Point defects and thermal conductivity of C_{60}

B. Sundqvist

Department of Experimental Physics, Umeå University, S-90187 Umeå, Sweden

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Recent literature data for the thermal conductivity κ of single-crystal C_{60} are analyzed using a standard model. It is shown that in the intermediate range 100–250 K, below the rotational transition, κ can be described extremely well by a model taking into account phonon and point defect scattering only. The magnitude derived for the phonon-phonon scattering term agrees very well with an estimate from a simple model.

The thermal conductivity κ of single-crystal C_{60} has recently been measured by Yu and co-workers[1,2] in the temperature range $30 < T < 300$ K. κ was found to have a very small magnitude and a T dependence in general agreement with that expected from its crystal structure: In the rotationally disordered (plastic crystal) fcc high-T ($T > 260$ K) phase, κ was very low and almost independent of T, as commonly observed for other plastic crystal phases[3] with orientational disorder. At the rotational locking fcc-to-sc transition κ increased by about 25%, and below 260 K it had an approximate T^{-1} behavior as expected for a crystalline solid with both long- and short-range order. However, two anomalous features were noted: First, the temperature dependence was weaker than a true T^{-1} behavior, and second, below 90 K κ was time dependent, resulting in a shoulder structure in the measured data. This behavior was explained in terms of the accepted model for the low-T phase of C_{60}, in which molecules jump between several discrete orientational states in contrast to the almost free rotation in the fcc high-T phase. It was assumed that this jump motion scattered phonons at a rate inversely proportional to the average librational frequency of the molecules and a thermal activation factor $e^{-u/k_B T}$, where u is the energy barrier between the different orientational states. Although this model explained both the T dependence of κ and its low-T time dependence, it gave a somewhat too strong T dependence in the intermediate range 120–260 K. The weaker-than-T^{-1} behavior of the experimental data in this range is typical for insulators with point defects, however, and it was decided to investigate whether such a model would apply here. I show below that a better agreement with experiment is in fact found in this temperature range under the simpler assumption that the acoustic phonons responsible for heat transport[4] are scattered by each other and by point defects only. The point defects of this model might be either true point defects or the misoriented ratcheting molecules discussed above.

The thermal conductivity of electrically insulating solids is usually modeled in terms of the relaxation-time model, with the simplifying assumption that the phonon spectrum can be described in a Debye model characterized by a Debye temperature Θ_D. The latter should be a reasonable model for long-wavelength acoustic phonons in the simple lattice of C_{60}. The expression for κ is then[4]

$$\kappa = (k_B/2\pi^2 v)(k_B/\hbar)^3 T^3 \int_0^{\Theta_D/T} \tau x^4 e^x (e^x - 1)^{-2} dx \ , \quad (1)$$

where $x = \hbar\omega/k_B T$, τ is the relaxation time, and v ($= 2 \times 10^3$ m s^{-1}) the sound velocity. In the present case, τ is assumed to contain the two components τ_p due to phonon-phonon scattering and τ_d due to point defects. We assume that τ_p can be modeled by the standard term $\tau_p^{-1} = AT^3 x^2$, which is a good approximation above about $\Theta_D/4$; below this, the term predicts a constant κ in contrast to the rapid (exponential) increase in κ with decreasing T actually observed[4] in insulators because of the freezing out of umklapp processes. For point defects, $\tau_d^{-1} = T^4 x^4$. This term takes into account the density of real point defects in the material, such as impurities, vacancies, and interstitials, which should be fairly large in a weakly bound crystal such as C_{60}. However, such a term should also be able to describe approximately the interaction of a phonon with an orientationally ratcheting single molecule, which is basically also a point defect. The total relaxation time is thus written

$$\tau^{-1} = \tau_p^{-1} + \tau_d^{-1} = AT^3 x^2 + BT^4 x^4 \ . \quad (2)$$

Since it is usually not possible[4] to add phonon thermal resistivities directly we must insert (2) into (1) for the analysis.

