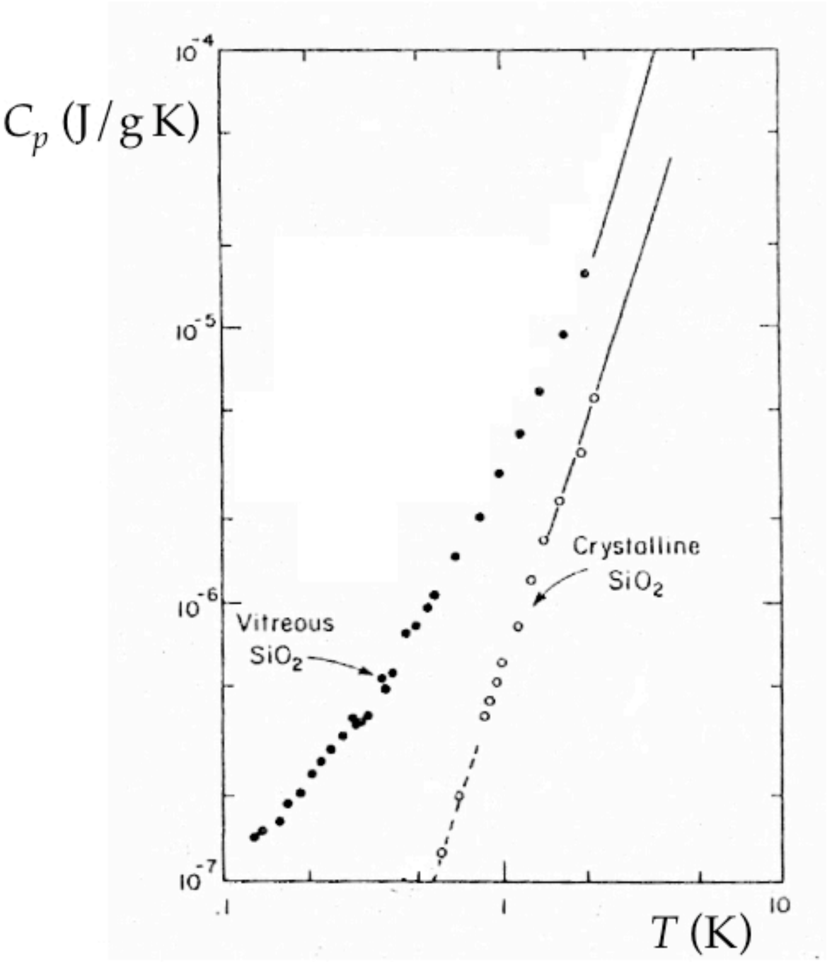
Lattice Excitations in Complex Structures

- Amorphous solids – thermal and elastic anomalies at low temperatures
- Umklapp processes in heterostructures and quasicrystals
- Structural scattering of the lattice excitations in quasicrystals
- Transport of heat in aerogels and opals

Amorphous solids—thermal and elastic anomalies at low temperatures

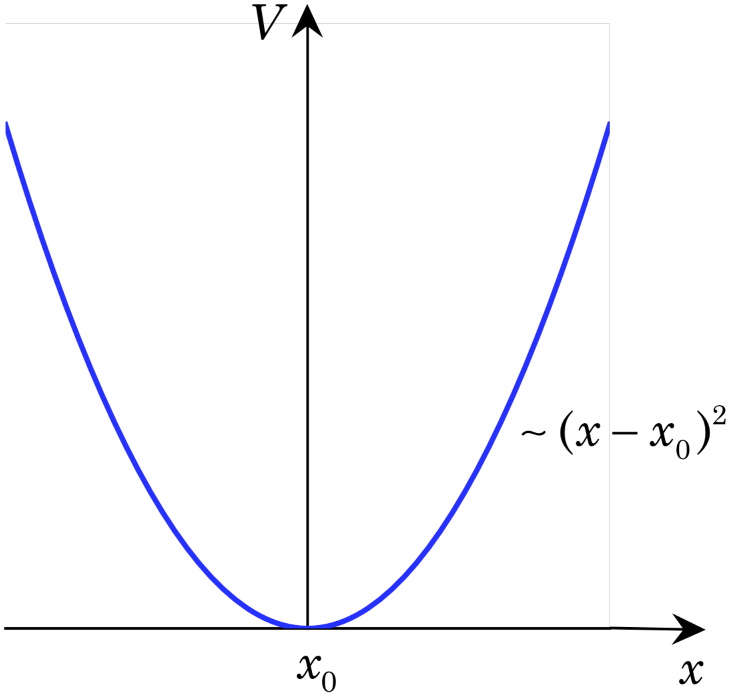
As we have established earlier, the low-temperature specific heat of glasses and amorphous solids does not follow the T^3 variation due to acoustic excitations and contains the excess contribution that varies as $T^\alpha, \alpha \approx 1$.



Such behavior can be explained by a specific dependence of the potential energy on the atomic displacement, namely, by anharmonic effects.

In harmonic approximation the potential energy is

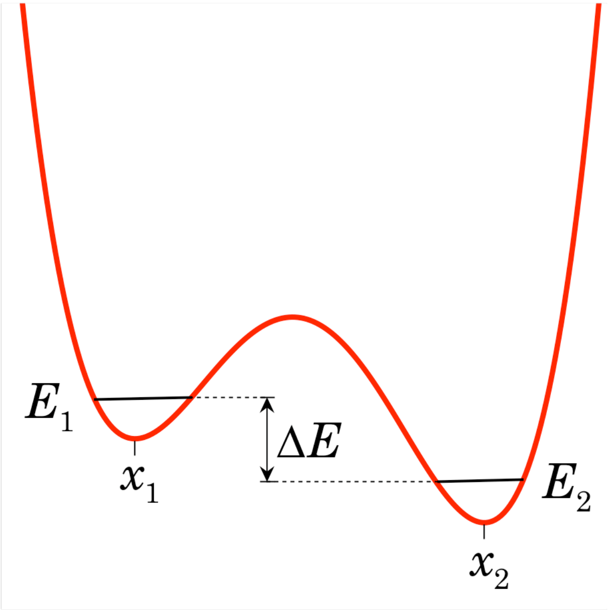
$$E_i = E_i^0 + a\left(\vec{r} - \vec{r}_0\right)^2 .$$



We have mentioned earlier that in contrast to periodically ordered crystals, in amorphous solids many realizations of the structure of almost equal potential energy are possible.

Consider the simplest model in which each atom has two possible positions with almost exactly equal potential energies.

The corresponding double well potential approximately as follows:



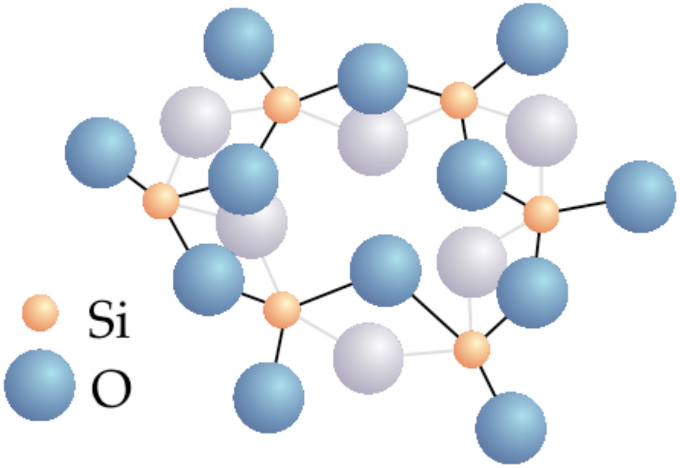
Such potential energy is strongly anharmonic, i.e., we are considering a system with strong anharmonicity.

