NR processes and the lattice thermal conductivity of polydiacetylene (PDA) single crystals at very low temperature

LETTER TO THE EDITOR

NR processes and the lattice thermal conductivity of polydiacetylene (PDA) single crystals at very low temperature

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Abstract. The lattice thermal conductivity of polydiacetylene (PDA) single crystals in the temperature range 0.5–1.5 K is studied. It is considered that the phonons of lower frequencies could combine to form ones of higher frequencies through combination processes (i.e. NR processes), and this scattering process can form a thermal resistance mechanism. A two-fluid model is used to discuss this phonon scattering process. The numerical calculation of thermal conductivity for PDA single crystals has been carried out over the above temperature range. Good agreement with experimental measurements was obtained.

In 1984, Wybourne and co-workers reported results of measurements of the thermal conductivity of polydiacetylene (PDA) single crystals [1]. The results presented a broad plateau in the thermal conductivity between 1 K and 50 K for PDA single crystals, characteristic of an amorphous material. However, there is a lot of evidence indicating that the samples were macroscopic crystals of high quality. In order to explain the anomalous thermal conductivities in PDA single crystals, they attributed it to scattering of acoustic phonons by low-energy optical phonons. Each optical mode was described as a two-energy-level system, the scattering being elastic. The results agree with experiments very well above 4 K and below 100 mK. In the intervening region an overestimation of the thermal conductivity appears and the peak is located at 0.8 K. In order to eliminate this non-conformity, they introduced stacking faults. When they calculated τ_{TLS}^{-1}, the energies of the optical modes which were used in the summation were 0.5, 1.0, 1.55, 1.72 and 2.33 meV respectively, and most of these modes correspond to the infrared modes above 4.2 K [2], since the value of $k_B T$ when $T = 1$ K is about 0.86 meV. So around 0.8 K, most optical modes are not excited. Therefore, their theoretical treatment is questionable.

In this Letter, we will give a new explanation for the thermal conductivity around 0.8 K in PDA single crystals. We consider that this thermal resistance is due to the phonons of lower frequencies combining ones of higher frequencies to form through a combination process (i.e. NR process as below). In previous theories of thermal conductivity, it is usual to treat N and U processes respectively, assuming that N processes do not contribute to thermal resistance and U processes do. We will see below that two phonons having lower frequencies could combine to produce one phonon
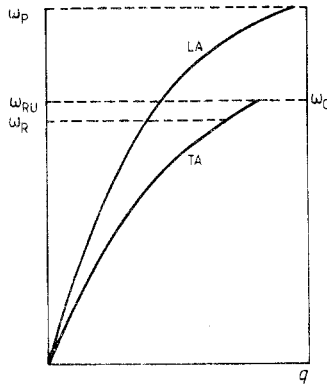
Figure 1. Frequency construction for propagating and reservoir modes for ideal phonon dispersion.

having a higher frequency, whose wavevector is in the region where the phonon scattering process can form thermal resistance. A two-fluid model [3] will be used to discuss the phonon scattering processes.

In the two-fluid model, the vibrational modes are divided into two groups, the propagating modes and the reservoir modes. The propagating modes contain the momentum of the phonon gas in a temperature gradient, and the reservoir modes, which are close to equilibrium, act as a momentum sink via the anharmonic processes between these two groups. The modes having lower frequencies are non-dispersive and provide thermal transport processes (anharmonic N processes), ones having higher frequencies control thermal resistive processes. The modes which can form thermal resistance are called the resistive group or the reservoir group and include: (i) those lying between ω_{RU} and ω_P, which are highly dispersive and have low group velocities, near the Brillouin-zone boundary (BZB), where wavevector reduction occurs for U processes; (ii) those which lie between ω_R and ω_{RU}, where U processes do not occur, non-intrinsic resistive processes (such as isotope, defect and dislocation scattering) whose dependence on frequency becomes an important factor.

In order to clarify the functions of N and U processes involving only phonons with frequencies less than ω_R they were called NN processes, and they do not contribute to entropy production; those processes which link the propagating modes with the reservoir modes (with a resultant phonon of frequency greater than ω_R), were called NR processes. The NR transitions which transfer momentum from propagating to reservoir modes are dominated by those processes in which a low-frequency mode ω combines with one of much higher frequency ω', and $\omega + \omega'$ must now exceed ω_R. Using the notation of Armstrong [3], the relaxation rate for the NR process is

$$\tau_{NR}^{-1} = (\gamma^2 T \omega \pi / 4 \rho \bar{V}^2) \Delta C(\omega_R, \omega_C) \tag{1}$$

where γ, the Grüneisen constant, is a measure of anharmonicity, ρ is the density, and $\bar{V}$ is the Debye average of the phonon velocity. The specific heat per unit volume C is broken up into spectral components, and $\Delta C(\omega_R, \omega_C)$ denotes the contribution to C from all the reservoir modes, i.e. modes for which $\omega_R \leqslant \omega \leqslant \omega_C$, ω_C being the boundary frequency.

The NN process does not contribute to thermal resistance. It is only necessary to include the boundary and NR scattering for the thermal conductivity near 0.8 K. When we calculate τ_{NR}^{-1}, we only need to include those modes which lie between ω_R and ω_C.

Table 1. The parameters used in calculating the lattice thermal conductivity κ of PDA single crystals.

B^{-1} (s^{-1})	$\bar{V}$ (ms^{-1})	θ_D (K)	ρ (kg m^{-3})	γ	ρ_a (m^{-3})
1×10^7	1×10^3	50	1422	1.5	9.415×10^{28}

The Debye approximation is used, but the integral regime could be varied, so we have [4]

$$\Delta C = 9\rho_a k_B \left(\frac{T}{\theta_D}\right)^3 \int_{x_R}^{x_C} \frac{e^y y^4}{(e^y - 1)^2} \, dy \tag{2}$$

where $x_C = \hbar\omega_C/k_B T$, $x_R = \hbar\omega_R/k_B T$ and $\rho_a = N/V$ is the number of atoms per unit volume. Substituting (2) into (1)

$$\tau_{NR}^{-1} = \frac{\gamma^2 T \omega \pi}{4\rho \bar{V}^2} 9\rho_a k_B \left(\frac{T}{\theta_D}\right)^3 \int_{x_R}^{x_C} \frac{e^y y^4}{(e^y - 1)^2} \, dy. \tag{3}$$

The total scattering rate is given by

$$\tau_T^{-1} = \tau_B^{-1} + \tau_{NR}^{-1} \tag{4}$$

where τ_B^{-1} is a frequency-independent geometric scattering rate and τ_{NR}^{-1} is a frequency-dependent term given by equation (3).

After finding out the total scattering rate, the thermal conductivity is given by [5]

$$\kappa = \frac{k_B}{2\pi^2 \bar{V}} \left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\theta_D/T} \tau_T(x) \frac{x^4 e^x}{(e^x - 1)^2} \, dx \tag{5}$$

where $x = \hbar\omega/k_B T$. The parameters which were used in the calculation are given in table 1.

The numerical calculation of thermal conductivity for PDA single crystals from (5) have been carried out over the temperature range 0.5–1.5 K. Good agreement with the results of measurements over the above temperature range was obtained. The only adjustable parameter is ω_R. With increasing temperature, the optical modes were excited gradually, the optical–acoustic phonon scattering becoming the main scattering mechanism, according to the interpretation of Wybourne.

References

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