Specific heat of \( C_{60} \) and \( K_3C_{60} \) thin films for \( T = 6 - 400 \) K

K. Allen and F. Hellman

Department of Physics, University of California, San Diego, California 92093

(Received 13 January 1999; revised manuscript received 14 May 1999)

Using a microcalorimeter, we have measured the specific heat of \( C_{60} \) and \( K_3C_{60} \) thin films from 6–400 K. The results can be understood by analyzing the phonon modes; the electronic specific heat of \( K_3C_{60} \) is a small fraction of the total. While \( C_{60} \) displays a clear separation of energy levels between interball and intraball modes, the added (alkali) optical modes in \( K_3C_{60} \) blur this separation because they appear in the gap. Additionally, the acoustic modes of \( K_3C_{60} \) soften compared to pure \( C_{60} \).

I. INTRODUCTION

\( C_{60} \) was discovered in 1985 (Ref. 1) and has been widely available since 1991.\(^2\) Shortly thereafter it was found that \( K_3C_{60} \) is a metal and a superconductor,\(^3\) with the surprisingly high transition temperature of 19 K. This marked the beginning of a full-blown research effort to understand all kinds of fullerene, with particular emphasis on alkali-intercalated \( C_{60} \) materials.

Pure \( C_{60} \) draws research interest as a novel molecular solid because the molecular units are so large and symmetric. Structural and bonding issues are of primary importance, not only intrinsically but also in their effects on electronic properties. The \( A_1C_{60} \) materials are interesting because they are not conventional metals, as numerous experiments have shown. The most striking evidence for atypical behavior comes from the nonsaturation of the resistivity with temperature.\(^4\) Both \( K_3C_{60} \) and \( Rb_3C_{60} \) have room-temperature resistivity near 1.5 \( \mu \)Ohm cm, four times larger than the Ioffe-Regel limit, implying a mean free path shorter than even the intermolecular spacing. As the temperature increases up to 800 K, the resistivity never levels off, rising beyond the point where the mean free path is shorter than even the interatomic spacing. Thus, the simple Drude formula for mean free path is inappropriate for these materials.

In addition, the weak bonding and consequently large distance between the cages results in a narrow \( [\approx 0.5 \text{ eV} \text{ (Ref. 5)]} \) conduction band, nearly an order of magnitude smaller than for conventional metals. The low electron density in \( K_3C_{60} \) (4 \times 10^{21} \text{ cm}^{-3} \text{ (Ref. 6)} \) implies poor screening. Numerous theoretical models and experiments show a large electron correlation energy, on the order of 1.0–1.8 eV,\(^7\) meaning that electron-electron interactions are strong. The transport properties of \( K_3C_{60} \) are strongly affected by such unconventionality; for instance, this material can be driven from superconducting to insulating solely by the addition of disorder, extremely rare for a three-dimensional system.\(^8\)

All of these factors indicate the anomalous electronic properties of \( A_1C_{60} \), but in addition, there are important questions of bonding. Pure \( C_{60} \) has only weak van der Waals bonds between the neutral balls; \( K_3C_{60} \) has \( K^+ \) ions filling the spaces between \( C_{60} \) molecules, so that the interaction is primarily ionic. The structure and lattice constant of \( C_{60} \) and \( K_3C_{60} \) are nearly the same. One can ask how the presence of the \( K \) between the \( C_{60} \) molecules affects the phonon spectrum.

Some of the questions about these materials can be addressed through heat-capacity measurements. There have been many previous specific-heat studies of pure \( C_{60} \) (Refs. 9–14) and \( K_3C_{60} \) (Ref. 15). Despite some initial confusion due to differences in sample quality, the vibrational modes and bonding in pure \( C_{60} \) have been well understood through \( C_p \) measurements, as we will describe in detail in Sec. III A. Our pure \( C_{60} \) results are fully consistent with past studies.

Because \( K_3C_{60} \) is a metal and a superconductor, one would like to learn from \( C_p \) measurements the value of \( \gamma \), the coefficient of the electronic specific heat (\( C_{\text{electronic}} = \gamma T \)), which is proportional to the density of electronic states at the Fermi level \( N(\epsilon_F) \), as well as the value of the discontinuity in \( C_p \) at the superconducting transition. Beyond metallic properties, heat capacity can reveal how strongly the lattice specific heat is affected by the changes in intermolecular potential from the different bonding in \( C_{60} \) and \( K_3C_{60} \). The only previous measurement of the specific heat of \( K_3C_{60} \) (Ref. 15) addresses the first two electronic issues (as discussed in Sec. III B), but not the lattice properties.

