produced in irradiation experiments and the high grain abundances (for example, 50% with respect to H_2O) predicted by interstellar chemistry models. Given interstellar cloud lifetimes, slight warming should suffice to convert the H_2CO to POM derivatives. These may be detectable as substructure near 1000 cm^{-1} (10 μm) on the interstellar silicate feature at the precise peak positions listed in Table 1. Furthermore, the compounds produced could participate in other reactions, providing a new set of complex organics not previously considered. In dense, hot cores where ice grains would evaporate, some of the products might be observable in the gas phase (*13*).

There are already applications for these results to comet science. We can use the H_2CO and NH_3 abundances determined for Comet Halley from ground-based and in situ measurements by Giotto and Vega to estimate that ~3% of the organic in Comet Halley are produced by thermal H_2CO reactions in the nucleus. These molecules would be very oxygen-rich (C/O ≈ 1) and would have alcohol-, ether-, and amine-type properties. The nature of the products and their relative abundances strongly depend on the initial ice composition and would therefore be a sensitive tracer of the chemical conditions inside the nucleus. Furthermore, these materials could contribute to the IR emission already detected from comets. Several of their CH stretching bands peak at positions spanned by the "3.4-μm" cometary emission feature (*14*).

Chemical analysis of the products of low-temperature H_2CO reactions are necessary to better characterize the molecules that are expected under astrophysical conditions. Such studies are essential to understand the origin of the organic molecules observed in the interstellar medium and in comets as well as the processes and the chemical conditions in the ices where they were formed.

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Specific Heat and Thermal Conductivity of Solid Fullerenes

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Evidence is presented that the lattice vibrations of compacted C_{60}/C_{70} fullerite microcrystals consist predominantly of localized modes. Vibrational motions of the rigid molecules ("buckyballs") have been identified as well as their internal vibrations. Debye waves play only a relatively minor role, except below ~4 kelvin. By comparison with other crystalline materials, for these materials the Einstein model of the specific heat and thermal conductivity of solids, which is based on the assumption of atoms (in this case, buckyballs) vibrating with random phases, is in much better agreement with the measurements than the Debye model, which is based on collective excitations.

The first model for lattice vibrations of solids was proposed in 1907 by Einstein, who applied the quantum concept to the mechanical motion of individual atoms in a crystal lattice that he assumed to be vibrating with random phases (*1*). He subsequently found that this model was inadequate, its most drastic shortcoming being that it led to a thermal conductivity that disagreed with the observation on crystals both in magnitude and in temperature dependence (*2*). This disagreement was removed by Debye (*3*) and by Born and von Karman (*4*), who demonstrated that in crystalline solids the atoms vibrate collectively as elastic waves. This picture has been tested extensively and is now generally accepted. Exceptions have been noted, however. In amorphous solids and certain disordered crystals, for example, the thermal conductivity above ~50 K can be well described with Einstein's picture (*5, 6*) (although the cause for the random phase of vibration of the neighboring atoms, the crucial assumption in Einstein's picture, is not yet understood). Also, in some crystalline polymeric solids, the specific heat has been shown to be well described over a wide temperature range with a set of Einstein modes consisting of vibrational motions of certain molecular units (*7*). However, in crystal lattices of simple atomic constituents, the model of collective wave motion has always been found to be correct.

We report here on a polycrystalline disordered solid of a rather simple composition in which the lattice vibrations are predominantly localized. Above ~4 K, both its specific heat and its thermal conductivity can be quantitatively described with Einstein's model, thus showing clearly the limitations of the commonly used picture that is based on plane waves.

