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Calorimetric measurements on Li_4C_{60} and Na_4C_{60}

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ABSTRACT

We show specific heat data for Na_4C_{60} and Li_4C_{60} in the range 0.4-350 K for samples characterized by Raman spectroscopy and X-ray diffraction. At high temperatures the two different polymer structures have very similar specific heats both in absolute values and in general trend. The specific heat data are compared with data for undoped polymeric and pristine C_{60} . At high temperatures, a difference in specific heat between the intercalated and undoped C_{60} polymers of $100 \text{ JK}^{-1}\text{mol}^{-1}$ is observed, in agreement with the Dulong-Petit law. At low temperatures the specific heat data for Li_4C_{60} and Na_4C_{60} are modified by the stiffening of vibrational and librational molecular motion induced by the polymer bonds. The covalent twin bonds in Li_4C_{60} affect these motions to a somewhat higher degree than the single intermolecular bonds in Na_4C_{60} . Below 1 K, the specific heats of both materials become linear in temperature, as expected from the effective dimensionality of the structure. The contribution to the total specific heat from the inserted metal ions can be well described by Einstein functions with $T_E = 386 \text{ K}$ for Li_4C_{60} and $T_E = 120 \text{ K}$ for Na_4C_{60} , but for both materials we also observe a Schottky-type contribution corresponding to a first approximation to a two-level system with $\Delta E = 9.3 \text{ meV}$ for Li_4C_{60} and 3.1 meV for Na_4C_{60} , probably associated with jumps between closely spaced energy levels inside “octahedral-type” ionic sites. Static magnetic fields up to 9 T had very small effects on the specific heat below 10 K.

I. INTRODUCTION

Doped and undoped C_{60} polymers are two classes of materials with very diverse structural and electronic properties^{1,2}. Pure C_{60} can be polymerized by irradiation with photons, electrons or ions, or by the simultaneous application of high temperature and high pressure¹⁻³, and in the latter case several well-ordered structural phases can be obtained under different conditions¹⁻³. Alkali metal intercalated C_{60} also often forms ordered, metastable polymeric structures at room temperature due to the charge transfer to the C_{60} molecules and it has been shown that the polymeric lattice structure is determined primarily by the amount of charge transferred to the fullerene molecules⁴. Li_4C_{60} and Na_4C_{60} are two compounds of particular interest since both have unique, two-dimensionally (2D) polymerized layered lattice structures near room temperature. Li_4C_{60} forms a quasi-tetragonal structure with $I2/m$ space group where the lattice angle is about 90.5 degree and the difference between the a and b lattice parameters is very small⁵. The structure is based on parallel molecular chains which are internally bonded by covalent intermolecular [2+2] cycloaddition bonds and cross-linked by single covalent bonds (see Figure 1). Except for the single bonds in the a direction⁵ and the resulting rotation of the cycloaddition-bonded chains, this structure is very similar to that of the 2D pseudo-tetragonal polymer of C_{60} ^{1,2,6}. Na_4C_{60} has only *single* covalent intermolecular bonds in both directions^{7,8}, which because of the molecular geometry results⁷ in a monoclinic $I2/m$ structure with a lattice angle of 78°. In both materials, the metal ions are located close to positions corresponding to the intermolecular voids in the original face-centered cubic (fcc) lattice of unpolymerized C_{60} , with a single ion in each (small) tetrahedral site and two ions in each (large) octahedral one. The conduction band of C_{60} can accommodate up to six electrons per molecule and assuming full charge transfer both Li_4C_{60} and Na_4C_{60} might be expected to be metallic, but band structure changes upon polymerization open gaps at the Fermi surface transforming both into small band gap semiconductors. However, both materials have been reported to transform into

