Low-temperature thermal conductivity of a single-grain Y-Mg-Zn icosahedral quasicrystal

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We report measurements of the thermal conductivity $\kappa(T)$ of a single-grain icosahedral $Y_{8.6}Mg_{34.6}Zn_{56.8}$ in the temperature range between 0.1 and 300 K. The quasilattice thermal conductivity κ_{ph} increases monotonically with T by three orders of magnitude between 0.1 and 23 K. Above 23 K, $\kappa_{ph}(T)$ decreases substantially with increasing temperature, typical for high-quality single grain quasicrystals. The decrease ends in a minimum at approximately 140 K. The interpretation of our data is based on a Debye-type relaxation time approximation. At very low temperatures, the corresponding fit reveals that the phonon mean free path is of the order of the smallest sample dimension, while at high temperatures, a power-law decrease of the phonon scattering time with increasing temperature evidences the effect of structural scattering on the mean free path of itinerant quasilattice excitations. The behavior of $\kappa_{ph}(T)$ at intermediate temperatures may best be fit by assuming the existence of stacking-fault-like phonon scatterers. No clear evidence for a scattering of phonons by tunneling states has been observed. If compared to previously reported measurements of the thermal conductivity of quasicrystals, these data indicate the very high structural perfection of this quasiperiodic material.

I. INTRODUCTION

Since the discovery of the first quasicrystalline material by Shechtman *et al.* in 1984,[1] much effort has been put into identifying distinct effects on the physical properties that would be characteristic of the quasiperiodicity of these alloys. One of the remarkable features of quasicrystals is, for instance, the apparent conflict between the high structural quality of these materials and their thermal and electrical conductivities, which are much lower than in periodically structured metallic solids.

In 1993 a stable icosahedral phase (*i*-phase) was discovered in the system (Y,RE)-Mg-Zn (RE=rare earth) by Luo *et al.*[2] In contrast to most of the other known *i* phases this system is based on Zn—and not Al—as the main constituent. Another interesting feature of this quasicrystalline alloy is the possibility to substitute other RE elements for Y. Detailed investigations showed the stability of the *i* phase for RE=Gd, Tb, Dy, Ho, and Er.[3,4] These alloys are so far the only stable materials which allow to study the behavior of localized 4*f* magnetic moments embedded in a quasiperiodic structure. In addition, an examination of how crystalline electric field effects and the rare-earth concentration affect their magnetic properties is possible in this new class of substances. Neutron diffraction experiments on single-grain samples[5,6] show no evidence for long-range magnetic order, in contrast to earlier measurements that were performed using multiphase polygrain materials.[7] At temperatures below 10 K, both ac- and dc-susceptibility measurements on the rare-earth containing samples exhibit classical spin-glass features which are consistent with the geometrical frustration of the magnetic moments in an aperiodic structure.[8]

Previous studies on *i*-$Y_{8.6}Mg_{34.6}Zn_{56.8}$ have mainly concentrated on establishing its structural characteristics. Available information on the physical properties of this compound includes data of the low-temperature magnetic properties and the electrical transport properties of single grain samples,[8] the magnetoresistance properties of bulk and ribbon samples,[9] the electronic structure,[10] the electronic specific heat,[11] and the optical properties of single-grain samples.[12,13] Recent advances in the growth of large single-grain (Y,RE)-Mg-Zn quasicrystals[14,15] allow the study of transport properties without the unwanted effects of second phases and grain boundaries upon the measured quantities. Reports on the low-temperature thermal transport properties of Y-Mg-Zn are still missing. In this work, we present the results of measurements of the thermal conductivity of a high-quality, single-grain Y-Mg-Zn icosahedral quasicrystal. The paper is organized as follows. In Sec. II we start with a brief description of the sample preparation and the experimental setup used for measuring the thermal conductivity κ between 0.1 and 300 K. In Sec. III, we show the results of our measurements and present a quantitative description of the data. Finally, in Sec. IV, we discuss the physical implications of our analysis.

II. EXPERIMENTAL

A large single-grain sample of $Y_{8.6}Mg_{34.6}Zn_{56.8}$ has been grown from the ternary melt, i.e., via a self-flux method.[14] In brief, this method involves the slow cooling of a ternary melt intersecting the primary solidification surface of the icosahedral phase, as identified by Langsdorf, Ritter, and Assmus.[16] The obtained sample has a dodecahedral morphology, with clearly defined pentagonal facets.

In order to measure the thermal conductivity κ of this material, a specimen in the form of a bar with dimensions $1.9\times1\times0.6$ mm^3 was cut from the single grain by spark erosion. The sample faces were then polished using emery paper.

The cooling of the sample was achieved by using a dilution refrigerator from 0.1 to 0.5 K, a ^{3}He cryostat between 0.3 and 2 K, and a ^{4}He flux cryostat between 1.5 and 300 K. The thermal conductivity was measured by a standard steady-state heat-flow technique. At one end the bar-shaped sample was glued to a heat sink made of OFHC copper by means of EpoTek H20E. The sample heater, attached to the other end with the same glue, consisted of a 100 Ω ruthenium-oxyde chip resistor. At temperatures below 2 K, we measured the temperature gradient along the sample with two carbon resistor thermometers which were calibrated against the heat sink temperature when no heat-flux was applied. The thermal contact of the thermometers to the sample was made by 0.1 mm diameter gold wires which were attached to one flat surface of the specimen by means of EpoTek H20E. In order to measure the thermal gradient along the sample above 2 K, we preferred the use of calibrated chromel-gold/iron thermocouples. The advantage here is that the thermocouples have a much smaller surface than the carbon resistors, which results in a substantial reduction of thermal radiative losses. Very thin (25 μm in diameter) and long (up to 10 cm) wires have been chosen in order to reduce the heat flow through the thermocouples.

