

Origin of the Exceptionally-Low Thermal Conductivity of Fullerene-Derived PCBM Thin Films

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Abstract

I. INTRODUCTION

Phase change random access memory (PRAM) is unique among semiconductor devices because heat is intrinsic to the operation of the device, not just a by-product. Here, we apply a material that is exotic in the context of typical semiconductor devices but has highly desirable properties for PRAM. Thin films of C60 are semiconducting and show very low thermal conductance. By inserting a C60 layer between the phase change material and the metal electrode, we dramatically reduced the heat dissipation and, thereby, the operating current. A PRAM device incorporating a C60 layer operated stably for more than 105 cycles.[?]

A novel type of multi-layer vacuum insulation based on carbon nano-materials, namely fullerenes, has been demonstrated. The design is based on unique thermal insulation properties of fullerenes, arising from their electronic structure, as well as proprietary deposition technique using thin layers of reflective material as a support. As a result of experimental testing, the fabricated samples of fullerene-based insulation were shown to possess R-values of 36 to 40 per inch of thickness at cryogenic temperatures, which considerably exceeds those of commonly available insulation materials (for example, polyurethane (R6.7), expanded polystyrene (R3.8), and even vacuum insulated panels (R924)). Application of such insulation will result in significant size and weight reduction while maintaining cost-effectiveness.[?]

We have argued that our sample of C60 exhibits a substantial amount of disorder. An indication of this is given by the phonon mean free path. The mean free path l can be estimated using the simple Debye formula for which is given by $(1/3) c_v l$, where c is the phonon velocity and v is the heat capacity per unit volume of the phonons which are responsible for the heat transport. We associate the vibrating unit with the C60 molecule $c_v = 25 \text{ J mol}^{-1} \text{ K}^{-1}$, 2400 mol m^{-3} and approximate c with the sound velocity 2103 m s^{-1} , which yields $l \approx 50$ at 200 K about three lattice constants. Although the absolute value for l obtained in this way needs to be treated with caution, the true l is almost certainly rather small. It probably follows that the amount of defects must be substantial but a quantification is not possible without specific knowledge of their ability to scatter phonons.[?]

Using a microcalorimeter, we have measured the specific heat of C60 and K3 C60 thin films from 6400 K. The results can be understood by analyzing the phonon modes; the electronic specific heat of K3C60 is a small fraction of the total. While C60 displays a clear

separation of energy levels between interball and intraball modes, the added alkali optical modes in K₃C₆₀ blur this separation because they appear in the gap. Additionally, the acoustic modes of K₃C₆₀ soften compared to pure C₆₀.[?]

The phonon component (γ 55.4 K) is evaluated on the basis of the Debye model using the Debye temperature (θ_D). Debye parameters are calculated from the known sound velocities. The general and partial Grüneisen parameters are calculated as functions of temperature. The results obtained for the high-temperature phase indicate that rotations of C₆₀ molecules are strongly hindered and intercorrelated.[?]

Using a novel microcalorimeter, we have performed the first specific heat measurements of C₈₄, Sc₂@C₈₄, C₈₂, and La@C₈₂ 10300 K. We analyze these results using a framework based on the phonon modes in these materials. C₈₄ compares qualitatively to C₆₀ with a clear separation between inter- and intraball modes, although the interball modes are significantly softer in C₈₄. For Sc₂@C₈₄ the added optical modes due to the metal atoms are high-energy Einstein modes comparable to the on-ball modes. Thus, the specific heat of Sc₂@C₈₄ is very similar to that of C₈₄; and likewise, the specific heat of La@C₈₂ resembles that of C₈₂. Remarkably, however, C₈₂ contrasts sharply with the other empty fullerenes in that it shows no separation of energy levels between inter- and intraball modes. We speculate about possible causes of this anomalous behavior. In conclusion, we have shown from specific heat experiments that C₈₄ behaves qualitatively like C₆₀ in terms of a separation of energy levels between interball and intraball modes. Thus, C₈₄ is a molecular solid like C₆₀ with weak bonds between the balls and strong bonds on the balls. However, C₈₄ shows significantly softer interball modes than C₆₀, saturating by 10 K, implying that the highest energy interball modes are below 1 eV. Adding Sc inside the balls to make Sc₂@C₈₄ makes almost no difference to C₈₄ because the Sc optical modes are high-energy modes that add into the intraball modes instead of appearing in the gap as they do for K₃C₆₀.¹⁶ C₈₂, however, differs even more severely from the other pure fullerenes studied. It shows no two-tiered behavior in C₈₂, and hence no separation of energy levels. La@C₈₂ actually shows somewhat more separation of energy levels than pure C₈₂ due, we suggest, to a stiffening of low-energy on-ball modes from the LaC bond, but it too has no true separation of energy levels.[?]

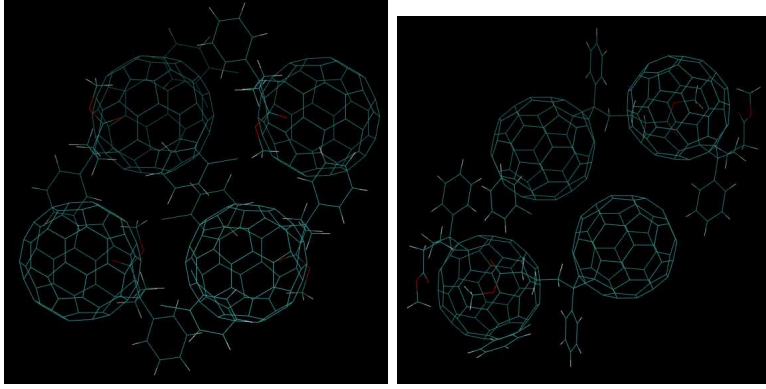


FIG. 1: film thickness dependant thermal conductivity of a-Si from experiment.

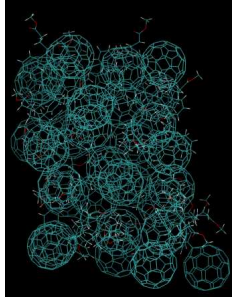


FIG. 2: film thickness dependant thermal conductivity of a-Si from experiment.

II. THEORETICAL FORMULATION

A. Vibrational Thermal Conductivity

$$k_{vib} = k_{ph} + k_{AF}, \quad (1)$$

III. SUMMARY