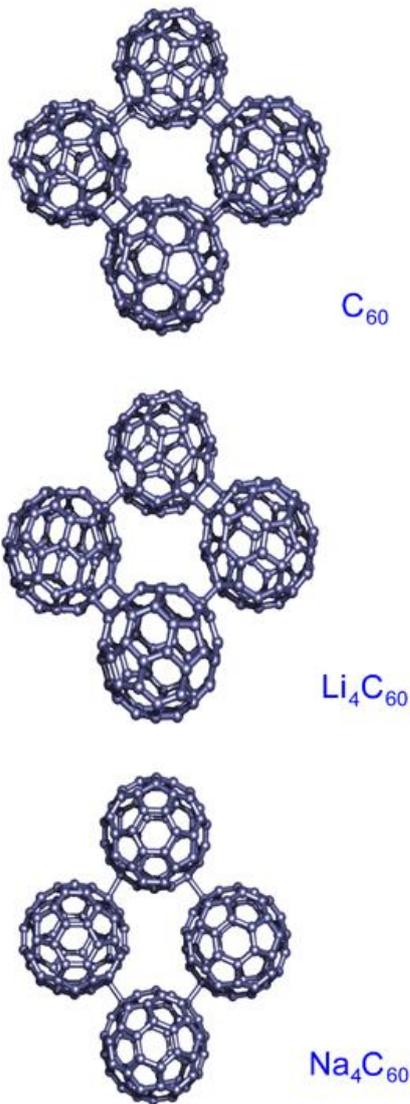


FIG. 1. From top down: the polymer structures of undoped, tetragonal C_{60} , Li_4C_{60} , and Na_4C_{60} .

metallic phases at high temperature^{9,10}. Li_4C_{60} has also recently been reported to be a superionic conductor at room temperature¹¹, although there are some questions regarding this identification^{12,13}. The physical properties of both materials have been well studied by many methods but some questions still remain, in particular regarding their structural and magnetic properties at low temperature. In this paper we report the results of a calorimetric study of Li_4C_{60} and Na_4C_{60} using adiabatic and relaxation calorimetric measurements. The specific heat is an important material property that can give valuable information on both lattice dynamics and on different types of structural or magnetic transformations, and also further insights on the structural differences between the two materials.

II. EXPERIMENTAL SECTION

Polycrystalline powder samples of Li_4C_{60} and Na_4C_{60} were produced by mixing stoichiometric amounts of Li (99 % purity) or Na (99.5% purity) with C_{60} (99.95 % purity, Term, USA) and treating the mixture at 523 K for several weeks in an argon atmosphere with oxygen and water levels below 1.0 ppm, following a procedure described earlier¹⁴. The samples were ground once every week to increase homogeneity. After synthesis the samples were transferred to 1.5 mm Lindemann capillaries (Hilgenberg, Germany) and sealed in an argon atmosphere. The powder samples were characterized by X-ray diffraction in a Siemens D5000 using the Cu K_α line ($\lambda = 1.54 \text{ \AA}$). Raman studies were performed using a Renishaw 1000 grating spectrometer with a notch filter to remove the Rayleigh line and a Peltier cooled CCD-detector. Laser powers below 10 Wcm^{-2} were used to avoid laser heating. Specific heat data were measured between 3 and 350 K by adiabatic calorimetry using samples loaded in gold plated copper vessels. The amounts used were $247.68 \text{ mg} = 0.33094 \text{ mmol}$ and $113.82 \text{ mg} = 0.14007 \text{ mmol}$ for Li_4C_{60} and Na_4C_{60} , respectively. To promote thermal equilibration He gas was introduced, and as a consequence the data below 60 K are not considered fully reliable due to the possibility of gas condensation. Relaxation calorimetry was carried out between 0.4 and 100 K by using a ^3He -probe, both without a magnetic field and in fields of 1 and 9 T. Although care was taken to keep the samples from exposure to air or moisture the relaxation results for the first sample of Na_4C_{60} indicated possible air contamination and the relaxation measurements were thus repeated on a second set of samples from a fresh batch of material. The amounts used for relaxation calorimetry were $6.060 \text{ mg} = 8.097 \text{ }\mu\text{mol}$ and $2.581 \text{ mg} = 3.449 \text{ }\mu\text{mol}$ for the first and second measurements on Li_4C_{60} , respectively, and $6.251 \text{ mg} = 7.693 \text{ }\mu\text{mol}$ for the second sample of Na_4C_{60} .

The activation energy barrier (E_a) and the corresponding transition states (TS) were computed using the climbing image nudged elastic band (CI-NEB) method¹⁵ as implemented in the Quantum Espresso code.¹⁶ After the initial and final configurations of the reaction path are known, the intermediate configurations are determined by a linear interpolation followed by energy minimization across the minimum energy path. The electronic structure was solved using ultrasoft pseudopotentials¹⁷ and the generalized gradient approximation with the model of Perdew, Burke and Ernzerhof as the exchange-correlation functional. The kinetic energy cutoff for wavefunctions was set to 40 Ry and 350 Ry for the charge density. A Marzari-Vanderbilt¹⁸ smearing of 0.02 Ry is used to aid convergence.

