Unusual Freezing and Melting of Gallium Encapsulated in Carbon Nanotubes

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The freezing and melting behavior of gallium (Ga) encapsulated in carbon nanotubes was investigated through *in situ* observation in a transmission electron microscope. It is shown that Ga remains liquid up to $-80\,°C$ when encapsulated in carbon nanotubes. Results of detailed electron diffraction analysis show that the encapsulated Ga can crystallize in either β phase or γ phase rather than the common α phase upon freezing. Both β-Ga and γ-Ga melt at around $-20\,°C$. While this is very close to the melting point of bulk β-Ga ($-16\,°C$), it is considerably higher than that of bulk γ-Ga ($-35.6\,°C$). It was observed that upon solidification, Ga has its unique crystallographic orientation relative to the host carbon nanotube.

It is well known that the behavior of a liquid confined in very small pores can be very different from its behavior in the normal bulk form [1–4]. Significant melting point depression and large hysteresis between melting and freezing (solidification) have been observed for cryogenic fluids [1,5,6] and low melting point metals [7–14]. There are also reports [15,16] showing that nanoclusters consisting a few tens of atoms display much higher melting points than in the bulk form. In this Letter we discuss the freezing and melting behavior of Ga encapsulated in carbon nanotubes. The carbon nanotubes containing Ga were synthesized using the previously described method [17,18]. It was found that Ga encapsulated in carbon nanotubes may remain liquid up to $-80\,°C$. Upon solidification, both β-Ga and γ-Ga can be formed. It is shown that β-Ga melts at about the same temperature as that of its bulk form, whereas γ-Ga melts at a considerably higher temperature as that of its bulk form.

Ga displays a complex phase diagram with many stable and metastable crystalline phases. The stable phase at normal conditions is α-Ga which possesses a *Cmca* (space group) structure with an orthorhombic symmetry. Ga has two other stable phases at high pressure [19], the GaII, a body-centered cubic structure, and the GaIII, a face-centered tetragonal structure. In addition, a number of metastable phases have also been identified at atmospheric pressure and designated as β [20], γ [21], δ [22], and ϵ [23]. The crystal structure of β-Ga is monoclinic. It is a metasable phase obtained by supercooling the liquid [22] or by heating amorphous Ga [23]. The crystal structure of γ-Ga is orthorhombic [21]. The crystallographic data of α-, β-, and γ-Ga is listed in Table I. The cell density ratios shown in Table I are calculated values using the Ga atomic radius of 1.26 Å in covalent-metallic bonding. It can be seen that β-Ga and γ-Ga are two more denser states than α-Ga.

Using a Gatan model 900 cold stage, the freezing and melting of Ga encapsulated in carbon nanotubes were directly observed in a transmission electron microscope

(TEM) and recorded using the CCD camera attached to the microscope. The Gatan cold stage uses liquid nitrogen for cooling and its cooling rate can be easily adjusted by changing the heating current. The cooling rate was set as low as $0.5\,°C/\text{min}$ prior to freezing and melting. To minimize electron beam heating, the smallest condenser aperture (4th, 20 μm) was used, resulting in the electron beam intensity of nearly 40 times weaker than under normal imaging conditions (1st condenser aperture, 150 μm).

Figure 1 shows a carbon nanotube encapsulated with Ga at various temperature stages during cooling and heating. The carbon nanotube was cooled down from room temperature ($21\,°C$) to $-90\,°C$, then reheated to $90\,°C$ (Fig. 2). In liquid state the length of the encapsulated Ga column varied linearly with temperature. Freezing (solidification) occurred at $-80\,°C$. This was evidenced by a sharp Ga volume decrease at this temperature (see both Figs. 1 and 2) and confirmed by electron diffraction. The sudden sharp volume (length) decrease of the encapsulated Ga column upon solidification obviously indicated that the encapsulated Ga crystallized in another phase rather than the α phase. Ga is an ice-type element and it expands 3.1% on solidifying in α phase. Results of detailed nanobeam electron diffraction