Because the low-temperature specific heat anomalies discussed above have been measured on SiO_2, we choose this substance as our model substance.

Many modifications of SiO_2 contain oxygen tetrahedra filled with one silicon atom.

We can construct an amorphous structure as a random network of such tetrahedra.

Here we show a schematic two-dimensional representation of two structures with almost equal potential energies. We assume that light oxygen atoms are more disposed to small displacements than heavy silicon atoms.



The model assumption is that only the lowest vibrational state, or ground state, is predominantly occupied in each potential well, i.e., $k_B T \ll \hbar\omega$.

The tunneling probability between the two states is such that an exchange is possible during the typical time of a specific heat experiment, i.e., $10^{-3}\ \mathrm{s} < t < 10^{3}\ \mathrm{s}$.

The tunneling barrier height can be chosen to be in the range between 0.1 and 1 eV.

Bonding between an oxygen atom and its neighbors allows reaching thermal equilibrium, and the temperature is defined.

We assume that all N oxygen atoms are in identical conditions. In thermal equilibrium the ratio of the occupation numbers of the two levels is

$$\frac{N_2}{N_1} = \frac{e^{-E_2/k_B T}}{e^{-E_1/k_B T}} = e^{(E_1 - E_2)/k_B T} = e^{\Delta E/k_B T} \quad . \tag{7.1}$$

Since

$$N_1 + N_2 = N \quad , \tag{7.2}$$

we find

$$N_1 = \frac{1}{e^{\Delta E/k_B T} + 1} \quad . \tag{7.3}$$

The energy is given by

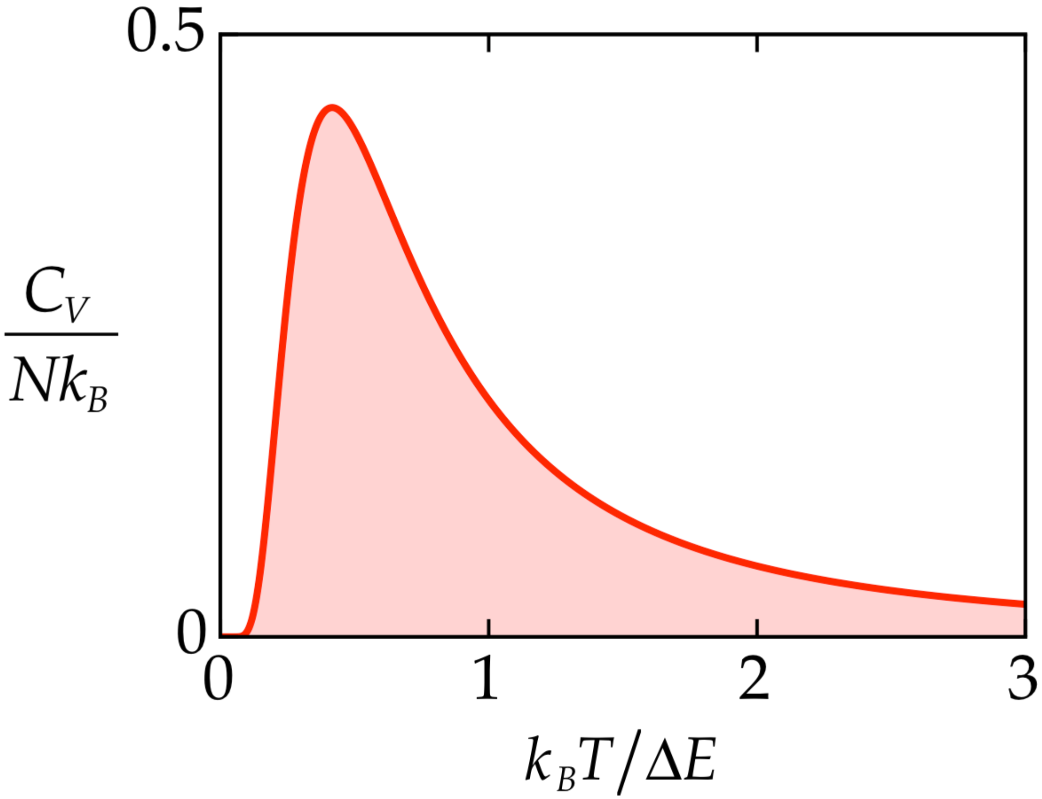
$$U = N_1 E_1 + N_2 E_2 = N_1 \Delta E + N E_2 \ .$$

The temperature dependent contribution to the energy is

$$U(T) = N_1 \Delta E = \frac{N \Delta E}{e^{\Delta E / k_B T} + 1} \ . \qquad (7.4)$$

Therefore,

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{\left(\Delta E / k_B T \right)^2 e^{\Delta E / k_B T}}{\left(e^{\Delta E / k_B T} + 1 \right)^2} N k_B \ . \qquad (7.5)$$



Here we show the temperature variation of the specific heat.

The specific heat of this type is typical of systems, in which internal degrees of freedom result in discrete energy spectra with level separations that fall into the temperature range measured.

The function $C_V(T)$, known as the Schottky anomaly, slowly increases with increasing temperature and reaches a maximum at $T \sim \Delta E / k_B$.

Asymptotic behavior of the Schottky anomaly:

Low temperatures $T \ll \frac{\Delta E}{k_B}$: $C_V\left(T\right) = k_B \left(\frac{\Delta E}{k_B T} \right)^2 e^{-\Delta E/k_B T}$.

High temperatures $T \gg \frac{\Delta E}{k_B}$: $C_V\left(T\right) = \frac{k_B}{4} \left(\frac{\Delta E}{k_B T} \right)^2$.

The specific heat of an ensemble of N two-level systems with equal ΔE

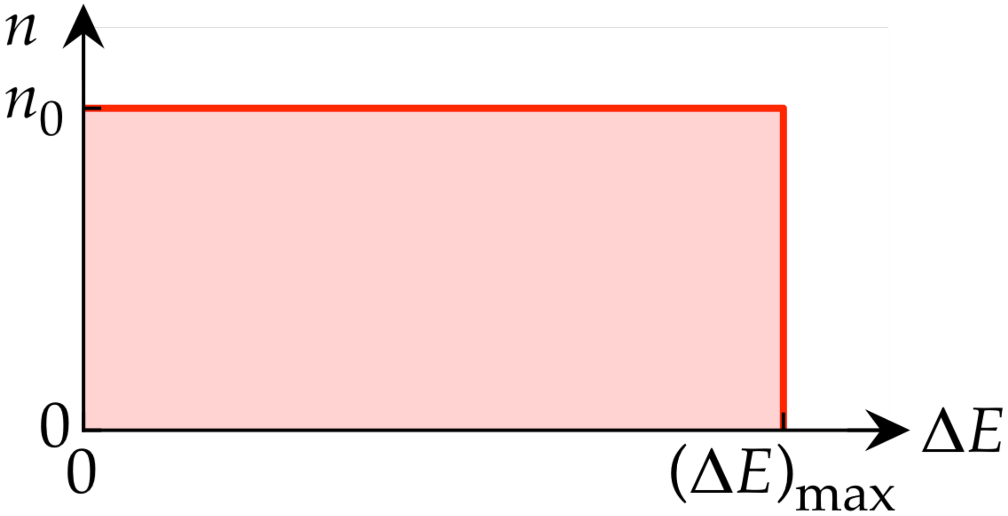
$$C_V = \frac{\left(\Delta E/k_B T\right)^2 e^{\Delta E/k_B T}}{\left(e^{\Delta E/k_B T} + 1\right)^2} N k_B$$

cannot describe the experimental data.