III. RESULTS AND DISCUSSION

The X-ray diffraction patterns of polycrystalline Li_4C_{60} and Na_4C_{60} are shown in Figure 2 and are in excellent agreement with the patterns observed by other groups^{5,7}, consistent with a quasi-tetragonal structure⁵ with space group $I2/m$ for Li_4C_{60} and a monoclinic structure⁷ with the same space group for Na_4C_{60} . Figure 3 shows the Raman spectra for Li_4C_{60} and Na_4C_{60} obtained using a 633 nm He-Ne laser for excitation. This wavelength is very appropriate for the analysis of these phases, since the pentagonal pinch mode area (around 1469 cm^{-1} for pristine C_{60}) is not as dominant as when exciting the sample with an argon ion laser (514 nm),

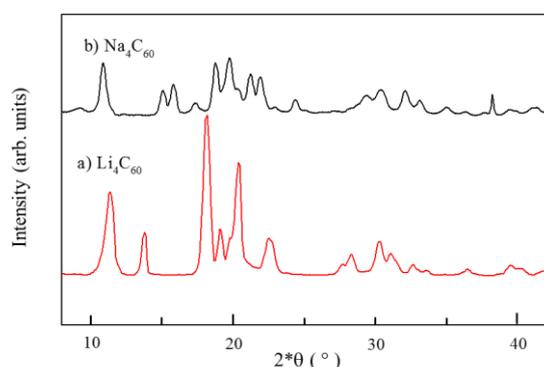


FIG. 2. X-ray diffraction patterns of Li_4C_{60} and Na_4C_{60} .

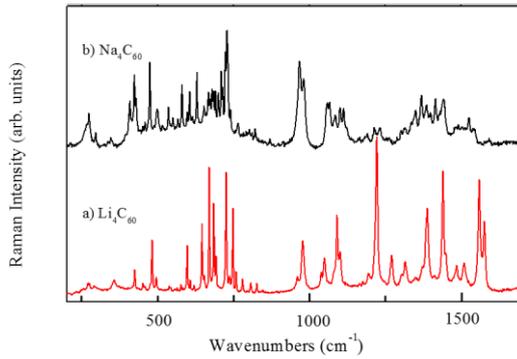


FIG.3. Raman spectra obtained using He-Ne laser, 633 nm, for Li_4C_{60} and Na_4C_{60} .

making it easier to detect impurity phases from unreacted C_{60} or from other non-polymeric intercalated C_{60} phases. The Raman spectra for the two phases show all signs of fully evolved two-dimensional Li_4C_{60} and Na_4C_{60} polymer structures. The pentagonal pinch mode, originally at 1469 cm^{-1} for pristine C_{60} , is shifted to 1441 cm^{-1} , in perfect agreement with earlier observations^{5,8,19,20}. The appearance of new modes at $960/978\text{ cm}^{-1}$ and $966/980\text{ cm}^{-1}$ for Li_4C_{60} and Na_4C_{60} , respectively, are also distinct signatures of polymeric phases and their positions can be used as fingerprints to distinguish between different types of polymer structures, in the same way as the shift of the pentagonal pinch mode. Distinct evidence for Li_4C_{60} and Na_4C_{60} polymers are also the large splitting of the H_g modes which is especially obvious for the Na_4C_{60} Raman spectra. For a more detailed discussion of the Raman spectra of Li_4C_{60} and Na_4C_{60} we refer to earlier studies²⁰.

Turning now to the calorimetric measurements, we show the measured specific heats of Li_4C_{60} and Na_4C_{60} as functions of temperature, T , in the range from 0.4 to 350 K in figure 4. The data shown were measured on one sample of each material by the adiabatic method and on one sample of Na_4C_{60} and two samples of Li_4C_{60} by the relaxation method (below 100 K). The data obtained by the relaxation method for the two Li_4C_{60} samples agreed to well within the experimental scatter and we show data for the first sample only. It is of obvious interest to compare these results with data for pristine C_{60} and for undoped C_{60} polymers. A detailed

