Kondo-like phonon scattering in thermoelectric clathrates

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Crystalline solids are generally known as excellent heat conductors, amorphous materials or glasses as thermal insulators. It has thus come as a surprise that certain crystal structures defy this paradigm. A prominent example are type-I clathrates and other materials with guest-host structures. They sustain low-energy Einstein-like modes in their phonon spectra, but are also prone to various types of disorder and phonon-electron scattering and thus the mechanism responsible for their ultralow thermal conductivities has remained elusive. While recent \textit{ab initio} lattice dynamics simulations show that the Einstein-like modes enhance phonon-phonon Umklapp scattering, they reproduce experimental data only at low temperatures. Here we show that a new effect, an "all phononic Kondo effect", can resolve this discrepancy. This is evidenced by our thermodynamic and transport measurements on various clathrate single crystal series and their comparison with \textit{ab initio} simulations. Our new understanding devises design strategies to further suppress the thermal conductivity of clathrates and other related materials classes, with relevance for the field of thermoelectric waste heat recovery but also more generally for phononic applications. More fundamentally, it may trigger theoretical work on strong correlation effects in phonon systems.
INTRODUCTION

The increasing worldwide energy consumption and the associated climate change call for enhancing the overall energy efficiency of technological energy conversion processes. Thermoelectrics\textsuperscript{1–6} can convert waste heat into electricity and could thus contribute to such an efficiency increase. The perfect thermoelectric material combines low phonon thermal conductivity with high electrical conductivity and high thermopower. Materials classes with cage-like structures such as the clathrates\textsuperscript{7,8} or skutterudites\textsuperscript{4,9} show surprisingly low phonon thermal conductivities $\kappa_{\text{ph}}$, even in perfect single crystals. Type-I clathrates $\text{G}_8\text{H}_{46}$, that show promising thermoelectric figures of merit\textsuperscript{5,10,11}, consist of host atoms (H) that encapsulate guest atoms (G) in a framework of oversized cages (Fig. 1a). Recent inelastic neutron and X-ray scattering studies uncovered energetically low-lying optical phonon modes which were attributed to a “rattling” motion of the guest atoms in the cages and are thus referred to as Einstein modes\textsuperscript{12,13,17}. Similar observations were also made for skutterudites\textsuperscript{9} and clathrate hydrates\textsuperscript{18}. A severe flattening of the acoustic phonon branches at energies near the optical modes was observed\textsuperscript{12,13,17}, and attributed to a finite coupling between the guest atoms and the host cages. Early thermal conductivity studies on type-I clathrates\textsuperscript{19,20}, inspired by investigations on glasses\textsuperscript{21}, tried to capture this guest-host coupling by including terms for resonance scattering, originally proposed to describe the resonance interaction between phonons and non-paramagnetic defects\textsuperscript{22}, and for scattering from tunneling states\textsuperscript{21} into phenomenological treatments\textsuperscript{23}. Whereas empirical multi-parameter fits including these terms can indeed model thermal conductivity data of several type-I clathrates below about 50 K (Refs. 19,20), inconsistencies with other results have been pointed out more recently. Notably, such modelling can neither explain the exceptionally long phonon lifetimes\textsuperscript{17,24} nor the large thermal conductivity differences between structurally very similar n- and p-type versions of these materials\textsuperscript{25}. The recent achievement of \textit{ab initio} calculations of the thermal conductivity of a type-I clathrate, based on intrinsic phonon-phonon Umklapp scattering processes\textsuperscript{15}, represents a major step forward. It showed that, unlike in the resonance scattering picture, the phonon lifetimes are reduced in a wide frequency range. Nevertheless, these calculations can explain experimental thermal conductivity data only below about 50 K. Here, we propose a new mechanism, the “all phononic Kondo effect”, that extends the agreement all the way up to room temperature. As we will show, the pronounced difference in temperature dependence is due to the disentanglement of Kondo-coupled acoustic
and rattling phonon modes above the phonon Kondo temperature.

In general terms, the Kondo effect describes non-commutative scattering of an extended wave from a localized entity with internal degree of freedom. It has been studied in many different settings, including magnetic, orbital, charge, and local vibrational degrees of freedom (see Supplementary Material S8 for more details). However, to the best of our knowledge, it has never been studied in an all phononic context.

To demonstrate this new effect, we had to go beyond the state-of-the-art in thermoelectric clathrates’ research in several respects. Firstly, to overcome the bottleneck of large uncertainties and systematic errors of standard thermal conductivity measurements at elevated temperatures, we developed a high-precision implementation (Fig. 2a and Materials and Methods) of the 3ω technique\textsuperscript{26}. A second key ingredient for our work are sample series of single crystals, which allow us to pin down the dominating \textit{intrinsic} phonon scattering mechanisms by employing an empirical model\textsuperscript{23}, modified to be in line with the most recent findings\textsuperscript{15,24} on the phonon band structure and phonon dynamics in type-I clathrates. Thirdly, we compare both the thermal conductivity data and thermodynamic data to \textit{ab initio} lattice dynamics calculations, thereby providing compelling evidence for the phonon Kondo effect.

RESULTS

We start by giving an overview of the phonon thermal conductivities $\kappa_{\text{ph}}$ of all type-I clathrate single crystals studied here (Fig. 2b). Although type-I clathrates are often referred to as model systems for the enigmatic phonon-glass electron-crystal concept\textsuperscript{1}, the most prominent feature of $\kappa_{\text{ph}}(T)$ is a large crystal-like maximum. It is narrow and occurs at a surprisingly low temperature of only about 10 K. As will be further detailed below, this narrow low-temperature maximum is a strong indication for the phonon transport not being controlled by the natural energy scale $k_B\Theta_D$ of the Debye temperature $\Theta_D$ but by a much smaller energy scale $k_B\Theta_E$.

To visualize the effect of a reduced Debye temperature we use a simple phenomenological lattice thermal conductivity model: A modified version of the standard Callaway model\textsuperscript{23} where we replaced the Debye temperature $\Theta_D$ by a variable temperature $\Theta_E$ (Supplementary Material S1). The left panel of Fig. 1d shows temperature dependencies of normalized phonon thermal conductivities calculated within this model for a series of different char-
acteristic energies $k_B \Theta_E$, keeping fixed scattering rates $\tau_D^{-1}$ for defect scattering, $\tau_B^{-1}$ for boundary scattering, and $\tau_{ph-el}^{-1}$ for phonon-electron scattering. Resonance scattering is of minor importance here (Supplementary Fig. 4). With decreasing $\Theta_E$ the broad maximum sharpens and is shifted to lower temperatures. This is attributed to a strongly enhanced Umklapp scattering rate $\tau_U^{-1}$ (Supplementary Material S1) that results from successively limiting the energy range of the contributing acoustic phonons as $\Theta_E$ decreases.

This effect can be directly observed by experiments. The right panel of Fig. 1d compares the phonon thermal conductivities of a Ge-based type-I clathrate single crystal (BCGG1.0, see Supplementary Table 1) and single crystalline Ge, irradiated$^{27}$ to a similar defect concentration. Both materials have similar Debye temperatures (Supplementary Material S2), but in the clathrate the low-lying Einstein temperature dominates the behaviour.

Next we prove, with two clathrate single crystal series, that the strong Umklapp scattering due to the new low-energy scale indeed dominates the lattice thermal conductivity in a wide temperature range. In the first such series, $\text{Ba}_8\text{Cu}_{4.8}\text{Ge}_{41.2-x-y} \square_y \text{Ga}_x$ ($x = 0, 0.2, 0.5, 1.0$, see BCGG$x$ in Supplementary Table 1), an increasing Ga content $x$ is accompanied by a decreasing content $y$ of host atom vacancies $\square$. This is supported by the increase of the lattice parameter $a$ (Fig. 3a) and the Hall mobility $\mu_H = R_H/\rho = 1/(ne\rho)$ (Fig. 3c) with $x$, as well as by the charge neutrality of this substitution (both the electronic $\gamma$ term of the specific heat and the charge carrier concentration $n$ are essentially independent of $x$, see Fig. 3b, c bottom), as discussed in the Supplementary Material S3. Because the mass difference between Ga and Ge is very small, Ga represents a much weaker scattering potential$^{32}$ in $\text{Ba}_8\text{Cu}_{4.8}\text{Ge}_{41.2-x-y} \square_y \text{Ga}_x$ than a vacancy. Thus, we expect a decrease of defect scattering with $x$. The low-temperature phonon thermal conductivity $\kappa_{ph}(T)$ of all samples in this series shows a maximum at low temperatures that is systematically enhanced at nearly constant temperature with increasing $x$ (Fig. 3d left). This trend is indeed well reproduced by a decrease of the point-defect scattering rate $\tau_D^{-1}$ with $x$, as seen by the good agreement of simulation and data for this case (full and dashed lines in Fig. 3d left). A much less satisfying agreement is observed if the boundary scattering rate $\tau_B^{-1}$ is allowed to change with $x$ instead (Fig. 3d right). The phonon-electron scattering rate $\tau_{ph-el}^{-1}$ can be assumed to be $x$ independent because of the above discussed charge neutrality. Above about 50 K, however, the $\kappa_{ph}(T)$ data for different $x$ merge (Fig. 3d left), indicating that scattering from point defects has become negligible. This can be rationalized by comparing
the (Debye) phonon wavelength $\lambda = \frac{2\pi v_s}{\omega}$, where $v_s$ is the sound velocity (Fig. 1c right), with the size of the scattering center. A vacancy with the distortion surrounding it was estimated to have a diameter $d \approx 5 \text{Å}$ (Ref. 33). Strong point-defect scattering of Rayleigh type, with an $\omega^4$ dependence, occurs only if $\lambda$ is at least an order of magnitude larger than $d$, corresponding to phonon energies $\hbar \omega$ of 2.5 meV (30 K) and below. At much larger energies (and temperatures), defect scattering should be weak and frequency independent.

