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Instability and thermal conductivity of pressure-densified and elastically altered orientational glass of Buckminsterfullerene

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Abstract

We report on the temperature, pressure and time (T, p and t)- dependent features of thermal conductivity, κ, of partially ordered, non-equilibrium state of C_{60}-OG, the orientational glass of Buckminsterfullerene (at T below the orientational freezing temperature T_{og}) made more unstable (i) by partially depressurizing its high-p formed state to elastically expand it, and (ii) by further pressurizing that state to elastically contract it. The sub-T_{og} effects observed on heating of C_{60}-OG differ from those of glasses, because phonon propagation depends on the ratio of two well-defined orientational states of C_{60} molecules and the density of the solid. A broad peak-like feature appears at T near T_{og} in the κ-T plots of C_{60}-OG formed at 0.7 and heated at 0.2 GPa, which we attribute to partial overlap of the sub-T_{og} and T_{og} features. A sub-T_{og} local minimum appears in the κ-T plots at T well below T_{og} of C_{60}-OG formed at 0.1 GPa and heated at 0.5 GPa, and corresponds to the state of maximum disorder. Although Buckminsterfullerene is regarded as an orientationally-disordered crystal, variation of its properties with T and p is qualitatively different from other such crystals. We discuss the findings in terms of the nature of its disorder, sensitivity of its rotational dynamics to temperature and the absence of the Johari-Goldstein relaxation. All seem to affect the phenomenology of its glass-like transition.

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I. INTRODUCTION

Rigid $C_{60}$ molecules of Buckminsterfullerene form an orientationally disordered crystal (ODIC). On cooling, the extent of the disorder changes and, ultimately, a certain extent of orientational disorder of its $C_{60}$ molecules becomes kinetically frozen in the crystal, and it becomes an orientational glass. An illustration of a $C_{60}$ molecule and their arrangement in a cubic lattice is provided in Fig. 1. Buckminsterfullerene crystal is distinguished from other ODICs, because it shows a $\lambda$-shape peak in the heat capacity, $C_p$, and has no underlying state of complete order.\cite{1,2} The dynamics of rotational motions of its $C_{60}$ molecules differs from that of the molecules in other ODICs, and does not show the Johari-Goldstein (JG) relaxation in its normal or orientationally-frozen state. There is a time-, and temperature-dependent equilibrium between two well-defined orientations of the $C_{60}$ molecules in its structure.\cite{1,2} These orientations involve relative positions of the pentagonal and hexagonal rings of the adjacent $C_{60}$ molecules. These rings and the location of the double bonds in them are illustrated in Fig. 1.

The high temperature crystal phase of $C_{60}$ has a face-centered cubic ($fcc$) structure in which the $C_{60}$ molecules undergo continuous rotations at temperatures above 260 K. On cooling through 260 K, the four molecules in the unit cell acquire different orientations which change the $fcc$ structure to simple cubic structure, or the $sc$ phase in space group $P\bar{a}3$. The $sc$ phase is partially disordered at all temperatures, $T$, and pressures, $p$, at least at pressures below 0.7 GPa. Its $T$ and $p$-dependent disordering involves change in the equilibrium population of two orientations of $C_{60}$ molecules, (i) the P-orientation in which molecules are oriented in such a way that the pentagonal ring (P) formed by the C atoms of one $C_{60}$ molecule faces the inter-pentagon double bond of the adjacent $C_{60}$ molecule, also known as normal orientation or ground state, and (ii) the H-orientation in which the hexagonal ring (H) formed by the C atoms faces the inter-pentagon double bond of the adjacent $C_{60}$ molecules, also known as misorientation or the (high
energy) misoriented state. The two orientations differ in energy by a relatively small amount of ~1.1 kJ/mol.\textsuperscript{1} In a neutron scattering study of the C\textsubscript{60} crystal under high pressures at 150 K, David and Ibberson\textsuperscript{2} showed that P- and H-orientations have the same energy at \( p = 0.2 \) GPa.

Therefore, while the energy of the P-orientation is lower than that of the H-orientation at \( p < 0.2 \) GPa, it is higher at \( p > 0.2 \) GPa. At \( p < 0.2 \) GPa, most molecules are in the P-orientation and as \( T \) decreases, most molecules are in the P-orientation. The percentage of H-orientations increases as \( p \) is increased even from the ambient pressure, and it decreases on cooling at \( p > 0.2 \) GPa.\textsuperscript{3} The \( \text{sc} \) phase is fully disordered when the fraction of P-orientations, \( R_p = \frac{[P]}{([H]+[P])} \) is equal to 0.5, where square brackets indicate the molar concentration. This occurs at \( p \) of 0.2 GPa at 150 K\textsuperscript{2,4} and at \( p \) of 0.15 GPa at \( T \) near 100 K.\textsuperscript{5,6,7,8,9} Other values of \( R_p \) indicate partial ordering, viz., \( R_p < 0.5 \) indicates increase in ordering towards higher [H], and \( R_p > 0.5 \) increase in ordering towards higher [P]. Variation in volume, enthalpy and entropy of the \( \text{sc} \) phase with \( T \) is precisely defined in terms of a change in \( R_p \). This change is clearly observed as change in thermal conductivity, \( \kappa \)\textsuperscript{10} and in thermal expansion coefficient, \( \alpha \).\textsuperscript{11}