TABLE I. Crystallography data of α-, β-, and γ-Ga

	α-Ga	β-Ga	γ-Ga
Symmetry	orthorhombic	monoclinic	orthorhombic
Space group	*Cmca*	*C2/c*	*Cmcm*
Lattice parameters (Å)	$a = 4.519$	$a = 2.766$	$a = 10.593$
	$b = 7.660$	$b = 8.053$	$b = 13.523$
	$c = 4.525$	$c = 3.332$	$c = 5.203$
		$\beta = 92°$	
No. of atoms/cell	8	4	40
Cell density	0.43	0.45	0.45
Melting point	$29.8\,°C$	$-16.3\,°C$	$-35.6\,°C$
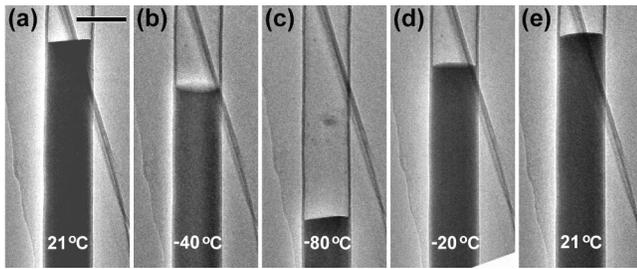
FIG. 1. TEM micrographs showing Ga volume contraction and expansion inside a carbon nanotube upon cooling and heating. The background feature is a carbon film. Scale bar = 100 nm. (a) At room temperature, 21 °C, before cooling. (b) At −40 °C. (c) At −80 °C, solidification occurred. (d) The crystallized Ga was melted at −20 °C. (e) Reheated to room temperature, 21 °C.

analysis show that the encapsulated Ga crystallized in β phase. A typical electron diffraction pattern of the β-Ga in [100] zone axis is shown in Fig. 3(a). A calculated pattern in the same zone axis is presented in Fig. 3(b).

Obviously, the volume of the solidified Ga should increase upon melting. This enabled us to measure the melting point free of electron irradiation (Fig. 4). The melting point of the encapsulated β-Ga was measured as −20 °C which is very close to the melting point of bulk β-Ga (− 16.3 °C) [20].

The encapsulated Ga can also crystallize in γ phase. Figure 5(a) shows a carbon nanotube with two encapsulated Ga columns separated by a small gap. Upon cooling, the upper column crystallized in γ phase at −70 °C while the lower column crystallized in β phase at −80 °C. Figures 5(b) and 5(c) are two electron nanobeam diffraction patterns of the γ-Ga in the [010] and [123] zone axes, respectively, while Figs. 5(d) and 5(e) correspond to β-Ga in the [310] and [510] axes, respectively. The measured values of some specific plane spacings of β-Ga and γ-Ga
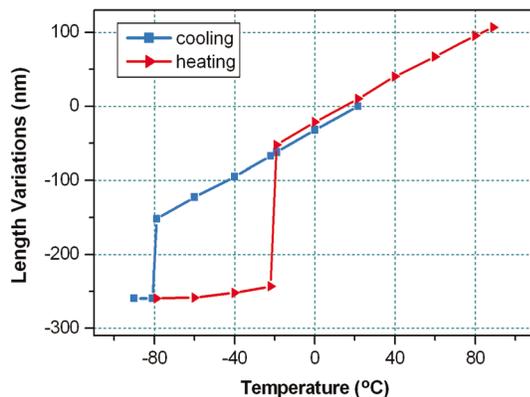
FIG. 2 (color). The Ga column length variations plotted against temperature. The length variations are relative length changes compared with the initial length at 21 °C before cooling. The blue curve corresponds to cooling and the red curve corresponds to heating.
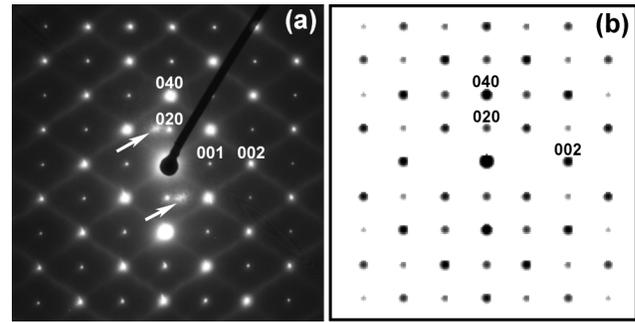
FIG. 3. Identification of β-Ga through electron diffraction analysis. (a) An experimental electron diffraction pattern in [100] zone axis. The $(00l)$ reflections with l being odd are kinematically forbidden but appeared here as double diffractions. The two arrowed reflections are the (002) and (00$\bar{2}$) reflections of a carbon nanotube. (b) A calculated pattern in the same zone axis.

are presented in Table II. The measured melting point of the encapsulated γ-Ga is around −21 °C, which is considerably higher than the melting point (−35.6 °C) of bulk γ-Ga [21]. The freezing and melting of both β-Ga and γ-Ga encapsulated in the same carbon nanotube are shown in Fig. 6. The sudden large volume contractions occurred at −70 °C and −80 °C [Figs. 6(b) and 6(c)] indicate freezing of γ-Ga (upper Ga column) and β-Ga (lower Ga column), respectively. We also managed to capture the moments of melting of the two phases [Fig. 6(e), γ-Ga; Fig. 6(f), β-Ga) which are only about 1 °C apart.