Thermal conductivity measurements of materials with low κ values are generally difficult to perform at high temperatures because of the detrimental effect of radiative losses on the results. In order to limit this type of energy dissipation, a cylindrical radiation shield in good thermal contact with the heat sink was installed. With this setup, the radiative losses in our measurements have been estimated to be below 1% of the applied power over the whole temperature range using the following arguments. At 300 K, the wavelength λ_m corresponding to the maximum of the energy density of radiation may be calculated by applying Wien's displacement law, which gives $\lambda_m = 9.66$ μm. The latter may be used for an estimate of the emissivity of $Y_{8.6}Mg_{34.6}Zn_{56.8}$ in the classical approximation. The theory of Drude yields a relation between the emissivity ϵ, the radiation wavelength $\lambda_m(\mu\text{m})$ and the dc electrical resistivity $\rho(\Omega\text{m})$ of a metal via the following expression:

$$\epsilon = 365\sqrt{\rho/\lambda_m}, \tag{1}$$

which is generally in good agreement with experimental data at elevated temperatures. Inserting the value of $\rho \sim 2\times10^{-6}$ Ω m, measured on our sample at room temperature, we obtain $\epsilon_{YMZ} = 0.17$ for $Y_{8.6}Mg_{34.6}Zn_{56.8}$. The literature value for the emissivity of oxidized copper, which was the material used for our radiation shield, is $\epsilon_{RS} = 0.6$. The power P_{rad}, effectively emitted by our sample via radiation, can now be calculated using Stefan's law

$$P_{rad} = \tilde{\sigma} E S_{RS}(T^4 - T_{RS}^4), \tag{2}$$

where T and T_{RS} are the mean sample and the radiation shield temperatures, respectively, S_{RS} is the surface of the radiation shield, and $\tilde{\sigma} = 5.67\times10^{-8}$ W/m^{2}K^4 is Stefan's constant. The constant E is the effective emissivity for coaxial cylinders and is given by[17]

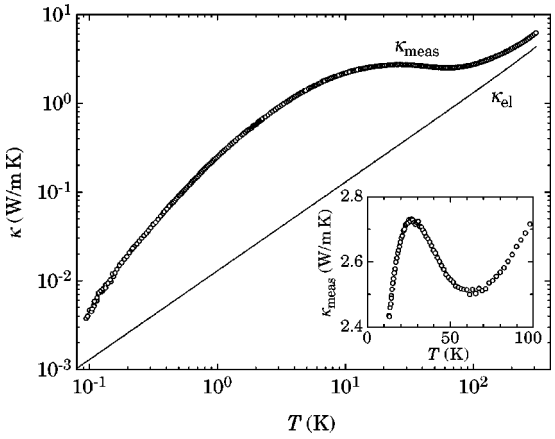

FIG. 1. Measured thermal conductivity κ_{meas} of icosahedral $Y_{8.6}Mg_{34.6}Zn_{56.8}$ as a function of temperature between 0.1 and 300 K. The solid line is an estimate of the electronic contribution κ_{el}, as explained in the text. The inset shows the region of the maximum and the minimum of κ_{meas} on linear scales.

$$E = \frac{\epsilon_{RS}\epsilon_{YMZ}}{\epsilon_{YMZ} + (S_{RS}/S_{YMZ})(1-\epsilon_{YMZ})\epsilon_{RS}}, \tag{3}$$

where S_{YMZ} is the surface of our sample. Since the temperature of the sample varies slightly along its length, Eq. (2) may, strictly speaking, only be applied to a layer of the sample with the temperature T. Nevertheless, since the temperature difference along the sample is small compared to its average temperature, the error made by using Eq. (2) can be neglected.

By using Eq. (2), we calculate $P_{rad}/P = \kappa_{rad}/\kappa_{meas} = 5\times10^{-3}$ at 300 K, where P is the power applied from the heater to our sample, κ_{rad} is the error due to radiation effects in the measurement of the thermal conductivity and κ_{meas} is the measured thermal conductivity. In a first order approximation, Eq. (2) may be written as $P_{rad} = 2\tilde{\sigma}ES_{RS}T^3\Delta T$, where ΔT is the temperature difference between the sample heater and the thermal sink. For this reason, radiation effects manifest themselves in the observation of a cubic-in-T dependence of the thermal conductivity. As will be shown below, the absence of such a T^3-regime in our data at the highest temperatures confirms the validity of our arguments in favor of a negligible influence of radiation losses on our data.

III. RESULTS AND ANALYSIS

In Fig. 1, we show the measured thermal conductivity κ_{meas} for the whole temperature range which has been covered in our study. The quasilattice contribution to the thermal conductivity κ_{ph} may in principle be obtained by subtracting off the electronic contribution κ_{el}. The latter has been estimated by using the data of the electrical conductivity measured on the same sample and assuming the validity of the Wiedemann-Franz law

$$\kappa_{el} = L_0\sigma T, \tag{4}$$

with the Lorenz number $L_0 = 2.44\times10^{-8}$ WΩ/T^2. Equation (4) has a very general range of validity. It usually holds for arbitrary band structures, as long as the change in energy

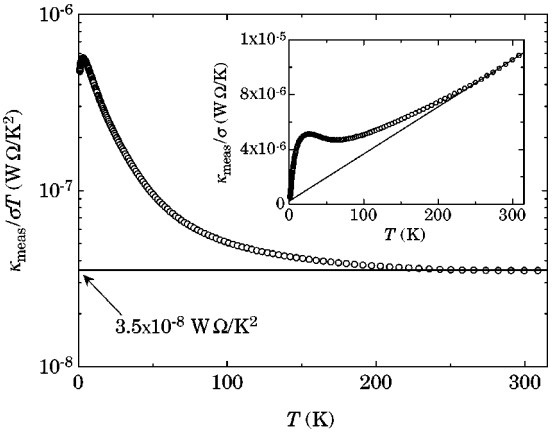

FIG. 2. $\kappa_{meas}/\sigma T$ as a function of temperature in $Y_{8.6}Mg_{34.6}Zn_{56.8}$. The solid horizontal line is a fit to the high temperature data. The inset shows the ratio κ_{meas}/σ as a function of temperature. The solid line is a fit consistent with that shown in the main frame, as explained in the text.

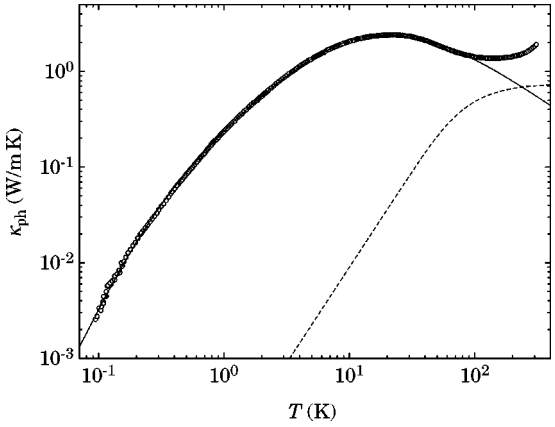

FIG. 3. The phonon contribution κ_{ph} to the thermal conductivity of icosahedral $Y_{8.6}Mg_{34.6}Zn_{56.8}$ as a function of temperature between 0.1 and 300 K. The solid line is a fit to the data based on Eq. (6). The dashed line is an estimate of the thermal conductivity due to diffusive phonon propagation using Eq. (13) (see text).

during an electron collision is small compared with $k_B T$. This happens to be the case at high temperatures, where the dominant source of the electron collisions is given by the thermal vibrations of the ions, as well as at low temperatures, where elastic impurity scattering is the dominant mechanism for the degradation of the electronic thermal current. Nevertheless, a direct evaluation of L_0 is still missing in quasicrystals, as its measurement by conventional techniques is inaccessible because of the high electrical resistivity of these materials. Considering the length of our sample and the lateral extension of the thermal contacts, the uncertainty in the geometrical factor has been estimated to be about 10%. In order to avoid additional uncertainties that arise in the subtraction of the electronic contribution κ_{el} from the measured thermal conductivity κ_{meas}, the same contacts used for the measurement of the temperature gradient along the sample were used as voltage terminals for the measurement of the electrical conductivity. The calculated electronic contribution to the thermal conductivity κ_{el} is shown in Fig. 1 as a solid line. Since κ_{el} is comparable to the total thermal conductivity at the lowest and at the highest temperatures, the estimated quasilattice contribution is expected to be sensitive to deviations from the Wiedemann-Franz relation in these temperature ranges.