The starting material was microcrystalline (~1 μm) commercial (*8*) fullerite powder containing ~85% C_{60} and ~15% C_{70} molecules (buckyballs), which had been extracted with toluene. Without any further treatment, the powder was compressed in a pellet press at 3000 atm, which resulted in pellets of a strength comparable to that of soft pencil graphite. This procedure enabled us to prepare samples of sufficient size to perform the measurements. Their mass density $\rho = 1.54$ g cm^{-3} (±10%) was close to the theoretical density ($\rho_{theor} = 1.676$ g cm^{-3}) of the face-centered-cubic (fcc) lattice. From Debye-Scherrer x-ray diffraction measurements, an fcc lattice constant of $a = 14.1 \pm 0.1$ Å was determined, near the accepted value for pure C_{60} ($a_{60} = 14.186$ Å) (*9*). X-ray line shapes of the powder as received and of the compact solid were virtually identical. We also investigated the thermal properties of compacts made of C_{60} starting material and obtained similar results (*10*). Thus, the presence of C_{70} appears to be irrelevant as far as the observations reported here and their interpretation are concerned. To avoid any ambiguity, however, we refer to the samples studied here as C_{60}/C_{70} compacts. Small changes of the low-temperature specific heat were also observed when the starting material or the

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compacted sample were vacuum-baked for 24 hours at 250°C. These changes, however, are also irrelevant at this point.

Specific heat was measured below 60 K with the transient heat pulse technique described in detail elsewhere (*11*), and between 30 and 300 K with an ac technique (*12*). Thermal conductivity was measured with the steady-state one-heater, two-thermometer method below 30 K, and with an ac technique [the 3ω method (*13*)] above 30 K. The metal film used for the latter (Ag, 30 μm wide, 2000 Å thick, 4 mm long, 20-ohm resistance at 300 K) was evaporated on the smooth surface of the pellet, which had been coated with a film of GE-7031 varnish <10 μm thick to improve the uniformity of the Ag film.

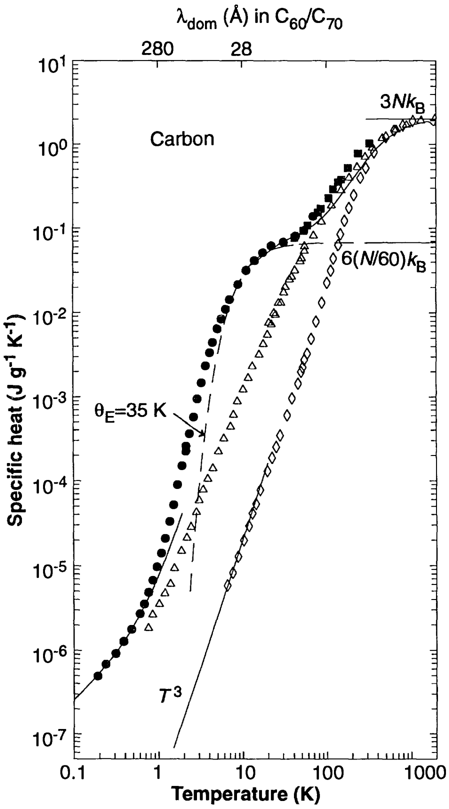

Fig. 1. Specific heat of microcrystalline compacts of C_{60}/C_{70} molecules (buckyballs) of composition 85%/15%, compared with that of diamond (diamonds) (*14*) and graphite (triangles) (*14, 15*). Solid circles, dc measurements; solid squares, ac measurements. Above ~80 K, the specific heat of the C_{60}/C_{70} compacts is close to that of graphite. The dashed line is an Einstein specific heat with the characteristic temperature θ_E = 35 K (ν_E = 7.3 × 10^{11} Hz), N is the number density (per unit mass) of carbon atoms, and $N/60$ is the approximate number density of the buckyballs. The term $6(N/60)k_B$ is a modified Dulong-Petit specific heat based on the assumption that the rigid clusters perform translational as well as torsional vibrations, with a total of six degrees of freedom. The solid curve above ~40 K shows the contribution to the specific heat expected for the intramolecular vibrations of the C_{60} molecules, calculated with the data in (*21*). Below ~2 K, the solid line is of the form $c_1T + c_3T^3$. If the cubic term is caused by waves that obey the Debye law, a Debye velocity v_D = 2.39 × 10^5 cm s^{-1} can be determined. From v_D, the dominant phonon wavelength λ_{dom} (*28*) in the C_{60}/C_{70} compact has been calculated, as shown on the upper horizontal scale (obviously not physically meaningful for values smaller than the lattice constant). The low-temperature specific heat of diamond is described with a Debye temperature θ_D = 2066 K, leading to a velocity v_D = 1.23 × 10^6 cm s^{-1}.