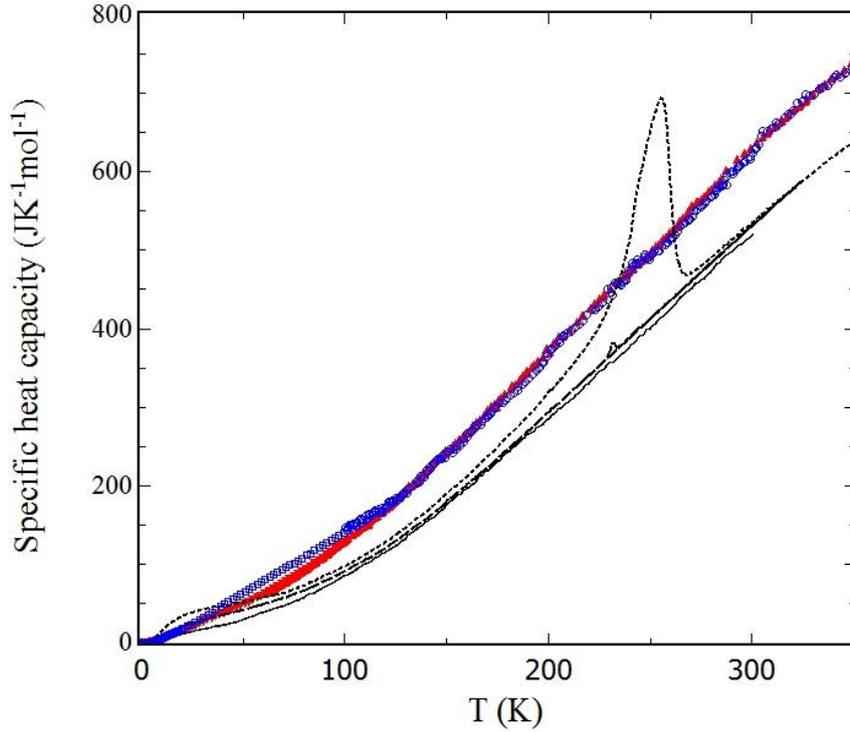


FIG. 4. Specific heat of Na_4C_{60} (blue rings) and Li_4C_{60} (red triangles) obtained by relaxation and adiabatic calorimetry in the range 0.4-350 K. Data for pristine C_{60} (dotted curve), 1D-polymerised C_{60} (dashed curve) and 2D-polymerised C_{60} (solid curve) are adapted from Inaba *et al.*²¹

measurement of the specific heat of C_{60} in both its pristine molecular phase and its tetragonal and orthorhombic polymeric phases has been reported by Inaba *et al.*²¹ and we have included their data in figure 4 for comparison. Other calorimetric studies of polymerized non-intercalated phases of C_{60} below 300 K have been reported for both dimer-rich material²² and for the orthorhombic²³, tetragonal²³ and rhombohedral²⁴ phases.

For Li_4C_{60} the data measured on different samples and with the two different methods are in excellent agreement in the ranges of overlap. Also, at temperatures above 120 K the specific heats of Na_4C_{60} and Li_4C_{60} are very similar both regarding actual values and general trends. The specific heat at these temperatures should be dominated by fullerene intramolecular

vibrations and it is therefore expected that different polymeric fullerene structures do not show any significant difference for this range. We note, however, that the specific heat of the intercalated polymers differs from that found²¹ for undoped C₆₀ polymers and for pristine C₆₀. The difference in magnitude becomes roughly constant at high temperatures at a value close to 100 J K⁻¹mol⁻¹. This value is in excellent agreement with the value deduced from the Dulong-Petit law, which predicts an excess specific heat of $4 \cdot 3 \cdot R = 99.77 \text{ J K}^{-1} \text{ mol}^{-1}$ due to the alkali ions. Here, the number three represents the degrees of freedom for the four metal ions in the structure. The good agreement shows that only weak interactions occur between the C₆₀ molecules and the intercalated alkali metal ions. The complete absence of a transition peak originating from the rotational transition in C₆₀ near 260 K in the data for the specific heat of Li₄C₆₀ and Na₄C₆₀ in figure 4 clearly shows that no unreacted C₆₀ is present in these samples.