Our experiments show that phonons and localized lattice excitations strongly dominate the specific heat at temperatures from 6 to 400 K. Due to the small electronic heat capacity, no information about the electronic term could be extracted. Therefore, we focus on drawing conclusions about the phonon density of states (DOS) and the bonding in \( C_{60} \) and \( K_3C_{60} \).

The lattice specific heat is related to the phonon density of states in energy space \( D(\omega) \) through

\[
C_{\text{lattice}}(T) = k_B \int_0^\infty \frac{x^2 e^x}{(e^x - 1)^2} D(\omega) \, d\omega,
\]

(1)

where \( x = h\omega/k_BT \) and \( k_B \) is the Boltzmann constant.\(^{16} \) We compare our \( C_p \) results to those obtained by integrating a published DOS (Ref. 17) from neutron scattering results. For the \( C_{60} \), the specific heat obtained from the published DOS matches our measured results moderately well, but for \( K_3C_{60} \), the match is quite poor. We then work backward from our data to construct a crude model of the difference in DOS between \( C_{60} \) and \( K_3C_{60} \), illuminating the essential
physics: C_{60} shows a clear separation of energy regimes in the DOS between low-energy interball modes and high-energy intraball (on-ball) modes, while in K_{3}C_{60} the separation is blurred due to the addition of alkali optical modes in the gap. Additionally, below 140 K—a temperature regime dominated completely by the acoustic phonon modes—the specific heat of K_{3}C_{60} is larger than that of C_{60}, showing that the acoustic modes of K_{3}C_{60} are softer than those of pure C_{60}.

II. EXPERIMENTAL DETAILS

A. Measurement method

The specific heat was measured with our thin-film calorimeter devices, which have been described in detail elsewhere. Briefly, the device consists of an 1800-Å amorphous SiN membrane, which serves to thermally isolate the sample, surrounded by a Si frame. A thin-film Pt heater and three thin-film thermometers cross the membrane, and each thermometer has an identical matching partner on the frame. One thermometer is Pt, working in the range 40 K–800 K; the other two are different geometries of amorphous Nb_{3}Si_{2}, together spanning the range 1 K–300 K. A metallic conduction layer is deposited on the center of the backside of the device so that it is in thermal, but not electrical, contact with the electronics on the front. This layer assures that the thermally isolated features on the membrane come to equilibrium among themselves much more quickly than any applied heat can leak back to the Cu block. The sample also goes on the backside, on top of the conduction layer. The sample and conduction layer are deposited through a shadow mask that sits less than 25 μm from the membrane surface to give a well-defined area.

The measurement is made using the standard relaxation method. Solving the heat-flow equation for this device yields the result C = kτ, where C is the heat capacity of everything in direct thermal contact with the conduction layer (sample, membrane electronics, a patch of membrane, the conduction layer itself); k is the thermal conductance of the leads and membrane that provide the heat link between the sample and the Si frame, which is thermally grounded to the cryostat block; and τ is the characteristic time for the heat to leak from sample to block. τ and k are measured by a standard ac bridge technique. The heat capacity of the thermometers, heater, membrane, and conduction layer (known as the addenda) were measured before depositing the sample. This addenda is then subtracted from the subsequently measured total heat capacity, which includes the sample. It accounts for 30–80% of the total heat capacity and was subtracted as a smooth curve.

The mass of the sample must also be measured in order to convert heat capacity (J/K) to specific heat (J/g K). The sample area was well known from the size of the shadow mask, and the thickness was determined by a crystal monitor located near the sample during deposition. The bulk density was used to calculate the mass, an assumption later justified for the pure C_{60} by comparing our measured specific heat to literature values. It is likely that the K_{3}C_{60} sample also had the bulk density because it was made by intercalating potassium into an already-deposited C_{60} film. For pure C_{60}, we have also checked the thickness by placing a blank substrate near the device during deposition, then measuring the film thickness directly on a profilometer after removal from the chamber. This method cannot be used for K_{3}C_{60} because the film immediately reacts with air, causing the potassium to migrate to the surface and form potassium oxides and the C_{60} lattice to relax.

B. Sample deposition

The samples were deposited onto devices already containing a conduction layer of 2500 Å of polycrystalline gold, evaporated at ambient temperature in a separate chamber. X-ray diffraction experiments that we performed on a C_{60} film grown on polycrystalline gold under somewhat different deposition conditions (0.2 Å/sec, 180 °C) showed a grain size of 4200 Å. Thus, we expect this sample had smaller grains.