Between room temperature and ~80 K, the specific heat of the C_{60}/C_{70} compacts shown in Fig. 1 is similar to that of crystalline graphite (*14, 15*), which has a layered structure. Within the graphite layer (in the *ab* plane), the atoms are strongly bonded, whereas the bonds between the planes are weak. The high-frequency vibrational spectrum of graphite is therefore dominated by vibrations of the two-dimensional *ab* plane (*16*). The similar specific heat observed in the fullerite compacts in this temperature range, which has also been observed by Atake *et al.* (*17*), indicates that the modes excited resemble those of the *ab* planes in graphite, that is, they are surface modes that are localized on the individual buckyballs. Atake *et al.* (*17*) also reported a pair of sharp peaks in the specific heat in C_{60} powder near 250 K, which they ascribed to a structural phase transition [between fcc and simple cubic (*18*)] and also to the onset of rotation of the C_{60} molecules. These peaks are absent in the compacts, but their specific heat is somewhat greater than that reported by Atake *et al.* between ~50 and 300 K. This difference may be evidence for some disorder in our samples.

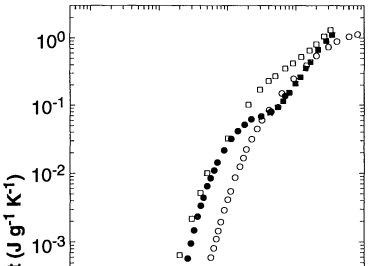

Fig. 2. Specific heat of the C_{60}/C_{70} compacts (filled circles and squares as in Fig. 1) compared with that of amorphous SiO_2 (open circles) and polystyrene (open squares) (*22*) to demonstrate the similar temperature dependence below ~1 K.

Below 80 K, the specific heat of the compact greatly exceeds that of graphite, dropping off steeply (almost exponentially) below 10 K. The specific heat below 40 K is well described with an Einstein specific heat (Fig. 1), with the characteristic temperature θ_E = 35 K ($k_B\theta_E$ = 3 meV, or ν_E = 7.3 × 10^{11} Hz, $\tilde{\nu}_E$ = 24 cm^{-1}, where k_B is Boltzmann's constant and ν_E is the characteristic Einstein vibrational frequency), and with a number density of the modes equal to $6(N/60)$, where N = 5 × 10^{22} g^{-1} is the number density (per unit mass) of carbon atoms in the compact, and therefore $N/60$ is (approximately) the number density of buckyballs in our sample. Thus, we can ascribe this Einstein specific heat to the vibrational motion of the rigid molecules. Both the translational and the torsional vibration, with three degrees of freedom each, appear to have similar frequencies. From neutron scattering experiments, Neumann *et al.* (*19*) have determined the energy of the torsional mode of C_{60} below 50 K to be $k_B\theta_E$ = 2.8 meV, which is in good agreement with the value reported here.

Thus, in the temperature range from 4 to 40 K, the vibrational spectrum is also dominated by localized excitations, which in this case are vibrations of the rigid buckyballs. Beyermann *et al.* (*20*) recently reported measurements of the specific heat of compressed C_{60} compacts between 1.4 and 20 K; their data agree well with ours, except in the region below 2.5 K, where their data lie considerably above ours (*20*).

As has been argued above, the rise of the measured specific heat above the Dulong-Petit value for the rigid buckyballs that sets in above 40 K indicates the onset of the intracluster vibrations (surface modes). Because these modes are known (*21*), their

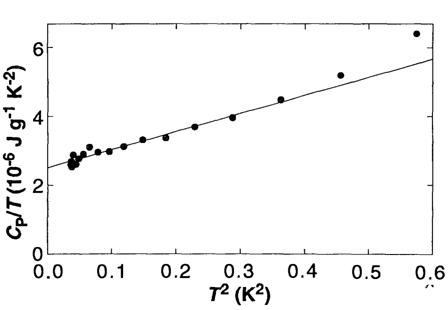

Fig. 3. Low-temperature specific heat of C_{60}/C_{70} compacts, plotted as C_p/T versus T^2. Below ~0.7 K, the data are well fitted with Eq. 1. See also the caption of Fig. 1 [the deviation of the experimental data from Eq. 1 as the temperature increases toward 1 K is common for amorphous solids (*23*)].

specific heat can be calculated; see the solid curve above ~10 K in Fig. 1, which agrees well with our measurements.

