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To cite this article: Anand P Tiwari et al 2017 J. Phys.: Condens. Matter 29 445701

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Superconductivity at 7.4 K in few layer graphene by Li-intercalation

Anand P Tiwari$^{1,2,4}$, Soohyeon Shin$^3$, Eunhee Hwang$^{1,2}$, Soon-Gil Jung$^3$, Tuson Park$^3$ and Hyoyoung Lee$^{1,2}$

$^1$ Centre for Integrated Nanostructure Physics (CINAP), Institute for Basic Science (IBS), Suwon 16419, Republic of Korea
$^2$ Department of Chemistry, Sungkyunkwan University (SKKU), Suwon 16419, Republic of Korea
$^3$ Department of Physics, Sungkyunkwan University (SKKU), Suwon 16419, Republic of Korea
$^4$ Department of Material Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea

E-mail: hyoyoung@skku.edu and tp8701@skku.edu

Received 3 July 2017, revised 20 August 2017
Accepted for publication 29 August 2017
Published 3 October 2017

Abstract
Superconductivity in graphene has been highly sought after for its promise in various device applications and for general scientific interest. Ironically, the simple electronic structure of graphene, which is responsible for novel quantum phenomena, hinders the emergence of superconductivity. Theory predicts that doping the surface of the graphene effectively alters the electronic structure, thus promoting propensity towards Cooper pair instability (Profeta et al (2012) Nat. Phys. 8 131–4; Nandkishore et al (2012) Nat. Phys. 8 158–63) [1, 2]. Here we report the emergence of superconductivity at 7.4 K in Li-intercalated few-layer-graphene (FLG). The absence of superconductivity in 3D Li-doped graphite underlines that superconductivity in Li-FLG arises from the novel electronic properties of the 2D graphene layer. These results are expected to guide future research on graphene-based superconductivity, both in theory and experiments. In addition, easy control of the Li-doping process holds promise for various device applications.

Keywords: few layer graphene, superconductivity, quantum confinement, intercalation

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)
However, when the intercalant distance $h$ is too small, as in LiC$_6$ graphite ($h = 1.85$ Å), the superconductivity can be completely destroyed because a strong confinement of the interlayer state in a narrow region shifts the intercalant band well above the Fermi energy [14]. A band structure calculation predicts that the empty interlayer state can be returned to the Fermi level by removing the quantum confinement [1]. In the 2D graphene LiC$_6$, where the quantum confinement is removed, the electron–phonon coupling from the low-energy lithium modes and carbon out-of-plane vibrations is predicted to be strong enough to induce superconductivity at as high as 8.1 K. Here we report the discovery of the SC phase below 7.4 K in the Li-intercalated few-layer-graphene (FLG). Zero-field-cooled (ZFC) magnetization ($M$) measurements of the Li-FLG reveal a sharp suppression below 7.4 K due to the Meissner effect, where $T_c$ is progressively suppressed with increasing magnetic field. Magnetization hysteresis loop as a function of magnetic field, which arises due to the trapped magnetic flux lines, becomes more pronounced with decreasing temperature. The upper critical field $H_{c2}$ from the $M$–$T$ measurements is 1538 Oe and the lower critical field $H_{c1}$ is 124 Oe, indicating that the Li-FLG is a prototypical type II superconductor with the Ginzburg–Landau parameter $\kappa (= \lambda / \xi)$ of 3.52. Here, $\lambda$ and $\xi$ is the penetration depth and SC coherence length, respectively. Observation of $T_c$ at 7.4 K in the graphene-based LiC$_6$ and its good agreement with the predicted $T_c$ indicate that the intercalant-derived band and the carbon out-of-plane vibrations are important to forming the SC Cooper pairs [1].