As is the case with the Einstein model, an assumption that the same value of ΔE can be assigned to all N atoms, is most likely incorrect.

Because of the randomness of the amorphous network the parameter ΔE does not have a well-defined value. It is expected to vary over a wide range.

We assume ΔE to have a constant distribution in the range between zero and $(\Delta E)_{\max}$.



The energy is now

$$U(T) = \int_0^{\Delta E_{\max}} n(\Delta E) \frac{\Delta E}{e^{\Delta E/k_B T} + 1} d(\Delta E) \ . \qquad (7.6)$$

Changing the integration variable in to $\Delta E/k_B T = x$ yields

$$U(T) = n_0 \left(k_B T\right)^2 \int_0^{x_{\max}} \frac{x}{e^x + 1} dx \ . \qquad (7.7)$$

Here the upper limit of integration is $x_{\max} = (\Delta E)_{\max}/k_B T$.

Since we are interested only in very low temperatures $T < 1\,\mathrm{K}$, and the typical values of $(\Delta E)_{\max}$ are in the range between 0.1 and 1 eV, we estimate $x_{\max} \sim 10^3 - 10^4$.

In the low-temperature limit $T \ll (\Delta E)_{\max}/k_B$

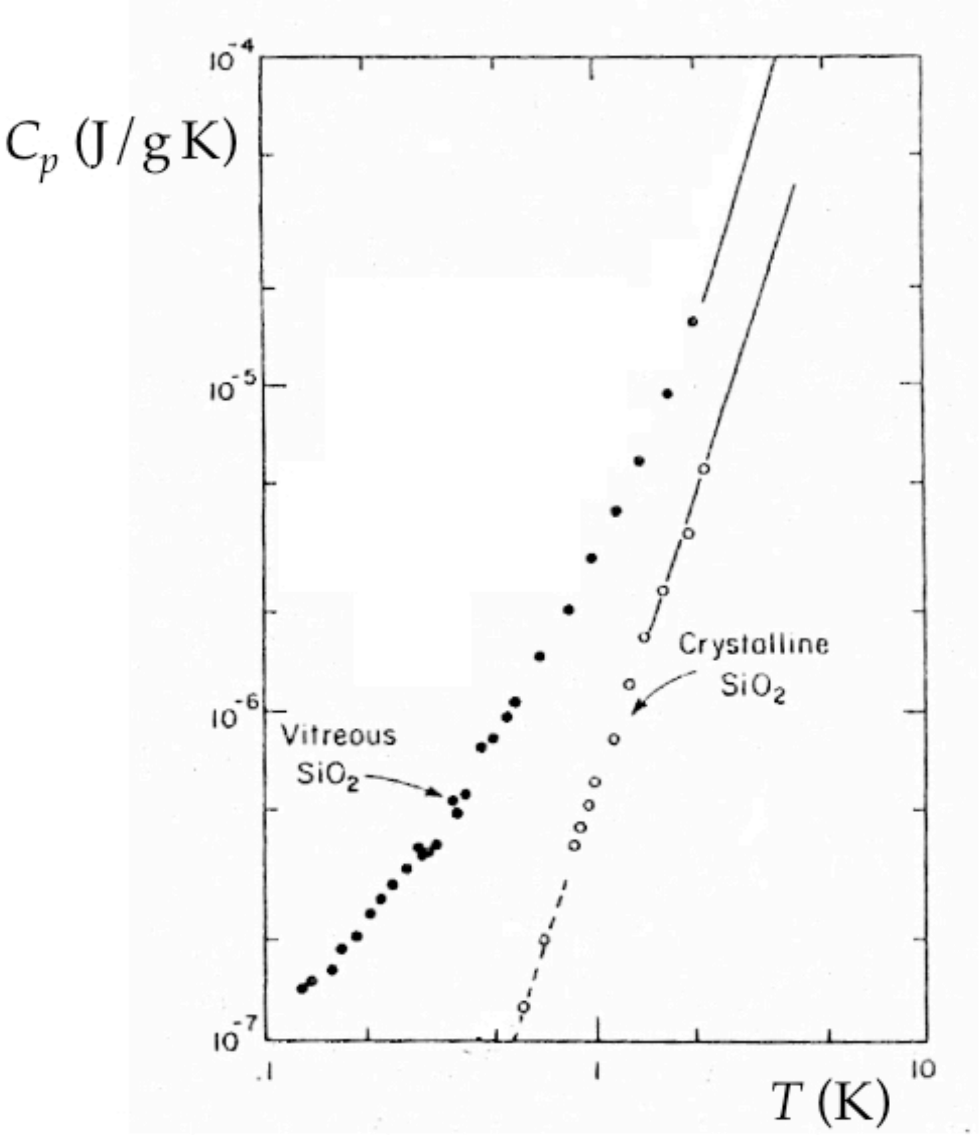
$$U(T) = n_0 \left(k_B T\right)^2 \underbrace{\int_0^\infty \frac{x}{e^x + 1}\,dx}_{\frac{\pi^2}{12}} \quad . \tag{7.8}$$

This definite integral can be evaluated exactly.

The low-temperature specific heat is

$$C_V = \frac{\pi^2}{6} n_0 k_B^2 T \quad . \tag{7.9}$$

The specific heat of amorphous SiO_2 at $T' = 0{,}1$ K, where the contribution varying as T^3 can be neglected, is about 10^{-7} J/g·K or $6 \cdot 10^{-6}$ J/mol·K.



The density of states n_0 with this $C_V(T')$ value is

$$n_0 = \frac{36 \cdot 10^{-6}}{\pi^2 k_B^2 T'} = 1,92 \cdot 10^{41}\ \text{J}^{-1}\text{mol}^{-1} = 3,06 \cdot 10^{22}\ \text{eV}^{-1}\text{mol}^{-1}. \quad (7.10)$$

Assuming that upper limit for the separation $(\Delta E)_{\max}$ between the levels is 0.1 eV we find the number of two-level systems

$$N_{\text{TLS}} = n_0 (\Delta E)_{\max} = 3,06 \cdot 10^{21}\ \text{mol}^{-1}\ , \qquad (7.11)$$

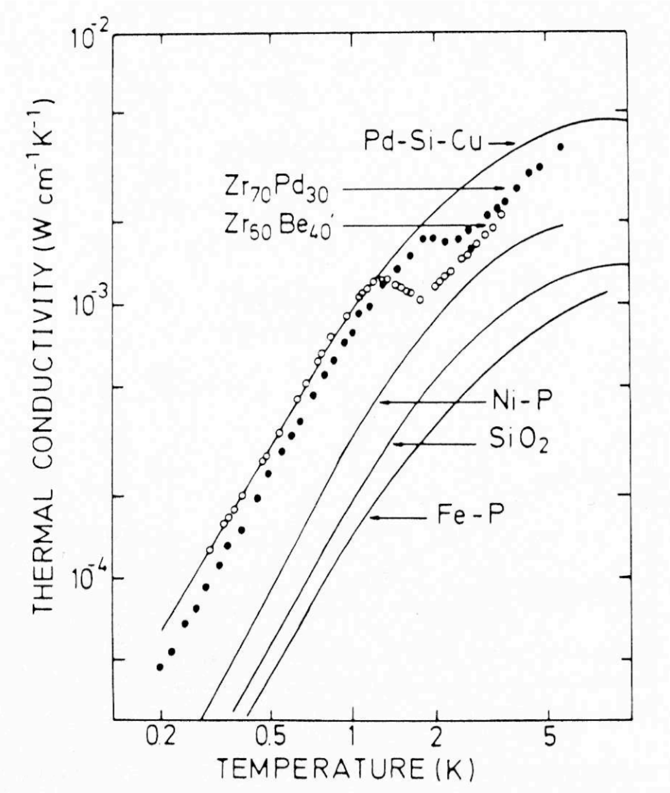
i.e., one two-level system per about two hundred SiO_2 groups.