The basic structure of the \( \text{sc} \) phase at \( T < 260 \) K is identical to the structure of the \( \text{fcc} \) phase except that the four molecules in the cubic unit cell have different orientations. When the \( \text{sc} \) phase of C\textsubscript{60}-crystal is cooled, its properties change because fluctuations in local density and structure resulting from rotational motions become progressively slower. Cooling under \( p < 0.2 \) GPa increases \( R_p \),\textsuperscript{1} which causes the volume to increase, but the total volume still decreases on cooling due to decrease in anharmonic effects. Hence the \( T \)-dependence of the volume of \( \text{sc} \) phase is different from the \( T \) dependence of the volume of liquids and ODICs. When the time scale of local density and structure fluctuations becomes longer than the time scale determined by the cooling rate, the \( \text{sc} \) phase becomes an orientational glass, C\textsubscript{60}-OG, at the orientational
freezing temperature $T_{og} \sim 86$ K at ambient $p$, and the extent of disorder kinetically freezes at $\sim 83.5\%$ or at $R_p = 0.835$.\(^1\) Pressurizing of the $sc$ phase also causes the density and structure fluctuations to become slower, and would produce $C_{60}$-OG at a fixed $T > 90$ K. So, if the pressure of orientational freezing, $p_{og}$, were known from the $\kappa$ against $p$ plots at a fixed $T$ then $R_p$ at $p_{og}$ can be determined. In such a case, there would be pairs of $T_{og}$ and $p_{og}$ at a given $R_p$.

Numerous studies have reported that the $sc$ phase of $C_{60}$ shows thermodynamic and dynamic features of liquid to glass transition on cooling and of glass to liquid transition on heating. Readers interested in details may consult the brief reviews given in Refs. 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, a comprehensive review on the high pressure studies by Sundqvist\(^10\) and also two recent studies devoted to the structure of the $C_{60}$-crystal and the P- and H-orientations in it.\(^22,23\) Since disorder in liquids and ODICs cannot be quantified, the knowledge of $R_p$ makes $C_{60}$-OG unique among disordered solids. Absence of JG relaxation in $C_{60}$-OG further makes it unique among glasses and ODICs. To distinguish it from a $C_{60}$ molecule and from $C_{60}$-OG, hereafter we refer to the kinetically unfrozen orientational state of the $sc$ phase as $sc$-$C_{60}$.

Since there is no ordered state of the $sc$ phase of $C_{60}$, it is not in a supercooled metastable state at ambient pressure. Therefore, the Kauzmann-type extrapolation\(^24\) of the entropy to lower $T$ and its consequences, as discussed for liquids\(^25\) and ODICs,\(^26,27\) are irrelevant to thermodynamic description of $sc$-$C_{60}$. Its residual entropy cannot be determined from the $C_p$ integral as used for a glass and other ODICs, and it had to be estimated by using a model.\(^28\)

Lundin and co-workers\(^29,30\) studied the bulk modulus of $sc$-$C_{60}$ as a function of $p$ at 152 K and 236 K, and found changes in the slope of its plots against $p$ at $p > \sim 0.7$ GPa, which they interpreted to be a result of change to an almost fully ordered H-orientation state of $C_{60}$ at high $p$,\(^29,30\) but no such state has been found at ambient pressure.
C_{60}-OG inherits the structure and $R_p$ of $sc$-$C_{60}$ at $T = T_{og}$, and, like those of other kinetically frozen ODICs $^{31,32}$ and of glasses, its properties change with time. We refer to this as the natural instability of the non-equilibrium state of a solid. It exists because the vibrational state of C_{60}-OG at $T < T_{og}$ does not correspond to the (kinetically-frozen) partially disordered (equilibrium) structure at $T_{og}$. At $T$ slightly below $T_{og}$, the orientational order of C_{60}-OG, as defined by $R_p$, increases with time and the properties change until an equilibrium state of higher $R_p$ is isothermally reached. Yu et al.$^{33}$ investigated the effect of cooling rate on the natural instability and the temperature-, and time-dependence of $\kappa$ of C_{60}-OG at ambient pressure. They found that $\kappa$ of C_{60}-OG increases as $R_p$ increases with time and C_{60}-OG becomes more ordered.

The subject of pressure-densified glasses was reviewed in the context of a mistaken second glass transition of water.$^{34}$ It is now of interest for investigating the elastic modulus,$^{35}$ the source of the JG relaxation, and of other features of the glassy state.$^{36,37,38,39}$ A recent paper$^{40}$ formally described the excess free energy of elastically expanded glasses and related it to increase in the solubility of a glass in a given solvent. As mentioned earlier here, in contrast to glasses and the OGs made from other ODICs, orientational disorder of C_{60} molecules in $sc$-$C_{60}$ and C_{60}-OG is precisely defined.$^{41}$ So we interpret the loss of $p$-induced (added) instability on heating in terms of change in $R_p$. To add instability, we elastically expand the high-$p$ formed C_{60}-OG by decreasing the pressure in one case, and elastically contract the high-$p$ formed C_{60}-OG by increasing the pressure in the second case.

Previously, we investigated the effect of added instability on the (irreversible) sub-$T_g$ features of glasses.$^{42,43}$ In order to determine whether or not this effect is independent of the type of disorder, a study of an orientational glass was needed. We chose to study C_{60}-OG, because of its unique type of disorder, and because two of us$^{3,41}$ had already obtained a large set of data on $\kappa$ of $sc$-$C_{60}$ and of C_{60}-OG, but had published only the data of contemporary relevance. The
remaining unpublished data presented here give us an opportunity for a detailed discussion of the effects of high $p$ on $\kappa$ of $sc$-C$_{60}$ and of an in-depth understanding of the vibrational-configurational changes in C$_{60}$-OG, a solid that physically ages towards an equilibrium state defined by $R_p$, but does not show the JG relaxation.