Natural graphite flakes (Alfa Aesar 99.9%), with a mean diameter of 1 mm, and Li (Sigma Aldrich) are taken for the reaction. First, the graphite flakes are placed in a round-bottom flask; Li is added and then degassed in a vacuum while heating. The resulting mixtures are raised to 200 °C for 24 h. Then, 150 ml 1,2-Dimethoxyethane (99.9%, Sigma Aldrich) is added in a freshly-prepared alloy of graphite and Li, and the Li-intercalated graphene is dispersed via ultrasonication for 24 h. The reaction mixture solution is then stirred for 7 d at room temperature. After standing for 24 h, the solution displays stratification, the upper clear solution can be poured off and the medial part of the solution evaporated. The sample must be kept in an argon atmosphere for 24 h to enhance the stability of Li between the layers of few-layer graphene.

The sample is washed with ethanol for several minutes to remove the absorbed Lithium on the surface of the FLG. The resulting sample is then placed in a vacuum chamber overnight to remove the residual ethanol and homogenize the distribution of Lithium. The structural and microstructural characterizations of the sample are studied via x-ray diffraction (XRD) (Rigaku Ultima IV), x-ray photoelectron spectroscopy (ESCA 2000, VG Microtech), atomic force microscopy (AFM) (Agilent 5100 AFM/SPM system), and transmission electron microscopy (TEM) (JEOL JEM-2100F). Magnetic properties, such as the temperature dependences of magnetization ($M$) and magnetic hysteresis ($M$–$H$) loops, for a pellet of Li-doped FLG flakes are investigated via a magnetic property measurement system (MPMS) Quantum Design).

Results and discussions

Li-intercalated few-layer graphene (FLG) samples are synthesized via a solution reaction of graphite flakes and Li, through several successive steps. All reactions for sample preparation are performed in a glove box with purified argon atmosphere. Figure 1(a) compares XRD patterns of the as-synthesized, Li-deposited few-layer graphene (Li-FLG) and pristine graphite in the top and bottom parts, respectively. The (0 0 2) reflection of the graphite precursor at 26.4° indicates that the material is AB stacked [21]. The width of the (0 0 2) reflection of the Li-FLG is significantly broadened due to the Li intercalation and the peak position slightly moved to a smaller angle of 26.11°, indicating that the interlayer spacing of the graphene layers is almost same (3.42 Å) as that of the graphite

Figure 1. Structural characterization of the Li-intercalated few-layer-graphene (FLG). (a) X-ray diffraction patterns of Li-intercalated FLG and graphite are plotted as a function of the diffraction angle $2\theta$ in the top (blue line) and bottom (black line) parts, respectively. (b) Surface image of atomic force microscopy and (c) its corresponding line profile of as-synthesized Li-FLG.
(3.33 Å). AFM image displays the Li-intercalated graphene flakes (bright spots) on the silicon surface where the dimension is approximately 30 × 20 × 2 nm3 (see figure 1(b)). The line profile of the Li-FLG, as shown in figure 1(c), shows that the average height of the flakes is ~2 nm, implying that 5–6 layers of graphene are formed on the substrate [22]. X-ray photoelectron spectroscopy (XPS) analysis (see figure S2, supplementary material) shows that 3.09 atomic % of Li atoms were intercalated in the graphene flakes.

Magnetization of Li-intercalated graphene at 20 Oe is shown as a function of temperature in figure 2(a). Both ZFC and field-cooled (FC) magnetization for a pellet of Li-FLG flakes is plotted as a function of temperature for 20 Oe. The onset of the SC phase transition is marked by an arrow. (b) The superconducting shielding fraction of the Li-FLG is estimated for 20 (squares), 100 (circles), 200 (up triangles), 300 (down triangles), 500 (diamonds), and 1000 Oe (hairs). Here the background was approximated as the FC susceptibility because there was negligible change at Tc in the FC magnetization. Arrows indicate the onset of the Meissner effect for each field.