The C_{60} and K_{3}C_{60} were evaporated from thermal sources in an ultrahigh vacuum (UHV) deposition chamber, which contains three thermal evaporation sources and a liquid-nitrogen-cooled shroud to reduce the deposition pressure. Under the conditions used in the present work, the pressure of the chamber prior to evaporation is 5 × 10^{-10} torr. The C_{60} source was sublimed powder from MER Corporation loaded into a baffled tungsten boat, while the potassium was grown from getter sources from SAES Inc. Both the C_{60} and the K (when used) were thoroughly outgassed before deposition. The substrate temperature during deposition was 135 °C; the pressure during deposition was 3 × 10^{-8} torr. In the case of pure C_{60}, we used a deposition rate of 1 Å/sec, growing the film to 7000-Å thick (mass 7.4 μg).

Growing the best K_{3}C_{60} film required balancing the competing factors of grain size, deposition rate, and alkali intercalation. A compromise between these considerations led to the following growth scheme: The 4500-Å K_{3}C_{60} film (5.5 μg) was grown in three separate sequential steps, each 1500-Å thick (i.e., 1500 Å of pure C_{60} was grown and then potassium was intercalated into it, three times in a row). The deposition rates were 0.2 Å/sec for C_{60} and 0.1 Å/sec for K. For each 1500-Å step, the four-wire resistance of the film was monitored using a SiN substrate with prepatterned contacts. The K was deposited until the film reached a resistivity first due to potassium from the lower layer and second K_{3}C_{60} was grown in three separate sequential steps, each 1500-Å thick (i.e., 1500 Å of pure C_{60} was grown and then potassium was intercalated into it, three times in a row). The deposition rates were 0.2 Å/sec for C_{60} and 0.1 Å/sec for K. For each 1500-Å step, the four-wire resistance of the film was monitored using a SiN substrate with prepatterned contacts. The K was deposited until the film reached a resistivity minimum, which corresponds to K_{3}C_{60}. Then the next layer was grown in a similar fashion. The resistance of the film after the second layer did not drop by a full factor of 2 compared to the first layer, which we take as evidence that the second and third C_{60} layers had smaller grains than the first due to potassium from the lower layer(s) diffusing into the fresh C_{60}. The film grown by this method showed resistivity characteristics similar to those seen in single crystals. It had positive (“metallic”) slope at high temperatures, low room-temperature resistivity for K_{3}C_{60} (2.5 mΩ cm), a high superconducting onset temperature (19.2 K), and a relatively narrow superconducting transition (2 K) (see Fig. 1).

C. Cryostats

Due to the great air sensitivity of K_{3}C_{60}, all measurements on this material must be performed in situ or on samples otherwise sealed from oxygen exposure. We measured the heat capacity of the K_{3}C_{60} sample in situ using a He cryostat mounted on top of the UHV deposition system,
FIG. 1. Resistivity of K$_3$C$_{60}$ sample, 4500 Å, substrate temperature during deposition 135 °C. The substrate was a-SiN covered by 2500 Å polycrystalline gold. This sample was grown simultaneously with the heat-capacity sample, next to the C$_p$ device.

with a cold finger which extends into the chamber. This cryostat has been constructed with UHV-compatible materials (for example, high-melting-temperature solder was used and vacuum grease was not). Its temperature range of operation is 2.5 K to 500 K; other details have been published previously. The calorimeter device with the less air-sensitive pure C$_{60}$ was removed from the deposition chamber and measured ex situ in two systems. The low-temperature cryostat, designed by RMC (now Desert Cryogenics), has a standard copper cold finger and radiation shield, and a brass vacuum attached by a greased taper seal. The temperature range of operation is 1.5–310 K. For the high-temperature C$_{60}$ data (300–400 K), a different ex situ setup was used, which has been described previously.

III. RESULTS AND DISCUSSION: C$_{60}$ AND K$_3$C$_{60}$

Figure 2 shows the specific heat of C$_{60}$ and K$_3$C$_{60}$ as a function of temperature in units of J/g K. Both these units and J/mol K have conceptual advantages and disadvantages for these materials. Comparing units, numbers of modes, and the density of states for C$_{60}$ and K$_3$C$_{60}$ is subtle; the details are worked out explicitly in the Appendix. For convenience in this text, we will treat the units of J/g K as primary; to convert to J/mol K, where a mole refers to carbon atoms for C$_{60}$ and average atoms for K$_3$C$_{60}$, multiply the C$_{60}$ data by 12 and the K$_3$C$_{60}$ data by 13.3. For moles of molecules, multiply the per gram results by 720 for C$_{60}$ and 837 for K$_3$C$_{60}$.