Surprisingly, the values of the excess specific heat are similar for different types of amorphous materials.

The thermal conductivity $\lambda(T)$ of amorphous materials also behaves anomalously at low temperatures. It is considerably lower than that of periodic crystals and depends only slightly on chemical composition.

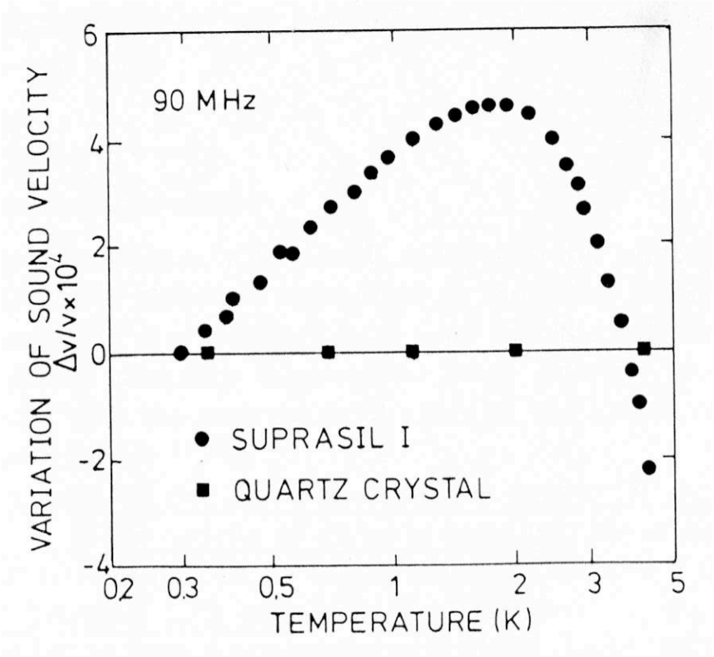
Below 1 K $\lambda(T)$ of amorphous materials is limited by phonon scattering involving two-level systems and it varies approximately as T^2.

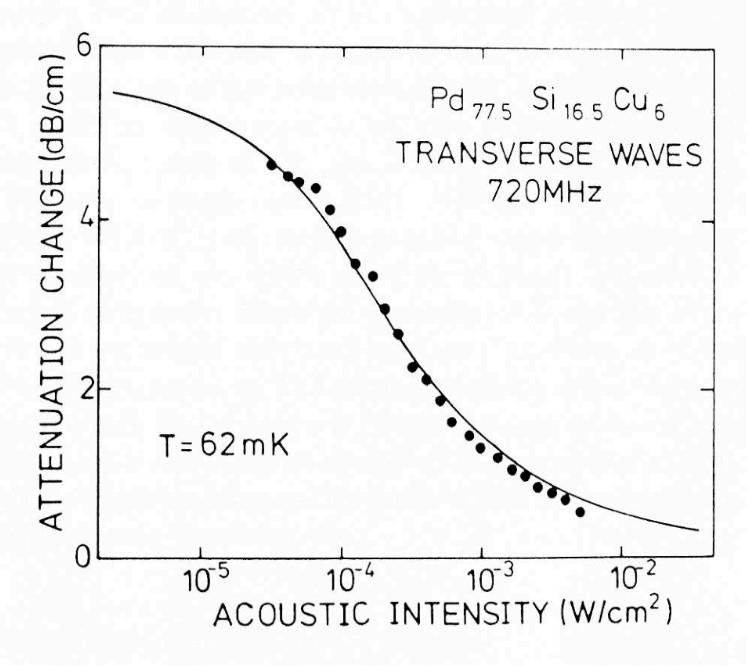
This scattering mechanism typically reduces $\lambda(T)$ to values an order of magnitude below the Casimir limit.



[from S. Hunklinger and A. K. Raychaudhuri, *Progress in Low Temperature Physics*, edited by D. F. Brewer (North-Holland, Amsterdam, 1986), Vol. IX, p. 265.]

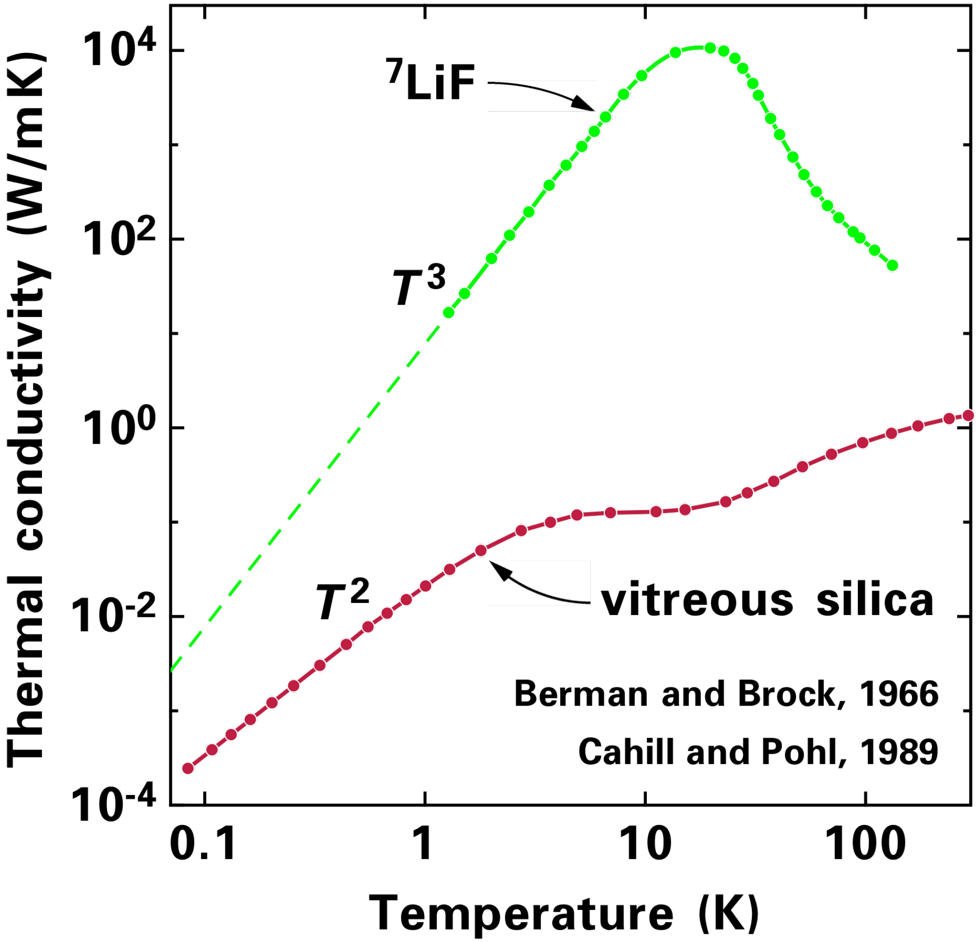
Interaction of the low frequency lattice excitations with two-level systems leads to anomalous temperature variation of the sound velocities and to saturation of the sound attenuation.





[from S. Hunklinger and A. K. Raychaudhuri, Progress in Low Temperature Physics, edited by D. F. Brewer (North-Holland, Amsterdam, 1986), Vol. IX, p. 265.]

