$ calculated in the same way as described above. The phonon thermal conductivity $\lambda_{\rm ph}^{q}$, obtained by subtracting $\lambda_{\rm el}^{q}$ from $\lambda_{\rm tot}^{q}$, is shown in Fig. 3(b). From 0.06 to 0.1 K, $\lambda_{\rm ph}^{q}$ increases rapidly with increasing temperature. From 0.2 to 0.8 K, the slope of $\lambda_{\rm ph}^{q}(T)$ is almost constant and $\lambda_{\rm ph}^{q}(T)$ is well fitted with $\lambda_{\rm ph}^{q} = AT^{n}$ with $n = 1.90$, again suggestive of the phonon scattering involving either itinerant electrons or tunneling states. The result of this fit is indicated by the solid line in Fig. 3(b). At higher temperatures, the slope $d\lambda_{\rm ph}^{q}/dT$ decreases gradually and $\lambda_{\rm ph}^{q}(T)$ saturates at about 25 K. From 30 to 70 K, $\lambda_{\rm ph}^{q}$ is almost temperature independent and slowly increases again above 70 K. A closer examination of $\lambda_{\rm ph}^{q}(T)$ reveals a shallow maximum at the lower end of the plateau region, as may be seen in the inset of Fig. 3(b).

The overall $\lambda_{\rm ph}^{q}(T)$ variation for decagonal $Al_{65}Cu_{20}Co_{15}$ described above is reminiscent of $\lambda_{\rm ph}(T)$ of icosahedral $Al_{70}Mn_{9}Pd_{21}$ [18], except for the rapid increase in the lowest temperature range between 0.06 and 0.1 K. A detailed analysis of $\lambda_{\rm ph}^{q}$ in this temperature range meets difficulties because of the large electronic contribution to the total thermal conductivity, as may be seen in Fig. 3(a). This problem is much less severe at higher temperatures, and we recall that a power law with an exponent close to 2 has also been observed for $\lambda_{\rm ph}(T)$ of icosahedral $Al_{70}Mn_{9}Pd_{21}$ [18]. In Ref. [18], this behavior has been analyzed in terms of the scattering of phonons by tunneling states, which is often also observed in amorphous solids [19,20]. Experimental investigations probing tunneling states directly, e.g., ultrasound experiments studying the temperature variation of the sound velocity and power dependence of the acoustic-wave attenuation in decagonal $Al_{65}Cu_{20}Co_{15}$, as they have been done for icosahedral Al-Mn-Pd [21], would be helpful.

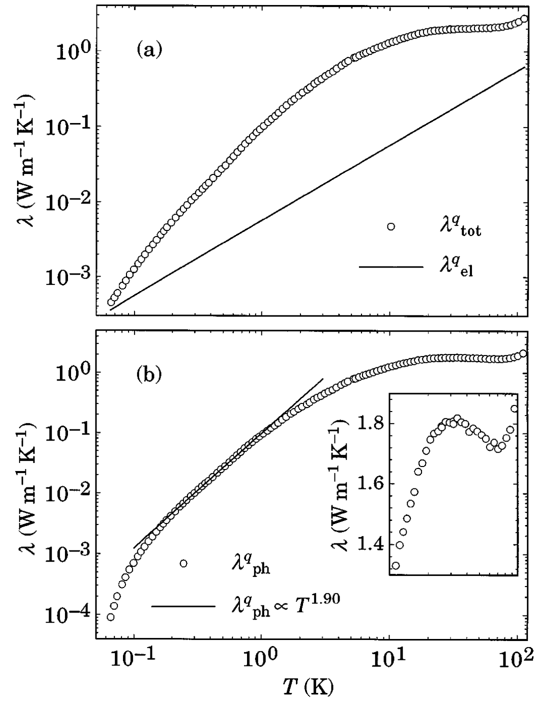

FIG. 3. (a) The total thermal conductivity $\lambda_{\rm tot}^{q}(T)$ of decagonal $Al_{65}Cu_{20}Co_{15}$ in a quasiperiodic direction between 0.06 and 110 K. The solid line is an estimate of the electronic contribution $\lambda_{\rm el}^{q}$ (see text). (b) Quasilattice thermal conductivity $\lambda_{\rm ph}^{q}(T)$. The solid line is a power-law approximation to the data between 0.2 and 0.8 K. The inset shows $\lambda_{\rm ph}^{q}$ between 10 and 100 K on an expanded vertical scale.

The occurrence of a plateau-type feature in the quasilattice thermal conductivity $\lambda_{\rm ph}^{q}$ of decagonal $Al_{65}Cu_{20}Co_{15}$ in the quasiperiodic plane [Fig. 3(b)] is compatible with the concept of generalized umklapp processes in condensed matter with quasiperiodic order recently proposed by Kalugin and co-workers [22]. In conventional crystals, the rate of the umklapp processes is expected to depend exponentially on temperature at low temperatures, as described above. Kalugin and co-workers argue that the rate of the generalized umklapp processes in quasicrystals should have a weaker power-law dependence, reflecting the fact that the momentum of vibrational excitations can be transferred to the quasilattice in inelastic scattering events by arbitrarily small portions, i.e., not limited in magnitude from below. This weaker temperature dependence would make the maximum in the $\lambda_{ph}^{q}(T)$ curve much more shallow or even turn it into a plateau, very much as what is displayed in Fig. 3(b). The plateau-type feature in the phonon thermal conductivity curve has previously been observed in icosahedral Al-Mn-Pd, Al-Cu-Fe, and Al-Re-Pd and seems to be a general observation for icosahedral quasicrystals [18,23,24].

In conclusion, the low linear-in-T contribution $\gamma T = 0.512$ mJ g atom^{-1} K^{-1} to the low-temperature specific heat $C_p(T)$ of decagonal $Al_{65}Cu_{20}Co_{15}$ suggests the existence of a pseudogap in the electronic density of states at the Fermi level. The cubic-in-T term to the specific heat is compatible with a Debye temperature Θ_D of 596 K, which is considerably higher than the Θ_D values previously reported for stable icosahedral quasicrystals. The dominant feature in the temperature dependence of the phonon-thermal conductivity λ_{ph}^{p} along the periodic direction is a distinct maximum at about 25 K. This feature can be attributed to a crossover between the Peierls regime of the usual umklapp phonon scattering and the regime of phonon-electron scattering. On the other hand, the phonon-thermal conductivity λ_{ph}^{q} in the quasiperiodic plane is only weakly temperature dependent between 30 and 70 K, in agreement with the concept of generalized umklapp processes in quasiperiodic crystals. This direct comparison strongly supports the view that the characteristics of lattice dynamics in periodically or quasiperiodically structured condensed matter are distinctly different.

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