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Letters to the Editor

Negative thermal expansion of fullerite C_{60} at liquid helium temperatures

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The thermal expansion of fullerite C_{60} has been measured in the temperature range 2–9 K. A compacted fullerite sample with a diameter of about 6 mm and height of 2.4 mm was used. It was found that at temperatures below ~ 3.4 K the linear thermal expansion coefficient becomes negative. At temperatures above 5 K our results are in good agreement with the available literature data. A qualitative explanation of the results is proposed.

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A considerable body of data already exists on the physical properties of fullerites [1]. Regarding the thermal expansion, however, no data yet exist on the thermal expansion of C_{60} and other fullerites at temperatures below 5 K (Ref. 2), although one may expect that at liquid helium temperatures there are peculiarities typical of orientational glasses in the behavior of the thermal expansion of C_{60} . In this paper we report the results of measurements of the thermal expansion of C_{60} carried out in the temperature range 2–9 K. Since C_{60} has a cubic lattice, its thermal expansion is isotropic and fully described by a single thermal expansion coefficient. It is therefore not necessary to use single crystals in thermal expansion studies.

The sublimated C60 powder used in our experiment for sample preparation was supplied by Term USA, Berkely, CA, and had a nominal purity of better than 99.98%. No traces of solvents were found by Raman analysis within its accuracy (0.1% by mass). Room-temperature powder x-ray diffraction pattern of the material displayed sharp peaks from fcc structure (a = 14.13 Å). In an atmosphere of dry argon the C60 powder was loaded in a small piston-cylinder device used for the sample preparation. After subsequent compacting of the powder at about 1 GPa, the sample (pellet of 6 mm in diameter and about 2.4 mm in height) was immediately transferred into a glass tube and dried under dynamic vacuum 10^{-6} Torr for about 16 h. The compacting procedure was done in air and did not exceed 15 min. Finally, the sample was sealed in vacuum 10^{-6}, shielded from light, and kept in that state for 3 months until the beginning of dilatometric measurements. Before mounting the sample, the glass cell containing the sample was opened in argon atmosphere at excessive pressure of about 200 Torr. During insertion of the sample into the measuring cell of the dilatometer, the sample was exposed to air for no more than 20 min and then was evacuated. During the measurements the vacuum in the dilatometer cell was maintained at the level of 10^{-6} Torr.

The measurements of the linear thermal expansion were carried out in the ILTPE of the National Academy of Sciences of Ukraine by using a capacitive dilatometer [3], which was specially modified for the measurements on C_{60}. The resolution of the dilatometer was $2 \cdot 10^{-9}$ cm. The sample was transported to Kharkov in a vacuum glass cell shielded from light and was held in a high vacuum during the measurements.

The dilatometer was constructed in such a way that all its elements capable of affecting the measured thermal expansion of the sample due to their own thermal expansion were held at constant temperature in a liquid helium bath. The temperature of the sample was measured by a reference germanium resistance thermometer and a differential thermocouple. Since the sample was in a vacuum chamber, it was well insulated thermally. Figure 1 shows a schematic drawing of the measuring cell of the dilatometer. A thermometric block containing the sample thermometer, a thermometer to control the temperature, and a sample heater were mounted on the objective table (*4*) of the dilatometer with which a good thermal contact was established. The fullerite sample studied (*7*) was also located on this table. The temperature difference between the upper and lower parts of the sample was measured by a differential thermocouple (gold-iron alloy versus copper), which measured the temperature difference between the objective table (*4*) of the dilatometer and a fine aluminum foil gasket (*3*) 0.02 mm thick and a 7 mm wide, which is located between the upper part of the sample and a sapphire hemisphere (*6*). Thermal connections between the objective table and the structural elements of the dilatometer and those with the displacement gauge were made by sapphire-sapphire point contacts. Because of the hardness and thermal conductivity of single-crystal sapphire, such contacts were found to perform very well in dilatometers [4,5]. According to the data of Carr and Swenson [4], the thermal expansion of a sapphire single crystal along the direction making a 60° angle with respect to the hexagonal axis is $\alpha = 1.2T^{2.2} \cdot 10^{-11}$ K^{-1} in the temperature range under consideration. For the direction along the axis this magnitude is probably even smaller since at room temperature the linear thermal expansion of sapphire along the hexagonal axis is an order of magnitude smaller than that in the basal plane [6]. Therefore, in order to have a minimal thermal expansion the sapphire was cut from a single crystal of artificial sapphire in such a way that the direction along which thermal expansion measurements of the studied samples were made coincided with the direction of the hexagonal axis of the sapphire crystals. It should be noted that since we did not know the true contribution of the sapphire and the aluminum foil to the results of thermal expansion measurements of C_{60}, we made additional studies to determine this contribution. From the data obtained by us it was found that this contribution was smaller than the experimental resolution of our setup in the whole range of temperatures studied.