The phase coexistence of β-Ga and γ-Ga in the same carbon nanotube is consistent with the recently published result by Pochon et al. [24] which shows that β-Ga and γ-Ga can coexist in Ga nanopaticles controlled by electron excitation. No significant melting point deviation was observed for these Ga particles.

The presently observed Ga melting point deviation from its bulk forms could be due to a combination of a couple of factors. The primary factor is the interaction between Ga and the wall of the carbon nanotube. This interaction is especially prominent at low temperature. It
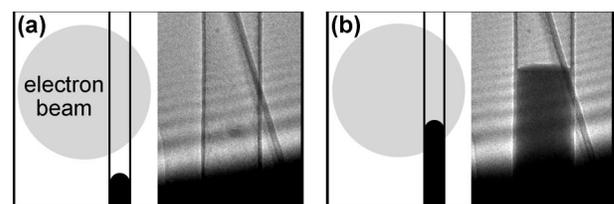
FIG. 4. Measuring the melting point of Ga encapsulated in a carbon nanotube free of electron irradiation. The left part of each graph is a schematic representation while the right part of each graph is a TEM image. (a) During heating, the electron beam was kept away but very close to the tip of the Ga column. (b) Upon melting due to expansion, the Ga tip can be seen without shifting the electron beam and the specimen.
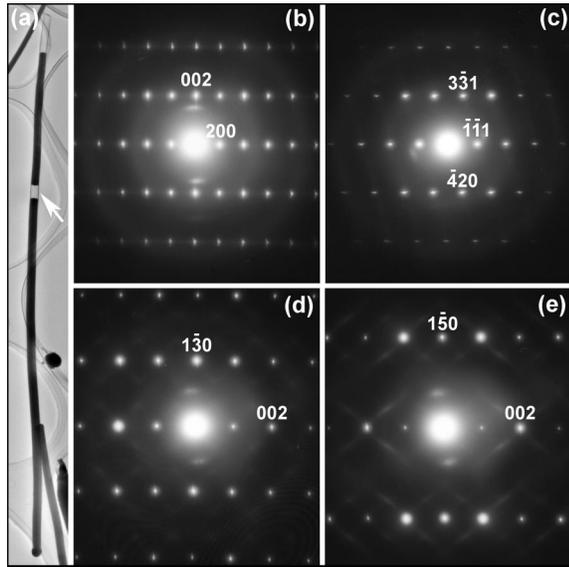
FIG. 5. Electron diffraction results showing crystallization of both β-Ga and γ-Ga in a same carbon nanotube. (a) TEM micrograph showing the carbon nanotube containing two Ga columns separated by a small gap (arrowed). (b)-(c) Electron diffraction patterns from upper Ga column which correspond to γ-Ga in [010] and [123] zone axis, respectively. (d)-(e) Electron diffraction patterns from lower Ga column which correspond to β-Ga in [310] and [510] zone axis, respectively.

is observed that the curvature of the Ga tip surface changed with temperature. Prior to solidification, the Ga tip surface can be very flat [see Fig. 1(b) and Fig. 6(b), the lower Ga column) rather than in a shape of a convex meniscus. Another possible factor could be the effect of uncontrollable impurity. Although it is undetectable by means of EELS (electron energy loss spectroscopy) and EDS (x-ray energy dispersive spectrometer) analysis, it is still uncertain if the encapsulated Ga contains very limited quantity of any impurity. The high vacuum in the TEM column may also slightly affect the melting point of the encapsulated Ga. It is believed that the carbon nanotube size confinement effect is negligible as the nanotube diameter is rather large (100 nm).

TABLE II. Plane spacings of β-Ga and γ-Ga

	Plane	Measured Spacing	Calculated Spacing
β-Ga	(020)	3.951	4.027
	(001)	3.267	3.332
	(021)	2.518	2.566
	(1$\bar{3}$0)	1.909	1.926
	(1$\bar{5}$0)	1.356	1.392
γ-Ga	(200)	5.160	5.296
	(1$\bar{1}$1)	4.321	4.414
	(002)	2.519	2.601
	(4$\bar{2}$0)	2.427	2.466
	(3$\bar{3}$1)	2.412	2.452

A series of observations on carbon nanotubes with different diameters ranging from 100 to 200 nm show no melting point dependence on the carbon nanotube diameter. In all cases, both β-Ga and γ-Ga melted at around $-20\,°C$.