Figure 2. Magnetic characterization of Li-FLG. (a) Zero-field-cooled (ZFC) and field-cooled (FC) magnetization for a pellet of Li-FLG flakes is plotted as a function of temperature for 20 Oe. The onset of the SC phase transition is marked by an arrow. (b) The superconducting shielding fraction of the Li-FLG is estimated for 20 (squares), 100 (circles), 200 (up triangles), 300 (down triangles), 500 (diamonds), and 1000 Oe (hairs). Here the background was approximated as the FC susceptibility because there was negligible change at Tc in the FC magnetization. Arrows indicate the onset of the Meissner effect for each field.

Magnetization of Li-intercalated graphene at 20 Oe is shown as a function of temperature in figure 2(a). Both ZFC and field-cooled (FC) data show a drop below 7.4 K, which manifests the Meissner effect of magnetic flux expulsion below the SC phase transition temperature (=Tc). The FC magnetization at 20 Oe drops slightly at the Tc onset and gradually increases with decreasing temperature, indicating the presence of local spins that may be introduced from such various defects on the graphene layers as vacancies, frustration, or hydrogen chemisorption [23–25]. The anomalous low-temperature upturn in magnetization can be described by the Curie–Weiss law, where the concentration of magnetic defects is estimated to be 0.012% with an assumption that the size of moment for each defect is 2 μB [26, 27] (see figure S3, supplementary material).

Figure 2(b) displays the evolution of the SC transition temperature and the SC shielding fraction 4π(χZFC − χbkg) for several magnetic fields. Since the FC magnetic susceptibility χFC has a negligible change near Tc from the Curie–Weiss background (see figure S4, supplementary material), it is approximated as the background χbkg, the magnetic susceptibility of the Li-FLG in the normal state. With increasing magnetic field, Tc is gradually suppressed. The SC shielding fraction is approximately 0.06% for the pellet of Li-FLG flakes, which reflects a small fraction of Li atoms that are successfully intercalated in the graphene flakes (see figure S2, supplementary material). When the size of the SC grains is comparable to the London penetration depth, small SC volume fraction is often reported in the powder form of the specimen because the magnetic flux expulsion arises from the aggregated SC grains: the SC shielding fraction was reported to be 0.05% for graphite–sulfur (C–S) composites [28, 29].

The dependence on magnetic field of magnetization M(H) of Li-doped FLG is displayed in figure 3(a), where ΔM is the magnetization after subtracting M at 10 K in the normal state.
of Li-FLG, i.e. \( \Delta M = M(H, T) - M(H, 10 \text{ K}) \) (see figure S5, supplementary material). At low fields, \( \Delta M \) at 2 K decreases linearly with increasing \( H \) due to the Meissner effect, deviates from the linear dependence above \( H_c1 \) (which is marked as an arrow in the inset to figure 3(a)), and starts to increase with further increasing magnetic field due to vortices in the mixed phase of the type II superconductor. At higher fields, \( \Delta M \) crosses zero to a positive value and increases with field. These peculiar \( M-H \) hysteretic loops below \( T_c \) can be explained by the superposition of the SC diamagnetic component and the paramagnetic contribution from the local spins that caused the anomalous upturn in the temperature dependence of \( M \) below \( T_c \) (see figure 2(a)). When temperature is raised close to \( T_c \) of 7.4 K, the hysteretic behaviour in the \( M-H \) curve is almost negligible.

