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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 C₆₀-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 C₆₀-OG differ from those of glasses, because phonon propagation depends on the ratio of two well-defined *orientational states* of C₆₀ molecules and the density of the solid. A broad peak-like feature appears at T near T_{og} in the κ - T plots of C₆₀-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 C₆₀-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 λ -shape peak in the heat capacity, C_p , and has *no* underlying state of complete order.^{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.^{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 $Pa\bar{3}$. 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.¹ In a neutron scattering study of the C₆₀ crystal under high pressures at 150 K, David and Ibberson² 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 is decreased at $p < 0.2$ GPa, the percentage of P-orientations increases. The percentage of H-orientations increases at a fixed T when p is increased even from the ambient pressure, and it increases on cooling at $p > 0.2$ GPa.³ The *sc* phase is fully disordered when the fraction of P-orientations, $R_P (= [P]/([H]+[P]))$ is equal to 0.5, where square brackets indicate the molar concentration. This occurs at p of 0.2 GPa at 150 K^{2,4} and at p of 0.15 GPa at T near 100 K.^{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 *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, κ ¹⁰ and in thermal expansion coefficient, α .¹¹

The basic structure of the *sc* phase at $T < 260$ K is identical to the structure of the *fcc* phase except that the four molecules in the cubic unit cell have different orientations. When the *sc* phase of C₆₀-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 ,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 *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 *sc* phase becomes an orientational glass, C₆₀-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 κ 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 Sundqvist¹⁰ 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 extrapolation²⁴ of the entropy to lower T and its consequences, as discussed for liquids²⁵ 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.

C₆₀-OG inherits the structure and R_p of *sc*-C₆₀ 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 C₆₀-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 C₆₀-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 κ of C₆₀-OG at ambient pressure. They found that κ of C₆₀-OG increases as R_p increases with time and C₆₀-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 paper⁴⁰ 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 C₆₀ molecules in *sc*-C₆₀ and C₆₀-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 C₆₀-OG by decreasing the pressure in one case, and elastically *contract* the high-*p* formed C₆₀-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 C₆₀-OG, because of its unique type of disorder, and because two of us^{3,41} had already obtained a large set of data on κ of *sc*-C₆₀ and of C₆₀-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 κ of sc -C₆₀ and of an in-depth understanding of the vibrational-configurational changes in C₆₀-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 C₆₀ 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 C₆₀ 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 κ was thus determined. Different cells and samples from the same batch were used, which partly contributed to the inaccuracies and uncertainties in κ 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 C₆₀, 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 ~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 κ 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 ~ 70 K and in one case from 250 K to ~ 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*-C₆₀ 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 κ measured during heating for these protocols is plotted against T as curves 1 and 2 in Fig. 3. The κ 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 κ values against T measured on heating C₆₀-OG that had been formed by cooling under 0.2 GPa pressure. For comparison, we include the κ - 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 C₆₀-OG samples of different p - T history. The C₆₀-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 κ was measured during the heating. Curve 1 in Fig. 4 shows the plot of the measured κ against T . The C₆₀-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*-C₆₀ and pressure-densified C₆₀-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 , κ , R_P , and the T - p history of both *sc*-C₆₀ and C₆₀-OG. As mentioned earlier here, on cooling through T of 260 K, the *fcc* structure changes to the *sc* structure and the C₆₀ 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*-C₆₀ change together, and on cooling from T_{og} , only vibrational state changes, the configurational state of *sc*-C₆₀ 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 κ - 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.⁵¹) In this sense, *sc*-C₆₀ behaves like a liquid or like the usual ODIC and C₆₀-OG behaves like a glass or an orientationally-frozen ODIC. Nevertheless, there are two remarkable differences, (i) α of the *sc*-C₆₀ *increases* on cooling through T_{og} at p below 0.15 GPa,^{5,11} which is the opposite of the generally found

decrease in α 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 $sc\text{-C}_{60}$ 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 κ 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_{phonon} , used in the relation $\kappa = \rho C_v l_{\text{phonon}} / 3$, where ρ is the density and C_v is the specific heat at constant volume, becomes of the order of the phonon wavelength. On heating, l_{phonon} ultimately becomes of the order of the interatomic spacing. This was discussed by Taraskin and Elliott⁵² in relation to the theory of Ioffe and Regel.⁵³ This theory⁵³ has been discussed by several groups and was reviewed and further analyzed by Beltukov et al⁵⁴ by using a harmonic oscillator model. Since α is zero in this model and α is positive for $\text{C}_{60}\text{-OG}$, 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 κ and its change with T .^{55,56}

B. Thermal conductivity features on cooling and kinetic freezing

Previous studies have shown that κ of most ODICs and of the fcc phase of C_{60} at ambient pressure is almost *independent* of temperature.^{31,32} In contrast, κ of a single crystal $sc\text{-C}_{60}$ at ambient pressure varies roughly as $1/T$,³³ which is also the typical behavior of crystalline phases. The difference is attributed to the partial order of $sc\text{-C}_{60}$ 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 -C₆₀ and single crystal C₆₀-OG would be due mainly to three-phonon Umklapp scattering. Polycrystalline samples of sc -C₆₀ and C₆₀-OG here and elsewhere^{3,41} show both a lower magnitude of κ and a weaker T -dependence than those observed for single crystal sc -C₆₀ and C₆₀-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 κ and its T -dependence.⁵⁷ Hence, κ of a given sc -C₆₀ 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 κ . 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 -C₆₀.³³ The superimposed effect of phonon scattering from orientational disorder becomes clearer when C₆₀ 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 κ of our polycrystalline C₆₀ 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 C₆₀-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 C₆₀-OG fine powder.⁵⁹ Also, the increase in C_p at T_{og} of single crystal C₆₀-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 C₆₀-OG at comparable cooling and heating rates.⁵⁹ So, although the change in C_p of C₆₀-OG powder relative to the single crystal is significant when C₆₀-OG is heated, the change in κ 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 -C₆₀ and C₆₀-OG single crystal in Fig 1 in Ref. 33, and the plots in Fig. 2 here for the sc -C₆₀ and C₆₀-OG powder. Only the $\kappa(T)$ of the isobarically cooled or heated powdered state without the sub- T_{og} pressure treatments of C₆₀-OG is the intrinsic value of $\kappa(T)$.