It is noted that upon solidification, Ga has its unique crystallographic orientation relative to the host carbon nanotube. This can be clearly seen from the electron nanobeam diffraction patterns in which the (002) and (00$\bar{2}$) reflections of the carbon nanotube always appear. Such a relationship is maintained not only in every carbon nanotube but also each time when the Ga in the same carbon nanotube is melted and refrozen. It is believed that such kind of confinement effect could affect the thermal stability of the encapsulated Ga. It is now generally accepted that melting starts from the solid surface. For α-Ga, it has been known that the thermal stability of its crystallographic planes is different from one to another [25,26]. Similar effects may also exist for β-Ga and γ-Ga. When Ga is encapsulated in carbon nanotubes, upon solidification, the crystallographic plane of its tip surface is uniquely determined by the host carbon nanotube, and therefore this kind of confinement effect will inevitably affect the thermal stability of the encapsulated Ga. Such kind of interaction between Ga and the carbon nanotube may also favor Ga nucleation in β and γ phases. Earlier studies [9,10] on Ga droplets of 100–1000 nm in diameter confined in epoxy resin also verified the occurrence of β-Ga and γ-Ga, and the lack of α-Ga when the Ga droplets were supercooled and solidified at $-123\,°C$ (150 K). In these studies it is explained that geometrical confinement may prevent solidification in the stable α phase since Ga is an ice-type element, for which the liquid phase is denser than the solid phase at ambient conditions. This is apparently not the case for the present situation where Ga can expand along the carbon nanotube freely.
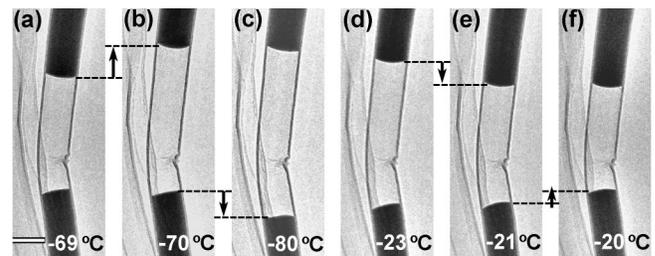
FIG. 6. TEM micrographs showing solidification and melting of both β-Ga and γ-Ga in the same carbon nanotube. The arrows and the dashed lines indicate the sudden large volume contractions and expansions upon solidification and melting. Scale bar = 100 nm. (a) At $-69\,°C$, both Ga columns were liquid. (b) The upper Ga column crystallized in γ phase at $-70\,°C$. (c) The lower Ga column crystallized in β phase at $-80\,°C$. (d) At $-23\,°C$. Both Ga columns were in solid state. (e) γ-Ga (upper column) was melted at $-21\,°C$. (f) β-Ga (lower column) was melted at $-20\,°C$.

It can be seen from Fig. 2 that the linear portions of the two curves which correspond to the liquid Ga state do not overlap. This is because the Ga tip surface did not return to the same positions upon melting and reheating to the former temperatures. We found that this irreversible effect was caused by a slight shape change of the carbon nanotube upon freezing of Ga. It seemed that the carbon nanotube diameter decreased slightly upon Ga solidification. After ten cycles of freezing and melting treatment the measured diameter of the carbon nanotube is only about 96% of its original value. While it is hard to believe that the diameter of the carbon nanotube could be reduced so much, as it would involve the expulsion of some of the carbon atoms from the shell network, it is likely that the carbon nanotube might have been slightly flattened each time when Ga solidified.

If the encapsulated Ga is cooled down but is not frozen, its tip surface will return to its initial position when reheated to the former temperature, and the characteristic curve of Ga volumetric-expansion is a single straight line. Therefore, a carbon nanotube encapsulated with Ga serves as a perfect nanothermometer and it can be used in a far longer temperature range (-69–$500\,^\circ$C) than it was initially thought (50–$500\,^\circ$C)[18]. The upper limit is set at about $500\,^\circ$C, as it was found that in TEM, Ga starts to evaporate quickly from $\sim 600\,^\circ$C.

In macroscopic state, the volumetric change of a liquid is directly related to temperature and can be expressed as $v_t = v_0[1 + \lambda(t - t_0)]$, where λ is the volumetric-expansion coefficient, while v_t and v_0 are the volumes at temperatures t and t_0, respectively. The expansion coefficient of liquid Ga is 0.1015×10^{-3} per $^\circ$C in a temperature range of 30–$977\,^\circ$C, as derived from density measurement [27]. Our calculations show that this value applies to far more lower temperatures for Ga encapsulated in carbon nanotubes. Based on volume changes, we derived a value of λ at 0.1008×10^{-3} in the temperature range of -69–$90\,^\circ$C. This value is exceptionally consistent with that of bulk Ga.