In order to present the connection between thermal and electrical conduction, we plotted the ratio $\kappa_{meas}/\sigma T$ in the whole temperature range covered by our experiment in Fig. 2. The data seem to reach asymptotically a constant value L in the limit of high temperatures. This value is about 40% higher than the Lorenz number ($L = 3.5 \times 10^{-8}$ W/ΩK^2). In the inset of Fig. 2, we plotted the ratio κ_{meas}/σ and a fit linear in temperature, to the last points taken at the highest temperatures reached in our experiment. The constant zero temperature component resulting from the fit is within the error margins of the extrapolation from high to low temperatures. On the basis of our data alone we are thus in principle not able to exclude that the upturn of the measured thermal conductivity at high temperatures has to be assigned completely to heat conduction via conduction electrons. Nevertheless, an increase of the thermal conductivity at high temperatures has also been observed in icosahedral quasicrystals with negligible electronic thermal conduction.[18] We are therefore confident that at least part of the high temperature thermal conductivity increasing with T is due to quasilattice vibrational modes. For this reason, we will base our analysis on the assumption that the classical Lorenz number approximately also applies for the material investigated here.

In Fig. 3, we show the calculated quasilattice contribution $\kappa_{ph} = \kappa_{meas} - \kappa_{el}$ to the thermal conductivity of icosahedral $Y_{8.6}Mg_{34.6}Zn_{56.8}$ where κ_{el} has been evaluated according to Eq. (4). The lattice conductivity increases monotonically with T between 0.1 and 23 K. Between 23 and 140 K, $\kappa_{ph}(T)$ decreases to almost half of its maximum value but increases again with further increasing temperature above 140 K. As we argued above, the rather unusual increase of κ_{ph} with increasing temperature above the temperature region where structural scattering is dominant, and which is commonly not observed in crystals with periodic structures, cannot simply be ascribed to radiative thermal losses.

In what follows, we present a quantitative analysis of our data in the long-wavelength limit. As it will be shown, our experimental results can successfully be described in a quantitative way between 0.1 and 70 K, i.e., over almost three orders of magnitude.

Bloch-type wave functions are generally not the appropriate description of lattice excitations in quasicrystals.[19] The eigenstates in quasiperiodic structures are always affected by an intrinsic decay rate and are not localized in momentum space as they are in periodically structured materials.[20] For this reason, the calculation of the dynamical response for three-dimensional quasilattices is a difficult task. Nevertheless, we may assume the validity of the use of quasi-Bloch states in the long-wavelength limit where their decay rate is so low that other scattering mechanisms will certainly dominate.[19] Thus, in the following we may identify the itinerant quasilattice excitations as phonons and we will speak about phonon momentum as if it were a good quantum number. Well defined phonons whose energy width is limited by the instrumental resolution have in fact been observed in the long-wavelength limit by means of inelastic neutron scattering experiments.[21,22]

Theoretical calculations of the dynamical properties of one-dimensional Fibonacci chains predict a linear phonon dispersion relation in the long-wavelength limit, where the quasicrystal can be regarded as a continuum.[23,24] Isotropic linear phonon dispersion relations are also predicted and have been observed in the long-wavelength limit of three-dimensional icosahedral quasicrystals.[21,25] For these reasons, we have based the analysis of our data at low temperatures where only long-wavelength states can thermally be excited, on a Debye-type relaxation time approximation.

In a relaxation-time approximation, the quasilattice thermal conductivity $\kappa_{\rm ph}$ can be written as

$$\kappa_{\rm ph}^{\rm fit}=\frac{1}{3}\int C_{\rm v}(\omega,T)v_{\rm ph}^2\tau(\omega,T)d\omega, \tag{5}$$

where $C_{\rm v}(\omega,T)$ is the quasilattice specific heat and $\tau(\omega,T)$ is the mean lifetime of a phonon. In the Debye model, the phonon dispersion relation is approximated by linear branches for which $v_{\rm ph}$ in the expression above is simply a constant mean phonon velocity, extending over all wave vectors up to the Debye wave-vector $k_{\rm D}$. In this simplification, the density of phonon states is quadratic in ω, and Eq. (5) may be rewritten as

$$\kappa_{\rm ph}^{\rm fit}=3nk_{\rm B}\left(\frac{T}{\Theta_{\rm D}}\right)^3 v_{\rm ph}^2\int_0^{\Theta_{\rm D}/T}\frac{x^4e^x}{(e^x-1)^2}\tau(x,T)dx, \tag{6}$$

where $n=1/6\pi^2(k_{\rm B}\Theta_{\rm D}/\hbar v_{\rm ph})^3$ is the number density of atoms in the quasicrystal, $x=\hbar\omega/k_{\rm B}T$, and $\Theta_{\rm D}$ is the Debye temperature. The value of $\Theta_{\rm D}=348$ K corresponding to a phonon velocity $v_{\rm ph}=3040$ m sec^{-1} may be extracted from specific-heat measurements which have been performed on the same sample.[13]

Some comments about the range of the validity of Eq. (6) seem in order. As we mentioned above, inelastic neutron scattering experiments showed a linear phonon dispersion relation up to wave vectors with approximately $q\sim 0.3$ Å^{-1} in icosahedral Al-Mn-Pd.[21] A phonon density of states quadratic in ω has been estimated by Hafner and Krajčí for higher-order rational approximants to *i*-Al-Mg-Zn quasicrystals up to energies of the order of magnitude of 10 meV, which also correspond to wave vectors with $q\sim 0.3$ Å^{-1}.[25] If we assume the existence of a similar ''well behaved'' phonon-spectrum for $Y_{8.6}Mg_{34.6}Zn_{56.8}$ at low q's, we expect the Debye approximation to be valid at those temperatures where the thermal excitation of phonons with a wave vector $q<0.3$ Å^{-1} is dominant. By considering

$$g(\omega,T)=\frac{3}{2\pi^2v_{\rm ph}^3}\frac{\omega^2}{\exp\left(\frac{\hbar\omega}{k_{\rm B}T}\right)-1}, \tag{7}$$

where $g(\omega,T)$ expresses the density of the thermally excited phonons at a given temperature and frequency, this is the case for temperatures lower than 50 K.