The second sample series is the prototypal clathrate $\text{Ba}_8\text{Ga}_{16-x}\text{Ge}_{30+x}$ that has been much investigated in the past. It is an ideal system to study the importance of phonon-electron scattering because it has a low and essentially constant amount of point defects (as seen above and shown in Ref. 32, Ga does not act as strong point defect in Ge clathrates) but a charge carrier concentration that varies strongly with $x$ (Ref. 35). Indeed, different $\text{Ba}_8\text{Ga}_{16-x}\text{Ge}_{30+x}$ single crystals reported in the literature show severely different $\kappa_{\text{ph}}(T)$ at low temperatures. Figure 3e replots two extreme cases. The red line is our low-temperature fit ($T < \Theta_E/2$) with the modified Callaway model (Supplementary Eqn. 1) to the data of Ref. 30. It takes Umklapp scattering ($\tau_U^{-1}$), defect scattering ($\tau_D^{-1}$), boundary scattering ($\tau_B^{-1}$), and phonon-electron scattering ($\tau_{\text{ph-el}}^{-1}$) into account. The latter is calculated from the reported materials properties using Supplementary Eqn. 8. Interestingly, the $\kappa_{\text{ph}}(T)$ data of a different $\text{Ba}_8\text{Ga}_{16-x}\text{Ge}_{30+x}$ single crystal can be very well reproduced by strongly increasing $\tau_{\text{ph-el}}^{-1}$ and by only slightly adjusting $\tau_U^{-1}$ (dashed line in Fig. 3e). Above about 50 K, the differences in $\kappa_{\text{ph}}$ caused by a different $\tau_{\text{ph-el}}^{-1}$ vanish. This observation is in line with the fact that phonon-electron scattering can only occur for phonons with a wave vector $q$ smaller than twice the Fermi wave vector $k_F$. For the crystal of Ref. 30 we estimate this to hold below about 140 K (Supplementary Material S2). At higher temperatures phonon-electron scattering is unlikely to be relevant.

A suppression of large low-temperature differences in $\kappa_{\text{ph}}(T)$ at higher temperatures has also been seen in other type-I clathrate single crystal series, but precise high-temperature data on these are not available to date.

Taking both our clathrate series together we have managed to rule out the influence of defect and phonon-electron scattering on $\kappa_{\text{ph}}(T)$ of various type-I clathrates above 50 K. In addition, boundary scattering cannot contribute significantly in single crystals at these temperatures. Thus, at elevated temperatures, $\kappa_{\text{ph}}$ is dominated by intrinsic phonon-phonon (Umklapp) scattering. This allows us to pin down its microscopic origin, as shown in what
follows.

Remarkably, a broad range of clathrates, including even a gas hydrate $^{18,38–40}$, shows a universal scaling of the room-temperature phonon thermal conductivity with the product of sound velocity and Einstein temperature of the lowest-lying rattling mode(s), $\kappa_{ph} \propto v_s \Theta_E$ (Fig. 4). The simple kinetic gas relation $\kappa_{ph} = c_s v_s^2 \tau/3$ predicts $\kappa_{ph}$ to depend on the square of the sound velocity. In the Debye model the sound velocity is proportional to the Debye temperature and thus $\kappa_{ph} \propto v_s^2 \propto \Theta_D^2$ is expected for simple Debye solids. The modified scaling $\kappa_{ph} \propto v_s \Theta_E \propto v_s^2 \cdot (\Theta_E/\Theta_D)$ shows that the above discussed energy renormalization is universal in clathrates.

A similar energy renormalization is seen in heavy fermion metals, where the (spin) Kondo effect rescales the Fermi temperature $T_F$ to the (spin) Kondo temperature $T_K$ (Refs. 42, 43). Figure 1c illustrates this analogy with schematic dispersion relations for electrons and phonons. In a band picture for heavy electron systems (left) a broad conduction band (blue) hybridizes with a flat, essentially non-dispersing $4f$ band of (renormalized) energy $\epsilon_{4f}$ (red). The hybridized bands (violet) are extremely flat near $\epsilon_{4f}$, corresponding to quasiparticles with strongly renormalized effective masses. In the phonon case the strongly dispersing acoustic phonon mode, approximated here by the linear dispersion of the Debye model, takes the role of the broad conduction band, and the flat Einstein-like rattling mode at $\hbar \omega_E = k_B \Theta_E$ corresponds to the narrow $4f$ band. The resulting hybridized band is again extremely flat in large portions of the Brillouin zone, giving rise to “heavy” phonons with extremely low group velocity $v_g$ at finite wave vectors. Even though the resulting $T = 0$ dispersion relation may look similar to the one obtained from \textit{ab initio} lattice dynamics simulations$^{15}$, there is an important difference: Being a strong correlation phenomenon, the phonon Kondo effect has a characteristic temperature dependence. Well above the Kondo temperature, the interacting states (violet) go over to the non-interacting ones (red and blue), an effect referred to as crossover from infrared slavery to asymptotic freedom$^{43}$, which is absent in the lattice dynamics simulations (see also Discussion).

The fact that the observed universal scaling of $\kappa_{ph}$ still contains $v_s$ (to linear power) is attributed to the absence of a Fermi level in phonon systems. Whereas the electrical resistivity in heavy fermion metals is dominated by the heavy electrons at the Fermi wavevector $k_F$, phonons of all wave vectors, including long-wavelength ones propagating with $v_s$, contribute to $\kappa_{ph}$. 

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Finally, we compare specific heat, thermal expansion, and thermal conductivity data for the prototypal clathrate Ba$_8$Ga$_{16}$Ge$_{30}$ with *ab initio* lattice dynamics calculations (see Materials and Methods) and reveal key characteristics of the Kondo effect. For the specific heat, the agreement between experiment and theory is excellent at low and high temperatures, but a distinct deviation is seen in between (Supplementary Fig. 1b). This difference gives rise to an “anomaly” near $\Theta_E$ (Fig. 1e). It releases an entropy of order $R \ln 2$ per rattling atom at the 6$d$ site. This is the behaviour expected for any Kondo effect involving a 2-fold degenerate localized entity: Its degeneracy is lifted by the Kondo interaction, giving rise to the above entropy release. The entropy reaches 0.4$\ln 2$ at 28 K. Twice this temperature is generally considered as good estimate of the Kondo temperature$^{44,45}$, which is thus very close to $\Theta_E$. The experimental thermal expansion is sizeably smaller than the theoretical prediction below 150 K, but agrees well with it above this temperature (Supplementary Fig. 2b). The difference between the theoretical and experimental curve closely resembles the specific heat anomaly (Fig. 1e). These discrepancies in specific heat and thermal expansion translate into a corresponding discrepancy in the Grüneisen parameter: *Ab initio* calculations predict an upturn at low temperatures, an effect usually associated with enhanced phonon anharmonicity at low frequencies, that is however absent in the experimental curve (Supplementary Fig. S2c). Finally, the experimental phonon thermal conductivity is well described by the *ab initio* calculations below 50 K, but severely overshoots them at higher temperatures (Supplementary Fig. 3b). The difference, plotted as inverse to represent a thermal resistivity (Fig. 1f), increases with decreasing temperature, with a slow (about $-\ln T$) dependence, the hallmark of incoherent Kondo scattering above $T_K$ in the original spin Kondo effect$^{42,43}$.

**DISCUSSION**

To understand these results it is important to assess the limitations of the used *ab initio* calculations (see Materials and Methods). The phonon density of states (DOS) and the specific heat are calculated in the harmonic approximation, the thermal expansion in the quasi-harmonic approximation, and the thermal conductivity from anharmonic interatomic force constants$^{15}$. The latter thus takes phonon-phonon interactions to lowest order into account. However, temperature dependencies resulting from strong phonon correlation effects, most notably the Kondo disentanglement of acoustic and rattling modes above the
phonon Kondo temperature, cannot be captured by these simulations. This is why the comparison of experimental data and such calculations can be used to extract the characteristic temperature dependencies due to the correlations (somewhat like non-\( f \) reference materials are used as background to reveal Kondo physics in heavy electron compounds – unfortunately, “empty” type-I clathrates without the rattling atoms, that would represent such background here, do not exist). Specifically, the temperature-dependent specific heat is overestimated by the calculations as, unlike in the Kondo effect, no entropy is released by Bose populating temperature-independent anticrossings (circles in Fig. 1e). The thermal expansion calculations do not contain the non-trivial temperature dependence of the anharmonicities due to the phonon Kondo interaction, which leaves a corresponding imprint in the thermal expansion difference (stars in Fig. 1e). Finally, the strong Umklapp scattering that is captured by the thermal conductivity calculations does not contain the weakening above \( T_K \) characteristic of an asymptotically free theory (Fig. 1f).