In summary, it has been found that when encapsulated in carbon nanotubes, Ga remains liquid up to $-80\,^\circ$C. The encapsulated Ga can crystallize in either β phase or γ phase rather than the common α phase. While the melting point of the encapsulated β-Ga is very close to the melting point of its bulk form, the encapsulated γ-Ga, however, melts at a substantially higher temperature than that of the bulk γ-Ga. Upon crystallization Ga has its unique crystallographic orientation relative to the host carbon nanotube.

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[1] J. Warnock, D. D. Awschalom, and M. W. Shafer, Phys. Rev. Lett. **57**, 1753 (1986).
[2] C. Liezhaoo, D. F. Brewer, C. Girit, J. D. Reppy, and E. N. Smith, Phys. Rev. B **33**, 106 (1986).
[3] D. D. Awschalom and J. Warnock, Phys. Rev. B **35**, 6779 (1987).
[4] J. H. Strange, M. Rahan, and E. G. Smith, Phys. Rev. Lett. **71**, 3589 (1993).
[5] P. E. Sokol, W. J. Ma, K. W. Herwig, W. M. Snow, Y. Wang, J. Koplik, and J. R. Banavar, Appl. Phys. Lett. **61**, 777 (1992).
[6] E. Molz, A. P. Y. Wong, M. W. Chan, and J. R. Beamish, Phys. Rev. B **48**, 5741 (1993).
[7] Y. A. Kumzerov, A. A. Nabereznov, S. B. Vakhrushev, and B. N. Savenko, Phys. Rev. B **52**, 4772 (1995).
[8] C. Tien, C. S. Wur, K. J. Lin, J. S. H., E. V. Charnaya, and Y. A. Kumzerov, Phys. Rev. B **54**, 11880 (1996).
[9] A. Di Cicco, Phys. Rev. Lett. **81**, 2942 (1998).
[10] A. Di Cicco, S. Fusari, and S. Stizza, Philos. Mag. B **79**, 2113 (1999).
[11] E. V. Charnaya, C. Tien, K. J. Lin, and Y. A. Kumzerov, Phys. Rev. B **58**, 11089 (1998).
[12] K. M. Unruh, T. E. Huber, and C. A. Huber, Phys. Rev. B **48**, 9021 (1993).
[13] B. F. Borisov, E. V. Charnaya, P. G. Plotnikov, W. D. Hoffmann, D. Michel, Y. A. Kumzerov, C. Tien, and C. S. Wur, Phys. Rev. B **58**, 5329 (1998).
[14] B. F. Borisov, E. V. Charnaya, W. D. Hoffmann, D. Michel, A. V. Shelyapin, and Y. A. Kumzerov, J. Phys. Condens. Matter **9**, 3377 (1997).
[15] A. A. Shvartsburg and M. F. Jarrold, Phys. Rev. Lett. **85**, 2530 (2000).
[16] G. A. Breaux, T. S. R. C. Benirschke, B. S. Kinnear, and M. F. Jarrold, Phys. Rev. Lett. **91**, 215508 (2003).
[17] Z. Liu, Y. Gao, and Y. Bando, Appl. Phys. Lett. **81**, 4844 (2002).
[18] Y. Gao and Y. Bando, Nature (London) **415**, 599 (2002).
[19] L. Bosio, J. Chem. Phys. **68**, 1221 (1978).
[20] L. Bosio, A. Defrain, H. Curien, and A. Rimsky, Acta Crystallogr. Sect. B **25**, 995 (1969).
[21] L. Bosio, A. Rimsky, M. Dupont, and H. Curien, Acta Crystallogr. Sect. B **28**, 1974 (1972).
[22] L. Bosio, H. Curien, M. Dupont, and A. Rimsky, Acta Crystallogr. Sect. B **29**, 367 (1973).
[23] A. Bererhi, L. Bosio, and R. Cortes, J. Non-Cryst. Solids **30**, 253 (1979).
[24] S. Pochon, K. MacDonald, R. J. Knize, and N. I. Zheludev, Phys. Rev. Lett. **92**, 145702 (2004).
[25] R. Trittibach, C. Grutter, and J. H. Bilgram, Phys. Rev. B **50**, 2529 (1994).
[26] C. Grutter, R. Trittibach, and J. H. Bilgram, Helv. Phys. Acta **67**, 215 (1994).
[27] D. R. Lide, *CRC Handbook of Chemistry and Physics* (Chemical Rubber, Cleveland, 1990), 71st ed.