Data for κ vs T in C_{60} were obtained by digitizing Fig. 1 of Ref. 1 and the model described was fitted to these data between 125 and 250 K using the same nonlinear gradient search method as used in a recent study[5] of κ in a high-T_c superconductor. Literature data for Θ_D, as obtained from the specific-heat capacity, usually range[6,7] from 50 to 70 K and an intermediate value of 60 K was chosen for this fit. The resulting parameter values found were then $A = 2.51 \times 10^5$ K^{-3} s^{-1} and $B = 2.70 \times 10^4$ K^{-4} s^{-1}, and the fitted function is shown in Fig. 1. The agreement between the data and the fitted function is excellent, with a rms difference of only 6.7 mW m^{-1} K^{-1} between the data and the function in the range studied. Only in the range below 90 K, where κ is time dependent, is there a significant difference between the fitted function and the data. Below 60 K the agreement between model and data again improves, which is probably a coincidence. The deviations between the data and the fitted function were not very sensitive to the choice of Θ_D; over

the range $50 < \Theta_D < 90$ K the rms difference varied from 6.6 to 6.8 mW m^{-1}K^{-1}, with higher values for Θ_D giving a better fit. Different choices of Θ_D result, of course, in different values for the fitted parameters, such that A increases from 2.1×10^5 to 3.8×10^5 when Θ_D increases from 50 to 90 K, while B decreases from 3.3×10^4 to 1.7×10^4 over the same range. Since the correct value for Θ_D is uncertain, there is a significant uncertainty in the parameter values, but the actual magnitudes of the scattering terms depend only weakly on Θ_D.

A comparison between Fig. 1 and the corresponding figures in Refs. 1 and 2 shows that the present model gives a better fit to the data in the range 100–250 K than that used previously. The model implicitly assumes a constant point defect density, while the rate of orientational jumps should be rather strongly temperature dependent because of the thermal activation term mentioned above. A reasonable conclusion is that true crystal point defects, such as vacancies, are common in the material and should be taken into account in the analysis. On the other hand, it is difficult to account for the time dependence of κ below 90 K in the present model. A possible explanation might be a slow continuous orientational ordering at low T, connected with "freezing" of the orientational jumping: Above 90 K the effective point defect density is approximately constant, but below this an orientational locking begins. The time dependence of κ might then be caused by a slow, continuous ordering with time as molecules form orientational domains (or such domains coalesce) during a long-time anneal. However, the final decrease in $|d\kappa/dT|$ below 80 K remains unexplained.

κ is dominated by phonon-phonon interactions at high T, and if we neglect point defect scattering τ_p alone, inserted into (1), gives $\kappa = 170/T$ W m^{-1}K^{-1}. We can compare this with the predictions of Slack's well-known formula[4,8]

$$\kappa = BMan^{1/3}(\Theta_D)^3/T\gamma^2 . \tag{3}$$

Here, B is a numerical constant, M is the average molecular weight of the atoms or molecules, a is the cube root of the atomic volume, n is the number of atoms in the unit cell, and γ is the Grüneisen parameter. For γ, it is common practice to use the thermal average, and here we should use a value pertaining to intermolecular vibrations
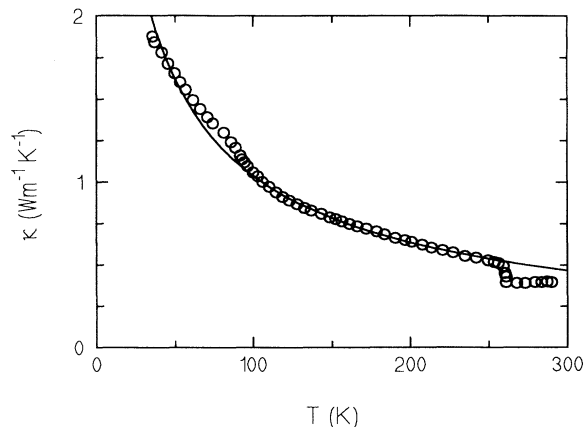

FIG. 1. Thermal conductivity κ for C_{60} vs temperature T. Circles are data from Ref. 1, while the curve is fitted to these data using Eq. (1).

only. Lundin et al.[9] recently gave a value $\gamma = 1.40$ for this quantity in the low-T phase; however, they used the total specific heat when calculating this value. Using instead the component due to the molecular vibrations of the lattice only[6] results in the surprisingly high value $\gamma = 9.8$. However, inserting this into (3) together with the chosen value for $\Theta_D = 60$ K and literature data for the other parameters gives $\kappa = 174/T$ W m^{-1}K^{-1}. The excellent numerical agreement is of course a coincidence, but it is gratifying to see that the fitted parameters have a reasonable magnitude.

In conclusion, I have shown that a simple point defect model can describe the thermal conductivity of C_{60} very well in the intermediate temperature range. The model is unable to describe the low-T time dependence observed in κ, however. Since point defects should be common in these materials they should be included in a detailed model for κ vs T, and it is suggested that a combined model containing both point defect scattering and the effects of orientational jumps would probably be necessary for a complete and accurate description of κ in C_{60}.

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