Below ~4 K, the specific heat decreases less rapidly than predicted for Einstein oscillators, and at the lowest temperatures of our measurements the specific heat approaches a linear temperature dependence. In this temperature range (<4 K), the specific heat resembles that of amorphous solids, as shown in Fig. 2 through the comparison with the specific heat of amorphous SiO_2 and polystyrene (*22*). In amorphous solids, the low-temperature ($T < 1$ K) specific heat C_p can be described well by a polynomial of the form (*23*)

$$C_p = c_1 T + c_3 T^3 \qquad (1)$$

The same polynomial can also be used to fit our data below 0.7 K (Fig. 3). By plotting (C_p/T) versus T^2 on linear scales, we obtain a straight line. The intercept at $T = 0$ yields $c_1 = 2.5 \times 10^{-6}$ J g^{-1} K^{-2}. The slope of the straight line yields $c_3 = 5.3 \times 10^{-6}$ J g^{-1} K^{-4}. The solid curve in Fig. 1 is an extension of Eq. 1 up to 2 K. The magnitude of c_1 lies in the range found in all amorphous solids (*23*). Although such low-energy excitations [believed to be caused by tunneling (*24*)] have also been observed in certain chemically disordered crystalline solids [reviewed in (*6*)], they have not been observed previously in a solid of a single chemical species. As mentioned above, the presence of C_{70} molecules appears to be unimportant, we are thus led to conclude that some other form of disorder causes the glasslike behavior in our compacts. In our measurements, both c_1 and c_3 are somewhat sample dependent (to within ~20%); the origin of this effect is under investigation (*10*).

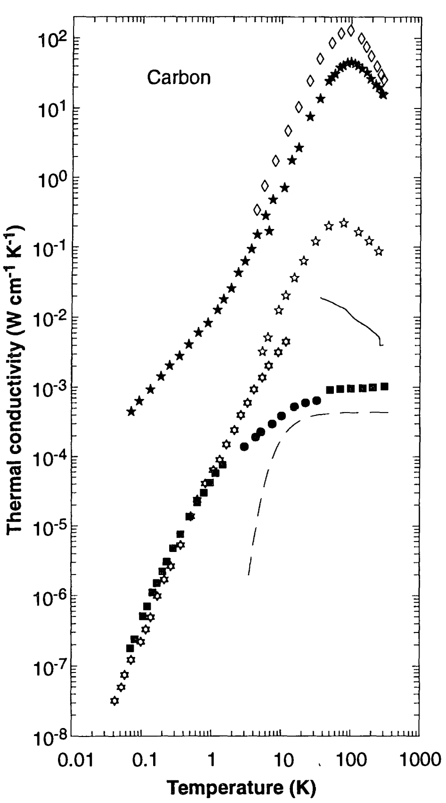

Fig. 4. Thermal conductivity of carbon in its three phases: diamond (diamonds) (*29*); single-crystal C_{60} (solid line) (*30*) and single-crystal graphite, heat flow in the *ab* plane (filled stars) and perpendicular to it (open stars), that is, along the *c* axis (*31*), compared to that of C_{60}/C_{70} compacts (filled circles and squares as in Fig. 1). In all single crystals, heat transport by lattice waves (phonons) is observed. The dashed line is the thermal conductivity based on Einstein's theory, assuming that only the rigid buckyballs carry heat in a random walk, and not phonons.