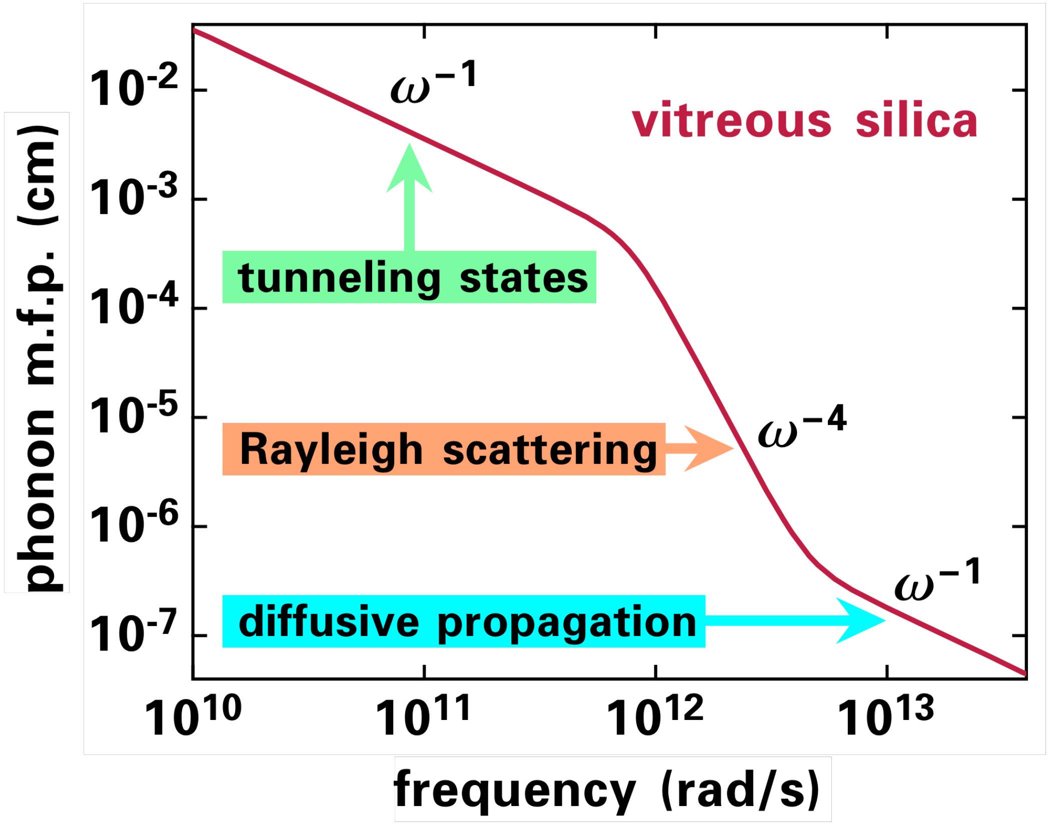
Transport of heat via lattice excitations



$$\lambda(T) = \frac{1}{3}\sum_i \int_0^\infty g_i(\omega) C_i(\omega,T)\, v_i\, l_i(\omega,T)\, \mathrm{d}\omega$$

$$l(\omega,T) = l(\omega)$$

Zaitlin and Anderson, 1975



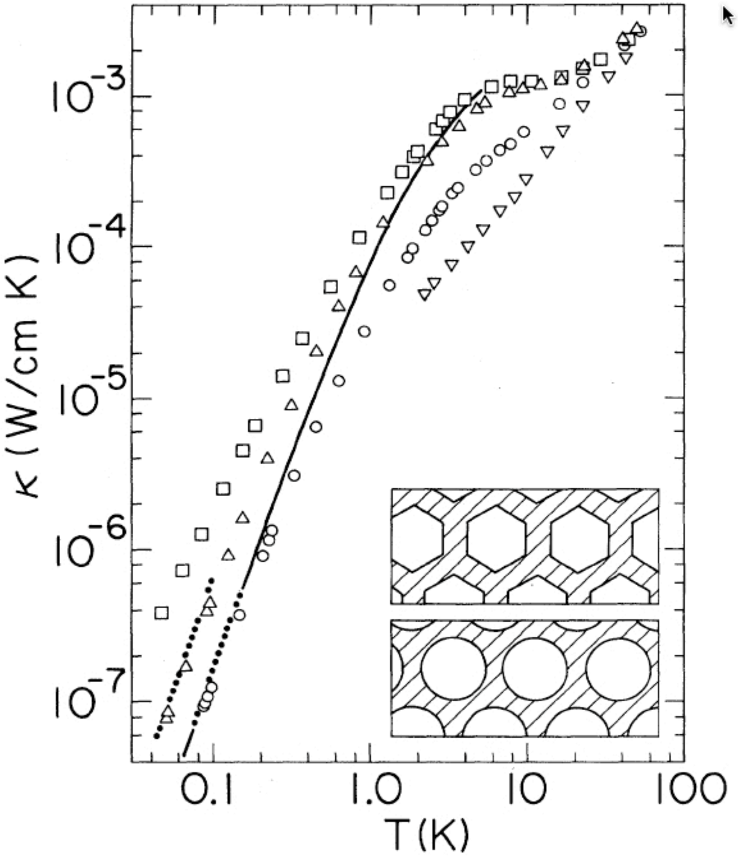
Composite glassy systems:

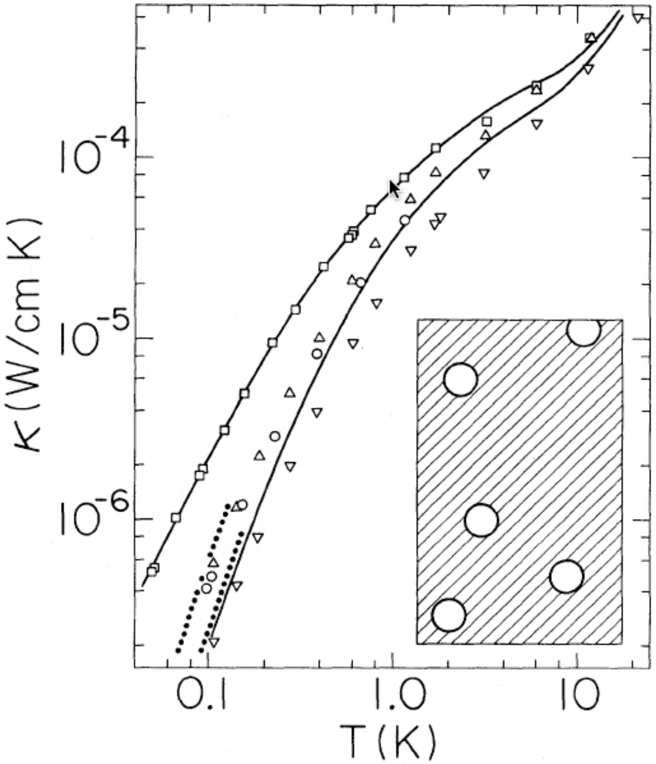
- fused capillary arrays of boro-silicate glass or policarbonate,
- boro-alumino-silicate glass containing mica crystallites.

Introduction of holes or crystallites in a glassy matrix produces a frequency-independent phonon mean free path.

This results in a suppression of the phonon mean free path below the value determined by the phonon scattering on tunneling states alone. The thermal conductivity of composite glassy systems shows a gradual increase of slope in $\lambda(T)$ with decreasing temperature.

At the lowest temperatures the $\lambda(T)$ variation is reported to be close to T^3.