As already mentioned, it has been argued that the phonon eigenstates in quasicrystals are always affected by an intrinsic decay rate.[19] However, this decay is exponentially slow in the long-wavelength limit, and other scattering mechanisms will dominate. In order to take into account the different phonon scattering mechanisms, we used the following expression for the total phonon scattering rate τ^{-1}:

$$\tau^{-1}(\omega,T)=(\tau_{\rm Cas}^{-1}+\tau_{\rm sf}^{-1}+\tau_{\rm U}^{-1})(\omega,T). \tag{8}$$

In Eq. (8), the different scattering rates represent possible individual scattering channels. At very low temperatures we may expect a temperature independent mean free path for phonons, known as Casimir limit, such that $\tau_{\rm Cas}=l_{\rm Cas}/v_{\rm ph}$. The term $\tau_{\rm sf}^{-1}=A\omega^2$ is introduced to describe the scattering rate due to phonon interactions with stacking fault-like defects. For the power law describing Umklapp scattering,[19] we found that a rate $\tau_{\rm U}^{-1}=B\omega^3T$ provides the best fit to our data. We attempted to fit our data using Eq. (8), letting $l_{\rm Cas}$, A, and B as free parameters. The resulting curve which reproduces our data below $\sim$70 K very well is displayed in Fig. 3 as a solid line.

Previously reported results of thermal conductivity measurements on icosahedral quasicrystals were characterized by a temperature regime in which $\kappa_{\rm ph}$ varied approximately proportional to T^2, suggestive for a term $\tau^{-1}\sim\omega$ in the scattering rate.[26,18] Scattering of phonons by two-level systems as well as phonon-electron scattering do account for such terms in the scattering rate. Since a scattering of phonons on electrons was not expected to be dominant in these previously investigated materials, the $\kappa_{\rm ph}\sim T^2$ dependence was interpreted as being due to the presence of tunneling states in the investigated quasicrystals. This observation was also supported by the fact that tunneling states in *i*-Al-Mn-Pd have been observed by analyzing the results of ultrasound experiments.[27] Phonon interactions with two-level systems are described by a scattering rate

$$\tau_{\rm TS}^{-1}=\frac{\overline{P}\gamma^2}{\tilde{\rho}v_{\rm ph}^2}\pi\omega\tanh\left(\frac{\hbar\omega}{2k_{\rm B}T}\right), \tag{9}$$

where $\overline{P}$ is the density of tunneling states, γ decribes the average coupling between them and the phonons, and $\tilde{\rho}$ is the mass density of $Y_{8.6}Mg_{34.6}Zn_{56.8}$.[28,29] As we tried to use the additional term $\tau_{\rm TS}^{-1}$ in the scattering rate given by Eq. (8) and leaving $\overline{P}\gamma^2$ as a free parameter, the quality of our fit did not improve and the free parameter tended to be zero. Attempts to fix the factor $\overline{P}\gamma^2$ to values of the same order of magnitude as those observed in *i*-Al-Mn-Pd[26] or *i*-Al-Re-Pd[18] lead to nonconvergent fits, suggesting that tunneling states in $Y_{8.6}Mg_{34.6}Zn_{56.8}$ if present at all, are characterized by a coupling parameter $\overline{P}\gamma^2$ which is much lower than those observed in other icosahedral quasicrystals. It has been argued that tunneling states might not necessarily be an intrinsic feature of quasicrystalline materials.[18] The absence of any evidence in our data for a scattering of phonons by tunneling states supports this point of view.

By inspecting the insert of Fig. 1 it may well be seen that the measured total thermal conductivity $\kappa_{\rm meas}$ exhibits a distinct maximum around 25 K. This feature, even more prominent for $\kappa_{\rm ph}$, is typical for periodic crystals and quite different from the plateau-type behavior of $\kappa_{\rm ph}$ of amorphous materials. The appearance of a plateau in the thermal conductivity of *amorphous* solids is thought to be the consequence of a rapidly decreasing phonon mean free path with

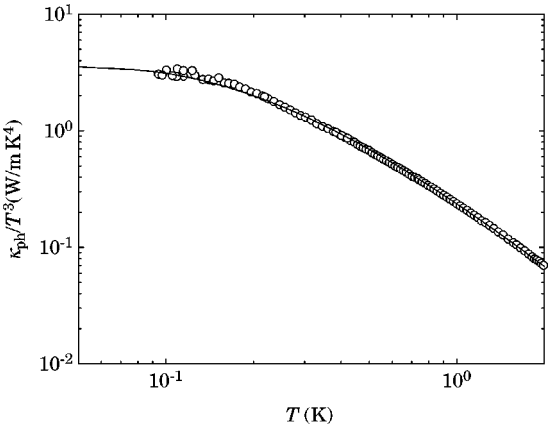

FIG. 4. κ_{ph}/T^3 vs T of icosahedral $Y_{8.6}Mg_{34.6}Zn_{56.8}$ below 2 K. The solid line corresponds to the fit to our data as explained in the text.

increasing frequency. Zaitlin and Anderson[30] were able to describe this feature by introducing a term $\tau_{Ray}^{-1} \propto \omega^4$ which has been compared to theoretical estimates of Rayleigh scattering. Such a term clearly fails to describe the features measured on $Y_{8.6}Mg_{34.6}Zn_{56.8}$ where the appearance of a maximum implies that the mean free path of phonons with a given frequency decreases with increasing temperature, whereas in amorphous solids an explicit temperature dependence of τ is not required. For these two reasons, i.e., the absence of tunneling states and absence of a plateau region at intermediate temperatures, it is definetely misleading to characterize the quasilattice thermal conductivity κ_{ph} of quasicrystals as ''glasslike.''

In what follows we discuss in more detail and quantitatively the parameters that follow from the measured temperature dependence of κ_{ph} in this quasicrystalline material.