From the cubic term, c_3, we determine the Debye temperature $\theta_D = 80$ K of the bulk solid with zero porosity (based on the theoretical number density of buckyballs), and the Debye velocity $v_D = 2.39 \times 10^5$ cm s^{-1}. From low-temperature measurements of the Young's modulus on single crystals of C_{60}, Hoen *et al.* (*25*) determined a Debye temperature of ~80 K. Preliminary ultrasonic measurements on compacts in our laboratory (*26*) at 300 K have yielded a transverse velocity $v_t = 1.9 \times 10^5$ cm s^{-1} and a longitudinal velocity $v_\ell = 3.3 \times 10^5$ cm s^{-1}. Shi *et al.* (*27*) recently reported an increase of the Young's sound velocity of 22% as the single-crystal C_{60} was cooled from 300 to 10 K. Assuming the same stiffening in our samples and allowing for a porosity of 8%, we calculate a low-temperature Debye velocity of 2.68×10^5 cm s^{-1} in the zero-porosity solid, in satisfactory agreement with the v_D determined from the specific heat. From v_D a dominant phonon wavelength $\lambda_{\rm dom}$ (the wavelength of the phonons carrying the bulk of the heat at a given temperature in the Debye approximation) can be determined from $\hbar\omega_{\rm dom} = 4.25\ k_BT$, that is, $\omega_{\rm dom}/2\pi = (90\ {\rm GHz\ K^{-1}})T$ ($\hbar = h/2\pi$, where h is Planck's constant) (*28*). Values for $\lambda_{\rm dom}$ in the C_{60}/C_{70} compacts are shown at the top of Fig. 1.

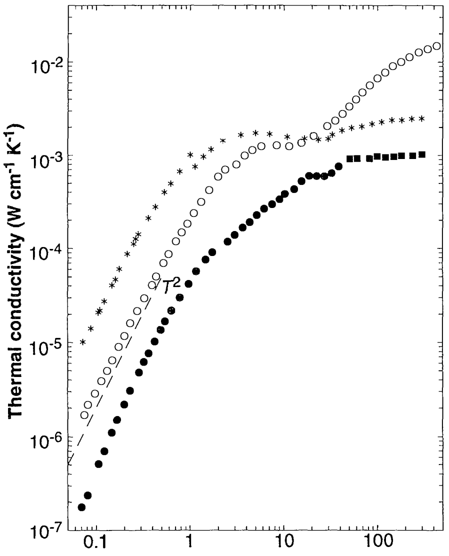

Fig. 5. Thermal conductivity of polycrystalline C_{60}/C_{70} compacts (filled circles and squares) compared with that of amorphous SiO_2 (open circles) and amorphous As_2S_3 (asterisks); solid circles, dc measurements, solid squares, 3ω measurements. The dashed line shows a T^2 dependence, drawn to show the smallest thermal conductivity known for an amorphous solid (Ca, KNO_3) (*32*). The T^2 thermal conductivity of the C_{60}/C_{70} compacts is approximately one-quarter as large

On the basis of the specific heat measurements, we conclude that the thermally excited vibrations below ~4 K, corresponding to a dominant phonon frequency of 400 GHz, are predominantly collective excitations and tunneling states as characteristic for amorphous solids. Above this temperature, the specific heat is dominated by Einstein oscillators, which are believed to be the vibrational motions of the rigid buckyball molecules, and, above 40 K, by surface modes, which are normal modes within the molecules. These conclusions can be verified through thermal conductivity measurements (Fig. 4), which are shown together with measurements on diamond (*29*), on a single crystal of C_{60} (*30*), and on graphite for heat flow both in the tightly bonded *ab* plane and in the direction perpendicular to it (*31*). Except for the C_{60}/C_{70} compacts, all crystals show the decrease of the thermal conductivity with increasing temperature near 300 K, which is characteristic for crystals and which results from the increased probability for phonon scattering by Umklapp processes. In the compacts, by contrast, the conductivity increases with increasing temperature and is practically temperature independent above ~10 K. This behavior suggests a different mechanism for the heat transport. In Einstein's theory, the heat is transported in a random walk among harmonically coupled localized oscillators, assumed to vibrate with random phases (*2*). In that case, the jump time of the elastic energy is close to one-half of the period t_0 of that oscillation ($t_0 = 2\pi/\omega_E$). This model leads to a thermal conductivity $\Lambda_{\rm Eins}$ (*5*):