II. EXPERIMENTAL METHODS

Details of the sample and measurement method are given in previous papers.$^{3,41,44,45}$ Briefly, the stated purity of C$_{60}$ powder was $>99.9\%$ and it was further dried in vacuum. A transient hot wire method was used to measure thermal conductivity. The probe, surrounded by ~2 g of polycrystalline C$_{60}$ was heated by a 1.4-s pulse of approximately constant power and the wire resistance was measured with time during the heat pulse. A theoretical expression for the temperature rise was fitted to the data points, and $\kappa$ was thus determined. Different cells and samples from the same batch were used, which partly contributed to the inaccuracies and uncertainties in $\kappa$ and $T_{og}$. There is also an uncertainty in $T_{og}$, which is due to different kinetics of structural arrest during the cooling and of structural release during the heating of C$_{60}$, and there is some uncertainty due to the different particle sizes and the defect states of the $sc$ phase itself. The samples were loaded in cylindrical cells made of Teflon in an atmosphere of dry argon and the sealed cells were inserted in a piston-cylinder apparatus of 45 mm internal diameter. The cylinder was placed in a vacuum chamber and load was applied using a 5 MN hydraulic press. The cylinder was cooled with a closed helium gas cycle refrigerator and heated by an electrical heated wound around the cold head, which has been described in detail elsewhere.$^{46}$ The heating and cooling rates were $\sim$0.3 K/min in the OG-ODIC transition range of 87 K - 134 K for pressures up to 0.7 GPa, and the pressurization and depressurization rates were typically in the 0.05-0.2 GPa h$^{-1}$ range.
We stress that the commonly used procedure of extracting the sample by forced, and sudden ejection out of the pressure vessel causes the ejected sample to contain internal stresses. Since these stresses affect the magnitudes of properties measured at ambient \( p \) and these stresses are released only on heating, showing artifacts of the stress release, \(^{47}\) measurements on depressurized samples need to be performed in situ. For that reason, the \( C_{60} \) samples in our study were depressurized to a \( p \) slightly higher than ambient pressure. This procedure had the additional advantage of preventing the often observed malfunctioning of thermal contacts between the hot wire and the sample at ambient pressure. As mentioned here earlier, the data we report were obtained in the 1990s, but not published. They are new to the readers, and so we refer to those as new data.

Importance of thermal conductivity for investigating the effect of the nature of disorder on phonon propagation is currently a subject of interest, and several kinetically frozen ODICs have been studied, \(^{48-50}\) and their features compared against those of glassy state of the same material. \(^{49}\) It has also been used to study the vibrational density of states at low temperatures. \(^{50}\)

We will discuss the effects on the features of other ODICs \(^{31,32}\) and their \( T_{og} \) in Sect. IV.

III. RESULTS

For clarity, we divided the measured \( \kappa \) at temperature \( T \) under each pressure \( p \) by its value at 70 K at that \( p \). The ratio, \( (\kappa_T/\kappa_{70})_p \) for each of the four pressures is plotted against \( T \) in Fig. 2. These data were measured during the cooling of \( sc-C_{60} \) (kinetically-unfrozen state of the \( sc \) phase) at fixed \( p \) of 0.1 GPa, 0.22 GPa, 0.4 GPa, and 0.7 GPa from 298 K to \( \sim \) 70 K and in one case from 250 K to \( \sim \) 70 K. The plots show that when \( T \) is decreased, both the slope of the plots and the \( (\kappa_T/\kappa_{70})_p \) value for \( p \) of 0.1 GPa and of 0.7 GPa increase initially and below a certain \( T \) at all pressures, the \( (\kappa_T/\kappa_{70})_p \) value begins to decrease. Hence, there is slope inversion
from negative to positive, or change in slope, which is most clearly evident in the plots for $p$ of 0.1 GPa and 0.7 GPa in Fig. 2. (Slope inversion at $p = 0.22$ GPa is affected by the nearly equal energies of the P- and H-orientations at this pressure.) The temperature at which the slope inversion occurs at a given $p$ is equal to $T_{og}$ at that $p$ for a given cooling rate.

In a second set of experiments, $sc$-$C_{60}$ was cooled from 275 K to $T < T_{og}$ of 133 K at 0.7 GPa. Subsequently, the pressure was slowly decreased from 0.7 GPa to 0.2 GPa while $T$ was gradually decreased to 77 K to remain below $T_{og}$. The sample was then heated under a fixed $p$ of 0.2 GPa, and two sets of studies were performed using this $T$-$p$ protocol. The $\kappa$ measured during heating for these protocols is plotted against $T$ as curves 1 and 2 in Fig. 3. The $\kappa$ values in these two curves differ by less than 1% which is well within the expected experimental errors of $\sim 3\%$ at 70 K.

In Fig. 3, curve 4 shows a plot of new set of $\kappa$ values against $T$ measured on heating C$_{60}$-OG that had been formed by cooling under 0.2 GPa pressure. For comparison, we include the $\kappa$-$T$ plot taken from Ref. 3 here as curve 3, which was obtained by cooling the sample from 250 K to 70 K under 0.1 GPa, pressurizing to 0.2 GPa at 70 K, and finally heating under $p$ of 0.2 GPa.

We report two further sets of new data which were obtained for the C$_{60}$-OG samples of different $p$-$T$ history. The C$_{60}$-OG of one sample was formed by cooling the $sc$ phase under 0.1 GPa, then pressurized to 0.5 GPa at 74 K and finally heated under 0.5 GPa where $\kappa$ was measured during the heating. Curve 1 in Fig. 4 shows the plot of the measured $\kappa$ against $T$. The C$_{60}$-OG of the second sample was formed by cooling the $sc$ phase under 0.25 GPa, then pressurized to 0.4 GPa at 74 K and finally heated under 0.4 GPa. Curve 2 in Fig. 4 shows the results.
V. DISCUSSION

A. General features of sc-C$_{60}$ and pressure-densified C$_{60}$-OG

In addition to the effects of the rates of cooling and heating and of pressurization and depressurization, we need to consider five interconnected variables, $T$, $p$, $\kappa$, $R_P$, and the $T$-$p$ history of both sc-C$_{60}$ and C$_{60}$-OG. As mentioned earlier here, on cooling through $T$ of 260 K, the fcc structure changes to the sc structure and the C$_{60}$ molecules’ orientational dynamics change from continuous rotational diffusion to jumping motions between discrete orientations, P and H. Neither the sc nor the fcc phase is 100% orientationally-ordered, i.e., neither of the two phases has all P-type orientations or all H-type orientations. (Neither $R_P = 0$ nor $R_P = 1$.) The structure of the sc phase with partial disorder is stabilized by both a Lennard-Jones atomic pair potential and Coulombic forces arising from excess electrical charge in the carbon-carbon double bonds. The sc phase remains partially disordered, with the populations of the P- and H-orientations at equilibrium at a given $T$ and $p$, as in a chemical equilibrium.