IV. DISCUSSION

A. The temperature independent mean free path τ_{Cas}

At the lowest temperatures reached in our experiment, κ_{ph} varies approximately as T^3, as may be seen in Fig. 4. This trend suggests that the mechanism which limits the phonon mean free path at the lowest temperatures is temperature- and frequency-independent. The fit to our data using a term $\tau_{Cas}^{-1} = v_{ph}/l_{Cas}$ with l_{Cas} as a free parameter and v_{ph} fixed to the value given above, leads to a mean free path $l_{Cas} = (9.8 \pm 0.7) \times 10^{-4}$ m, which is of the same order of magnitude as the lateral dimensions of our specimen. The size-limited thermal conductivity of solids due to nonspecular scattering of phonons at the sample surface, known as the Casimir limit, is well documented for periodic crystals,[31] but is usually not observed in amorphous substances. It has been argued that the absence of a temperature- and frequency-independent phonon mean free path in glassy materials is due to the fact that the defects responsible for diffusive scattering of phonons at the surfaces of periodic crystals are not present in amorphous solids.[32] Attempts to roughen or damage the flat surfaces of glassy materials did not suppress specular surface-reflection of phonons, which is a process which leaves the flow of heat unaltered.[32] It is still not known whether the necessary kind of defects exists at surfaces of quasicrystals. Previous low-temperature measurements of the thermal conductivity on *i*-Al-Mn-Pd[26] seemed to suggest that the scattering of phonons on microholes or on grain boundaries were responsible for the appearance of a rather long temperature-independent mean free path $l = 2.5 \times 10^{-4}$ m.

According to Zaitlin *et al.*,[32] $l = \alpha(4A/\pi)^{1/2}$ is a good approximation for the boundary limited phonon mean free path for samples with a square cross section A. Taking into account the finite sample length by introducing the factor $\alpha = 0.6$, as derived by Berman *et al.*,[31] we calculate $l = 5.2 \times 10^{-4}$ m for our sample, which is shorter than the temperature independent mean free path imposed by the size of the sample. This can be explained by using arguments given in Ref. 31, stating that only about half of the phonons undergo diffusive boundary reflection. Thus our measurements seem to provide evidence that also in quasicrystals, as in periodic structures, phonons are thermalized so that upon leaving the surface they are, at least partly, independent of the incident phonons in energy as well as in the direction of propagation.

B. Scattering of phonons on defects

In order to reproduce our thermal conductivity data, we had to assume a term $\tau_{sf}^{-1} \propto \omega^2$ in the total phonon scattering rate τ^{-1} given in Eq. (8). According to Klemens,[33] such a frequency dependence of the scattering rate can be ascribed to the presence of stacking faults. By following this approach, the effective value of τ_{sf}^{-1} is

$$\tau_{sf}^{-1} = 0.7 \frac{a^2}{v_{ph}} \gamma^2 \omega^2 N_s, \tag{10}$$

where a is an averaged lattice constant, v_{ph} is the phonon velocity, γ is the Grüneisen-constant and N_s is the number of stacking faults crossing a line of unit length.

The measured thermal expansion of *i*-Al-Mn-Pd does not differ more than 50% from the thermal expansion of the isolated elements,[34] and the low temperature limit of the Grüneisen parameter has been calculated to be $\gamma = 1.14$–1.32 for Mg and $\gamma = 2.15$–2.24 for Zn.[35] By averaging these values for Mg and Zn, using the formula ratio as a weighing factor, we get $\gamma = 1.8$ for $Y_{8.6}Mg_{34.6}Zn_{56.8}$. Therefore, taking $A = 2.9 \times 10^{-16}$ sec from the fit shown in Fig. 3 and using the value $a = 2.96$ Å from Ref. 3, we get $N_s = (5.1 \pm 0.1) \times 10^6$ m^{-1} for the linear stacking fault-density on $Y_{8.6}Mg_{34.6}Zn_{56.8}$. This value has simply to be understood as a rough estimate of the stacking fault density. Nevertheless, the calculated N_s is comparable with those reported for Al-Mn-Pd ($N_s \sim 1.5 \times 10^7$ m^{-1}), Al-Cu-Fe ($N_s \sim 6.3 \times 10^6$ m^{-1}), and Al-Ni-Co ($N_s = 2.4 \times 10^7$ m^{-1}).[36,37] An analysis of our sample using scanning and transmission electron microscopy is in progress for confirming the presence of such stacking faults in $Y_{8.6}Mg_{34.6}Zn_{56.8}$. It is not clear whether either phason walls or similar sheetlike defects can manifest themselves in the same manner as stacking faults would.

C. Generalized Umklapp processes

The concept of generalized Umklapp processes in quasiperiodic structures has been introduced by Kalugin *et al.*[19] It

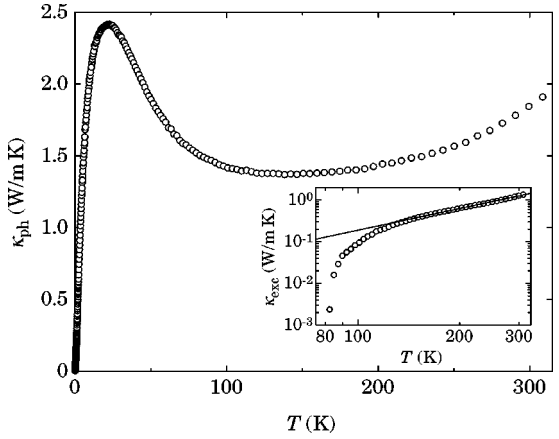

FIG. 5. The phonon contribution κ_{ph} to the thermal conductivity of icosahedral $Y_{8.6}Mg_{34.6}Zn_{56.8}$ as a function of temperature between 0.1 and 300 K on linear scales. The inset shows the additional contribution to the thermal conductivity κ_{exc} above 70 K, as explained in the text.

has been argued that these processes lead to a power-law dependence of the mean free path of delocalized quasilattice excitations on temperature as opposed to the exponential temperature dependence of the phonon mean free path due to conventional Umklapp processes in periodic structures. Under the assumption that three-phonon processes are not prohibited by the conservation laws, it has been shown that $\tau_U^{-1} \propto \omega^2 T^4$ is expected for Umklapp processes in quasicrystals, which leads to a power-law dependence of the thermal conductivity $\kappa_{ph} \propto T^{-3}$.

The observation of the regime where the proportion of phonon-phonon interactions leading to U-processes ''freeze out'' is not trivial, even in periodic structures. Defects inevitably suppress the maximum which ought to appear in the crossover regime between the Casimir limit of boundary scattering leading to $\kappa_{ph} \propto T^3$ and the region of increasing importance of Umklapp processes which is supposed to lead approximately to $\kappa_{ph} \propto T^{-3}$. In comparison with $\kappa_{ph}(T)$ of an ideal, defect-free sample, the defect scattering mechanism presented in the previous section may also result in an overall shift of this maximum towards higher temperatures, eventually masking the manifestation of the theoretical low temperature dependence of τ_U^{-1}.