A. Pure C$_{60}$: Separation of energy levels

Our C$_{60}$ measurement covers the widest temperature range for a clean (sublimed) sample. A number of earlier results over smaller ranges or with lower quality samples have been published in the literature, and we note that our data match well with previous results.

The first-order orientational transition is clearly visible near 250 K. Using $S = \int (C/T) \, dT$ and $H = \int C \, dT$, we found the changes in entropy $\Delta S$ and enthalpy $\Delta H$ at the transition from our data by measuring the excess specific heat above a smooth background through 250 K: 30.5 J/g K and 6.67 J/g K, respectively. These values are in good agreement with model calculations (26.5 J/g K and 6.7 J/g K), as well as previous experimental results (41.7 J/g K and 5.9 J/g K).

The overall shape of the C$_{60}$ specific-heat curve can be understood in the following way, as articulated by Olson et al. Note that there is an initial rise in the specific heat, followed by a plateau near 80 K, then another steep, nearly linear rise. This two-tiered behavior corresponds to a separation of energy levels in the phonon spectrum. The low-energy excitations are translations and rotations (also called librations) involving the entire C$_{60}$ cage. Because the bonds between cages are weak van der Waals bonds, these low-energy modes saturate below 80 K. With six modes (three translational and three librational) and a molecular number density (N/60), the Dulong-Petit limit for the C$_{60}$ molecules is 6(N/60)k_B = 69.3 mJ/g K, which matches the level of the plateau. Calculations and measurements of the speeds of sound in C$_{60}$ give a Debye temperature of about 90–100 K, reasonably consistent with this saturation occurring near 80 K in our data.

Above the temperature where the low-energy modes saturate, the higher-energy excitations on the ball start to be activated and contribute to the specific heat, causing the sharp rise above 100 K. The Dulong-Petit limit for the carbon atoms is equal to 3Nk_B = 2.08 J/g K. The saturation temperature is not reached in our experiment or any other published specific-heat results; based on the highest-energy on-ball mode (196 meV), this temperature is expected to be above 2500 K. (Since C$_{60}$ sublimes around 300 °C, it could not be observed anyway.) It is the large difference in bond strength...
between the covalent bonds on the cage and the molecular bonds between the cages that leads to the separation of energies in the phonon spectrum.

We note briefly that the roughly linear dependence of $C_p$ above 100 K corresponds to a broad, nearly constant density of phonon states, which arises from the multitude of on-ball modes (see Sec. III C).

Looking in more detail, we consider the low-temperature behavior of $C_p$. In the Debye model, the $T^3$ regime can be expected no higher than about 1/10 the saturation temperature, and a common rule of thumb (accounting for deviations from the Debye model) is 1/50. From the data, we see that the intermolecular modes of $C_{60}$ saturate near 80 K, and therefore the $T^3$ regime for the specific heat is not expected above 8 K and could occur below 2 K. Recall also that the intermolecular modes consist of both acoustic (translational) modes and librations. There is no reason to assume that these two kinds of excitations have the same saturation temperature; therefore, the shape of the $C_p$ curve below 80 K may be non-Debye-like even if both kinds of modes are well described by Debye functions. Indeed, Beyermann, Hundley, and Thompson have analyzed their specific-heat data in the regime 1–20 K, and they find that a sum of two Einstein terms, a Debye term, and a linear term is required to accurately model the data. Our data are nearly identical to theirs in the overlapping region (6–20 K). Therefore, there is no true low-temperature “Debye regime” above 6 K in which the excitations are in the long-wavelength continuum limit.

A low-temperature $T^3$ behavior in $C_p$ arises from a phonon density of states $D(\omega)$ that varies as $\omega^2$. The lack of a $T^3$ regime implies that the DOS does not vary as $\omega^2$ until below the energy corresponding to 6 K [=0.52 meV/$h$].