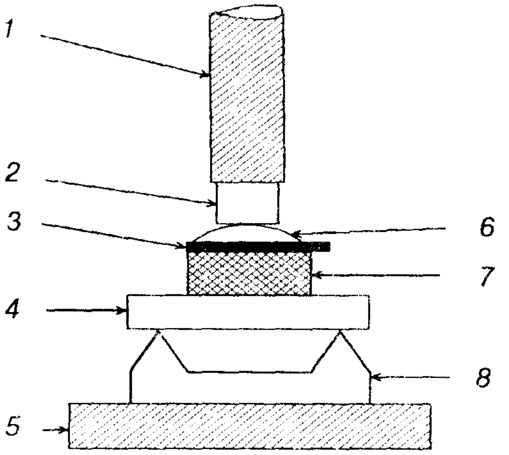

Fig. 1. Schematic drawing of the measuring cell of the dilatometer: rod to sensitive displacement transducer (*1*); sapphire tip (*2*); aluminum packing (*3*); sapphire objective table of the dilatometer (*4*); base for the objective table (*5*); sapphire hemisphere (*6*); C_{60} sample (*7*); sapphire support for the dilatometer objective table (*8*). Elements *1*, *2*, *5*, and *8* are in a liquid helium bath held at constant liquid helium temperature.

Temperatures below 4.2 K were obtained by pumping out liquid helium into a small container which was in thermal contact with the sample and by continuously refilling it by using the capillary method of DeLong et al. [7]. The elongation of the sample was measured by a two-terminal capacitive gauge connected so as to determine the frequency of a tunnel diode oscillator circuit. The block containing the capacitive displacement gauge and the tunnel diode oscillator were also placed in a liquid helium bath at constant temperature.

The change in the length of the sample was determined by increasing the temperature and decreasing it. Data on the temperature and sample length were measured once a minute and processed in real time by a computer.

The measurements were made by a temperature step technique. At the beginning of each measurement the sample was held at constant temperature T_1 and the output of the displacement gauge was constant. The temperature of the objective table with the sample was then changed to a temperature T_2, which from that moment was held constant. When the temperature variation of the sample no longer exceeded 0.001 K per minute, we determined the change in its length because of the temperature

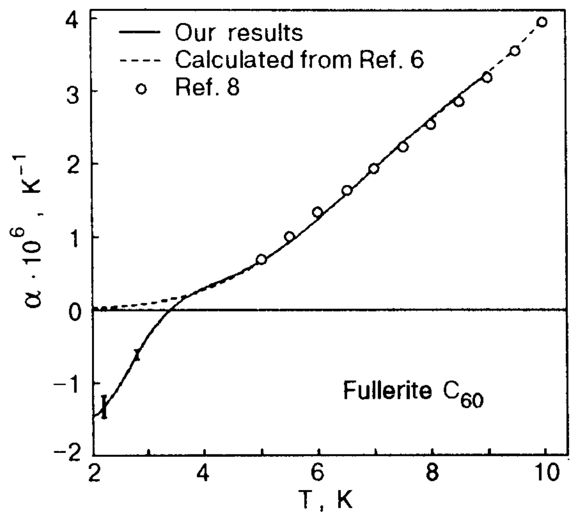

Fig. 2. Linear thermal expansion coefficient of fullerite C_{60}.

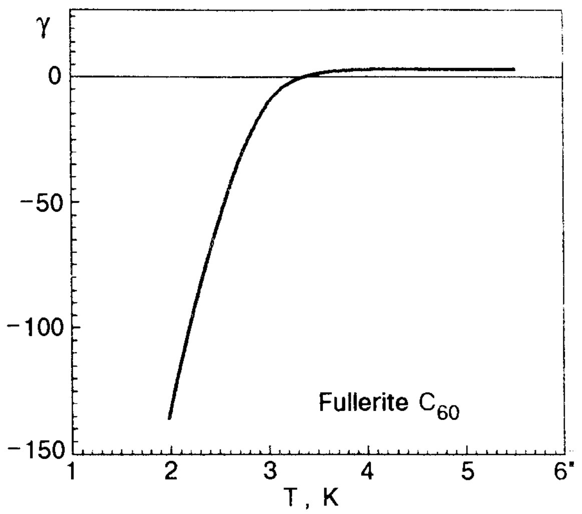

Fig. 3. The Grüneisen coefficient of fullerite C_{60}.

change from T_1 to T_2. The temperature steps were 0.1–0.3 K, depending on the temperature region. In the temperature range below 4.2 K eight runs were made as the temperature was raised and then lowered, while in the temperature range above 4.2 K three runs were made.