On cooling towards $T_{og}$, the configurational and vibrational states of sc-C$_{60}$ change together, and on cooling from $T_{og}$, only vibrational state changes, the configurational state of sc-C$_{60}$ remains fixed at the $R_P$ value at $T = T_{og}$. The phonon properties at $T < T_{og}$ differ from those at $T_{og}$, as is evident from the slope inversion of the $\kappa$-$T$ plot at $T = T_{og}$. On structural relaxation, both the vibrational and configurational states change until equilibrium is reached, i.e., the departure of a property from its equilibrium state value, $\Delta \xi$, becomes zero. (At $T = T_{og}$, $\Delta \xi$ is equal to 0, and as $T \rightarrow 0$ K, $\Delta \xi$ approaches a maximum value.) In this sense, sc-C$_{60}$ behaves like a liquid or like the usual ODIC and C$_{60}$-OG behaves like a glass or an orientationally-frozen ODIC. Nevertheless, there are two remarkable differences, (i) $\alpha$ of the sc-C$_{60}$ increases on cooling through $T_{og}$ at $p$ below 0.15 GPa, which is the opposite of the generally found
decrease in $\alpha$ when a liquid is cooled through its kinetics freezing temperature at all pressures, and (ii) P-orientations convert to H-orientations on pressurizing because of the increase in the energy term $pdV$. Since one expects configurational entropy to be maximum at $R_p = 0.5$, a correlation between increase in entropy with decrease in the relaxation time would suggest that the relaxation time of $sc$-$C_{60}$ would be minimum for a structure at $R_p = 0.5$. Whether or not that occurs is yet to be investigated.

There are no free electrons in the structure of Buckminsterfullene. Therefore, it is worth comparing the features of its $\kappa$ against the theories used for amorphous electrical insulators which are based on phonon propagation mediated by localized vibrational excitations. In these cases, the mean free path of phonons, $l_{\text{phonon}}$, used in the relation $\kappa = \rho C_v l_{\text{phonon}}/3$, where $\rho$ is the density and $C_v$ is the specific heat at constant volume, becomes of the order of the phonon wavelength. On heating, $l_{\text{phonon}}$ ultimately becomes of the order of the interatomic spacing. This was discussed by Taraskin and Elliott\textsuperscript{52} in relation to the theory of Ioffe and Regel.\textsuperscript{53} This theory\textsuperscript{53} has been discussed by several groups and was reviewed and further analyzed by Beltukov et al\textsuperscript{54} by using a harmonic oscillator model. Since $\alpha$ is zero in this model and $\alpha$ is positive for C$_{60}$-OG, one expects the potential function to include anharmonic forces, which in turn are known to be prerequisites for the phonon-phonon scattering process. In view of these arguments we can only qualitatively discuss the magnitude of $\kappa$ and its change with $T$.\textsuperscript{55,56}

**B. Thermal conductivity features on cooling and kinetic freezing**

Previous studies have shown that $\kappa$ of most ODICs and of the $fcc$ phase of C$_{60}$ at ambient pressure is almost independent of temperature.\textsuperscript{31,32} In contrast, $\kappa$ of a single crystal $sc$-$C_{60}$ at ambient pressure varies roughly as $1/T$,\textsuperscript{33} which is also the typical behavior of crystalline phases. The difference is attributed to the partial order of $sc$-$C_{60}$ described in terms of the $R_P$ value. Both
low $R_p$ and high $R_p$ values indicate low degree of orientational disorder. Because of this low
degree of disorder, phonon scattering in single crystal sc-C$_{60}$ and single crystal C$_{60}$-OG would be
due mainly to three-phonon Umklapp scattering. Polycrystalline samples of sc-C$_{60}$ and C$_{60}$-OG
here and elsewhere$^{3,41}$ show both a lower magnitude of $\kappa$ and a weaker $T$-dependence than those
observed for single crystal sc-C$_{60}$ and C$_{60}$-OG.$^{33}$ The reason is that the sub-mm size sc crystals in
the samples of our study contain lattice defects such as dislocations and vacancies, which
amounts to a certain extent of positional disorder, and in addition there are inter-grain boundaries
or inter-crystal surfaces. Altogether these constitute the “static sample-effect”, which is in
addition to the orientational disorder. The static sample effect adds to the phonon scattering and
the three-phonon Umklapp scattering from orientational disorder thereby reducing $\kappa$ and its $T$-
dependence.$^{57}$ Hence, $\kappa$ of a given sc-C$_{60}$ sample depends on $T$ and $p$ and its $R_p$ as well as the
static disorder, and the microscopic state of the sample adds to $\kappa$. These effects are difficult to
separate here.