Further support, independent of any theoretical modeling, comes from recent inelastic neutron scattering experiments. They reveal unexpected changes of the optical dynamical structure factors as function of temperature\(^{24} \) that could be an indication of such a disentanglement of interacting acoustic and rattling modes at high temperatures. All these observations provide strong evidence for a new correlation effect – an all phononic Kondo effect – as microscopic origin of the peculiar thermodynamic and thermal transport behaviour of clathrates.

We do not want to conclude without proposing a possible microscopic realization of the phonon Kondo effect in clathrates. The rattling motion of the guest atoms at the crystallographic 6\( d \) site within a soft plane\(^{17,31,46} \) in the tetracaidecahedra (Fig. 1b) is known to have the lowest frequency\(^{15} \). Within this plane, due to the four-fold symmetry of the potential well, rattling occurs preferentially along two perpendicular soft directions\(^{16,25,47} \), that we refer to as “1” and “2”. The two corresponding rattling modes (\( e_1 \) and \( e_2 \) in Fig. 1b), which are degenerate in energy for symmetry reasons, are thus identified as the pseudospins of the Kondo model (they represent “spin up” and “spin down” in the spin Kondo effect). They can be approximated as simple Einstein oscillators, with the first excited state corresponding to the “Einstein temperature” \( \Theta_E \) observed in inelastic scattering experiments\(^{12,13,17} \). The two polarizations of the transverse acoustic phonons represent the corresponding degree of freedom of the itinerant species (\( e_{T1} \) and \( e_{T2} \) in Fig. 1b, thus repre-
senting the conduction electrons in the spin Kondo effect). The hybridization of the local (rattling) and extended (acoustic) phonon modes has been observed in inelastic neutron and X-ray scattering experiments\textsuperscript{12,13,17,18,38}. A spin flip process in the spin Kondo effect corresponds to a scattering process with polarization change in the phonon Kondo effect. It can be visualized as follows: Assume the guest atom rattles in mode $e_1$ and a propagating phonon of polarization $e_{T2}$ “hops” onto the cage, creating a distortion of the cage that resembles the effect of mode $e_2$. This additional cage distortion will facilitate a change of rattling direction from $e_1$ to $e_2$, and an accompanying change in polarization of the outgoing acoustic wave from $e_{T2}$ to $e_{T1}$. Such an interaction of two modes with “opposite” polarization is analogous to an antiferromagnetic exchange interaction in the spin Kondo effect. Further details as well as a suggestion for a mapping of these ingredients onto a Kondo-type Hamiltonian are given in the Supplementary Material S8.

Our discovery of Kondo physics in an all phononic system is not only of fundamental interest (see discussion of non-canonical Kondo physics in other settings in Supplementary Material S8), but also has practical implications. First, it gives a concise description of how to tailor “rattling materials” for thermoelectric applications at elevated temperatures, which are most relevant for waste heat-recovery applications: Materials with the lowest possible Einstein and thus phonon Kondo temperatures should be found. Microscopically, this might be achieved by changing the mass and size of the guest atoms, but also by structural disorder on the guest site\textsuperscript{48,49} and/or tailored guest-host charge transfer\textsuperscript{48}.

An equally striking consequence is that Cahill’s definition of the minimum thermal conductivity $\kappa_{\text{min}}^{\text{ph}}$ (Ref. 41), that is being referred to so extensively, needs to be reconsidered. With the energy renormalization also $\kappa_{\text{ph}}^{\text{min}}$ is drastically reduced (Supplementary Material S1). This implies that for the materials in Fig. 4 there is still room for further improvement as their phonon thermal conductivities all lie well above their respective new $\kappa_{\text{ph}}^{\text{min}}$ value (dashed red line in Fig. 4). Further lowering the $\kappa_{\text{ph}}$ of a given material could, for instance, be realized by nanostructuring or the introduction of dense dislocation arrays\textsuperscript{50}. Long-wavelength phonons that are only weakly affected by the phonon Kondo effect could, at high temperatures, be effectively scattered by nanostructures that are small compared to their mean free path. Indeed, a few clathrates and skutterudites appear to violate the original Cahill $\kappa_{\text{ph}}^{\text{min}}$ limit, though this has not been explicitly recognized in these works (Supplementary Material S2). We expect our results to trigger more systematic efforts along these lines.
The occurrence of low-lying Einstein-like phonon modes that interact with acoustic phonons is not limited to the class of clathrates and related cage-like materials. For the recently discovered family of Cu$_{12-x}$M$_x$Sb$_4$S$_{13}$ (M = transition metal) tetrahedrites, optical phonon branches involving out-of-plane vibrations of the three-fold coordinated Cu ions were predicted by \textit{ab initio} calculations and were suggested as origin of the low thermal conductivities\textsuperscript{51}. Interestingly, $\kappa_{ph}$ of this new material fits perfectly into our universal scaling plot (Fig. 4). Other candidate materials are, e.g., PbTe (Ref. 52), Bi$_2$Te$_3$ (Ref. 53), BiCu(Se,Te)O (Ref. 54), Cu$_3$SbSe$_3$ (Ref. 55), and rattling-induced superconductors such as the $\beta$-pyrochlore oxides\textsuperscript{56}, dodecaborides\textsuperscript{57}, or VAl$_{10}$ (Ref. 58), and possibly even amorphous and glassy materials\textsuperscript{59}. Detailed investigations, such as presented here, are needed to test whether also in these materials the phonon Kondo effect is at work.

Phonon Kondo systems transfer heat largely via low frequency phonons of long mean free paths. As such they are promising \textit{intrinsic} “thermocrystals”, for applications such as heat waveguides or thermal diodes in the emerging field of phononics\textsuperscript{60}.

**MATERIALS AND METHODS**

\textbf{Synthesis and structural characterization} As starting material for the single crystal growth of BCGG$_x$, two cylindrical rods with the same nominal composition Ba$_8$Cu$_{4.8}$Ge$_{41.2-x-y}$\sq Ga$_x$ (BCGG$_x$) were prepared for each sample with $x = 0.0, 0.2, 0.5, \text{and } 1.0$ from high-purity elements using a high-frequency induction furnace. One rod with 7 mm in diameter and 60 mm in length served as the feed rod, the other one with the same diameter and 20 mm in length as the seed for the crystal growth. The single crystal growth was performed in a 4-mirror furnace equipped with 1000 W halogen lamps. The pulling speed of the rod was 3-5 mm/h. Both rods rotated in opposite direction (speed: $\sim$8 revolutions per minute) to ensure efficient mixing of the liquid and a uniform temperature distribution in the molten zone. A pressure of 1.5 bar Ar was used during the crystal growth.

X-ray powder diffraction data on BCGG$_x$ were collected using a HUBER-Guinier image plate system (Cu K$_{\alpha1}$, $8^\circ \leq 2\theta \leq 100^\circ$). The lattice parameters (Fig. 3a) were obtained from least squares fits to indexed $2\theta$ values employing Ge ($a_{Ge} = 0.5657906$ nm) as internal standard.

\textbf{Thermal conductivity} Commonly used laser flash methods measure the thermal diffusiv-
ity and thus need to be combined with specific heat and density measurements to calculate the thermal conductivity, which typically reduces the accuracy of this technique. By contrast, the $3\omega$ method is an ac technique for direct thermal conductivity measurements. During a $3\omega$ experiment the sample is heated locally and thus, in contrast to steady-state heat-flow experiments, errors due to radiation at elevated temperatures are reduced to a negligibly low level\textsuperscript{26}. Furthermore, this method is insensitive to geometrical errors. This is because the only geometrical parameter entering is the length of a line heater. As it is usually prepared by means of photo or electron-beam lithography and sputtering, its length is very well defined (see below). In fact, the error of our $3\omega$ thermal conductivity data, which we estimate to be below 5%, is dominated by uncertainties in the heater resistance and its temperature dependence.

For our studies, the narrow metal line serving as both the heater and the thermometer had a width of 20 $\mu$m and a length of 1 mm, with an uncertainly of 1 $\mu$m. To avoid electrical contact between heater and sample a thin layer of SiO$_2$ was first deposited on the polished sample surfaces by chemical vapor deposition. Then, a 4 nm thick titanium sticking layer and the 64 nm thick gold film were sputtered in an Ardenne LS 320 S sputter system. The heater structures were made by standard optical lithography techniques using a Karl Susse MJB4 mask aligner.