At low temperatures the specific heat data for the polymers show much more distinct differences, as shown in Figure 5. The specific heat data for Li₄C₆₀ overlap almost perfectly for different samples and lie between those for the 1D and 2D polymers of C₆₀ at the lowest temperatures. Although there is also an almost perfect overlap between the data for the two intercalated polymers above 125 K, the specific heat for Na₄C₆₀ is significantly higher than that of Li₄C₆₀ at temperatures below this. We note that the specific heat is dominated by contributions from low energy modes, such as fullerene lattice modes and molecular librations, at low temperatures. For polymeric C₆₀ structures this leads to very obvious effects due to the stiffness induced by the polymerisation, as shown by Inaba *et al.*²¹. The increased stiffness shifts most vibrational frequencies to higher energies and the low temperature specific heats of the pure and intercalated polymers thus drop well below that of pristine, molecular C₆₀. As mentioned above, a first Na₄C₆₀ sample showed specific heat values close to that of pristine C₆₀ at the lowest temperatures, indicating that the intermolecular bonds had

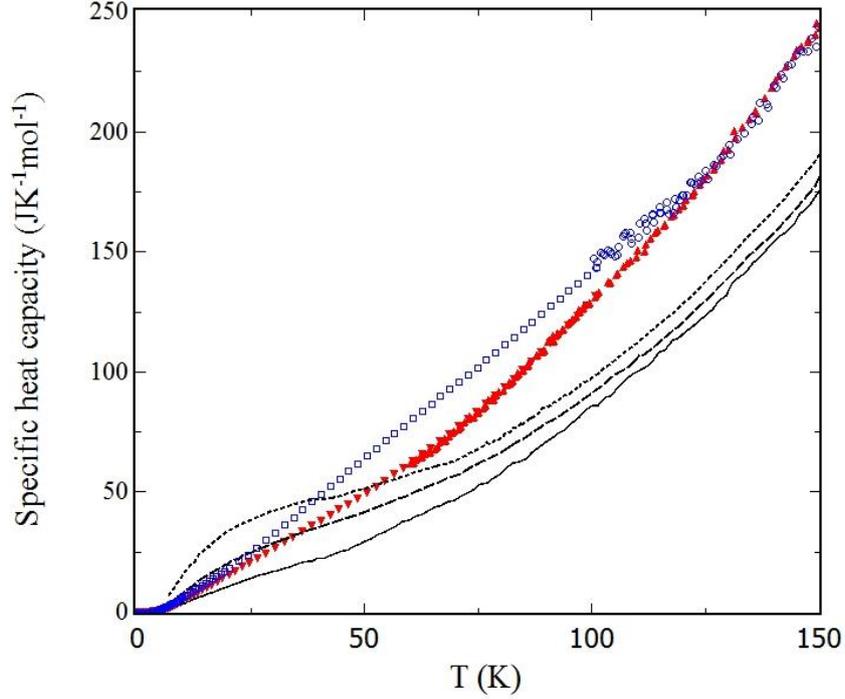


FIG. 5. Specific heat of Na_4C_{60} (blue rings) and Li_4C_{60} (red triangles) obtained by relaxation and adiabatic calorimetry in the range 0.4-150 K. Data for pristine C_{60} (dotted curve), 1D-polymerised C_{60} (dashed curve) and 2D-polymerised C_{60} (solid curve) are adapted from Inaba *et al.*²¹

broken up during mounting for the relaxation experiment, probably due to contamination by oxygen or water. The data for this sample were thus discarded and in the final analysis of Na_4C_{60} we have only used the data for sample 2 below 100 K and the data from the adiabatic calorimetry for sample 1 above 100 K.

Finally, below 10 K we also measured the specific heat for both materials in applied magnetic fields of 1 and 9 T. Between 2 and 10 K data in different fields were practically identical, except that data at 9 T fall slightly ($\approx 5\%$) below data measured at the lower fields in the center of the interval. Below 1 K, stronger deviations were found but because the absolute

magnitudes were small, experimental uncertainties are significant and we will not discuss these data further.

Li_4C_{60} is known to be bonded by 2+2 cycloadditions in one direction and by single covalent bonds in the other (see Figure 1). Librations and longitudinal waves should thus stiffen significantly in two dimensions but we cannot rule out the possibility that there might still be some freedom for transverse vibrations and for librations of the cycloaddition-bonded chains around their axes, perpendicular to the single bonds. The lattice of Na_4C_{60} should be less rigid because all intermolecular links are single C-C bonds. Effects due to the structure of the polymerized lattice are best seen at very low temperature, and we show in Figure 6 data for the specific heat of Na_4C_{60} and Li_4C_{60} between 0.4 and 30 K, plotted on logarithmic axes to show clearly the functional dependence. We expect that fullerene lattice vibrations and librations dominate the low-temperature behavior because the contribution from the metal ions should decrease exponentially with temperature (see below). Below 10 K the specific heat of both materials is roughly proportional to T^3 as expected in a Debye solid, but below about 2 K the dependence on temperature becomes weaker as lattice modes in the polymerized planes freeze out. For metals, an electronic specific heat term linear in T is