B. $K_3C_{60}$: Small electronic term

Figure 2 shows our measurement of the specific heat of $K_3C_{60}$ compared to that of $C_{60}$. We first note that $K_3C_{60}$ shows no orientational transition below 400 K associated with the breaking of spherical symmetry when the balls stop rotating freely, consistent with NMR experiments.27 The presence of the potassium hinders rotation. The balls sit in one of two inequivalent orientations, which is called “merohedral disorder,” at all temperatures relevant to this study.26

We now turn to the analysis of the electronic contribution to the specific heat: the value of $\gamma$ and the jump at $T_c$. The first has only been measured indirectly, and the second only measured once. The relevant experiments were performed by Ramirez et al. and Burkhart and Meingust. They measured the heat capacity of a thick film of $K_3C_{60}$ deposited on the inside of a quartz ampule from 4–25 K. Using the jump in the specific heat at $T_c$ and information about the superconducting parameters from other experiments, Ramirez et al. calculated a value for $\gamma$: 3.1x10^-5 J/g K^2. Burkhart and Meingust measured the volume expansion coefficient of $K_3C_{60}$ pellets, from which $\gamma$ can also be calculated; they found 3.7x10^-5 J/g K^2. For comparison, a typical metal has $\gamma$ about an order of magnitude smaller. The large value in $K_3C_{60}$ is due to a high density of electronic states $N(E_f)$, which results from the narrow conduction band.

The electronic term associated with the average calculated $\gamma$ value (3.4x10^-5 J/g K^2) is plotted in Fig. 3, along with the low-temperature portion of our $K_3C_{60}$ data and Ramirez’ results, which span the range 4–25 K. We see that even below 50 K, the electronic contribution to the total specific heat of $K_3C_{60}$ is small; it is even smaller at higher temperatures. The superconducting transition is at 19 K, and below $T_c$, the electronic heat capacity drops exponentially and is even less of the total.

The dashed vertical line in Fig. 3 represents $T_c$, the superconducting transition temperature. By plotting their data on a log-log scale, Ramirez et al. find an experimental value of $\Delta C=1.6$ mJ/g K. Using the calculated $\gamma$ of 3.1x10^-5 J/g K^2, $C_{\text{electronic}}$ at $T_c$ is 5.89x10^-4 J/g K, so that the ratio of $\Delta C$ to $C_{\text{electronic}}$ at $T_c$ is 2.72, somewhat higher than the predicted BCS value of 1.43 (Ref. 16) (this has been interpreted as strong electron-phonon coupling in fullerene superconductors). Going the other way, Burkhart’s $\gamma$ of 3.7x10^-5 J/g K^2 in conjunction with these values for the ratio gives a jump in the specific heat of 1–2 mJ/g K. These values for the jump are below the level of the noise in our data, and indeed, we see no evidence of a jump, so it was not possible for us to estimate $\Delta C$.

It is clear from Fig. 3 that the specific heat of $K_3C_{60}$ is dominated by nonelectronic terms to which we now turn.

C. Blurred energy levels and the density of states

Figure 2 shows that in $K_3C_{60}$, unlike $C_{60}$, there is no clear saturation of low-energy modes and no plateau in $C_p$. As determined in the Appendix, the saturation value for all modes not on the ball in $K_3C_{60}$ is 150 mJ/g K. There is a slight flattening in $C_p(T)$ near this value, but not as distinct as in the case of $C_{60}$.

The differences between $C_p$ in $C_{60}$ and $K_3C_{60}$ can be explained by the changes in the acoustic modes due to the K ions, as well as the appearance of new alkali optical modes. Some of the modified modes are very soft, contributing weight at the lowest energies, which accounts for $K_3C_{60}$’s larger specific heat at low temperature, while the alkali optical modes appear in the gap between interball and intraball modes and cause the blurring of the separation.
For K$_3$C$_{60}$, the charge transfer is nearly complete,$^{30}$ so the crystal consists of K$^+$ and C$_{60}^{-3}$ ions, giving K$_3$C$_{60}$ a different intermolecular potential than that of the neutral molecular solid C$_{60}$. It is not clear what the effect on the phonons will be: On the one hand, ionic bonds should stiffen the lattice because the attraction of the charged units exceeds the attraction of the induced dipoles of van der Waals bonds, and steric hindrance could possibly play a stiffening role also. On the other hand, metallic screening tends to soften the phonons. Raman and IR spectroscopy indicate that most shifts in on-ball modes between C$_{60}$ and K$_3$C$_{60}$ are small ($\leq$ a few percent).$^{31}$ Further, neutron studies show that the repulsive part of the A-C$_{60}$ potential is as important as the Coulombic part in determining the orientational potential.$^{32}$ Note from Fig. 2 that the specific heat of K$_3$C$_{60}$ exceeds that of C$_{60}$ from $\sim$6–140 K, indicating that the low-energy intermolecular modes shift to lower energy, and therefore these cannot be the source of the lack of $C_p$ plateau and blurred energy levels.