The metal line was heated by an oscillating current at a circular frequency $\omega$, which thus leads to a $2\omega$ temperature oscillation of both the heater and the sample. Due to the linear temperature dependence of the metallic heater, the $2\omega$ temperature oscillation translates into a $3\omega$ voltage oscillation, which is detected using a lock-in amplifier (7265, Signal Recovery). Applying the $3\omega$ method\textsuperscript{26} to bulk geometry, the measured in-phase temperature oscillation of the heater/thermometer line is expected to be linear in logarithmic frequency $f$ as long as the thermal penetration depth is large compared to the heater half width $b$ and at least five times smaller than the sample thickness $t$ (see boundaries indicated in Fig. 2a). The thermal conductivity $\kappa$ of the material can then be extracted from the slope of the in-phase temperature oscillation $\Delta T$ vs log $f$.

Prior to the thermal $3\omega$ voltage detection, the first harmonic and all related higher harmonics are subtracted from the signal using a carefully gain and phase calibrated active filter\textsuperscript{26} based on a technique that allows to adjust the magnitude and phase of a reference signal as a function of frequency. In this way the main error sources of a $3\omega$ experi-
ment, spurious $3\omega$ signals arising from harmonic distortions of the involved amplifiers, can be largely eliminated. Using an ultra-precise 100 $\Omega$ Z-foil resistor (temperature coefficient $\pm 0.05$ ppm/°C, tolerance $\pm 50$ ppm; Vishay) as a sample we found the background signal to be negligibly small within the entire frequency range (0.5 Hz to 50 kHz) of the experiment. With the same resistor, the accuracy of our voltage controlled AC constant current source was found to be within $\pm 0.1\%$ within the whole frequency range and for all tested excitations (100 $\mu$A to 10 mA). By further measurements on different resistors, load dependencies were ruled out.

$3\omega$ measurements were done in the temperature range between 80 and 330 K. With this setup, we reproduced the thermal conductivity data on single crystalline $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ of Sales et al.\textsuperscript{16} within the error bar, estimated to only 3\% in that work. This precision, which is remarkable for a steady-state experiment, was reached with special radiation shields and specific sample geometries\textsuperscript{16,61}.

Below 100 K the data were completed by additional steady-state heat-flow experiments. The phonon thermal conductivities of all investigated materials were calculated by subtracting an electronic contribution, determined using the Wiedemann-Franz law with a constant Lorenz number of $L_0 = 2.44 \cdot 10^{-8} \text{W}\Omega\text{K}^{-2}$ and electrical resistivity data measured on the same samples.

**Specific heat** The specific heat was measured with a relaxation-type method using the $^4\text{He}$ specific heat option of a Physical Property Measurement System (PPMS) from Quantum Design. The addenda was measured separately prior to each sample measurement.

To study the phonon contribution to $C_p$, first the electronic contribution was determined. At low temperatures, the specific heat can be approximated by $C_p/T = \gamma + \beta T^2$, where the Sommerfeld coefficient $\gamma$ represents the electron contribution and the $\beta$ parameter quantifies the Debye-like phonon contribution. For BCGG$x$, the data below 3.5 K are very well described by such linear fits (not shown).

Rattling modes, originating from localized oscillations of the guest atoms, can be revealed by analyzing $C_p/T^3$ vs log $T$. Within such a representation, rattling modes appear as bell-shaped contributions on top of a Debye-like phonon background (not shown).

**Hall effect and electrical resistivity** The electrical resistivity and the Hall coefficient were determined by a standard 6-wire technique using the horizontal rotator option
of a Physical Property Measurement System (PPMS) from Quantum Design. Temperature
dependent Hall effect measurements were performed in a magnetic field of 9 T. The Hall
resistivity was confirmed to be linear in fields up to 9 T at all temperatures down to 2.5 K.
The Hall coefficient was analyzed within a simple one-band model, \( R_H = 1/ne \).

**Thermal expansion** Measurements of the coefficient of thermal expansion \( \alpha_L(T) = l^{-1}dl/dT \) were carried out by using a high-resolution capacitive dilatometer\(^6\), which enables the detection of length changes \( \Delta l \geq 10^{-2} \) Å. Relative length changes were measured along a principle axis of cubic Ba\(_8\)Ga\(_{16}\)Ge\(_{30}\). \( \alpha_L(T) \) is obtained by numerical differentiation of the \( \Delta l(T)/l \) data with respect to temperature (Supplementary Material S7).

**Ab initio calculations** *Ab initio* density functional theory (DFT) simulations were conducted using the Vienna Ab initio Simulation Package (VASP)\(^63\), applying the projector augmented wave method\(^64\) and the generalized gradient approximation (GGA) as proposed by Perdew and Wang (PW91)\(^65\). A fully ordered, cubic 54 atom unit cell of Ba\(_8\)Ga\(_{16}\)Ge\(_{30}\) with Ba at the Wyckoff sites 2\(a\) and 6\(d\), Ge at 6\(c\) and 24\(k\), and Ga at 16\(i\) was investigated, using a \( 5 \times 5 \times 5 \) \( k \)-point mesh and a plane wave cutoff of 500 eV. For a fixed lattice constant of 10.74 Å, corresponding to the experimental value, the atomic positions were relaxed. After reaching convergence (residual forces of less than \( 10^{-3} \) eV/Å), symmetry non-equivalent displacements were introduced into the relaxed structure. For displacements of 0.02 Å, the restoring forces were determined, again by using the VASP code with the above described settings. From the obtained forces, the dynamical matrix was extracted and the alamode\(^{15,66}\) code was used to determine the phonon DOS and the specific heat (Supplementary Fig. 1, main parts and insets) in the harmonic approximation.

The thermal expansion coefficient was determined within the quasi-harmonic approximation. For this purpose, the ground state structure and energy were determined for a series of unit cells with fixed cubic lattice parameter, corresponding to both decreased and increased cell volumes. For each of these volumes the dynamical matrix was then obtained in the same way as described above for the experimental volume. By using the phonopy code\(^67\) the dynamical matrix could be used to determine the free energy at the given volume and as a function of temperature. The free energy as a function of the volume for a given temperature was then fitted to the Vinet equation of state, again using the phonopy code. Finally, from the free energy minima at a given temperature, the corresponding equilibrium volume at this
temperature can be extracted, which then allows to access the thermal expansion coefficient. GGA generally slightly overestimates bonding. Thus, the \textit{ab initio} thermal expansion curves are rescaled to match the high-temperature data (Supplementary Fig. 2).

For the thermal conductivity, \textit{ab initio} results obtained by Tadano et al.\textsuperscript{15} using anharmonic interatomic force constants are used. We reproduced these calculations to within a factor of 1.1 (the difference is likely due to a slightly different lattice constant used in our calculations).

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AUTHOR CONTRIBUTIONS

M.I. and S.P. designed the research. X.Y., P.T., and A.P. synthesized the materials. M.I. and R.S. designed the 3\textomega setup. M.I., L.P., X.Y., P.T., G.L., S.H., and E.G. performed the measurements. M.L. supervised the thermal expansion work. M.I. analyzed the data. H.E. performed the \textit{ab initio} calculations. M.I. and S.P. interpreted the results and prepared the manuscript. All authors contributed to the discussion.

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ADDITIONAL INFORMATION

Supplementary Information accompanies the paper on XXX (doi: XXX).

COMPETING INTERESTS

The authors declare no competing interests.
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electrons phonons

\[ \kappa_{\text{ph}} / \kappa_{\text{ph}}^{\text{max}} \]

\[ T (K) \]

\[ \frac{1}{\kappa} \text{ (W}^{-1}\text{Km)} \]

\[ \frac{\Delta S/6R}{\Delta C_{/R}} \]

\[ \frac{\Delta \alpha/\alpha}{\Delta S/6R} \]

\[ T/\theta_E \]

\[ \theta_E \]

50 K

300 K

\[ \kappa_{\text{exp}} (Sales et al.) - \kappa_{\text{calc}} (Tadano et al.) \]