Although the “static sample-effect” causes strong phonon scattering in our polycrystalline
solid, it has been shown that the temperature of the slope change in $\kappa(T)$ in Fig. 2, $^{3,41}$ is in
qualitative agreement with the corresponding slope change observed in $\kappa(T)$ of single crystal sc-
C$_{60}$.$^{33}$ The superimposed effect of phonon scattering from orientational disorder becomes clearer
when C$_{60}$ goes through the state of maximum orientational disorder on heating, as shown by
curve 3 in Fig. 3. We stress that the origin of the weak $T$-dependence of $\kappa$ of our polycrystalline
C$_{60}$ is different from that of the plastic crystal phases,$^{58}$ e.g. those of the high temperature phases
of cyclo-hexanol and cyclo-octanol ODICs,$^{31,32,48}$ whose entropy differs little from that of their
liquids state, and similarly of some other ODICs with a significant entropy from orientational
configurations.$^{49}$
One expects that change in $T$ would change the inter-crystal surface area in our samples and thus change the static sample-effect, but this change would be small in comparison to change due to change in intermolecular interactions at the surface. In this context we point out a calorimetric finding, namely, that $T_{og}$ of single crystal C$_{60}$-OG, determined from the onset temperature of the $C_p$ increase measured in adiabatic calorimetry, is 84.6 K,$^1$ which is close to the $T_{og}$ of 86.0 K of C$_{60}$-OG fine powder.$^59$ Also, the increase in $C_p$ at $T_{og}$ of single crystal C$_{60}$-OG is 3.6 J K$^{-1}$ mol$^{-1}$, which is about 80% of the value (of 4.40 J mol$^{-1}$ K$^{-1}$ at 80 K) for the fine powder of C$_{60}$-OG at comparable cooling and heating rates.$^59$ So, although the change in $C_p$ of C$_{60}$-OG powder relative to the single crystal is significant when C$_{60}$-OG is heated, the change in $\kappa$ and in $d\kappa/dT$ due to changes in phonon scattering rate, the phonon velocity, and $C_p$ are relatively small. These changes are seen in the plot of $sc$-C$_{60}$ and C$_{60}$-OG single crystal in Fig 1 in Ref. 33, and the plots in Fig. 2 here for the $sc$-C$_{60}$ and C$_{60}$-OG powder. Only the $\kappa(T)$ of the isobarically cooled or heated powdered state without the sub-$T_{og}$ pressure treatments of C$_{60}$-OG is the intrinsic value of $\kappa(T)$.

Looking into still lower temperature features, Beyermann et al.$^60$ reported $C_p$ of polycrystalline C$_{60}$ in the 1.5 - 20 K range, analyzed the results in terms of the Debye and the Einstein theory and showed that a peak appears in the plots of $C_p/T^3$ against $T$, which is similar to the peak found for structural glasses and ODICs. This means that the low $T$ peak in $C_p$ is also qualitatively unaffected by the nature of disorder.

We now consider the shape of the $\kappa$-$T$ plots shown in Fig. 2. For the $sc$-C$_{60}$ cooled under $p$ close to 0.2 GPa, kinetic freezing of disorder is detected as a weak, almost imperceptible change in $d\kappa/dT$ at $T_{og}$ in Fig. 2. This is consistent with the finding$^2$ that at 0.2 GPa the P- and H-orientations are almost energetically equivalent at all temperatures. (Cooling causes the
pressure at which these orientations are energetically equivalent to decrease slightly.\(^{2,5,6}\) Alternatively stated, \(R_P\) would not increase on cooling or decrease on heating when the sample is under \(p\) of 0.2 GPa. Therefore, there would be no slope inversion and indeed only a little change in \(d\kappa/dT\) to indicate \(T_{og}\) in the \(\kappa-T\) plots. On cooling under \(p < 0.2\) GPa the \(sc\)-C\(_{60}\) would tend to order towards greater population of P-orientations and \(R_P\) would increase. In contrast, on cooling under \(p > 0.2\) GPa the \(sc\)-C\(_{60}\) would tend to order, towards greater H-orientation populations and \(R_P\) would decrease. At \(p > 0.2\) GPa and at \(p < 0.2\) GPa the slope inversion in \(\kappa-T\) plots at \(T_{og}\) becomes observable and it would become clearer when the sample is farther away from \(p\) of 0.2 GPa. The plot for 0.22 GPa in Fig. 2 shows \(T_{og}\) as a weak change in \(d\kappa/dT\), but no slope inversion is observed, despite the finding that \(T_{og}\) is also the onset temperature of change in \(R_P\) in the structure of the \(sc\) phase.

The plots in Fig. 2 show only a slope inversion. There is no additional and sharp peak at \(T\) near \(T_{og}\) that is observed in the \(\kappa-T\) plots of molecular glasses\(^{42,43,61,62,63}\) and polymers\(^{64,65,66}\) at \(T\) near their \(T_g\) and of ODICs\(^{31,32}\) at \(T\) near their \(T_{og}\). Since the peak arises from the time-dependence of the heat capacity, \(C_P\), at \(T\) near \(T_g\) and \(T_{og}\), this indicates that the time dependence of \(C_P\) of C\(_{60}\)-OG is too weak to produce the artificial peak.\(^{67}\) Therefore, an important aspect of our finding is that the \(\kappa-T\) plots of \(sc\)-C\(_{60}\) and C\(_{60}\)-OG in Fig. 2 differ from those for liquids and for other ODICs.

**C. Sub-\(T_{og}\) effects and the induced elastic instability**

Studies of glycerol\(^{43}\) and di-\(n\)-butyl phthalate\(^{42}\) glasses have shown that when their liquid state was cooled under a high \(p\), it kinetically froze to glass of a configurational state of high density. When the glass was then partially depressurized at \(T\) far below \(T_g\) to \(p\), say \(p_1\), it elastically expanded at a fixed configuration, and thus became more unstable than the glass
formed by cooling at \( p_1 \). When the elastically expanded glass was heated under pressure \( p_1 \), it showed an irreversible sub-\( T_g \) feature in which \( \kappa \) gradually decreased from its non-equilibrium high value at pressure \( p \) at \( T < T_g \) to its equilibrium value at \( T \) near \( T_g \) at pressure \( p_1 \). This sub-\( T_g \) feature is not observed for the glass heated at the same \( p \) under which it was formed.

In one study,\(^{42}\) the di-\( n \)-butyl phthalate glass was formed by cooling the liquid under a relatively low \( p \), and the glass at \( T \) below its \( T_g \) was pressurized to \( p_2 \). This caused the glass to elastically contract at a fixed configuration. The elastically contracted glass was also thermally more unstable than the glass formed by cooling under the higher pressure \( p_2 \). When heated under pressure \( p_2 \), it showed an irreversible sub-\( T_g \) feature in which \( \kappa \) increased over a broad \( T \) range from its non-equilibrium state value at \( p_2 \) to its equilibrium value at \( T \) near \( T_g \) at \( p_2 \). These sub-\( T_g \) effects were a result of the greater departure of the vibrational state from the configurational state of an elastically expanded or contracted glass.