To examine the phonon density of states in these materials more carefully, we first compared our specific-heat data to published neutron-scattering results. The DOS (Ref. 33) can be calculated from neutron-scattering results, combined with appropriate force constants known from theory.$^{34}$ Gompf et al. have done this for C$_{60}$ and K$_3$C$_{60}$ using a model based on strong (covalent) nearest-neighbor interactions on the C$_{60}$ molecules and weak van der Waals or weak ionic interactions between balls.

Using this calculated DOS for both C$_{60}$ and K$_3$C$_{60}$, we have done the integral in Eq. (1) to determine the corresponding $C_{\text{lattice}}$ in the range 1–400 K. (As a check, we also did the calculation up to 3500 K and confirmed that it approached the correct Dulong-Petit limit in each case.) The results are shown in Figs. 4 and 5, along with our own model which will be described shortly. For C$_{60}$, the calculated $C_{\text{lattice}}$ has the correct qualitative two-tiered shape but does not quantitatively match the data at low temperature, due either to inaccuracy of the low-energy neutron data or to incorrect mode counting in the model used to convert the neutron data to a DOS. For K$_3$C$_{60}$, the problems are more serious; the calculated $C_{\text{lattice}}$ does not even qualitatively match the blurred shape of the K$_3$C$_{60}$ $C_p$ data. First, it retains the two-tiered shape because too few modes appear in the gap to blur the separation of energy levels. Also, there is too little weight at the lowest energies; K$_3$C$_{60}$’s greater specific heat below 140 K requires the interball modes to become even softer than they are in pure C$_{60}$. (More detailed information about this comparison to neutron results can be found in Ref. 35.)

Using a different neutron scattering technique, Neumann et al.$^{32}$ focused their studies on the low-energy regime ($\leq$10 meV) in C$_{60}$, K$_3$C$_{60}$, and other fullerenes. Since they were primarily interested in the orientational potential of these materials, they did not calculate a phonon DOS, but some of their findings can be compared with our specific heat results. In particular, they find significant neutron-scattering intensity near 2.5 meV in C$_{60}$, which is due to the very soft librational modes. This is very close to the librational energy we found to best match our specific-heat results, as described below. However, Neumann’s results indicate that in K$_3$C$_{60}$ the acoustic modes are stiffer than those in C$_{60}$ (peaked near 4 meV), while we found that they had to be slightly softer to account for the larger $C_p$ in K$_3$C$_{60}$ at low temperature.

To understand more clearly how the differences between the specific heats of C$_{60}$ and K$_3$C$_{60}$ result from differences in the DOS, we constructed two crude model densities of states, based on knowledge of the relative weights of different modes (see the Appendix). We have confirmed that they approach the correct Dulong-Petit limits at high temperature: 2.08 J/g K for C$_{60}$ and 1.88 for K$_3$C$_{60}$. The models are shown in Fig. 6. The simple rectangular shapes are fairly accurate in the case of C$_{60}$, which has many excitations of similar energy,$^{26}$ but less accurate for K$_3$C$_{60}$. (Note that at the lowest energy, the true DOS must drop as $E^2$ in the elastic limit, so this simple model will not produce a specific heat that approaches zero correctly at the lowest temperature.)

![FIG. 4. Our C$_{60}$ data compared to our model (Fig. 6) and to the specific heat calculated [using Eq. (1)] from the published neutron DOS (Ref. 17). Neither our model nor the neutron result is expected to display the orientational peak because no provision was made in the calculations for the number of modes to change with temperature. Inset: The region below 50 K.](image1)

![FIG. 5. Our K$_3$C$_{60}$ data compared to our model (Fig. 6) and to the specific heat calculated [using Eq. (1)] from the published neutron DOS (Ref. 17). Inset: The region below 50 K.](image2)
FIG. 6. Model densities of states for C\textsubscript{60} and K\textsubscript{3}C\textsubscript{60}. The solid line model represents C\textsubscript{60}, with a well-defined separation of energy levels. The dashed line model simulates the case of K\textsubscript{3}C\textsubscript{60}, with weight shifted to lower energies and states in the gap. The states at the lowest energy (≈5 meV) are associated with acoustic modes, the large blocks at high energy (≈30 meV) with the numerous on-ball modes, and the peak between 10–15 meV with the optical modes of K\textsubscript{3}C\textsubscript{60}. The integrated DOS under each block was constrained to match the number of modes of each type (see the Appendix for details). Both models were tuned to produce C\textsubscript{p} curves that resemble our experimental results. Inset: The low-energy region. The real DOS must approach 0 as E\textsubscript{2}; this has no impact on C\textsubscript{p} in the measured temperature range.