BCG1.0

Ge, Vook et al.
FIG. 1: Comparison of spin and phonon Kondo effect. (a) Type-I clathrate crystal structure G$_8$H$_{46}$. Per unit cell 8 guest atoms (G, red) are situated in two different cages (smaller dodecahedra X$_{20}$ and larger tetrakaidecahedra X$_{24}$) built by the host (H, blue) atoms. The different crystallographic sites are labeled. (b) Sketch of an X$_{24}$ cage with the two soft rattling directions $e_1$ and $e_2$ within the easy plane parallel to the two hexagonal faces of the cage. Each soft direction is parallel to the longest secant of one of the two hexagons, both defined by the 6c site (black atoms) of the structure. Incoming acoustic phonons with the two different transverse polarizations $e_{T1}$ and $e_{T1}$ are sketched by the sinusoidal waves. (c) Schematic dispersion relations for electrons in heavy electron systems (left) and phonons in an analogously defined “heavy” phonon system (right). The blue and red curves represent the non-interacting dispersive and localized entities, respectively, the violet curves the hybridized interacting states. As function of temperature, the system evolves from non-interacting well above the Kondo temperature to interacting well below it. For simplicity, phonon branches above $\omega_E$ are neglected. This is justified in real clathrates by the presence of multiple Einstein temperatures, resulting in multiple anticrossings$^{12,13}$. The Debye model (blue line, right) assumes $\omega = v_s q$ where $v_s$ is the sound velocity. The new dispersion relation (violet, right) is characterized by the group velocity $v_g = \partial \omega / \partial q$. It equals the sound velocity only at low wave vectors and frequencies. (d) Temperature dependent phonon thermal conductivity, normalized to its maximum, calculated using a modified Callaway model (Supplementary Information S1) for various Einstein temperatures $\Theta_E$ (left) and corresponding data for the Ge-based type-I clathrate BCGG1.0 (Supplementary Table 1) and elemental Ge, electron irradiated and annealed at 77 K to similar defect densities$^{14}$ (right). (e) Specific heat and thermal expansion phonon Kondo anomaly, obtained by subtracting the experimental from the theoretical specific heat and thermal expansion curves of Ba$_8$Ga$_{16}$Ge$_{30}$ (left axis, see Supplementary Figs. 1b and 2b and Materials and Methods) and the corresponding entropy (right axis). (f) The inverse difference of calculated$^{15}$ and experimental$^{16}$ phonon thermal conductivities of Ba$_8$Ga$_{16}$Ge$_{30}$ (Supplementary Fig. 3b), showing the $-\ln T$ hallmark (full red line) of incoherent Kondo scattering in the spin Kondo effect above the Kondo temperature (dashed vertical line). The error bars represent the error of $\pm 3\%$ specified for the thermal conductivity data$^{16}$. 

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FIG. 2: Thermal conductivity data of type-I clathrate single crystals. (a) Exemplary frequency scan in the $3\omega$ setup. Rectangles show the in-phase, circles the out-of-phase contribution of the temperature oscillation $\Delta T$. The expected linear-in-logarithmic-frequency dependence of the in-phase temperature oscillation of the heater/thermometer line, that is observed at intermediate frequencies (between the hatched areas), is measured with an extremely low noise level. The slope of this dependence (full line) is inversely proportional to the thermal conductivity $\kappa$ of the studied material. (b) Temperature dependent thermal conductivity of all studied materials. The data points represent the phonon thermal conductivities $\kappa_{\text{ph}}$, calculated by subtracting an electronic contribution (lines and identifier symbols) from the total measured $\kappa$. Each data point above 80 K is determined from the slope of an isothermal $\Delta T$ vs $\log f$ curve (straight line in a). All sample compositions are given in the Supplementary Table 1.
FIG. 3: Scattering contributions in clathrate single crystal series. (a) Lattice parameter vs \( x \) for Ba\(_8\)Cu\(_{4.8}\)Ge\(_{41.2-x}\ homoepitaxial (BCGGx, Supplementary Table 1) and comparison with the series Ba\(_8\)Ga\(_{14+x}\)Ge\(_{32-x}\) (BGG are polycrystals synthesized by us, BGG1 are single crystals 4 and 6 from Ref. 28, and BGG2 is a single crystal from Ref. 29), which was shifted downwards by 89.6 mÅ for better readability. For the linear fits see Supplementary Information S3. (b) Coefficients \( \gamma \) and \( \beta \) of linear fits \( C_p/T = \gamma + \beta T^2 \) to the specific heat data, normalized to their respective value for \( x = 0 \), of Ba\(_8\)Cu\(_{4.8}\)Ge\(_{41.2-x}\ homoepitaxial below 3.5 K (not shown) vs \( x \). (c) Electrical resistivity (top) and charge carrier concentration (bottom), determined from the Hall coefficient in a one-band model, \( R_H = 1/ne \), as function of temperature for all Ba\(_8\)Cu\(_{4.8}\)Ge\(_{41.2-x}\ homoepitaxial samples. (d) Phonon thermal conductivity vs temperature for all Ba\(_8\)Cu\(_{4.8}\)Ge\(_{41.2-x}\ homoepitaxial samples (symbols), together with fits with the modified Callaway model (Supplementary Information S1) to the \( x = 0 \) data (red full line) and simulations (dashed lines) using the parameters of the \( x = 0 \) fit except for the defect scattering rate \( \tau_D^{-1} \) (left) and the boundary scattering rate \( \tau_B^{-1} \) (right). The respective scattering rate was decreased to the indicated percentage in direction of the arrow. The speed of sound of each sample was determined from \( \beta \), the Einstein temperature \( \Theta_E \) from bell shaped contributions to \( C_p/T^3 \) versus log\( T \). (e) Phonon thermal conductivity vs temperature for two different
FIG. 3: (cont.) Ba$_{8}$Ga$_{16-x}$Ge$_{30+x}$ samples from the literature$^{30,31}$, with lines corresponding to our fit to the data from Ref. 30 and a simulation using essentially the same parameters except for a strongly enhanced phonon-electron scattering rate $\tau_{\text{ph-el}}^{-1}$ for the data from Ref. 31.

FIG. 4: Universal scaling of the intrinsic phonon thermal conductivity of phonon Kondo compounds. Phonon thermal conductivities vs the product of sound velocity and lowest-lying Einstein temperature (Supplementary Information S5) for single crystalline intermetallic clathrates measured within this work (full circles), together with published data on intermetallic clathrates (full squares), a Xe-filled ice hydrate, and the tetrahedrite Cu$_{10.6}$Mn$_{1.4}$Sb$_4$S$_{13}$ (CMSS, see Supplementary Table 1 for all sample compositions and references). The open triangles are the minimum $\kappa_{\text{ph}}$ values derived using $\kappa_{\text{min}}$ of Ref. 41. The open squares are the minimum $\kappa_{\text{ph}}$ values estimated using Supplementary Eqn. 9.
Supplementary Material for

Kondo-like phonon scattering in thermoelectric clathrates

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Supplementary Discussion S1 - S8
Supplementary Equations S1 - S11
Supplementary Table S1
Supplementary Figures S1 - S4
Additional References
Supplementary Discussion

S1. Modified Callaway model

The Callaway model is a phenomenological treatment of the phonon thermal conductivity of solids. It is derived from the Boltzmann equation for an isotropic crystal with dispersionless acoustic phonon branches, assuming that all phonon scattering processes can be represented by frequency-dependent relaxation times. Both resistive three-phonon Umklapp scattering processes and total momentum conserving normal processes are considered. Its simplicity and early success in describing simple materials such as Germanium made it a popular choice to model experimental thermal conductivity data, even for more complex materials.

To model the low-temperature thermal conductivity of type-I clathrates we propose here a modified form of the Callaway model, namely

\[ \kappa_{ph} = \frac{k_B^4}{2 \cdot \pi^2 \cdot v_s \cdot h^3} \cdot \left[ \int_0^{\Theta_E} \tau \cdot \frac{x^4 \cdot e^x}{(e^x - 1)^2} \cdot dx + \frac{I_1^2}{I_2} \right] , \]

with

\[ I_1 = \int_0^{\Theta_E} \tau \cdot \frac{1}{\tau_N} \cdot \frac{x^4 \cdot e^x}{(e^x - 1)^2} \cdot dx , \]

\[ I_2 = \int_0^{\Theta_E} \frac{1}{\tau_N} \cdot \left( 1 - \frac{\tau}{\tau_N} \right) \cdot \frac{x^4 \cdot e^x}{(e^x - 1)^2} \cdot dx , \]

and

\[ \tau^{-1} = \tau_N^{-1} + \tau_D^{-1} + \tau_B^{-1} + \tau_U^{-1} + \tau_{ph-el}^{-1} . \]

It differs from the original Callaway model only by the substitution of the Debye temperature \( \Theta_D \) by the characteristic temperature of the lowest-lying Einstein contribution \( \Theta_E \). This approximation effectively cuts off all phonon modes above the lowest-lying optical mode, which is justified by the significantly smaller group velocities of the higher-lying modes\(^2,3\). At temperatures below \( \Theta_E/2 \), where we performed quantitative analyses (Fig. 1d, Fig. 3d, e of main part), errors arising from this approximation are negligible. The empirical scaling of the intrinsic phonon thermal conductivities of a large number of clathrates with only \( v_s \Theta_E \) observed at 300 K (Fig. 4 of main part) further supports this approximation because \( \Theta_E \) does not contain any information on the phonon spectrum above \( \Theta_E \).