Looking into still lower temperature features, Beyermann et al.⁶⁰ reported C_p of polycrystalline C₆₀ 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 κ - T plots shown in Fig. 2. For the sc -C₆₀ 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 finding² 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 κ - T plots. On cooling under $p < 0.2$ GPa the sc -C₆₀ 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 -C₆₀ 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 κ - 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 κ - 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 C₆₀-OG is too weak to produce the artificial peak.⁶⁷ Therefore, an important aspect of our finding is that the κ - T plots of sc -C₆₀ and C₆₀-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 glycerol⁴³ and di-*n*-butyl phthalate⁴² 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 κ 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 κ 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 , C₆₀-OG inherits the structure, configuration, or R_p of C₆₀ at $T = T_{og}$. So, we compare the behavior of C₆₀-OG in the same sequence as that of the glycerol⁴³ and *n*-dibutyl phthalate.⁴² The κ - T plot of the elastically expanded state of C₆₀-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 C₆₀-OG formed by cooling *sc*-C₆₀ 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 κ

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 κ approaches the equilibrium R_P more *slowly* than expected. This suggests that some orientational order persists even at $T > T_{og}$, which is similar to our previous interpretation.^{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 plot⁴¹ 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,⁴¹ we find no sub- T_{og} effect in the elastically expanded C₆₀-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.⁶⁸ Also, recent dilatometric studies by Casalini and Roland³⁸ 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 glycerol⁴³ and di-*n*-butyl phthalate.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.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 *sc*-C₆₀ or C₆₀-OG.

The study of elastically contracted C₆₀-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 κ observed on heating a C₆₀-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 κ - T plot at $T < 125$ K, coincides with T_{og} of 121 K of *sc*-C₆₀,⁴¹ 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, κ of C₆₀-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, κ in curve 1 follows the intrinsic κ of the *sc*-C₆₀ at 0.5 GPa, which has previously shown a maximum in κ at 190 K.⁴¹ The red arrow above curve 1 indicates the range of sub- T_{og} relaxation as suggested by the changes in κ with T at $T < T_{og}$.

Curve 2 in Fig. 4 shows the results obtained for elastically contracted C₆₀-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 κ than that of the intrinsic $\kappa(T)$ at T of ~ 102 K, which is below the slope inversion temperature or T_{og} of 116 K at 0.4 GPa. For comparison, κ 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*-C₆₀ is less. The higher κ 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 κ , the onset temperature obtained from the κ - T plots may not be 102 K. On heating above T_{og} , the κ value in curve 2, Fig. 4, follows the intrinsic κ of *sc*-C₆₀ at 0.4 GPa, which has shown a maximum at 170 K.⁴¹

A sub- T_g feature also appears in curve 3 of Fig. 3, which is for the C₆₀-OG formed under 0.1 GPa and heated under 0.2 GPa. Here κ begins to gradually decrease showing slope inversion

at T well below the T_{og} of 102.5 K at 0.2 GPa.⁴¹ 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, κ also shows a local minimum because the intrinsic κ 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 α and thus affects its intrinsic $d\kappa/dT$ but structural relaxation of single crystal C₆₀-OG on heating through T_{og} at ambient p decreases α .¹¹ One expects that the consequences of the opposite changes in α of glass vs. C₆₀-OG would be different for $d\kappa/dT$ on heating. It is difficult to envisage how a decrease in α on heating through T_{og} and an increase in α on cooling through T_{og} ¹¹ 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 κ vary also with the changing configuration. But when T and p of C₆₀-OG, of glasses, and of kinetically-frozen ODICs are varied, the vibrational density of states, phonon propagation, and κ vary at a fixed configuration. When T of the elastically expanded or elastically contracted C₆₀-OG is increased at a fixed p , there is an additional effect on κ 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 C₆₀-OG state, no sub- T_{og} effect on κ 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 κ of the elastically expanded glasses of glycerol⁴³ and di-n-butyl phthalate,⁴² 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, κ 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 κ 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, κ 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 κ - T plot. A minimum was observed also in an isothermal time-dependence of κ .⁴¹ 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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1 or $R_P = 0$ are never obtained. For C₆₀-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 C₆₀-OG increases or decreases (above 0.2 GPa). An increase in R_P isothermally with time, which would decrease T_f , increases κ at ambient pressure (Ref. 33).

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FIGURE CAPTIONS

FIG. 1. An illustration of the C_{60} molecule, and of the molecular arrangement in the *fcc* crystal lattice at $T > 260$ K. On cooling through T of ~ 260 K at ambient pressure, free rotations of the C_{60} 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, C_{60} -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 κ of C_{60} 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 ~ 170 K. In order to show the change in slope at $T = T_{og}$ more clearly, the κ 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 κ against T , measured on heating of two samples of C_{60} -OG of different p - T history. All samples were heated from ~ 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 κ against T measured during heating of two samples of C₆₀-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 C₆₀-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.