A decrease of the thermal conductivity with increasing temperature, compatible with a power-law decrease of the phonon mean free path, is observed in our experiment between 23 and 140 K. As can be seen in Fig. 5, $Y_{8.6}Mg_{34.6}Zn_{56.8}$ exhibits a very pronounced peak in the temperature dependence of the thermal conductivity κ_{ph}, at least when compared to analogous data on other quasicrystalline samples. For instance, the region with a negative slope $d\kappa_{ph}/dT$ is more extended in temperature than for any quasicrystalline system investigated so far. Also, the ratio $\kappa_{ph}^{max}/\kappa_{ph}^{min}$ between the values of the thermal conductivity maximum and the subsequent minimum at higher temperatures is 50% larger for $Y_{8.6}Mg_{34.6}Zn_{56.8}$ than reported for *i*-Al-Mn-Pd in Ref. 26.

The best fit to our data was achieved using a term $\tau_U^{-1} \propto \omega^3 T$, which leads to an approximate temperature dependence of the thermal conductivity $\kappa_{ph} \propto T^{-1}$ instead of T^{-3}. Since we do not take into account any dispersion in the phonon spectrum, the exponent in the frequency dependence of the given scattering rate τ_U^{-1} may actually be lower than three. A decrease of $\kappa_{ph} \propto T^{-1}$ with increasing temperature is usually obeyed in periodic systems at temperatures *above* Θ_D where the thermal resistivity is determined by three-phonon processes and the temperature variation of the thermal conductivity depends only on the variation in the population of the modes and not on the increasing ratio of the phonons undergoing structural scattering. We would like to mention here that the appearance of a gap in the phonon spectrum of *i*-Y-Mg-Zn at frequencies lower than the Debye frequency ω_D could lead to a T^{-1}-temperature dependence of the thermal conductivity at temperatures *below* the Debye temperature. Actually, an infinite number of gaps, opening in the dispersion curves of *i*-Y-Mg-Zn at any energy less than the Debye energy, is expected due to the quasicrystallinity of the sample.[19] The widths of these gaps are of no concern in the long-wavelength limit, as the spectrum appears as continuous.

Major gaps defining pseudo-Brillouin zone boundaries may be located by introducing quasiperiodicity as a weak perturbation.[21] The acoustic branches are expected to flatten out when crossing such a boundary. The calculated dispersion relations for *i*-Al-Mg-Zn meet with zero slope at wave vectors $q_{max} \sim 0.5$ Å^{-1}.[25] This has been identified as the crossing to a quasi-Brillouin-zone boundary where a gap opening could be expected. Phonons with wave vectors $q \sim q_{max}/2$ can thermally be excited at temperatures $T \sim 30$ K, i.e., just above the peak in the quasilattice thermal conductivity of $Y_{8.6}Mg_{34.6}Zn_{56.8}$. This means that if in *i*-Y-Mg-Zn a gap is situated at wave vectors $q_{max} \sim 0.5$ Å^{-1}, the U processes would ''freeze out'' at temperatures where the characteristic temperature behavior is masked by the defect scattering mechanism presented above. Nevertheless, we emphasize that, to the best of our knowledge, no gaps in the dispersion relation of quasicrystals have as yet been detected within the limits of instrumental resolution.[21]

D. Thermal conduction above 70 K

The increase of the quasilattice contribution to the thermal conductivity with T at high temperatures seems to be a general feature of quasicrystals.[26,38] It has been argued that above temperatures of the order of 100 K, quasilattice vibrational modes responsible for heat transport cannot be described as propagating collective excitations.[38] A localization of the high-frequency vibrational modes in Al-Mn-Pd quasicrystals has previously been claimed by de Boissieu *et al.*[21] by analyzing the results of inelastic neutron scattering experiments. In their data, a broadening of the acoustic modes occurs for wave vectors of about $q = 0.5$ Å^{-1}, corresponding to a wavelength of the order of 10 Å. Since this is the size of the Mackay icosahedra and of the intercluster bond length, it has been pointed out that the hierarchical and quasiperiodic tiling of these clusters might be at the origin of the localization of the phonons.[21]

In order to understand the deviation of the quasilattice contribution to the thermal conductivity from our low-

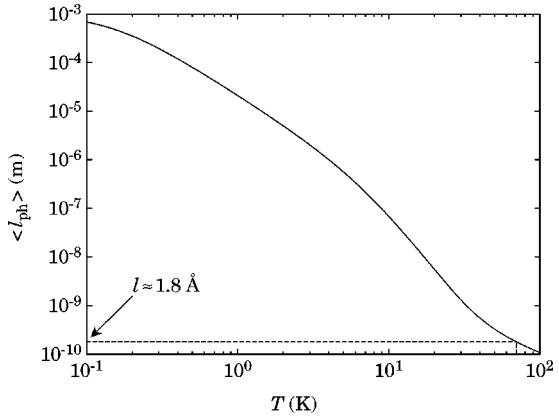

FIG. 6. The averaged phonon mean free path as a function of temperature calculated as explained in the text. The phonon scattering length corresponding to the quasilattice contribution to the thermal conductivity at 70 K is of the order of 2 Å .

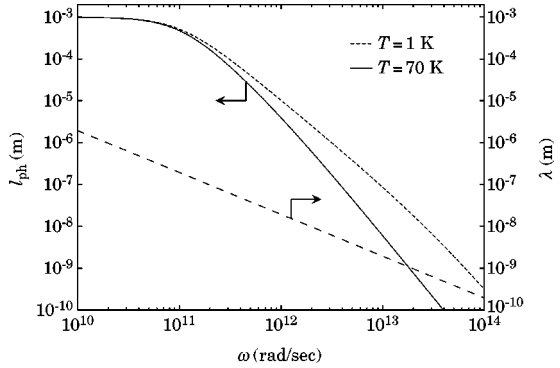

FIG. 7. The frequency dependence of the phonon mean free path at $T=1$ and 70 K and of the phonon wavelength λ (dash-dotted line) assuming a constant phonon velocity.

temperature fit above approximately 70 K, we have tried to relate κ_{ph} at 70 K to a characteristic phonon scattering length $\langle l_{ph}\rangle$, defined so that

$$\kappa_{ph}(T)=\frac{1}{3}C_v v_{ph}\langle l_{ph}\rangle(T). \tag{11}$$

The scattering length $l_{ph}(\omega,T)=v_{ph}\tau(\omega,T)$ is, as implied by Eq. (8), a function of temperature *and* frequency, and therefore needs to be averaged over the frequency spectrum with an appropriate weighing function. The proper way to calculate $\langle l_{ph}\rangle$, such that Eq. (11) is fulfilled, is mentioned in Ref. 39, and

$$\langle l_{ph}(T)\rangle^{-1}=C_v^{-1}(T)\int\frac{C_v(\omega,T)}{l_{ph}(\omega,T)}d\omega. \tag{12}$$