Normal processes are usually taken into account by

\[ \tau_N^{-1} = N \omega^a T^b . \] (S2)

However, for complex crystal structures or materials including a high defect concentration these processes have been shown to be negligible\(^4\) permitting us to omit the corresponding
I_2^2 term in Eqn. S1, in our analyses. At low temperatures, we describe defect scattering by Rayleigh scattering\(^5\)
\[
\tau_D^{-1} = D \cdot \omega^4
\]  
(S3)
and boundary scattering by the frequency independent scattering rate\(^5\)
\[
\tau_B^{-1} = B
\]  
(S4)
In analogy with the expression for the scattering rate due to three phonon Umklapp scattering within the Debye approximation\(^5\)
\[
\tau_U^{-1} \propto \omega^2 \tau_D^2 \left[ 1 + 6 \frac{T}{\Theta_D} + 24 \left( \frac{T}{\Theta_D} \right)^2 + 48 \left( \frac{T}{\Theta_D} \right)^3 \right] \quad \text{for} \ T < \Theta_D
\]  
(S5)
we derived\(^6\)
\[
\tau_U^{-1} \propto \frac{\omega^2}{\alpha^2} \tau_E^2 \left[ 1 + 2 \frac{\alpha T}{\Theta_E} + 2 \left( \frac{\alpha T}{\Theta_E} \right)^2 \right] \quad \text{for} \ T < \Theta_E
\]  
(S6)
for acoustic phonons scattering off a low-lying flat optical phonon mode with energy \(k_B \Theta_E\).
The exponential term of \(\tau_U^{-1}\) derived within the Debye approximation is scaled by \(\Theta_D\). By contrast, in the model proposed here, the Einstein temperature \(\Theta_E\) determines the Umklapp scattering rate. As in the original form\(^5\), the parameter \(\alpha\) scales the energy of the second phonon to be able to participate in three phonon Umklapp scattering. The upper limit of \(\alpha\) is determined by the dispersion of the acoustic branch. \(\alpha\) values around 2.3 obtained from fitting \(\kappa_{ph}\) of the BCGG series (not shown) are reasonable\(^5,7\).

An alternative relation for \(\tau_U^{-1}\) of type-I clathrates and related materials is obtained\(^8\) by substituting \(\Theta_D\) by \(\Theta_E\) in the empirical expression\(^9\)
\[
\tau_U^{-1} = U \omega^2 e^{-\frac{\Theta_D}{\pi \rho v_s}} \left( \frac{T}{\Theta_D} \right)^\beta
\]  
(S7)
Phonon-electron scattering is taken into account by the expression\(^10\)
\[
\tau_{ph-el}^{-1} = \frac{\pi n m^* v_F \omega}{6 \rho v_s} \quad \text{with} \quad q < 2k_F \quad \text{and} \quad q l_e >> 1
\]  
(S8)
where \(n\) is the charge carrier concentration, \(m^*\) is the effective electron mass, \(v_F\) is the Fermi velocity, \(\rho\) is the mass density, and \(l_e\) is the electron mean free path.

Finally we suggest a redefinition of Cahill’s minimum phonon thermal conductivity\(^11\) to the new form
\[
\kappa_{min}^{ph} = \frac{k_B^4 \cdot T^3}{2 \cdot \pi^2 \cdot v_k \cdot \hbar^3} \cdot \int_0^{\frac{\Theta_E}{\Theta_D}} \frac{x^3 \cdot e^x}{(e^x - 1)^2} \cdot dx
\]  
(S9)
Cutting off phonon modes above $\Theta_E$ is justified by the same arguments as in Eqn. S1. A direct confirmation of the need for a new $\kappa_{\text{ph}}^{\text{min}}$ limit is the experimental observation of the violation of the original (Cahill) limit (see section Materials above).

S2. Materials

Figure 1d right compares the phonon thermal conductivity of the single crystalline clathrate BCGG1.0 with elemental Ge. Both materials possess a similar Debye temperature (304 K for BCGG1.0, 362 K for Ge, Ref. 12). In both cases, phonon-electron scattering and boundary scattering are expected to be negligible. In contrast to the complex structure of BCGG1.0 built up of atoms with severely different masses, single crystalline Ge typically exhibits few defects and thus a very high thermal conductivity. Therefore, the phonon thermal conductivity of an electron-irradiated and post-annealed Ge sample (Ge II annealed at 77 K, Ref. 12) was chosen for comparison.

Figure 3e compares the phonon thermal conductivity of two type-I clathrate single crystals with nominal composition $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$. Phonon-electron scattering can only occur for phonons with a wave vector $q$ smaller than twice the Fermi wave vector $k_F$. Using the charge carrier concentration $n = 0.84 \cdot 10^{27} \text{e}^{-}/\text{m}^3$ and the sound velocity calculated from the Debye temperature $\Theta_D = 324\text{K}$ reported for crystal II of Ref. 13 we estimate that phonon-electron scattering should occur below 140 K.

For a few type-I clathrates$^{14,15}$ and skutterudites$^{16,17}$, phonon thermal conductivities have been reported that violate the Cahill $\kappa_{\text{ph}}^{\text{min}}$ limit, even though this was not explicitly stated in these works. For nanostructured $\text{Ba}_8\text{Cu}_x\text{Si}_{46-x}$ ($x = 3.6, 3.8$) prepared by ballmilling and hotpressing $\kappa_{\text{ph}}(800\text{K}) = 0.2\text{W/Km}$ was found$^{14}$. With the reported Debye temperature $\Theta_D = 420\text{K}$ we calculate a Cahill $\kappa_{\text{ph}}^{\text{min}}$ value of 0.85 W/Km. A less drastic violation seems to occur for $K_8\text{Ga}_8\text{Si}_{38}$ with $\kappa_{\text{ph}}(300\text{K}) = 0.5\text{W/Km}$ (Ref. 15). In the absence of reported $\Theta_D$ values we estimate a Cahill $\kappa_{\text{ph}}^{\text{min}}$ value of 0.7 W/Km as lower boundary by using $\Theta_D = 360\text{K}$ of the heavier-element Si-based clathrates La-BAS and Ce-BAS (Table S1) as lower $\Theta_D$ boundary. Likewise, also the high-pressure torsion-treated skutterudites $\text{DD}_x\text{Fe}_3\text{CoSb}_{12}$ with $x = 0.6$ (Ref. 16) and $x = 0.68$ (Ref. 17) show ultralow phonon thermal conductivities that appear to violate the respective Cahill $\kappa_{\text{ph}}^{\text{min}}$ limits.

Figure S1a shows the specific heat at constant volume ($C_V$) of Si versus temperature. The data were calculated from experimental specific heat values taken at constant pressure
(\(C_p\), Ref. 18) and the temperature dependent volumetric thermal expansion coefficient (\(\alpha_V\), Ref. 19) using the expression 
\[ C_p - C_V = \alpha_V^2 \cdot T \cdot V_{\text{mol}} \cdot B, \]
where \(V_{\text{mol}}\) is the molar volume and \(B = 97.8\) GPa is the bulk modulus of Si (Ref. 20). For \(\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}\) (BGG, Fig. S1b), the thermal expansion coefficient was taken from Ref. 21 and the bulk modulus from Ref. 22.

**S3. Filling of vacancies by Ga in \(\text{Ba}_8\text{Cu}_{4.8}\text{Ge}_{41.2-x-y}\square_y\text{Ga}_x\)**

Here we show that with increasing Ga content \(x\) in \(\text{Ba}_8\text{Cu}_{4.8}\text{Ge}_{41.2-x-y}\square_y\text{Ga}_x\) the content \(y\) of vacancies \(\square\) is successively reduced. We assume that, as in related systems\(^{23-25}\), both Cu and the vacancy occupy the 6c site (Fig. 1a,b). With the multiplicity 6 of this site and 4.8 Cu atoms this limits the maximum amount of vacancies to 1.2 per unit cell. The linear dependence of the lattice parameter \(a\) on the Ga content \(x\) with the slope \(\Delta a/\Delta x = 4.8\) mÅ (Fig. 3a) suggests that Ga successively fills the vacancies and that we thus have \(y = 1.2 - x\). In detail, this slope is well accounted for by a substitution of Ge for \(\square\) with \(\Delta a/\Delta x = 3.46\) mÅ (Ref. 23) in a first step, and by a substitution of Ga for Ge with \(\Delta a/\Delta x = 1.13\) mÅ (blue line in Fig. 3a) in a second step. Both steps together yield a slope of 4.59 mÅ (= 3.46 + 1.13), in good agreement with experiment (red line in Fig. 3a).

The filling of the vacancies by Ga is corroborated by our low-temperature specific heat \(C_p\) and electrical transport (resistivity \(\rho\) and Hall coefficient \(R_H\)) measurements. Whereas the prefactor \(\beta\) of the phonon \(T^3\) term of \(C_p(T)\) increases strongly with the rate \(\Delta \beta/\Delta x \approx 30\%\) (Fig. 3b), the electronic Sommerfeld coefficient \(\gamma\) (Fig. 3b) and the charge carrier concentration \(n\) (Fig. 3c bottom) are essentially independent of \(x\). This discards Ga substituting either Cu or Ge which, according to the Zintl-Klemm concept\(^{26}\) (see S4 below), would change the charge carrier concentration by +2 or -1 electron per formula unit, respectively, and suggests that the formal charge of the vacancy is -1, just as that of Ga. The observed increase of the charge carrier mobility \(\mu_H = R_H/\rho\) with increasing Ga content (Fig. 3c top and bottom) strongly supports the picture of vacancy filling because in a Ge-based clathrate electrons are expected to scatter much more strongly from vacancies than from Ga.