For C\textsubscript{60}, we chose two regions separated by a gap, indicative of the separation of energy levels. To obtain the correct C\textsubscript{p} shape in the range 100–200 K, it was necessary to add some structure to the intraball phonons, with less weight from 30–50 meV and more from 50–70 meV. The resultant specific heat is shown in Fig. 4 along with our C\textsubscript{60} data. Note that this sort of model is not expected to reproduce the orientational peak in the specific heat because that peak occurs when the number of phonon modes abruptly changes at 250 K. The overall match between our model and the data is excellent, including the initial rise at low temperature.

In the case of K\textsubscript{3}C\textsubscript{60}, some weight is shifted to even lower energies to reproduce the greater magnitude of the K\textsubscript{3}C\textsubscript{60} specific heat over the C\textsubscript{60} specific heat. Note that if the data were plotted as J/mol K instead of J/g K the difference at low temperature would be further enhanced, because K\textsubscript{3}C\textsubscript{60} has larger mass per mole than C\textsubscript{60}. We also added alkali optical modes in the gap to blur the separation of energy levels. The specific heat calculated from this model is comparable to our K\textsubscript{3}C\textsubscript{60} data in Fig. 5. The match is again quite good for such a simple model.

IV. CONCLUSIONS

In summary, our specific-heat measurements (6–400 K) indicate that the lattice contribution dominates C\textsubscript{p} in K\textsubscript{3}C\textsubscript{60} and that C\textsubscript{60} and K\textsubscript{3}C\textsubscript{60} have significantly different densities of phonon states. Pure C\textsubscript{60} exhibits a separation of energy levels in its DOS due to differing bond strengths on and between molecules, which results in a two-tiered shape to the specific heat as the intermolecular modes saturate before the on-ball modes become excited. The intermolecular modes are very soft, so that there is no T\textsuperscript{3} dependence to C\textsubscript{p} down to at least 6 K. In K\textsubscript{3}C\textsubscript{60}, the separation of energy levels is blurred so that the two-tiered behavior is not evident.

Using published densities of states for C\textsubscript{60} and K\textsubscript{3}C\textsubscript{60} calculated from neutron results to determine the specific heat, we find a consistent qualitative picture for the case of C\textsubscript{60}: the modes are separated into two regimes. But for K\textsubscript{3}C\textsubscript{60}, too few modes are added at low temperature and in the gap, so the model does not match the specific-heat data. More significant changes are needed to give K\textsubscript{3}C\textsubscript{60} a higher specific heat at low temperature and to eliminate the two-tiered shape of C\textsubscript{p}.

Our own simple model densities of states, constructed to resemble our specific-heat results upon integration, show that adding alkali optical states in the gap and at the lowest energies accounts well for the differences in specific heat between C\textsubscript{60} and K\textsubscript{3}C\textsubscript{60}.

APPENDIX: MODE-COUNTING AND THE DENSITY OF STATES IN C\textsubscript{60} AND K\textsubscript{3}C\textsubscript{60}

Enumerating the vibrational modes in these materials can become confusing, especially when translating between gram and molar quantities. In this appendix, we explicitly count the nonelectronic modes contributing to the specific heat of C\textsubscript{60} and K\textsubscript{3}C\textsubscript{60}, divide these into low- and high-energy portions, and calculate the weights of these modes in the densities of states.

C\textsubscript{60} is a pure material, so it is unambiguous to consider the density of states per atom (of carbon). We write this as

\[ D(E) = \frac{\text{number of modes}}{\text{eV (carbon atom)}}. \]  

(A1)

Since the total number of modes is 3\textsubscript{N}, where N is the number of carbon atoms, the area under D(E) is constrained:

\[ \int_0^\infty D(E) \, dE = 3. \]  

(A2)

Each unit cell contains 60 carbon atoms. Therefore, there are 180 total modes of vibration in this material. Recalling that C\textsubscript{60} displays a separation of energy levels between low-energy interball modes and high-energy on-ball modes, it makes sense to divide these modes into two categories: the first consisting of rotations of the entire ball, called librations (three modes), plus acoustic phonons (three modes), and the second consisting of on-ball modes. Thus, the interball modes account for 6 out of 180 modes, and the on-ball modes are the remaining 174. Integrating just the area of the DOS under the interball modes should give a value 3\times 6/180 = 0.1. The remaining 2.9 is the area under the on-ball modes, and a gap separates these two regions of the DOS.