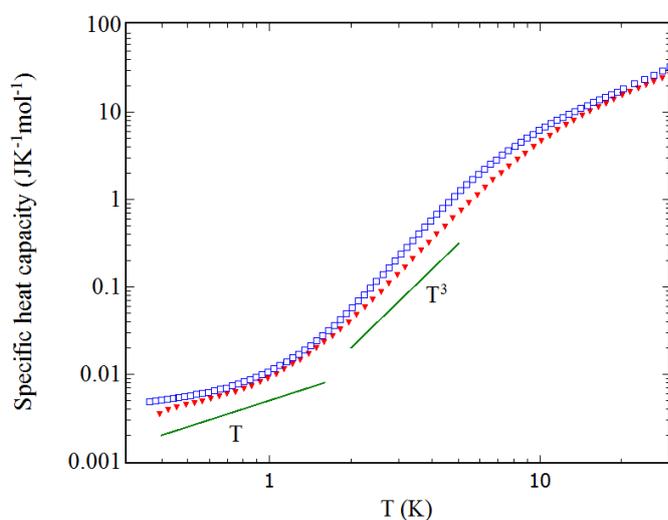


FIG. 6. Low-temperature data for the specific heat as a function of temperature T , plotted on a log-log diagram to show the functional dependence. Blue rings denote Na_4C_{60} , red triangles Li_4C_{60} .

expected, but both Li_4C_{60} and Na_4C_{60} are semiconductors¹³ with a very low conductivity and thus a negligible density of conduction electrons at very low T . However, at sufficiently low temperatures a stack of perfectly rigid planes should be a good approximation to a one-dimensional material with lattice vibrations only in the direction perpendicular to the sheets. Basic solid state theory predicts that the low-temperature specific heat of an N -dimensional material should be proportional to T^N , and we see that below 1 K both materials are very close to behave like ideal one-dimensional solids with a specific heat $c_p = c_o T$. For Na_4C_{60} the slope becomes even smaller below 0.6 K, but this might be an experimental artifact due to the very small magnitude of the total c_p .

A reasonable starting point for an analysis of the contribution from the alkali metal ions to the total c_p in Li_4C_{60} is that the specific heat of the fullerene structure should not be much different from that of the 2D tetragonal C_{60} polymer, since the geometry is very similar and the bonding pattern differs only by having single bonds in one direction. Assuming that the interaction between the fullerene lattice and the ions is very weak, as suggested from the high-temperature data, we can subtract the contribution of the former from the measured data for Li_4C_{60} to find the excess specific heat of the Li^+ ions (Kopp-Neumann law). This procedure might, however, overestimate slightly the contribution from the lithium ions, since the single bonds in the Li_4C_{60} are “softer” than the corresponding twin bonds of tetragonal C_{60} . As mentioned above, there are two sites for Li^+ ions^{5,11}, corresponding approximately to one ion in each tetrahedral void and two in each octahedral void in the original fcc lattice of C_{60} . However, there are several possible ionic positions in each of the octahedral sites and there is some uncertainty as to the exact ionic locations^{5,11,25}. The excess specific heat obtained by subtraction of the data for tetragonal 2D C_{60} can be analyzed in the light of our structural knowledge. Because there is no true Li^+ ion lattice an Einstein model for the specific heat is

preferred to a Debye model, and in principle two Einstein temperatures corresponding to the two different sites should be expected. Fitting Einstein models to the data we find reasonable agreement above about 100 K for an Einstein temperature $T_E = 386$ K. A somewhat better fit can be found using two Einstein functions of equal amplitude and with $T_{E1} \approx 300$ K and $T_{E2} \approx 550$ K, but the statistical quality of the single-function fit is better. We can compare the Einstein temperatures found with the Debye temperature of metallic lithium, 344 K. However, below 100 K the experimental data always significantly exceed the fitted functions. We do not believe that this is an experimental error, because measurements on two different samples give almost indistinguishable results and measurements with different methods are in excellent agreement in the range of overlap. While the excess specific heat in this temperature range might be a contribution from fullerene chain librations, it has a characteristic asymmetric peak shape suggesting a Schottky anomaly. Using the classical two-level expression²⁶