**S4. Zintl-Klemm concept**

For the BCGG series a nearly temperature and sample independent charge carrier concentration \(n\) was found. According to the Zintl concept, Ba is expected to donate 2 electrons to the host framework. In a first approximation, the tetrahedrally coordinated host atoms can be considered to form covalent bonds. The formal charge of a Ge/Ga/Cu atom within a
type-I clathrate host framework is expected to be close to 0/-1/-3. Therefore, one Ga atom
substituting for Ge (Cu) would change the charge carrier concentration by -1 (+2) electrons per formula unit. For the BCGG series, the variable amount of Ga incorporated into
the host framework leaves the charge carrier concentration nearly unchanged. Therefore, a
substitution of Ga for vacancies with a formal charge of -1 is the most likely scenario.

S5. Specific heat analysis
The phonon specific heat of type-I clathrates is typically described by the sum of a Debye
contribution and two Einstein contributions,
\[
C_p = 9N_D R \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx + \sum_{i=1}^2 p_i N_{Ei} R \left( \frac{\Theta_{Ei}}{T} \right)^2 \frac{e^{\Theta_{Ei}/T}}{(e^{\Theta_{Ei}/T} - 1)^2},
\]
where \( x = \hbar \omega/k_B T \) and \( N_D \) and \( N_{Ei} \) are the numbers of Debye and Einstein oscillators
per formula unit. \( \Theta_D, \Theta_{Ei}, \) and \( p_i \) are the Debye temperature, Einstein temperatures, and
the number of degrees of freedom related to the \( i \)-th vibrational mode of the guest atoms,
respectively, and \( R \) is the gas constant. In the fitting procedure we fixed \( p_1 = p_2 = 3 \)
and \( N_D + \sum N_{Ei} = 54 \). When presented as \( \frac{C_p}{T^2} \) vs log \( T \), Einstein contributions typically
have a bell-shaped appearance on top of a Debye background from which the corresponding
Einstein temperatures can be extracted by fitting with Eqn. S10.

Below 3.5 K, the specific heat of all samples analyzed here has the form \( C_p/T = \gamma + \beta T^2 \),
which was used to extract the sound velocity \( v_s \). The number of contributing atoms was
assumed to be 54. When inelastic neutron scattering data were available, \( v_s \) was extracted
from these using the relation \( v_s = \left[ 1/3 \cdot ((1/v_L)^3 + 2 \cdot (1/v_T)^3) \right]^{-1/3} \), where \( v_T \) and \( v_L \) are the
initial slopes of the transverse and longitudinal acoustic phonon branches, respectively. The
agreement between both methods is satisfying.

S6. Theoretical calculation of the specific heat
The vibrational properties of \( \text{Ba}_8\text{Ga}_{16}\text{Ge}_{30} \) and Si were computed with \textit{ab initio}
density functional theory (Methods). The specific heat at constant volume was calculated from
the phonon density of states \( D(\omega) \), shown in Fig. S1 insets, via
\[
C_V(T) = \frac{\partial}{\partial T} \int_0^\infty d\omega D(\omega) \left[ \frac{1}{e^{\frac{\hbar \omega}{k_B T}} - 1} \right] (\hbar \omega + \frac{1}{2}),
\]
(S11)
S7. Experimental determination of the thermal expansion

The linear coefficient of thermal expansion $\alpha_L(T)$ of single crystalline Ba$_8$Ga$_{16}$Ge$_{30}$ was determined from the experimentally revealed $\Delta l(T)/l$ data, with $\Delta l(T) = l(T) - l(200 \text{ K})$, by numerical differentiation with respect to temperature. For that purpose the $\Delta l(T)/l$ data were divided into equidistant intervals of width $\Delta T = 0.13 \text{ K}$, in each of which the mean slope was determined from linear regression. The experiment was carried out on a single crystal of length $l = 1.6 \text{ mm}$ along a principal axis of the cubic structure for which the volume expansion coefficient $\alpha_V$ is given by $\alpha_V = 3 \cdot \alpha_L$. Measurements were performed from 4.5 K up to 200 K upon increasing the temperature at a slow rate of 1.5 K/h to ensure thermal equilibrium. At low temperatures, the data are well described by $\alpha_V/T = a + bT^2$, with a negligibly small electronic contribution $a$ (not shown). Thus, $\alpha_L(T)$ is dominated by the phonon contribution.

S8. Phonon Kondo effect

The Kondo problem has a 50-year-old history of highly active research. It has been studied in settings ranging from bulk materials, to surfaces, 2-dimensional materials, mesoscopic systems, and ultracold atoms in optical lattices. Originally it was formulated for free conduction electrons interacting with spin-1/2 local magnetic moments$^{27-29}$. However, Kondo physics is a very broad phenomenon, with only a few fundamental requirements, most notably the non-commutative scattering of an extended wave off a localized entity with internal degrees of freedom. In addition to magnetic moments, the localized entities may take the form of orbital$^{30-32}$, charge$^{33}$, and local vibrational degrees of freedom$^{34-37}$. The extended wave component can also take various forms, in addition to conduction electrons in simple metals, it may also arise from fermions with pseudo-gapped electronic densities of states$^{38}$, Dirac particles$^{39,40}$, and bosonic baths$^{41,42}$. To the best of our knowledge Kondo physics has, however, never been considered in an entirely phononic context.

In the following we give an experimentalist’s sketch of how the basic physical picture of a Kondo interaction between rattling modes and the transverse acoustic phonons of a type-I clathrate, described in the main text, might be translated into a Kondo-type Hamiltonian.

The two degenerate Einstein modes associated with the two rattling directions ($\alpha = 1, 2$)
of the guest atoms in the large cages are described as

$$H_0 = \sum_{\alpha=1,2} \hbar \omega_E (b^\dagger_\alpha b_\alpha + \frac{1}{2}) + \frac{U}{2} (b^\dagger_1 b_1 + b^\dagger_2 b_2 - N_b)^2 \ ,$$

(S12)

where $b^\dagger_\alpha$ and $b_\alpha$ ($\alpha = 1, 2$) are the boson creation and annihilation operators, $N_b$ is an effective boson number, and $U$ is the interaction energy. We can absorb the first term into the second, writing

$$H_0 = \frac{U}{2} (n_1 + n_2 - N_b^*)^2 + \hbar \omega_E (1 + \frac{\hbar \omega_E}{2U} + N_b^*) \ ,$$

(S13)

where

$$N_b^* = N_b - \frac{\hbar \omega_E}{U}$$

and $b^\dagger_\alpha b_\alpha = n_\alpha$. Provided this quantity remains positive, then the ground state energy is minimized at $n_1 + n_2 = N_b^*$, and the energy of the states with one more, or one less phonon is $U/2$ higher. In this way, our local Hamiltonian has the effect of inducing a “phonon blockade”, the rattler analog of the Coulomb blockade of the spin Kondo effect, in which the states with $N_b^*$ phonons are degenerate, and split off beneath all states with larger, or smaller numbers of bosons. The Hamiltonian also ensures that there is an effective SU(2) degeneracy between the “1” and “2” bosons. However, it may well be that other formulations can be found that represent a phonon Kondo effect more elegantly.

The hybridization of the Einstein modes with the acoustic modes is described by

$$H_1 = \sum_{\mathbf{q},\alpha=1,2} V_{\mathbf{q}} (b_{\mathbf{q},\alpha} + b^\dagger_{-\mathbf{q},\alpha})(b_\alpha + b^\dagger_\alpha) \quad (S15)$$

where $V_{\mathbf{q}}$ is the hybridization strength. It does not conserve the boson number. This will produce additional Kondo terms in the Schrieffer-Wolff transformation, in which the number of acoustic bosons changes by $\pm 2$.

Finally, the acoustic modes themselves are described by

$$H_2 = \sum_{\mathbf{q},\alpha=1,2} \hbar \omega_{\mathbf{q},\alpha} (b^\dagger_{\mathbf{q},\alpha} b_{\mathbf{q},\alpha} + \frac{1}{2}) \ ,$$

(S16)

where $\mathbf{q}$ is the wave vector and $\alpha$ the polarization of an acoustic phonon. The total Hamiltonian of the interacting acoustic and rattling phonon system thus reads

$$H = H_0 + H_1 + H_2 \ ,$$

(S17)
which resembles an Anderson impurity model\textsuperscript{28}.