This procedure determined the relative elongation of the sample $(\Delta L/L_0)$ as a function of temperature, and the thermal expansion was determined by differentiating these results with respect to temperature.

Figure 2 shows the final results for the linear thermal expansion coefficient α of C_{60} as a function of temperature (the solid curve). The error bars show the estimated experimental errors. A marked increase in the error below 2.5 K is worth noting; however, we have failed to find the reason for this behavior. The most interesting and, at first glance, unexpected result is the negative thermal expansion observed below about 3.4 K. Such a phenomenon has been observed previously in other molecular crystals at liquid helium temperatures, namely, in methane below 8 K (Refs. 8–10) and in a dilute solution of nitrogen in argon at $T < 3.5$ K (Ref. 11). For comparison, we show as open circles the existing experimental data from dilatometric studies of the linear thermal expansion coefficient of a single crystal of C_{60} (Ref. 2). In the overlapping temperature range 5–9 K an excellent agreement is observed between these data and our results. As another comparison, the dashed curve shows the results of a calculation of linear thermal expansion coefficient obtained from data for the specific heat capacity of C_{60} (Ref. 12), assuming that the Grüneisen law $\gamma = 3\alpha V/C\chi$ is valid, i.e., the behavior expected for α in a quasi-harmonic model for the crystal lattice. Data for the compressibility χ and molar volume V were obtained from Refs. 12–14, and the Grüneisen coefficient γ is assumed to be equal to 3 (Ref. 13), which is close to the Grüneisen coefficients for rare gas solids and for simple molecular crystals with dominant central interactions [15,16]. If instead we use the present data for α to calculate an «effective» Grüneisen parameter as a function of temperature, we find that at temperatures below 3.4 K the Grüneisen coefficient is negative and reaches very large values (Fig. 3). For a glassy (disordered) material such as an orientationally disordered sc C_{60} we would expect to find a comparatively small contribution to the thermal expansion, which would be proportional to absolute temperature, but against the observed background of very large negative values such a component is impossible to see.

As mentioned above, a negative thermal expansion coefficient has previously been observed in some other molecular crystals, and it is reasonable to assume that the effect observed here arises from the same mechanism. In the case of molecular crystals a negative thermal expansion can arise from the tunneling of molecules between different orientational states with identical energies. It is well known [17] that tunnel energy levels split up into several levels E_i equal to the number of energy equivalent states of the molecule. The Grüneisen coefficient for such levels, $\gamma_i = -(d \ln E_i)/(d \ln V)$, is negative since the magnitude of the separation between the new levels increases with decreasing height and width of the barrier, which prevents a molecule from rotating. In turn, the indicated parameters of the barrier decrease with increasing volume V of the solid in such a way that the derivative of E_i with respect to V is positive and γ_i is negative. In the Grüneisen law approximation $\alpha = \gamma C$, where C is the specific heat and γ is the effective Grüneisen coefficient. It thus follows that at sufficiently low temperatures, where the rotational motion of molecules occurs mainly through tunneling, the thermal expansion coefficient must be negative. The tunnel splitting of energy levels depends exponentially on the height U of the barrier [17], while U, in turn, has a power dependence on the crystal volume V [18]. The result is that the Grüneisen coefficients are very large [19,20]. The unusually large negative values of γ obtained here are therefore strong evidence for the tunneling nature of the negative thermal expansion.

These considerations are, of course, common for all substances whose molecules have orientational degrees of freedom, but in most cases the thermal expansion becomes negative only at very low temperatures which are beyond the reach of experiment because of the presence of very high barriers that prevent the molecules from rotation. The barrier U, which prevents fullerene molecules from rotating in the solid phase, is also rather high [21] and it seems surprising that tunnel splitting of the levels can reveal itself at such a high temperature as a few degrees. The lowest librational energy levels of fullerite in a low-temperature phase are about 7.3 and 8.5 cm^{-1} (Refs. 22–24). A possible reason for the large tunnel splitting is that the low-temperature ($T < 90$ K) phase of C_{60} is an orientational glass, and for some molecules in the glass the barrier may appear to be significantly lower than that is observed in experiments on crystals with orientational order. Local deformations arising in C_{60} during the formation of the orientational glass [25] might also decrease the value of U. Note that the structure of the glass and, hence, the coefficients α and γ may depend on the history of fullerite samples, and on the type and number of impurities in them.

Finally, impurity atoms and small molecules can be located in interstitial voids and tunnel between them at low temperatures. In principle, this situation must lead to a splitting of their tunnel levels and account for the negative contribution to the thermal expansion. The presence of impurities in the molecular interstitials has also been shown to change the critical temperature for the orientational transition [26] and thus should also have an effect on the barrier U. We therefore note that a small concentration of argon may exist in our sample, which was prepared in an argon atmosphere. On the other hand, the probability of tunneling must be highest for light molecules such as H_2 and for He atoms, but significantly smaller for the comparatively heavy atoms of argon.