[from M. P. Zaitlin and A. C. Anderson, Phys. Rev. B **12**, 4475 (1975);
E. P. Roth and A. C. Anderson, Journ. Appl. Phys. **47**, 3644 (1976)]

The composite glassy systems represent cases of extremely strong additional phonon scattering corresponding to mean free paths of the order of $10^{-4} - 10^{-3}$ cm.

If the mean free path l due to excessive scattering is long enough, the T^3 regime will not be reached down to the lowest temperatures usually accessible to thermal-conductivity measurements of the order of 0.05 K.

Umklapp processes in heterostructures and quasicrystals

The large-period modulation of the acoustic impedance across the superlattice layers, e.g., $(\mathrm{GaAs})_n(\mathrm{AlAs})_m$ creates the so-called mini-Brillouin zones.

The reciprocal lattice vectors associated with the mini-Brillouin zones give rise to the mini-Umklapp processes, which increase the thermal resistance. The corresponding phonon mean free path Λ_{ph} is expected to vary with the temperature approximately as $e^{\hbar G' v_{\mathrm{s}}/2k_B T}$, where $G' \ll k_B \theta_D / \hbar v_{\mathrm{s}}$ is the size of the mini-Brillouin zone. For comparison, in periodic crystals Λ_{ph} varies with T as $e^{\theta_D/2T}$.

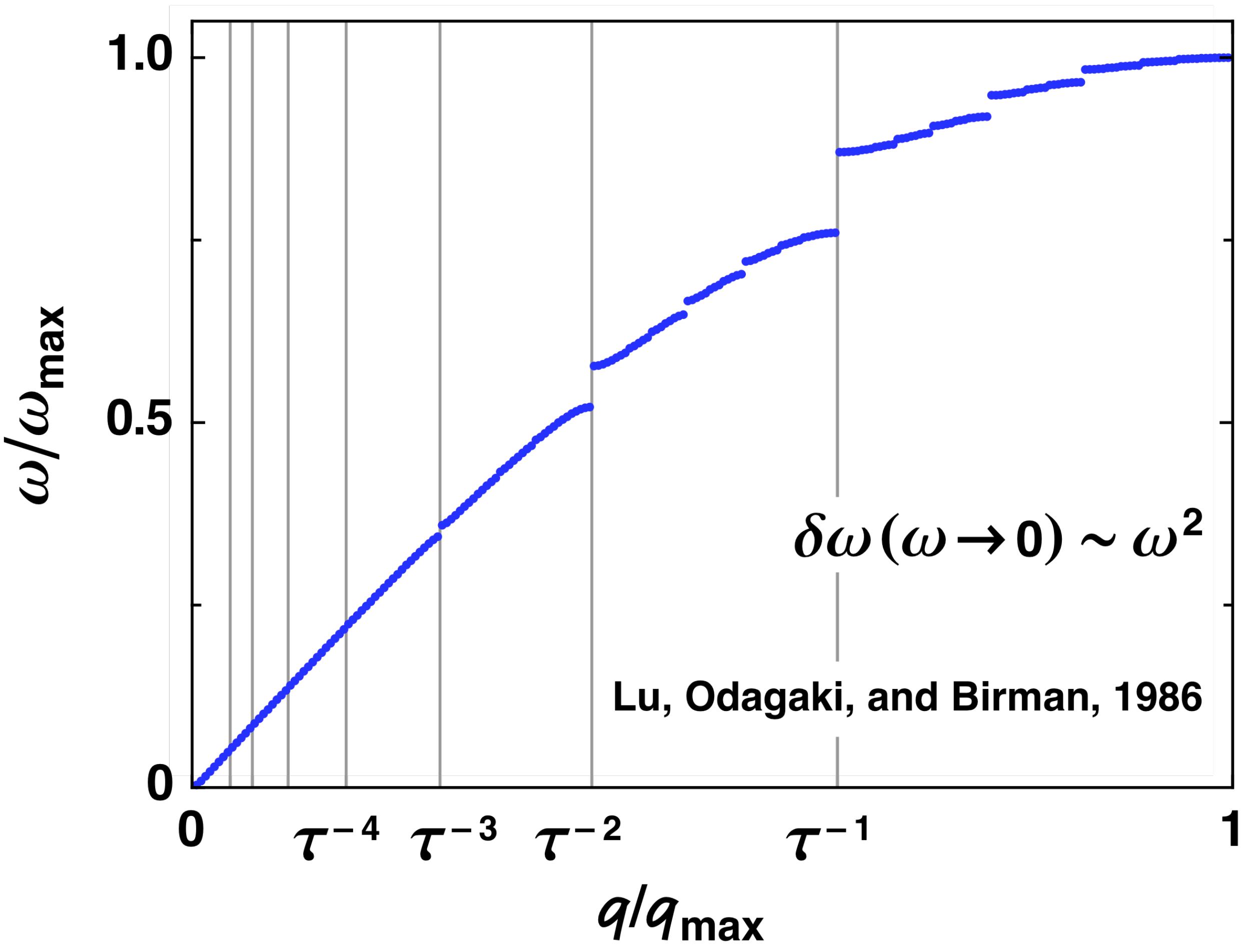
Quasicrystals

The characteristics of Umklapp scattering of lattice excitations in solids with periodic and quasiperiodic orders are distinctly different.

This is believed to be a direct consequence of the difference between the lattice excitation spectra of periodic and quasiperiodic lattices.

In a periodic crystal, the exponential decrease with decreasing temperature of high frequency phonons available for Umklapp processes leads to an exponential decrease of the Umklapp scattering rate of the phonons.

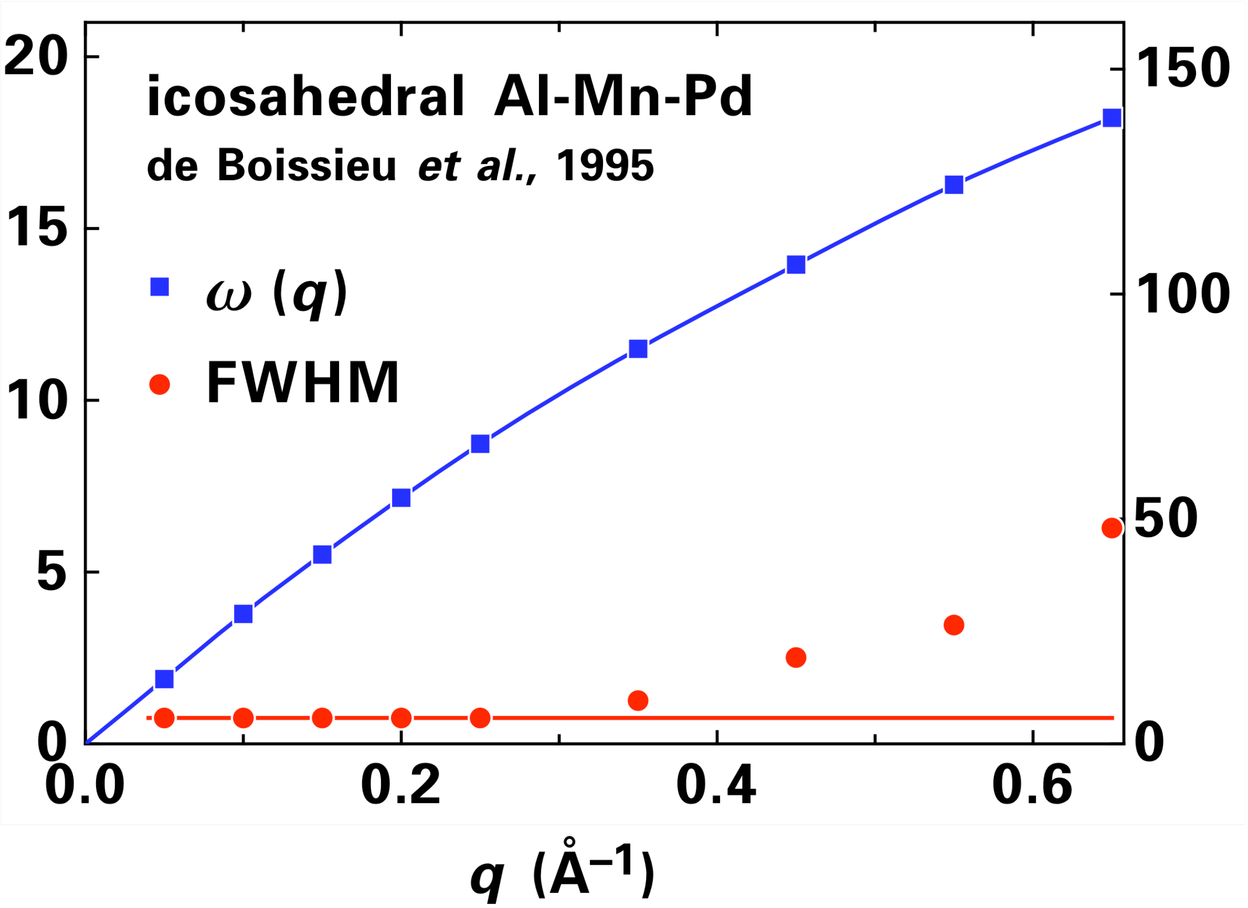
1D quasiperiodic lattice–excitation spectrum