It is obvious that on cooling under all conditions of \( p \), \( C_{60} \)-OG inherits the structure, configuration, or \( R_P \) of \( C_{60} \) at \( T = T_{og} \). So, we compare the behavior of \( C_{60} \)-OG in the same sequence as that of the glycerol\(^{43}\) and \( n \)-dibutyl phthalate.\(^{42}\) The \( \kappa - T \) plot of the elastically expanded state of \( C_{60} \)-OGs shown as curves 1 and 2 in Fig. 3 are for heating of the samples depressurized from 0.7 GPa to 0.2 GPa at \( T < T_{og} \). Both plots 1 (red circles) and 2 (blue circles) show slope inversion from positive to negative at about the same \( T \) of 104.5 ± 1.5 K at 0.2 GPa. This \( T \) is near the \( T_{og} \) of 102.5 K for the \( C_{60} \)-OG formed by cooling \( sc \)-\( C_{60} \) under 0.2 GPa.\(^{41}\) By using the energy difference at 150 K given by Ibberson and David,\(^{2}\) we calculate \( R_P \) of 0.07 for the kinetically frozen state of the sample cooled under 0.7 GPa and heated under 0.2 GPa. After the onset of rotational motions on heating this sample through \( T_{og} \), the non-equilibrium state’s \( R_P \) value of 0.07 changes towards the equilibrium state’s \( R_P \) value of ~0.5 at 0.2 GPa, and \( \kappa \).
decreases at \( T = T_{og} \). The data in curve 4 in Fig. 3, which were obtained during the heating to \( T \) above \( T_{og} \), show that \( \kappa \) approaches the equilibrium \( R_P \) more \textit{slowly} than expected. This suggest that some orientational order persists even at \( T > T_{og} \), which is similar to our previous interpretation.\textsuperscript{3,41} In contrast, the data for the equilibrium state provided in curve 4 show no observable change of slope, indicating that this change occurs at \( T \) near or at the \( T_{og} \) value calculated from the fit of the \( T_{og} \) against \( p \) plot\textsuperscript{41} and shown by a black arrow. On the basis of \( T_{og} \) of 102.5 K at \( p = 0.2 \) GPa, which is within the inaccuracy of the relaxation features observed in curves 1 and 2 and the fit of the \( T_{og} \) against \( p \) plot,\textsuperscript{41} we find no sub-\( T_{og} \) effect in the elastically expanded \( C_{60} \)-OG. We should also note that heat capacity studies of elastically expanded polystyrene have shown that a sub-\( T_g \) endothermic peak appears at \( T \) considerably below \( T_g \) and this peak moves to higher \( T \), and closer to \( T_g \), when the pressure under which the polystyrene glass was formed is decreased. Both features are expected on the phenomenological basis of glass formation.\textsuperscript{68} Also, recent dilatometric studies by Casalini and Roland\textsuperscript{38} have found that the sub-\( T_g \) feature has moved so close to \( T_g \) that it is observed as a low-temperature broadening of the \( T_g \). It is possible that our findings indicate a shift so large that the sub-\( T_{og} \) feature became undiscernible. Such a feature was discernible for glycerol\textsuperscript{43} and di-\( n \)-butyl phthalate.\textsuperscript{42} After a comprehensive discussion it was concluded that in these cases the average density does not govern the properties of the glass, but rather the local structure and barriers for thermal fluctuations of density are the main control parameters.\textsuperscript{38} We suggest that elastically altered states of glasses would show difference in the strength and dynamics of the JG relaxation. But no such relaxation has been known to occur in \textit{sc-}\( C_{60} \) or \( C_{60} \)-OG.

The study of elastically contracted \( C_{60} \)-OGs apparently shows the sub-\( T_{og} \) effect, which is more clearly observed when \( R_P \) crosses the value of 0.5. To elaborate, curve 1 in Fig. 4 shows several features of \( \kappa \) observed on heating a \( C_{60} \)-OG sample that had been elastically contracted
by pressurizing from 0.1 to 0.5 GPa at \( T < T_{og} \). One of these features, namely, the change in the slope of the \( \kappa - T \) plot at \( T < 125 \) K, coincides with \( T_{og} \) of 121 K of sc-C\textsubscript{60},\textsuperscript{41} as indicated by the vertical arrow in Fig. 4. Curve 1 in Fig. 4 also shows that at \( T \) below the \( T_{og} \) of 121 K at 0.5 GPa, \( \kappa \) of C\textsubscript{60}-OG first decreases from its value at 70 K and then increases, showing a local minimum at \( T = 107 \) K (somewhat below \( T_{og} \)), where disorder is maximum, or \( R_P = 0.5 \). On further heating, \( \kappa \) in curve 1 follows the intrinsic \( \kappa \) of the sc-C\textsubscript{60} at 0.5 GPa, which has previously shown a maximum in \( \kappa \) at 190 K.\textsuperscript{41} The red arrow above curve 1 indicates the range of sub-\( T_{og} \) relaxation as suggested by the changes in \( \kappa \) with \( T \) at \( T < T_{og} \).