$$\Lambda_{\rm Eins} = 2\frac{k_B{}^2}{\hbar}\,\frac{n_v{}^{1/3}}{\pi}\,\theta_E\,\frac{x^2e^x}{(e^x-1)^2} \qquad (2)$$

where $n_v = (N/60)\rho$ is the number density (per unit volume) of the buckyballs, θ_E is the Einstein characteristic temperature, and $x = \theta_E/T$. In applying this theory, we consider only vibrations of the rigid molecules and ignore their surface modes, because we do not believe that surface modes contribute to the transport of heat. However, we consider both the translational and the torsional vibrations of the rigid molecules. This leads to the factor of 2 in Eq. 2. With all quantities in Eq. 2 known, we can calculate Λ_{Eins} (dashed curve in Fig. 4). The agreement between theory and experiment from 300 to 10 K, achieved without any adjustable parameters, is taken as evidence that we correctly identified the excitations in the specific heat measurements and also the mechanism of the heat transport. The transition from torsional vibration to nearly free rotation expected to occur at ~250 K does not appear to have a noticeable effect. The excitations that dominate the specific heat above ~40 K (by as much as an order of magnitude at 300 K) do not appear to contribute to the heat flow at all, which means that they are truly localized.

Einstein's theory of thermal conductivity quite obviously fails below ~10 K [as it does in all amorphous solids as well (*5*)]. In this temperature range collective excitations become noticeable in specific heat, and they should contribute to the heat flow, thus increasing the thermal conductivity. As shown in Fig. 5, the thermal conductivity of the C_{60}/C_{70} compacts is similar in this temperature range to that observed in all amorphous solids, in which the phonon scattering by the low-energy [tunneling (*25*)] excitations leads to a thermal conductivity that varies as T^2. (Some additional grain boundary scattering appears to occur in the compacts, which decreases the conductivity at the lowest temperatures. Diffuse scattering with a mean free path of ~20 μm may be responsible for this effect.) Because both thermal conductivity and low-temperature specific heat of the compacts are similar to those of amorphous solids, we do not believe that some accidental random impurities are the cause. The origin of the glasslike excitations, which are obviously absent in the single-crystal C_{60} (see the thermal conductivity data in Fig. 4) are as yet unexplained. The point to be stressed here is the observation of a solid with lattice vibrations that are described by the Einstein localized oscillator model over a wide frequency range much better than by the standard Debye model, which is based on plane waves.

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Mid-Depth Circulation of the Subpolar North Atlantic During the Last Glacial Maximum

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Holocene and glacial carbon isotope data of benthic foraminifera from shallow to mid-depth cores from the northeastern subpolar Atlantic show that this region was strongly stratified, with carbon-13–enriched glacial North Atlantic intermediate water (GNAIW) overlying carbon-13–depleted Southern Ocean water (SOW). The data suggest that GNAIW originated north of the polar front and define GNAIW end-member carbon isotope values for studies of water-mass mixing in the open Atlantic. Identical carbon isotope values in the core of GNAIW and below the subtropical thermocline are consistent with rapid cycling of GNAIW through the northern Atlantic. The high carbon isotope values below the thermocline indicate that enhanced nutrient leakage in response to increased ventilation may have extended into intermediate waters. Geochemical box models show that the atmospheric carbon dioxide response to nutrient leakage that results from an increase in ventilation rate may be greater than the response to nutrient redistribution by conversion of North Atlantic deep water into GNAIW. These results underscore the potential rule of Atlantic Ocean circulation changes in influencing past atmospheric carbon dioxide values.

The general features of North Atlantic Ocean circulation during the last glaciation, ~18,000 to 15,000 years ago, are fairly well understood, but several outstanding questions remain. Among these uncertainties is the mode of formation and source region of high-$\delta^{13}C$ and low-Cd/Ca GNAIW as well as the origin of nutrient depletion in this water mass. Nutrient-poor (high $\delta^{13}C$, low Cd/Ca) lower North Atlantic deep water (NADW) now fills the deep northern and tropical Atlantic. During the last glaciation, this water mass was replaced by nutrient-rich SOW, whereas

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