The resulting function has been plotted in Fig. 6. As may be inferred from this diagram, the averaged phonon mean free path at 70 K, i.e., the temperature at which the experimental κ_{ph} starts to deviate from the calculated one, is close to 2 Å . This has to be compared with the results of a powder x-ray diffraction study of the Zn-Mg-Ho icosahedral phase, where atomic clusters which have been interpreted as extended Bergman clusters could be identified with shell-radii varying from 2.6 to 8.8 Å .[40]

In Fig. 7, we show the calculated phonon mean free path l_{ph} as a function of frequency for the temperatures $T=1$ and 70 K together with the phonon wavelength $\lambda=2\pi/k$, calculated by assuming a constant phonon velocity v_{ph}. At frequencies of the order of $\omega\sim 2\times 10^{13}$ rad/sec, the phonon mean free path at 70 K becomes smaller than the phonon wavelength λ and is of the order of 10 Å . A maximum in the density of states as given in Eq. (7) occurs at frequencies $\omega\sim 2\times 10^{13}$ rad/sec for temperatures around 90 K. The equality of l_{ph} and λ suggests that high frequency phonons at 70 K are localized and that this localization is related to some characteristic structural correlation length of the order of a few Å . It is not possible to exactly determine this characteristic length, since the calculation of it is based on the Debye model which is not expected to be valid at those temperatures, as discussed above.

In attempts to explain the thermal conductivity of systems where the high-frequency vibrational states are localized, several models have been proposed. In the following, we will compare our data with different theoretical predictions of κ_{ph}.

The concept of hierarchically variable-range hopping between localized states in quasicrystals was introduced by Janot.[41] In order to explain the increase of κ_{ph} at high temperatures, an interaction between high-energy localized modes and low-energy extended phonons is assumed. This interaction induces the hopping of localized states between equivalent sites of the structure. Since the quasicrystalline structure in this model is described as a hierarchically packed ensemble of pseudo-Mackay icosahedra,[41] the possible hopping distances corresponding to the distances between the equivalent sites of the structure are expected to scale with the cube of the golden mean τ. In this picture, a thermal conductivity $\kappa_{ph}\propto T^{\alpha-1}$ is expected, where α describes the damping of thermal propagation and depends on the hierarchical structure of the quasicrystal. Assuming for $Y_{8.6}Mg_{34.6}Zn_{56.8}$ a similar hierarchical structure as for *i*-Al-Mn-Pd where $\alpha=2.5$,[41] we would expect $\kappa_{ph}\propto T^{1.5}$.

The excess high temperature contribution to the thermal conductivity of $Y_{8.6}Mg_{34.6}Zn_{56.8}$, which cannot be described in the Debye approximation, can be expressed as $\kappa_{exc}=\kappa_{ph}-\kappa_{ph}^{fit}$. In the inset of Fig. 5, we have plotted κ_{exc} versus T on logarithmic scales. As may be seen, above 140 K κ_{exc} is nicely approximated by a power-law $\kappa_{exc}\sim T^n$ with $n=1.7$ which in the inset, is represented by the solid line. This value is close to the exponent $n=1.5$ which has been predicted for the hierarchical phonon hopping mechanism, provoked by the hierarchical structural characteristics of quasicrystals.

The temperature variation of $\kappa_{ph}\sim T^n$ with $n\geqslant 1.5$ ought to be compared with $\kappa_{ph}\sim T$, often observed in amorphous solids far above the κ-plateau, typical for this type of materials. This difference is again an indication that quasicrystals should not simply be regarded as another species of disordered solids.

Quite generally, the increase of the thermal conductivity of solids at elevated temperatures has, in some cases, successfully been described by using a model originally proposed by Einstein,[42] who assumed a mechanism of heat transport due to a random exchange of thermal energy between neigboring atoms vibrating with random phases. Cahill and Pohl[43] modified Einstein's result by dividing the

sample into regions of size $\lambda/2$, whose frequencies of oscillation are given by the low-frequency speed of sound $\omega = 2\pi v/\lambda$. This modification leads to a minimum thermal conductivity $\kappa_{\min}$

$$\kappa_{\min} = \left(\frac{3n}{4\pi}\right)^{1/3} \frac{k_B^2 T^2}{\hbar \Theta_D} \int_0^{\Theta_D/T} \frac{x^3 e^x}{(e^x - 1)^2} dx, \qquad (13)$$

where n is the number of atoms per unit volume. We have plotted $\kappa_{\min}$ as a dotted line in Fig. 3, using the value $\Theta_D = 348$ K from Ref. 13. Although previous measurements of the thermal conductivity of quasicrystals at high temperatures[18,38] were close to the prediction of Einstein's model, the minimum thermal conductivity model predicts $\kappa_{\min} = 0.71$ W/m K at 300 K for $Y_{8.6}Mg_{34.6}Zn_{56.8}$ which is distinctly less than the observed $\kappa_{ph} = 1.9$ W/m K.

V. SUMMARY AND CONCLUSION

Measurements of the thermal transport of *i*-$Y_{8.6}Mg_{34.6}Zn_{56.8}$ between 0.1 and 300 K have been reported and analyzed. The thermal conductivity data have been discussed on the basis of the Debye approximation in the temperature region below 70 K. At the lowest temperatures reached in our experiment, the phonon mean free path is close to the smallest lateral dimension of our sample. No evidence for a scattering of phonons by tunneling states has been observed. These latter two facts and the rather large absolute value of κ_{ph} at its maximum, at least in comparison with previously reported results of $\kappa(T)$ of quasicrystals, indicate a fairly high structural perfection of our sample. A term proportional to ω^2 in the phonon scattering rate had to be introduced for the description of our data at intermediate temperatures. This is usually ascribed to the presence of stacking faults. Evidence for the effect of generalized Umklapp-processes has been found between approximately 23 and 140 K. Above these temperatures, vibrational modes responsible for the heat transport cannot be described as propagating excitations. Einstein's model which considers the energy transfer between localized modes via a strong-coupling mechanism cannot successfully explain the measured high temperature thermal conductivity. Our data at high temperatures are, however, compatible with a variable-range hopping mechanism based on a hierarchical structural model of quasicrystals.

Taken altogether, our results provide strong evidence that the lattice properties of quasicrystals are indeed different from those of glassy materials. The very long mean free path, limited by the sample size, of itinerant lattice excitations at low temperatures, the lacking evidence for scattering at two level centers, the typical features of structural scattering in quasiperiodic lattices and the characteristics of the increase of the lattice conductivity at high temperatures, all point in this direction. The trends for this behavior were recognized and discussed in earlier work,[18,26,38] but it is, most likely, the high structural perfection of the specimen investigated in this work, which allows for a much more obvious identification of these features.