Curve 2 in Fig. 4 shows the results obtained for elastically contracted C\textsubscript{60}-OG formed under \( p \) of 0.25 GPa and heated under 0.4 GPa. This plot also shows weak features of the sub-\( T_g \) effect, which appears as a more abrupt rise of \( \kappa \) than that of the intrinsic \( \kappa(T) \) at \( T \) of \( \sim 102 \) K, which is below the slope inversion temperature or \( T_{og} \) of 116 K at 0.4 GPa. For comparison, \( \kappa \) is higher in curve 1 which is for a more elastically-contracted sample obtained by pressurizing to 0.5 GPa at which \( R_P = 0.15 \) at \( T_{og} \), than in curve 2 which is for a less elastically-contracted sample obtained by pressurizing to 0.4 GPa at which \( R_P = 0.23 \) at \( T_{og} \). This is due to the decrease in the orientational order at \( T > T_{og} \) when \( p \) on sc-C\textsubscript{60} is less. The higher \( \kappa \) in curve 1 would then be due to a combination of higher density at higher \( p \) and higher \( R_P \) at \( T > T_{og} \). The temperature range of the sub-\( T_g \) feature is smaller in curve 2 than in curve 1, but because of the intrinsic increase of \( \kappa \), the onset temperature obtained from the \( \kappa - T \) plots may not be 102 K. On heating above \( T_{og} \), the \( \kappa \) value in curve 2, Fig. 4, follows the intrinsic \( \kappa \) of sc-C\textsubscript{60} at 0.4 GPa, which has shown a maximum at 170 K.\textsuperscript{41}

A sub-\( T_g \) feature also appears in curve 3 of Fig. 3, which is for the C\textsubscript{60}-OG formed under 0.1 GPa and heated under 0.2 GPa. Here \( \kappa \) begins to gradually decrease showing slope inversion
at \( T \) well below the \( T_{og} \) of 102.5 K at 0.2 GPa.\(^4\) At 0.2 GPa, the equilibrium \( R_P \) is ~0.5. This means that the sample approaches maximum orientational disorder on heating to \( T_{og} \) and then remains in this state on further heating. In this case, \( \kappa \) also shows a local minimum because the intrinsic \( \kappa \) increases in the \( T_{og} \) range, as seen in Fig. 3. Structural relaxation of a glass on heating through \( T_g \) at ambient \( p \) increase \( \alpha \) and thus affects its intrinsic \( d\kappa/dT \) but structural relaxation of single crystal C\(_{60}\)-OG on heating through \( T_{og} \) at ambient \( p \) decreases \( \alpha \).\(^1\) One expects that the consequences of the opposite changes in \( \alpha \) of glass vs. C\(_{60}\)-OG would be different for \( d\kappa/dT \) on heating. It is difficult to envisage how a decrease in \( \alpha \) on heating through \( T_{og} \) and an increase in \( \alpha \) on cooling through \( T_{og} \)\(^1\) would affect the sub-\( T_{og} \) features observed in our study.

When \( T \) and \( p \) of liquids, of the \( sc \) phase, and of ODICs are varied the vibrational density of states, phonon propagation and \( \kappa \) vary also with the changing configuration. But when \( T \) and \( p \) of C\(_{60}\)-OG, of glasses, and of kinetically-frozen ODICs are varied, the vibrational density of states, phonon propagation, and \( \kappa \) vary at a fixed configuration. When \( T \) of the elastically expanded or elastically contracted C\(_{60}\)-OG is increased at a fixed \( p \), there is an additional effect on \( \kappa \) from (irreversible) change in the vibrational density of states on phonon scattering due to time- and \( T \)-dependent change in \( R_P \).

**V. CONCLUSION**

(1). On heating the elastically expanded C\(_{60}\)-OG state, no sub-\( T_{og} \) effect on \( \kappa \) is observed. We attribute it to partial overlap of the sub-\( T_{og} \) and \( T_{og} \) features. This is different from the sub-\( T_g \) effect on \( \kappa \) of the elastically expanded glasses of glycerol\(^4\)\(^3\) and di-n-butyl phthalate,\(^4\)\(^2\) which appears at \( T \) well-below \( T_g \).
(2). When the elastically-contracted state of the C₆₀-OG formed by cooling under a high \( p \) is heated, \( \kappa \) shows a sub-\( T_{og} \) feature due to the onset of orientational motions and irreversible change in \( R_p \) in the \( T \)-range well below \( T_{og} \). This is qualitatively similar to the findings for elastically- contracted glasses, which have shown an accelerated increase of \( \kappa \) as the glass irreversibly relaxes and configurationally densifies towards the equilibrium high-density state on heating. In contrast, when the elastically-compressed state of the C₆₀-OG formed at \( p < 0.2 \) GPa is heated under \( p > 0.2 \) GPa, \( \kappa \) shows a sub-\( T_{og} \) feature in the form of an initial decrease and thereafter an accelerated rise on heating up to \( T_{og} \) at \( p > 0.2 \) GPa, and hence a minimum in the \( \kappa \)-\( T \) plot. A minimum was observed also in an isothermal time-dependence of \( \kappa \). Here, it is attributed to the onset of sub-\( T_g \) orientational motions on heating through the sub-\( T_{og} \) range. It first decreases \( R_p \) from its (higher) value to 0.5 at which the state has maximum disorder, and then further decreases \( R_p \) from 0.5, which corresponds to an increase of orientational order, but with more H-orientations.

(3). The known increase in thermal expansion coefficient on cooling sc-C₆₀ through the \( T_{og} \) range indicates that consequences of change in the volume fluctuations in sc-C₆₀ differ from those of the change in entropy fluctuations, and the increase in the relaxation time on cooling is unaffected by change in volume. We stress that the new data discussed here are for an ODIC of large rigid molecules, with well-defined orientational disorder kinetically frozen on cooling, and no indication of the JG relaxation. A study of the usual ODICs, which mimic thermodynamic and relaxation features of a glass, may help in revealing the role of different types of disorder.

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References and Notes


4 David and Ibberson, Ref. 2, mentioned 2.6 kbar based on a calculation using earlier data but in their neutron scattering study of the structure of the sc phase, the energy difference becomes equal at $p$ slightly below 2 kbar, as shown by the data in their Fig 1.