$\delta\omega(\omega \to 0) \sim \omega^2$

Lu, Odagaki, and Birman, 1986

TA excitations–dispersion relation



In a quasicrystal the situation is apparently different, because the momentum of lattice excitations can be transferred to the lattice in inelastic scattering events by arbitrarily small portions, i.e., not limited in magnitude from below, resulting in a power-law decrease of the rate of Umklapp processes.

The average transport cross-section for the quasiperiodic Umklapp process is proportional to $\omega^2 T^4$, i.e., not exponential in frequency or temperature as is valid for Umklapp processes in periodic crystals.

Structural scattering of the lattice excitations in quasicrystals

Consider the “quasiperiodic” Umklapp processes, which involve both phonon-phonon scattering and Bragg reflections. Suppose, that the conservation laws do not prohibit the three-phonon processes.

Then, the frequency dependence of the transport cross-section is given by

$$\left\langle \sigma_{transp} \right\rangle = A\sigma\,\omega/\omega_{max} \;,$$

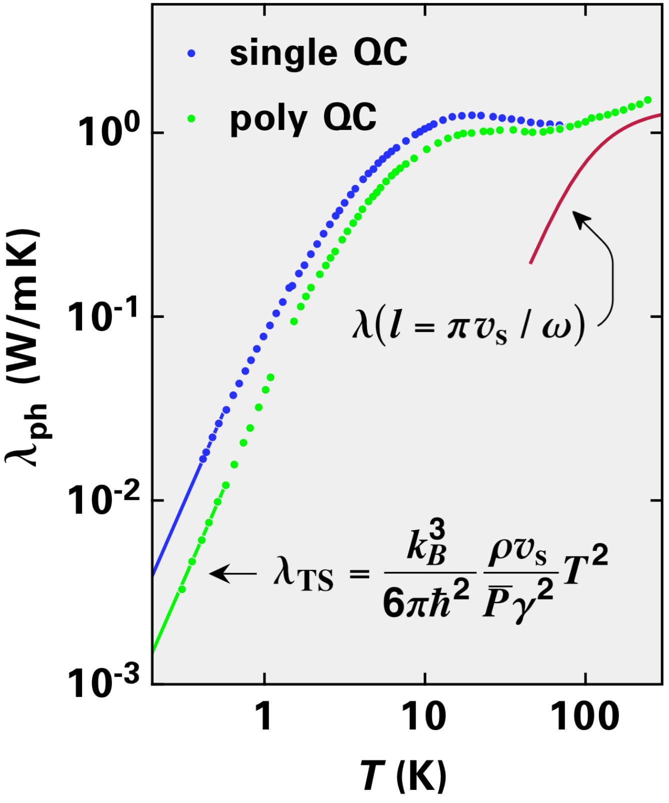
where σ is the full phonon-phonon scattering cross section. For three-phonon scattering the full cross-section is proportional to ωT^4, because the standard three-phonon matrix element is proportional to $\sqrt{\omega_1 \omega_2 \omega_3}$ and the phase volume rises as T^2 (six free components minus four conservation laws).

Here it is supposed that only one phonon in the three-phonon process has a low frequency and that the two others are merely thermal ones with their frequency proportional to the temperature.

The average transport cross-section for the anharmonic and quasiperiodic structural scattering, together denoted as quasiperiodic Umklapp process, is proportional to $\omega^2 T^4$.