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[1] D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).
[2] Z. Luo, S. Zhang, Y. Tang, and D. Zhao, Scr. Metall. Mater. **28**, 1513 (1993).
[3] A. P. Tsai, A. Niikura, A. Inoue, T. Masumoto, Y. Nishida, K. Tsuda, and M. Tanaka, Philos. Mag. Lett. **70**, 169 (1994).
[4] A. Niikura, A. P. Tsai, A. Inoue, and T. Masumoto, Jpn. J. Appl. Phys., Part 2 **33**, L1538 (1994).
[5] Z. Islam, I. R. Fisher, J. Zarestky, P. C. Canfield, C. Stassis, and A. I. Goldman, Phys. Rev. B **57**, R11047 (1998).
[6] T. J. Sato, H. Takakura, A. P. Tsai, and K. Shibata, Phys. Rev. Lett. **81**, 2364 (1998).
[7] B. Charrier, B. Ouladdiaf, and D. Schmitt, Phys. Rev. Lett. **78**, 4637 (1997).
[8] I. R. Fisher, K. O. Cheon, A. F. Panchula, P. C. Canfield, M. Chernikov, H. R. Ott, and K. Dennis, Phys. Rev. B **59**, 308 (1999).
[9] R. Kondo, T. Hashimoto, K. Edagawa, S. Takeuchi, T. Takeuchi, and U. Mizutani, J. Phys. Soc. Jpn. **66**, 1097 (1997).
[10] Z. M. Stadnik, D. Purdie, M. Garnier, Y. Baer, A. P. Tsai, A. Inoue, K. Edagawa, S. Takeuchi, and K. H. J. Buschow, Phys. Rev. B **55**, 10 938 (1997).
[11] Y. Hattori, K. Fukamichi, K. Suzuki, A. Niikura, A. P. Tsai, A. Inoue, and T. Masumoto, J. Phys.: Condens. Matter **7**, 4183 (1995).
[12] A. Langsdorf, W. Assmus, G. J. Babonas, and A. Reza, Lith. Phys. J. **37**, 40 (1997).
[13] M. A. Chernikov, S. Paschen, E. Felder, P. Vorburger, B. Ruzicka, L. Degiorgi, H. R. Ott, I. R. Fisher, and P. C. Canfield (unpublished).
[14] I. R. Fisher, Z. Islam, A. F. Panchula, K. O. Cheon, M. J. Kramer, P. C. Canfield, and A. I. Goldman, Philos. Mag. B **77**, 1601 (1998).
[15] A. Langsdorf and W. Assmus, Cryst. Res. Technol. **34**, 261 (1999).
[16] A. Langsdorf, F. Ritter, and W. Assmus, Philos. Mag. Lett. **75**, 381 (1997).
[17] H. Bougrine and M. Ausloos, Rev. Sci. Instrum. **66**, 199 (1995).
[18] M. A. Chernikov, A. Bianchi, E. Felder, U. Gubler, and H. R. Ott, Europhys. Lett. **35**, 431 (1996).
[19] P. A. Kalugin, M. A. Chernikov, A. Bianchi, and H. R. Ott, Phys. Rev. B **53**, 14 145 (1996).
[20] A. Yu. Kitaev, Pis'ma Zh. Éksp. Teor. Fiz. **48**(5), 270 (1988) [JETP Lett. **48**, 298 (1998)].
[21] M. de Boissieu, M. Boudard, R. Bellisent, M. Quilichini, B. Hennion, R. Currat, A. I. Goldman, and C. Janot, J. Phys.: Condens. Matter **5**, 4945 (1993).

[22] M. Quilichini and T. Janssen, Rev. Mod. Phys. **69**, 277 (1997).
[23] J. A. Ashraff and R. B. Stinchcombe, Phys. Rev. B **39**, 2670 (1989).
[24] J. P. Lu, T. Odagaki, and J. L. Birman, Phys. Rev. B **33**, 4809 (1986).
[25] J. Hafner and M. Krajčí, Europhys. Lett. **21**, 31 (1993).
[26] M. A. Chernikov, A. Bianchi, and H. R. Ott, Phys. Rev. B **51**, 153 (1995).
[27] N. Vernier, G. Bellessa, B. Perrin, A. Zarembowitch, and M. de Boissieu, Europhys. Lett. **22**, 187 (1993).
[28] P. W. Anderson, B. I. Halperlin, and C. M. Varma, Philos. Mag. **25**, 1 (1972).
[29] W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).
[30] M. P. Zaitlin and A. C. Anderson, Phys. Rev. B **12**, 4475 (1975).
[31] R. Berman, E. L. Foster, and J. M. Ziman, Proc. R. Soc. London, Ser. A **231**, 130 (1955).
[32] M. P. Zaitlin, L. M. Scherr, and A. C. Anderson, Phys. Rev. B **12**, 4487 (1975).
[33] P. G. Klemens, in *Solid State Physics: Advances in Research and Applications*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 7.
[34] A. P. Tsai, H. Suenaga, M. Ohmori, Y. Yokoyama, A. Inoue, and T. Masumoto, Jpn. J. Appl. Phys., Part 1 **31**, 2530 (1992).
[35] K. A. Gschneidner, in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1971), Vol. 16.
[36] S. Legault, B. Ellmann, J. Ström-Olsen, L. Taillefer, T. Lograsso, and D. Delaney, in *Quasicrystals. Proceedings of the 6th International Conference, Tokyo, Japan, 1997*, edited by S. Takeuchi and T. Fujiwara (World Scientific, Singapore, 1998).
[37] M. Matsukawa, M. Yoshizawa, K. Noto, Y. Yokoyama, and A. Inoue, Physica B **263-264**, 146 (1999).
[38] M. A. Chernikov, A. Bianchi, H. Müller, and H. R. Ott, in *Quasicrystals. Proceedings of the 5th International Conference, Avignon, France, 1995*, edited by C. Janot and R. Mosseri (World Scientific, Singapore, 1996).
[39] R. D. Barnard, *Thermoelectricity in Metals and Alloys* (Taylor & Francis Ltd., London, 1972), p. 123.
[40] T. Ohno and T. Ishimasa, in *Quasicrystals. Proceedings of the 6th International Conference, Tokyo, Japan, 1997*, edited by S. Takeuchi and T. Fujiwara (World Scientific, Singapore, 1998).
[41] C. Janot, Phys. Rev. B **53**, 181 (1996).
[42] A. Einstein, Ann. Phys. (Leipzig) **35**, 679 (1911).
[43] D. G. Cahill and R. O. Pohl, Solid State Commun. **70**, 927 (1989).