We do not use the concepts of the fictive temperature, $T_f$, and of the fictive pressure, $p_f$, because (i) as structural relaxation occurs isothermally, $T_f$ and $p_f$ change with time in opposite directions - $T_f$ decreases and $p_f$ increases, (ii) $p_f$ is rarely determined by isothermal structural relaxation, (iii) when an elastically expanded or elastically contracted state of pressure-densified state is heated, $T_f$ and $p_f$ change in a complicated manner, and (iv) ordering of the sc phase into P-orientations at $p < 0.2$ GPa changes to ordering into H-orientations at $p > 0.2$ GPa, i.e., there is an inversion of the population from predominantly P-orientations to predominantly H-orientations when $p$ is increased through the 0.2 GPa range, a state of $R_p = 0.5$ corresponds to a maximum disorder at a fixed $T$ and states of $R_p =$
1 or \( R_P = 0 \) are never obtained. For \( \text{C}_{60}\)-OG, the quantity \( \Delta \xi \) would refer to departure from the equilibrium state whose \( R_P \) differs from 0.5, and isothermal structural relaxation of pressure-densified \( \text{C}_{60}\)-OG increases or decreases (above 0.2 GPa). An increase in \( R_P \) isothermally with time, which would decrease \( T_f \), increases \( \kappa \) at ambient pressure (Ref. 33).


55 Although our \( \text{C}_{60}\) sample contains a significant number of structural defects, it is polycrystalline. If we reach the Ioffe-Regel limit at \( T \) near \( T_{og} \), the mean free path would be constant, and an increase in orientational disorder would not affect it. This limit is often discussed in connection with \( \kappa \) of amorphous solids and glasses but less often in crystals. It is discussed also in connection with deviations from a linear change in the electrical resistivity with \( T \), typically as “saturation” at high \( T \) in crystals, in the “Mott-Ioffe-Regel” limit (Ref. 56).


57 The equilibrium population of point defects in a crystal increases with \( T \), but that population has little effect on the entropy. Defects may cause some variation of \( \kappa \) from one sample to another in our studies, but they would not significantly contribute to the change in the entropy or in \( \kappa \) of a given sample with changes in \( T \) and/or in \( p \). Also, the initially applied uniaxial load to sub mm-size crystals in a sample of the \( sc \) phase may cause some plastic deformation and therefore further crystal defects, but this type of defects-disorder is likely to be static and would not vary with \( T \) and \( p \) enough to
change the entropy. The disorder at the crystal-crystal interface remains fixed unless crystal growth occurs.


67 Two of the OG states of cyclo-octanol do not show a peak (Ref. 32), and the peak for the third is small. Also, the peak diminishes when a polymer is cross-linked, the latter probably due to broadening of the relaxation times.

FIGURE CAPTIONS

FIG. 1. An illustration of the C60 molecule, and of the molecular arrangement in the fcc crystal lattice at $T > 260$ K. On cooling through $T$ of $\sim 260$ K at ambient pressure, free rotations of the C60 molecules become restricted to P and H-orientations, the lattice becomes sc, or simple cubic (space group $Pa\bar{3}$). On cooling the sc phase, equilibrium population of the P- and H orientations changes towards more P-orientations, the orientational fluctuations become progressively more slow and an orientational glass, C60-OG, forms on cooling through the 90 K to 80 K range. At $T_{og}$ of 86 K, observed for a certain heating rate, the population of the P-orientations is 83.5% at ambient $p$. This population is 50% at $p$ of 0.2 GPa at 150 K, and at $p$ of 0.15 GPa at $T$ near 100 K.

FIG. 2. Plots of the thermal conductivity $\kappa$ of C60 under pressures of 0.1 GPa (circles, plot 1), 0.22 GPa (upside down triangles, plot 2), 0.40 GPa (squares, plot 3), and 0.70 GPa (triangles, plot 4) obtained during the cooling of the samples’ (orientationally more ordered or less disordered) equilibrium state from $\sim 170$ K. In order to show the change in slope at $T = T_{og}$ more clearly, the $\kappa$ value was divided by its value at 70 K. The blue solid lines show the change in slope which occurs at $T = T_{og}$. Vertical dashed lines show the values of $T_{og}$ at different $p$. The pressure of 0.22 GPa is close to the $p$ (0.15-0.2 GPa$^{2,5,6,7}$) at which the P- and H-orientations are energetically equivalent, and therefore the changes of $d\kappa/dT$ at $T_{og}$ is the smallest. The slope changes in $\kappa(T)$ are similar as those reported before on heating at corresponding pressures and temperatures.$^{41}$

FIG. 3. Plots of $\kappa$ against $T$, measured on heating of two samples of C60-OG of different $p-T$ history. All samples were heated from $\sim 70$ K at $p = 0.2$ GPa. Curve 1 is for the OG that was
formed by cooling under $p$ of 0.7 GPa, depressurized to 0.2 GPa at $T < T_{og}$ and then heated.
Curve 2 is for a repeat experiment. Curve 3 is for the OG formed by cooling under 0.1 GPa, pressurized to 0.2 GPa at 72 K and then heated. Curve 4 is for the OG formed by cooling under 0.2 GPa and then heated. The black arrow indicates the onset temperature, $T_{og}$, for rotational motions of the state formed by cooling at 0.2 GPa. The red arrows indicate the onset of relaxation for the OGs depressurized or pressurized at $T < T_{og}$. The top panel provides a summary of the $p$-$T$ protocols.

FIG. 4. Plots of $\kappa$ against $T$ measured during heating of two samples of C$_{60}$-OGs of different $p$-$T$ history. Curve 1 is for the sample formed by cooling at 0.1 GPa, pressurized to 0.5 GPa at 74 K and then heated under 0.5 GPa. Curve 2 is for the C$_{60}$-OG formed by cooling at 0.25 GPa, pressurized to 0.4 GPa at 74 K and then heated under 0.4 GPa. Vertical arrows show $T_{og}$ at 0.4 and 0.5 GPa. Red horizontal arrows indicate the detectible range of sub-$T_g$ effects. See text for details.
Figure 1.
Figure 2.
Figure 3.
Figure 4.