Figure 3(b) describes the temperature dependence of the upper critical field, \( H_{c2} \), which was obtained from the \( M-T \) measurements. The orbital depairing field of Li-FLG is estimated to be 1538 Oe by using the Werthamer–Helfand–Hohenberg (WHH) model for the dirty type II superconductor [30], where the slope at \( T_c \) is \(-304 \text{ Oe}/K\): \( H_{c2}(T = 0) = -0.69T_c(dH_{c2}/dT)|_{T=T_c} \). The Ginzburg–Landau coherence length estimated from the relation \( H_{c2} \sim \Phi_0/2\pi\xi^2 \) is \( \xi = 462 \text{ Å} \), where \( \Phi_0 = (2.07 \times 10^{-15} \text{ T-m}^2) \) is a flux quantum. The lower critical field \( H_{c1} \), where magnetic flux begins to penetrate the Li-FLG, is multiplied by a factor of 2 for comparison, and is plotted as a function of temperature in figure 3(b). \( H_{c1} \) initially increases with decreasing temperature and saturates to 124 Oe at lower temperatures. When estimated from \( H_{c1} \) \((-\Phi_0/2\pi\lambda^2)\), the penetration depth \( \lambda \) by which the applied field extends into the SC state is estimated to be 1628 Å. The Ginzburg–Landau parameter, \( \kappa = (\lambda/\xi) \), is 3.52, indicating that the Li-FLG is a prototypical type II superconductor.

Electrical resistance measurements, \( R(T) \), were performed on a pellet of Li-FLG flakes, where the average dimension of the flakes is \( 30 \times 20 \times 2 \text{ nm}^3 \). Figure 4(a) representatively shows the zero-field resistance of the Li-FLG as a function of temperature. \( R(T) \) increases gradually with lowering temperature, but deviates from the linear increase, showing a strong enhancement below 7.4 K, the SC transition temperature determined from the \( M-T \) measurements. When the zero-field resistance was subtracted by the resistance for 2 kOe \((>H_{c2})\), \( \Delta R = R(0 \text{ kOe}) - R(2 \text{ kOe}) \), the anomalous enhancement is clearly distinguishable and reproducible in the measured pellets of the Li-FLG flakes, as shown in figures 4(b) and (c). The anomalous increase in \( R \) below \( T_c \) is similarly observed in 2D superconductors that are in the regime of weakly localized Cooper pairs [31]. When combined with the small SC shielding fraction, the anomalous upturn in \( R \) indicates that superconductivity is localized within the Li-FLG grains or islands. Future study on the nano-scale transport measurements such as scanning tunneling microscopy (STM), nano angle resolved photoemission spectroscopy (nanoARPES) [4] and magnetic force microscopy (MFM) is expected to provide direct information on the SC properties of the SC Li-FLG flake.

Observation of superconductivity in the Li-intercalated FLG flakes implies that the removal of the quantum confinement of the intercalated Li state is a key to superconductivity where the deconfinement returns the empty interlayer state across the Fermi level and enhances the electron–phonon coupling that was negligible in the bulk Li-graphite. The SC transition temperature 7.4 K is slightly lower than the predicted 8.1 K for the Li-intercalated single graphene layer [1], which could be ascribed to the magnetic defects that caused the unusual upturn in the \( M-T \) measurements and the paramagnetic background in the \( M-H \) hysteresis loop.

Conclusions
To summarize, we reported the superconductivity at 7.4 K for the Li-FLG, which is the highest \( T_c \) among the intercalant FLG compounds. The discovery not only confirms the theoretical prediction that the 2D graphene-based superconductivity is very different from the bulk graphite based counterpart, but also is expected to expedite further research on superconductivity in low-dimensional materials, particularly aiding in the ability to achieve higher \( T_S \) through the manipulating layer thickness and the adsorption process: 17–18 K of \( T_c \) is theoretically predicted in the graphene-based Li2C6 compound [1]. Successful synthesis of SC Li-FLG through wet chemistry holds promise for nanoscience applications because of its simple control afforded over the Li-doping process.
Acknowledgments

We thank S Oh for helping with magnetization measurements. This work was supported by IBS-R011-D1 and partially supported by the Creative Research Initiatives of Ministry of Science, ICT and Future Planning (2012R1A3A2048816).

Author contributions

APT and SS contributed equally to this work. All authors discussed the results and commented on the manuscript. EH performed the structural characterizations. SS and SGJ performed and analysed MPMS experiments. APT, SS, TP and HL wrote the manuscript.

ORCID IDs

Hyoyoung Lee https://orcid.org/0000-0002-8031-0791

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