$$c_s = R(\Delta E/k_B T)^2 \exp(\Delta E/k_B T) / [\exp(\Delta E/k_B T) + 1]^2 \quad (1)$$

with ΔE as fitting parameter resulted in a good fit, with fitted parameters indicating four Li^+ ions moving between two levels with an energy difference of $\Delta E = 9.3$ meV. We believe that this component corresponds to ions jumping between the different states inside the large octahedral voids, where two ions share several possible sub-sites but their total energy depends on their relative positions, as previously shown in NMR studies²⁵. In fact, an even better fit could be obtained by using the expression for two ions moving in a three-level system²⁷, with excited energy levels near 7 and 15 meV, but the large number of parameters made the fitted energies quite uncertain. It should be noted, however, that the latter system should be an excellent physical model for ions trapped in the octahedral voids with sites near

the corners. We show in Figure 7 the derived data for the excess specific heat of Li_4C_{60} together with the fitted single Einstein function and the two-level Schottky function (Eq. (1)) to show the quality of the fit. Note that both contributions discussed go exponentially to zero as $T \rightarrow 0$, validating the assumptions made in the analysis of the fullerene contribution. Also, the fitted Einstein function has an amplitude of 118 instead of $100 \text{ JK}^{-1}\text{mol}^{-1}$, corroborating our assumption above that the subtraction procedure used probably overestimates the excess specific heat of Li_4C_{60} . However, considering the many approximations made, the agreement between the derived data for the excess specific heat and the fitted functions is excellent.

To get more insight into the dynamics of these trapped ions we have performed density functional theory (DFT) calculations using the climbing image nudged elastic band (CI-NEB) method to calculate the activation energy associated with a coordinated jump to a new set of positions of the two Li^+ ions residing in the octahedral void, starting from a geometrically relaxed Li_4C_{60} unit cell corresponding to the report by Ricco *et al.*¹¹ It is clear from these calculations that the activation energy related to a full ionic swap is about two orders of magnitude higher than the energy levels found in our study (see figure S1 in supporting information). This strongly suggest that the observed excited levels in the range of tens of meV are instead associated with smaller positional jumps between local energy minima close to the ground state ionic positions.

For Na_4C_{60} a similar analysis will in principle be more uncertain because of the very different lattice structure. No pure C_{60} polymer with a single-bonded structure similar to that of Na_4C_{60} exists, and we have again used tetragonal C_{60} as reference material. The excess specific heat due to the Na^+ ions was found by subtracting the data for the latter from the data for Na_4C_{60} and we found again a behavior similar to that shown for Li_4C_{60} in figure 7, although shifted to

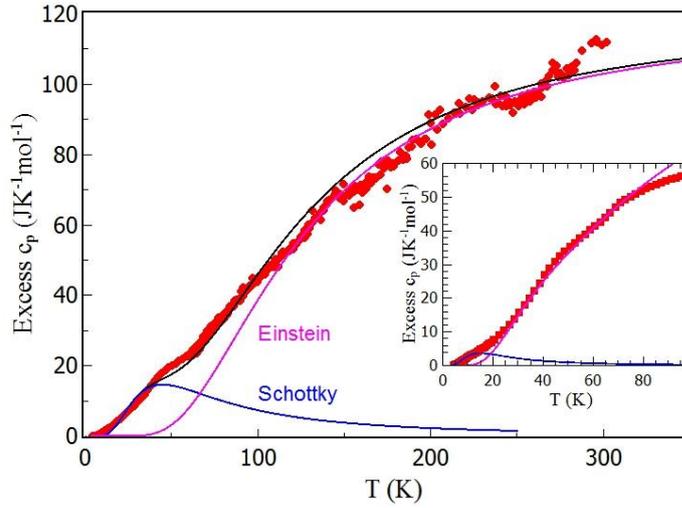


FIG. 7. Excess specific heat of Li_4C_{60} , obtained by subtraction of the data for 2D-polymerized C_{60} from those for Li_4C_{60} . Solid curves show an Einstein function with $T_E = 386$ K fitted to the data above 100 K, a Schottky function with $T_S = 108$ K fitted to the difference between the experimental data and the Einstein function, and the resulting total fitted specific heat. Inset shows the corresponding data for Na_4C_{60} below 100 K with $T_E = 122$ K and $T_S = 36$ K.