To map this Hamiltonian directly to a spin Kondo Hamiltonian (Schrieffer-Wolff transformation\textsuperscript{28,29}) we note that the two-fold degeneracy of the rattler modes ($\alpha = 1, 2$) resembles a spin, described in a Schwinger boson representation\textsuperscript{43–45} as

\begin{equation}
S_z = \frac{1}{2}(b_1^\dagger b_1 - b_2^\dagger b_2) , \tag{S18}
\end{equation}

where

\begin{equation}
S = \frac{1}{2}(b_1^\dagger b_1 + b_2^\dagger b_2) . \tag{S19}
\end{equation}

Interestingly, this means that the effective spin of the rattler is given by the Bose-Einstein function

\begin{equation}
2S = N_b = 1/(e^{\hbar \omega_E/(k_B T)} - 1) \tag{S20}
\end{equation}

and will thus grow with $k_B T/\hbar \omega_E$ at high temperatures. This distinguishes the all phononic Kondo effect from the usual spin Kondo effect in a simple metal, where the interaction does not disappear at $T = 0$. By contrast, it is similar to the Kondo effect in pseudo-gapped Fermi systems\textsuperscript{38} and in particular in fermionic systems with linear dispersion like graphene and 3-dimensional Dirac semimetals. Here the electronic density of states vanishes at the Fermi level and thus Kondo screening is expected to disappear below the Kondo temperature\textsuperscript{39}.

Interestingly, a $-\ln T$ dependence of the electrical resistivity is experimentally observed in defect-graphene in a rather extended temperature range above some cutoff temperature\textsuperscript{40}.

The acoustic phonon modes apparently have the ability to switch the polarization of the rattler, which can be visualized as follows: If an acoustic phonon of polarization 1 arrives at a cage with an atom rattling in polarization 2, it will be absorbed in the cage in the form of a distortion of the cage along 1, corresponding to an excited state (represented by the “Hubbard” term in Eqn. S12). This may lead to a change of the rattling direction (2 $\rightarrow$ 1), and the subsequent emission of an acoustic phonon of changed polarization (1 $\rightarrow$ 2). Such a process is governed by the “antiferromagnetic” exchange interaction

\begin{equation}
J \sim \frac{V^2}{U} \tag{S21}
\end{equation}

where, for simplicity, we have assumed the hybridization to be wave vector independent.

This leads to the well-known Kondo term

\begin{equation}
H_K \sim Js(0) \cdot 2S , \tag{S22}
\end{equation}

9
where \( s(0) \) represents the effective pseudospin

\[
s(0) = \phi_\alpha^\dagger \sigma_{\alpha\beta} \phi_\beta,
\]

(S23)
of the acoustic phonons at the position of the local pseudospin \( 2S \), \( \sigma_{\alpha\beta} \) are the Pauli matrices, and

\[
\phi_\alpha = \sum_q g_{q,\alpha}(b_{q,\alpha} + b_{-q,\alpha}^\dagger)
\]

(S24)
are the displacements of the acoustic modes that couple linearly to the rattler modes.

To treat this or equivalent formulations of the all phononic Kondo effect we believe to be realized in type-I clathrates and derive its physical properties for a realistic phonon density of states as function of the coupling strength is a task for future theoretical work. However, in analogy with related models (see above), it seems likely that archetype Kondo features such as the observed low-temperature \((- \ln T\)-like) increase of the thermal resistance would indeed result from such a model, at least in a limited temperature range.
Table S1: Materials obeying universal scaling. Type-I clathrate single crystals synthesized for this work (BCGGx, BGG) and materials used for comparison. All intermetallic clathrates except the large-grain polycrystal BAgG are single crystals. The other materials are polycrystals.

| Abbreviation | Composition | Reference |
|--------------|-------------|-----------|
| BCGG0.0      | Ba$_8$Cu$_{4.8}$Ge$_{40}$□$_{1.2}$ |          |
| BCGG0.2      | Ba$_8$Cu$_{4.8}$Ge$_{40}$Ga$_{0.2}$□$_{1.0}$ |          |
| BCGG0.5      | Ba$_8$Cu$_{4.8}$Ge$_{40}$Ga$_{0.5}$□$_{0.7}$ |          |
| BCGG1.0      | Ba$_8$Cu$_{4.8}$Ge$_{40}$Ga$_{1.0}$□$_{0.2}$ |          |
| BNG          | Ba$_8$Ni$_{3.5}$Ge$_{42.1}$□$_{0.4}$ | 23        |
| BAG          | Ba$_8$Au$_{5.25}$Ge$_{40.3}$□$_{0.45}$ | 24,46     |
| BAgG         | Ba$_8$Ag$_{4.1}$Ge$_{41.4}$□$_{0.5}$ | 25        |
| La-BAS       | La$_{1.23}$Ba$_{6.99}$Au$_{5.91}$Si$_{39.87}$ | 47        |
| Ce-BAS       | Ce$_{1.06}$Ba$_{6.91}$Au$_{5.56}$Si$_{40.47}$ | 47        |
| BGG          | Ba$_8$Ga$_{16}$Ge$_{30}$ | 48,49     |
| SGG          | Sr$_8$Ga$_{16}$Ge$_{30}$ | 49,50     |
| EGG          | Eu$_8$Ga$_{16}$Ge$_{30}$ | 49,51     |
| BGSn         | Ba$_8$Ga$_{16}$Sn$_{30}$ (n-type) | 52–54     |
| Xe hydrate   | Xe·6.2H$_2$O | 55–57     |
| CMSS         | Cu$_{10.6}$Mn$_{1.4}$Sb$_4$S$_{13}$ | 58        |
Figure S1: Specific heat of Si and Ba$_8$Ga$_{16}$Ge$_{30}$. Experimental (symbols) and calculated (lines) specific heat of (a) Si and (b) Ba$_8$Ga$_{16}$Ge$_{30}$ (BGG) versus temperature. Whereas for Si, the calculated specific heat is in good agreement with experimental data$^{18,19}$, for Ba$_8$Ga$_{16}$Ge$_{30}$ an extra contribution (red area) is observed between 10 and 100 K. As discussed in the main part, this contribution can be attributed to the weakening of the correlation between acoustic and optical phonon modes. The inset in both panels shows the ab initio phonon density of states (DOS) as a function of phonon energy, used for calculating the specific heat (see Methods and Supplementary Information S6).
Figure S2: Thermal expansion of Ge and Ba$_8$Ga$_{16}$Ge$_{30}$, and Grüneisen parameter of Ba$_8$Ga$_{16}$Ge$_{30}$. Experimental ($\alpha_{\text{exp}}^L$, symbols), calculated ($\alpha_{\text{calc}}^L$, gray lines), and rescaled ($\alpha_{\text{cs}}^L$, black lines) thermal expansion of (a) Ge and (b) Ba$_8$Ga$_{16}$Ge$_{30}$ (BGG) versus temperature. Whereas for Ge, the calculated (and rescaled) thermal expansion is in good agreement with experimental data, for Ba$_8$Ga$_{16}$Ge$_{30}$ an extra contribution (red area) is observed below 150 K. The difference between theory and experiment is plotted in the two insets. (c) Comparison of the experimental Grüneisen parameter $\Gamma = B\alpha_V/C_V$ of Ba$_8$Ga$_{16}$Ge$_{30}$, using either a temperature-independent bulk modulus $B$ of 65 GPa (black solid line) or the temperature-dependent one of Eu$_8$Ga$_{16}$Ge$_{30}$ (Ref. 62, gray circles), and the theoretical Grüneisen parameter determined from our \textit{ab initio} lattice dynamics calculations (crosses and gray line). $C_V$ is the specific heat at constant volume, $\alpha_V$ is the volumetric thermal expansion coefficient.
Figure S3: Thermal conductivity of Si and Ba$_8$Ga$_{16}$Ge$_{30}$. Experimental (symbols) and calculated (dashed lines) thermal conductivity of (a) Si and (b) Ba$_8$Ga$_{16}$Ge$_{30}$ (BGG) versus temperature. While for Si, the calculated thermal conductivity$^{63}$ is in good agreement with experimental data$^{64}$, for Ba$_8$Ga$_{16}$Ge$_{30}$ the calculated thermal conductivity$^{65}$ undershoots the experimental data$^{49,66}$ significantly above 50 K. As discussed in the main part, the inverse thermal conductivity difference shows approximate $−\ln T$ behaviour, the hallmark of incoherent Kondo scattering in spin Kondo systems.
**Figure S4: Enhanced Umklapp versus resonance scattering.** Temperature dependent phonon thermal conductivity, normalized to its maximum, calculated using a modified Callaway model for various Einstein temperatures $\Theta_E$ (left, replotted from Fig. 1d left) and for the $\Theta_E = 300 \text{ K}$ curve modified by resonance scattering according to $\tau_R^{-1} = \frac{C_R \omega^2}{(\omega^2_0 - \omega^2)}$, where $\omega_0$ is the circular frequency of the lowest-lying optical mode, with different scattering levels $C_R$ (right). Whereas enhanced Umklapp scattering leads to a sharpening of the phonon thermal conductivity maximum at low temperatures and a suppression of the thermal conductivity in a wide temperature range above the maximum, resonance scattering leads to an additional shoulder and a reduction of the thermal conductivity at low temperatures. Resonance scattering can thus be ruled out as an important scattering channel for the type-I clathrates studied here.
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