The Dulong-Petit limit is 25 J/mol K. Since a mole of carbon atoms has mass 12 g (i.e., a carbon atom weighs 12 amu), this limit becomes 2.08 J/g K for C\textsubscript{60}. (Caveat: the orientational transition at 250 K slightly changes this result, as described in the paragraph below. However, the small change does not affect the analysis in this paper.) Since the interball modes account for 6/180 total modes, the saturation value for the interball modes is 1/30 of 2.08 = 69 ml/g K.
As a brief aside, it is worth noting the effect of the orientational transition at 250 K in pure C\textsubscript{60} on the specific heat. Above this transition, the balls spin freely, which means that there is no potential energy associated with their rotational motion (because there is no restoring force). Recall that in the classical, high-temperature limit, each squared term in the Hamiltonian (called a degree of freedom) contributes $\frac{1}{2}k_B$ to the heat capacity per atom, so that usually a set of three modes will contribute $3k_B$, with three kinetic and three potential degrees of freedom. However, the three rotational modes in C\textsubscript{60} do not contribute the full $3(N/60)k_B$ to the specific heat above 250 K; they only contribute of 15 modes not on the ball. The remaining 174 are the modes that we counted above for the case of C\textsubscript{60}. This makes a total of 189 total modes, they should saturate at 1.88 J/g K. Although the modes do not clearly separate in this material (recall Fig. 2), we can derive a theoretical saturation value for the modes that are not on the ball. Since these modes account for 15 out of 189 total modes, they should saturate at $1.88 \times \frac{15}{189} = 0.143$. Thus, the total weight of non-on-ball modes is 0.24 in K\textsubscript{3}C\textsubscript{60} (within rounding). The on-ball modes have weight $3 \times \frac{60}{189} = 2.76$. Note that the total is still 3.

In terms of modes of average atoms, the Dulong-Petit limit is still 25 J/mol K. Since an average atom weighs 13.3 amu, this limit for K\textsubscript{3}C\textsubscript{60} translates to 1.88 J/g K. Although the modes do not clearly separate in this material (recall Fig. 2), we can derive a theoretical saturation value for the modes that are not on the ball. Since these modes account for 15 out of 189 total modes, they should saturate at $1.88 \times \frac{15}{189} = 0.143$. Thus, the total weight of non-on-ball modes is 0.24 in K\textsubscript{3}C\textsubscript{60} (within rounding). The on-ball modes have weight $3 \times \frac{60}{189} = 2.76$. Note that the total is still 3.

It is worth noting finally how to conceptualize the difference between $D(E)$ for C\textsubscript{60}, which is expressed in terms of carbon atoms, and $D'(E)$ for K\textsubscript{3}C\textsubscript{60}, which is expressed in terms of average atoms. We can write

\[
D'(E) = \frac{\text{number of modes}}{\text{eV (average atom)}},
\]

Equation (2) is still true for $D'(E)$—it just refers to the modes of the average atoms. The total area is still 3.

Dividing up the modes is somewhat more difficult. Consider all the modes that are not high-energy (on-ball) modes. This amounts to considering the C\textsubscript{60} molecule as a large “atom”—in other words, conceptually the material is K\textsubscript{3}X, with four “atoms” per primitive unit cell. We consider an fcc structure, ignoring the orientation of the balls because it does not affect the mode counting result. There are a total of 12 modes ($=4 \times 3$), of which 3 are acoustic. Therefore, nine are optical. We still must add in the three rotational modes that we counted above for the case of C\textsubscript{60}. This makes a total of 15 modes not on the ball. The remaining 174 are the on-ball modes (the same number as we found in the case of C\textsubscript{60}).

Since there are now 63 average atoms per unit cell, there are 189 total modes, which are distributed in the ratios derived in the previous paragraph. This makes the relative weights of the portions of the DOS slightly different: the acoustic and rotational modes have total area $3 \times \frac{6}{189} = 0.095$; the optical modes $3 \times \frac{9}{189} = 0.143$. Thus, the total weight of non-on-ball modes is 0.24 in K\textsubscript{3}C\textsubscript{60} (within rounding). The on-ball modes have weight $3 \times \frac{60}{189} = 2.76$. Note that the total is still 3.

ACKNOWLEDGMENTS

We thank S. Watson, R. Dynes, D. Arovas, and J. Ostrick for valuable discussions and insights. This work was supported by NSF Grant No. DMR-9208599.

---

11. T. Matsuo, H. Suga, W. I. F. David, R. M. Ibberson, P. Bernier,
33 The density of states from neutron results is often called the "generalized density of states" (GDOS) because the weights of the phonons are convoluted with the scattering power of each element making up the material. However, for pure or nearly pure materials like C60 and K 3 C 60 , the GDOS is essentially identical to the phonon density of states, and in this paper we ignore the difference.