lower temperatures as expected from the more rapid rise of c_p with temperature (figure 5). Again, the high-temperature data agreed well with the high-T Dulong-Petit limit and the low-temperature data (up to about 80 K) could be very well fitted with an Einstein function with $T_{E1} \approx 120$ K and an amplitude corresponding to the presence of two Na^+ ions per C_{60} molecule (see inset in Figure 7). The Debye temperature of Na, for comparison, is 158 K. No single Einstein-type curve gave a satisfactory fit to the data over the whole experimental range in temperature, but a reasonable result was obtained for a sum of two Einstein functions, each with an amplitude corresponding to two Na^+ ions and with $T_{E1} = 122$ K and $T_{E2} = 352$ K. Again, the Einstein functions did not describe the data well below 20 K, where there was an additional excess specific heat. This could be very well fitted with the Schottky expression

Eq. (1), now with an amplitude corresponding to a single ion moving between states $\Delta E = 3.1$ meV apart (see inset in Figure 7).

For both materials, the fitted theoretical models agree very well with the experimental data below about 90 K and in the range 200-300 K. Between 90 and 200 K the experimental data are 10-15 $\text{JK}^{-1}\text{mol}^{-1}$ lower than the fitted functions, with similar positive deviations above 300 K. The most probable reason for these deviations from a smooth behaviour is that the baseline, taken as the specific heat of 2D-polymeric C_{60} , is not a perfect model for the fullerene lattices in the fullerenes. The specific heat of the various structural varieties of pure C_{60} can be very roughly divided into a “Debye” region below 50-70 K, a region dominated by radial molecular modes above this and a region dominated by tangential molecular modes near and above room temperature. Intermolecular bonding stiffens the lattice, increasing the energy of the lattice modes and shifting the corresponding contributions to c_p to much higher temperatures. The in-plane bonding of the 2D polymers is weakest in Na_4C_{60} (single bonds only) and strongest in tetragonal C_{60} (twin bonds in both directions), and we thus expect that in the Debye region the fullerene-derived specific heat should be lowest in tetragonal C_{60} , slightly higher in Li_4C_{60} and highest in Na_4C_{60} . The subtraction procedure used to find the excess specific heat of the alkali ions will thus give slightly too high values for the intercalated polymers, especially Na_4C_{60} , in this range, which results in the observed deviations between the experimental data and the fitted models above 100 K.

We note that a structural phase transformation has been suggested^{7,19} to occur in Na_4C_{60} near or below 100 K, involving the fullerene lattice, the metal ions, or both. Several unexplained anomalies have been observed: data for the spin susceptibility found from ESR show an unusual temperature dependence with a change in slope^{7,19} near 100 K and a sharp peak¹⁹ near

40 K, and high temperature data cannot be fitted to standard Curie plus Pauli models. Kubozono *et al.*¹⁹ also find small anomalies in all lattice parameters near 50 K, but no appearance (or disappearance) of any diffraction lines. Although it might be possible that some of the scatter we observe at intermediate temperatures could be associated with such a transition, the inset in Figure 7 shows a complete absence of any sharp anomalies below 100 K that could indicate the existence of a structural transition in the material.

In summary, we have shown experimental data for the specific heat of Na_4C_{60} and Li_4C_{60} . At high temperatures the two different polymer structures have a very similar specific heat both in absolute values and general trend. A difference in specific heat between the intercalated structures and undoped polymeric C_{60} of about $100 \text{ J/K}^{-1}\text{mol}^{-1}$ is observed, in excellent agreement with the Petit-Dulong law. At low temperatures the general features of the specific heat data for Li_4C_{60} and Na_4C_{60} can be understood from a stiffening of the librational molecular motion induced by the polymer bonds, together with contributions from the thermal vibrations of the inserted alkali metal ions. We observe that covalent double bonds such as those in Li_4C_{60} affects the molecular motion to a somewhat higher degree than the single polymer bonds present in Na_4C_{60} , and for both materials we identify a contribution to the specific heat due to ionic jumps between states with similar energies inside the common fullerene enclosure. The standard two-level Schottky expression provides a reasonable functional dependence for this contribution but its amplitude is a factor of two higher than expected for Li_4C_{60} and a similar factor too low for Na_4C_{60} . This is probably caused by the use of an oversimplified model; in the real lattice a multi-level system with several degenerate or closely spaced sub-levels is expected in both materials. Finally, most of the observed deviations from a smooth Einstein behaviour of the difference between the specific heats of

the two intercalated polymers and tetragonal C_{60} are probably caused by the structural differences between the fullerene “backbones” of the materials studied.

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