Although we can thus explain qualitatively the effect which we observed, no detailed explanation has yet been found. The influence of, for example, the sample history and impurities on the effect requires further investigation, and it would also be interesting to extend the studies to lower temperatures.

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1. M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego (1996).
2. F. Gugenberger, R. Heid, C. Meingast, P. Adelmann, M. Braun, H. Wuhl, M. Haluska, and H. Kuzmany, *Phys. Rev. Lett.* **69**, 3774 (1992).
3. A. M. Tolkachev, A. N. Aleksandrovskii, and V. I. Kuchnev, *Cryogenics* **15**, 547 (1975).
4. R. H. Carr and C. A. Swenson, *Cryogenics* **4**, 76 (1964).
5. K. O. McLean, C. A. Swenson, and C. R. Case, *J. Low Temp. Phys.* **7**, 77 (1972).
6. *Fizicheskii Enziklopedicheskii Slovar'* [in Russian], Sovietskaja Enziklopedia, Moscow (1962), Vol. 2.
7. L. E. De Long, O. G. Symko, and J. C. Wheatley, *Rev. Sci. Instrum.* **42**, 147 (1971).
8. D. C. Heberlein and E. D. Adams, *J. Low Temp. Phys.* **3**, 115 (1970).
9. A. N. Aleksandrovskii, V. B. Kokshenev, V. G. Manzhelii, and A. M. Tolkachev, *Fiz. Nizk. Temp.* **4**, 915 (1978) [*Sov. J. Low Temp. Phys.* **4**, 435 (1978)].
10. Yu. A. Freiman, *Fiz. Nizk. Temp.* **9**, 657 (1983) [*Sov. J. Low Temp. Phys.* **9**, 335 (1983)].
11. A. N. Aleksandrovskii, V. G. Manzhelii, V. B. Esel'son, and B. G. Udovidchenko, *J. Low Temp. Phys.* **108**, 279 (1997).
12. W. B. Beyermann, M. F. Hundley, J. D. Thompson, F. N. Diederich, and G. Gruner, *Phys. Rev. Lett.* **68**, 2046 (1992).
13. M. A. White, C. Meingast, W. I. F. David, and T. Matsuo, *Solid State Commun.* **94**, 481 (1995).
14. A. Lundin and B. Sundqvist, *Phys. Rev.* **B53**, 8329 (1996).
15. M. Klein and A. J. Venables (eds.), *Rare Gas Solids*, Academic Press, London, New-York, San Francisco (1976).
16. *Physics of Cryocrystals*, V. G. Manzhelii and Y. A. Freiman (eds.), AIP Press, American Institute of Physics, Woodbury, New York (1997).

17. L. D. Landau and E. M Lifshitz, ***Quantum Mechanics*** [in Russian], Nauka, Moscow (1989).
18. V. G. Manzhelii, E. A. Kosobutskaya, V. V. Sumarokov, A. N. Aleksandrovskii, Yu. A. Freman, V. A. Popov, and V. A. Konstantinov, ***Fiz. Nizk. Temp.*** **12**, 151 (1986) [*Sov. J. Low Temp. Phys.* **12**, 86 (1986)].
19. C. R. Case K. O. McLean, C. A. Swenson, and G. K. White, *Thermal expansion-1971, AIP Conference Proc.*, New York (1972), p. 312.
20. G. R. Case and C. A. Swenson, *Phys. Rev.* **B9**, 4506 (1974)
21. C. Meingast and F. Gugenberger, *Mod. Phys. Lett.* **B7**, 1703 (1993)
22. G. Kato, C. Yokomizo, H. Omata, M. Sato, T. Ishii, and K. Nagasaka, *Solid State Commun.* **93**, 801 (1995).
23. S. Huant, J. B. Robert, G. Chouteau, P. Bernier, C. Fabre, and A. Rassat, *Phys. Rev. Lett.* **69**, 2666 (1992).
24. T. Yildirim and A. Harris, *Phys. Rev.* **B46**, 7878 (1992).
25. S. V. Lubenets, V. D. Natsik, L. S. Fomenko, A. P. Isakina, A. I. Prokhvatilov, M. A. Strzhemechny, N. A. Aksenova, and R. S. Ruoff, *Low Temp. Phys.* **23**, 251 (1997).
26. G. A. Samara, L. V. Hansen, R. A. Assink, B. Morosin, J. E. Schirber, and D. Loy, *Phys. Rev.* **B47**, 4756 (1993).