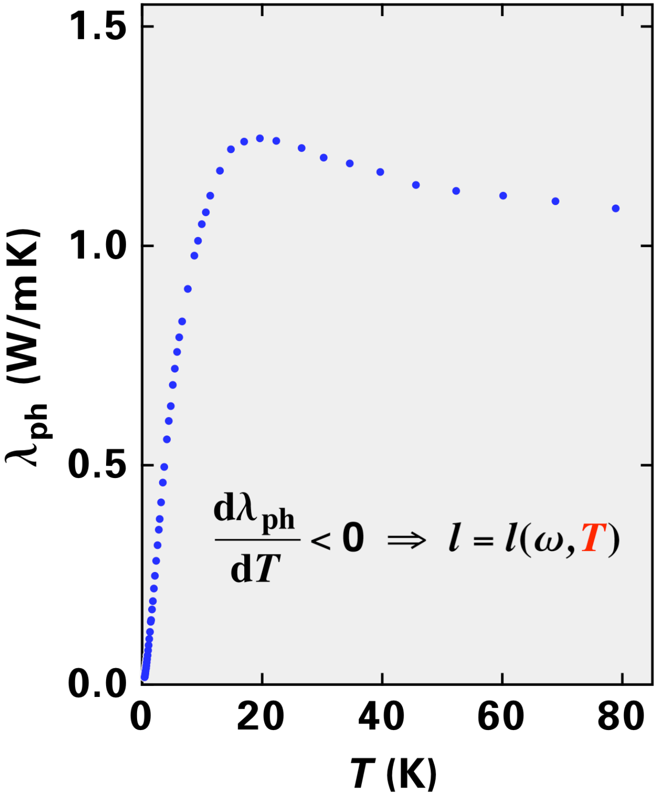
Lattice thermal conductivity

icosahedral Al-Mn-Pd QC's



Lattice thermal conductivity

Al-Mn-Pd single quasicrystal

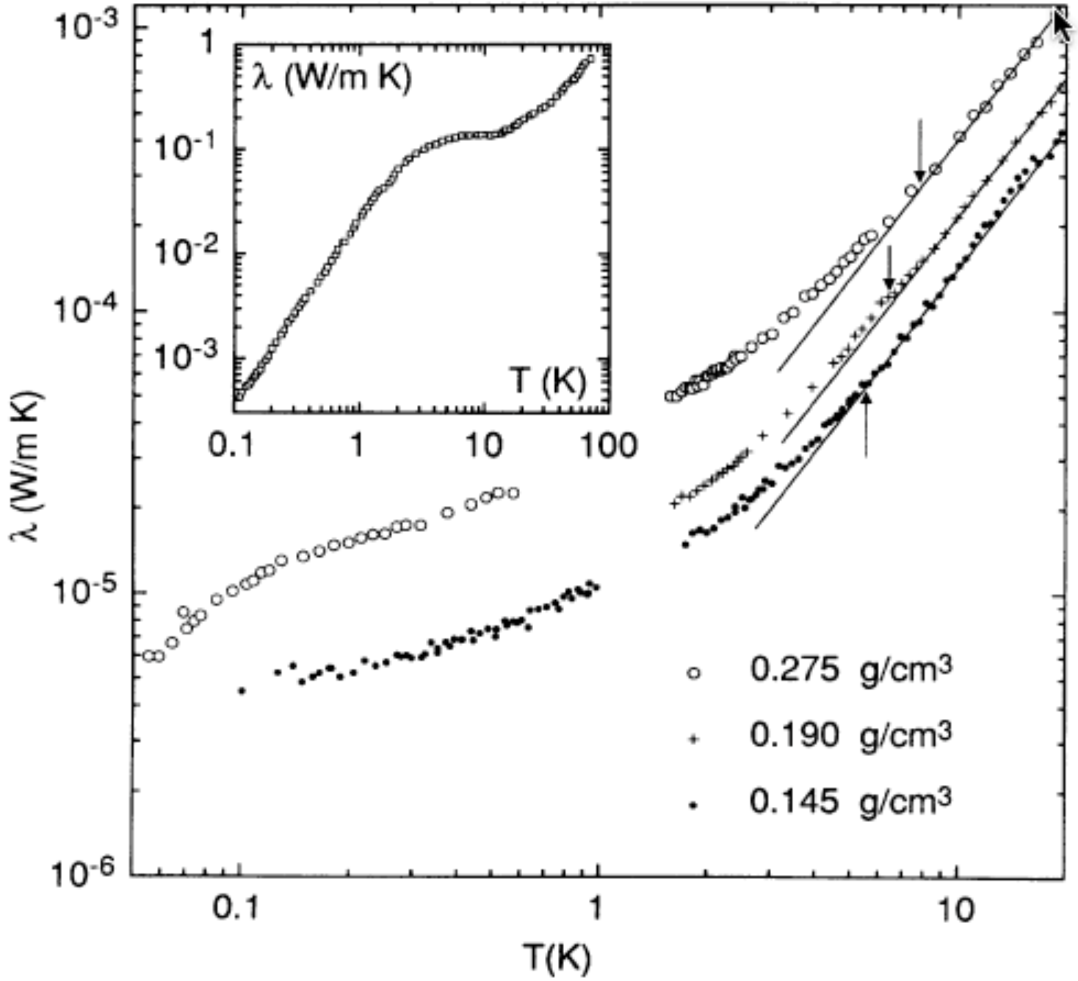


Transport of heat in aerogels and opals

The $\lambda(T)$ curves for silica aerogels of different densities.

At high temperatures the T dependence of λ is the same for different densities.

The inset shows $\lambda(T)$ for amorphous SiO_2.

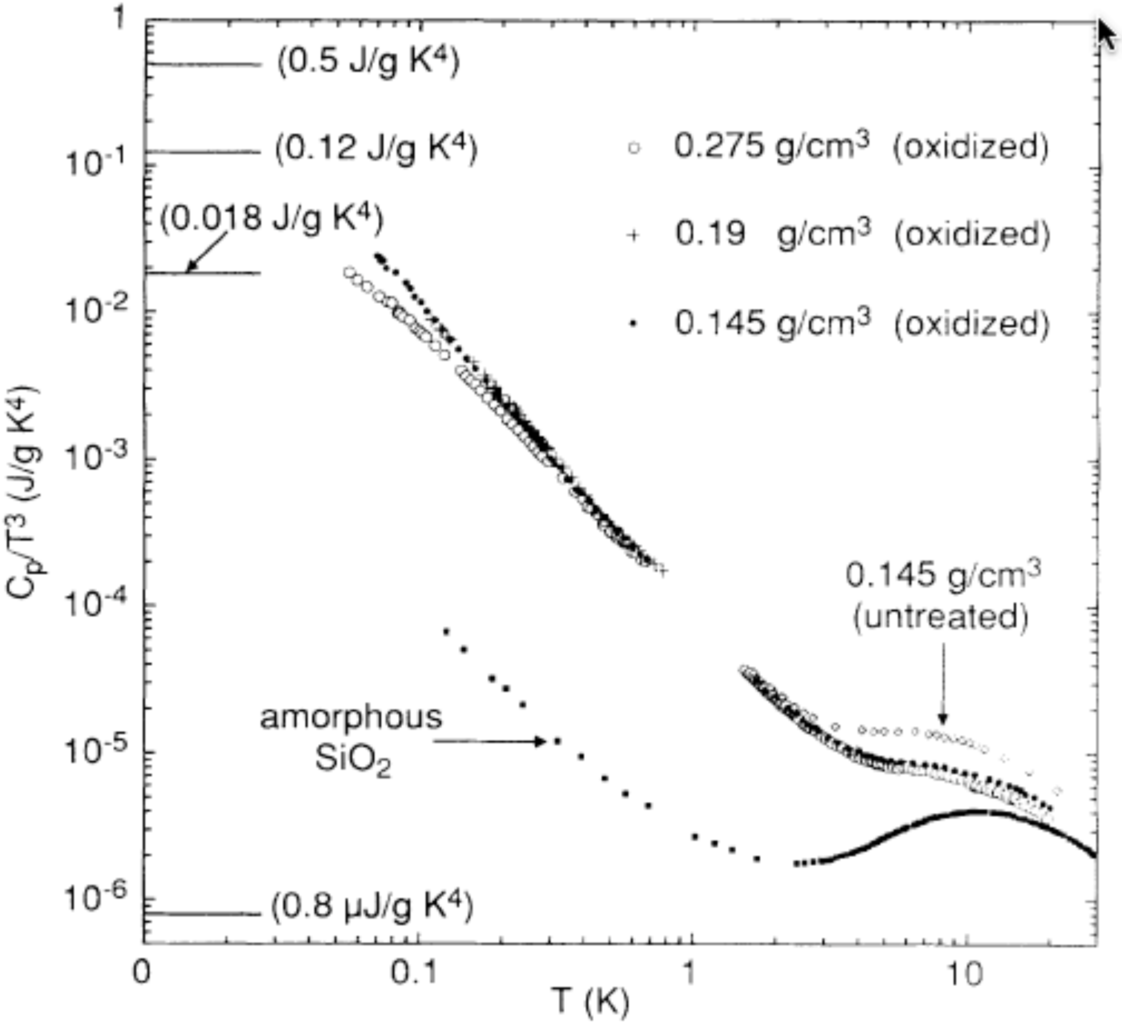


[from A. Bernasconi *et al.*, Phys. Rev. B **45**, 10363 (1992)]

Temperature dependence of the specific heat of various silica aerogel samples and of amorphous SiO_2.

Data are plotted as C_p/T^3 vs T on a double logarithmic scale.

Horizontal lines are the Debye limits.



[from A. Bernasconi *et al.*, Phys. Rev. B **45**, 10363 (1992)]

Opals are structures composed of the closed packing of silica spheres in the size range typically between 150 to 300 nm. Chemical formula $SiO_2 \cdot n\,H_2O$.

Depending on the method of preparation, the temperature variation of the thermal conductivity of opals can be either similar to $\lambda(T)$ of quasicrystals (type 1 opals) or amorphous solids (type 2 opals).