Model of an Exotic Chiral Superconducting Phase in a Graphene Bilayer

Mir Vahid Hosseini and Malek Zareyan

Department of Physics, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran

(Received 18 September 2011; published 2 April 2012)

We theoretically demonstrate the formation of a new type of unconventional superconductivity in graphene materials, which exhibits a gapless property. The studied superconductivity is based on an interlayer pairing of chiral electrons in bilayer graphene, which results in an exotic s-wave spin-triplet condensate order with anomalous thermodynamic properties. These include the possibility of a temperature-induced condensation causing an increase of the pairing gap with increasing temperature and an entropy of the stable superconducting state which can be higher than its value in the normal state. Our study reveals the analogy of the interlayer superconductivity in graphene materials to the color superconductivity in dense quark matter and the gapless pairing states in nuclear matter and ultracold atomic gases.

DOI: 10.1103/PhysRevLett.108.147001 PACS numbers: 74.78.−w, 12.38.−t, 73.22.Pr, 74.70.Kn

The microscopic Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity [1] is based on the formation of the so-called Cooper pairs between electrons with opposite spin and equal but opposite momentum, when a weak attractive interaction exists between the electrons. Despite first being applied specifically to explain metallic superconductivity, the BCS pairing was discovered later on to be a general effect which could appear in other areas of physics (see Ref. [2] for a recent overview). While in conventional metallic superconductors an energy gap is opened in the electronic excitation spectrum on the Fermi surface [3], unconventional pairing states can be realized in a wide range of fermionic systems in which superconductivity coexists with the gapless spectrum of the normal (N) phase. Great interest has been devoted to the BCS pairing in composite systems of two (or more) types of fermions with different Fermi surfaces, in which, despite a nonvanishing pairing gap (PG) or order parameter, there appears no energy gap on the Fermi surface due to a separation of N and superconducting (S) phases in the momentum space [4]. Gapless color superconductivity in dense quark matter at low temperatures [5] and its analogous gapless pairing states in nuclear matter [6] and ultracold atomic gases with two types of atoms or identical atoms with different spin states in an external magnetic (see, e.g., [7]) are famous examples of this kind.

The color superconductivity is the state of matter at highest densities and low temperatures which can be reached at the interior of dense neutron stars [5]. In this Letter, we report on the theoretical study of interlayer electronic pairing in pure bilayer graphene, which explores the potential of this carbon-based material to lend itself to an experimentally feasible study of the relativistic gapless superconductivity. This may also simulate the regime of color superconductivity. Graphene [8], the two-dimensional solid of carbon atoms with honeycomb lattice structure, has already been proven to exhibit a variety of compelling pseudorelativistic and quantum electrodynamics phenomena such as Klein tunneling [9], *Zitterbewegung* [10], and universal light absorption [11], to name a few. This is due to its unique zero-gap electronic band structure with conically shaped conduction and valence bands touching each other at the corners of the hexagonal first Brillouin zone, known as Dirac points [see Fig. 1(a)]. An important aspect in graphene is the connection between this specific band structure and the sublattice pseudospin degree of freedom, which makes electrons behave like two-dimensional massless Dirac fermions with a pseudorelativistic chiral property [12]. Here we find that, in bilayer graphene, the interplay between the interlayer pairing of electrons with the same sublattice chirality and the asymmetric arrangement of the sublattices of the two layers result in a gapless superconductivity which possesses an exotic s-wave spin-triplet symmetry of the order parameter and an anomalous N-S phase diagram, shown in Fig. 1(b). We further find that the entropy in the chiral S state can be higher than the entropy in the N state. This finding is in striking contrast to the common behavior of the entropy upon a phase transition.

We start with a qualitative description of the interlayer pairing in bilayer graphene, which reveals the key features of the chiral superconductivity and its anomalous properties. As is shown in Fig. 1(a), in bilayer graphene two monolayers with A_1 and B_1 triangular sublattices in the top layer and A_2 and B_2 triangular sublattices in the bottom layer are arranged according to Bernal stacking, in which every A_1 site of the top layer lies directly above a B_2 site of the bottom layer. In the absence of hopping between the layers ($t_\perp = 0$), the electronic states of the layers are not mixed in the N state. In layer 1 (2), the electronic states lie in two Dirac-cone bands on the two inequivalent $K_{1(2)}$ and $K'_{1(2)}$ valleys (Dirac points). In each layer, pseudospin chirality links the relative amplitude of the electron wave function (to be in the A or B sublattices) to the direction of

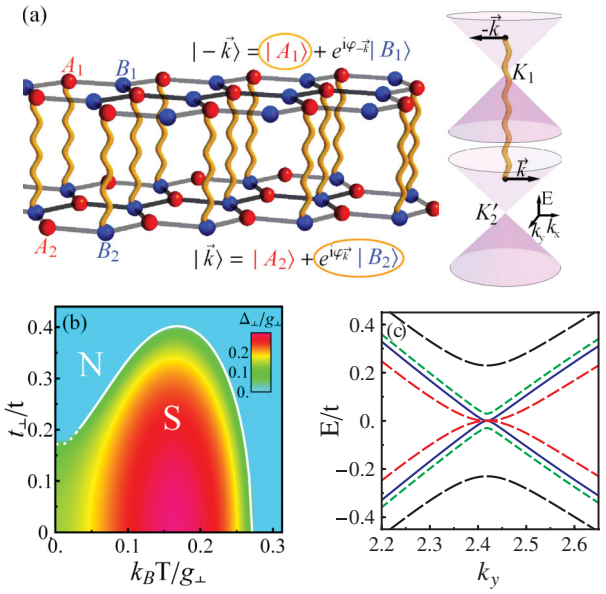

FIG. 1 (color). (a) Sketch of the bilayer graphene lattice structure with the interlayer chiral superconducting correlations (illustrated by wavy lines) between electrons of different types of sublattices. Dirac-cone bands of two monolayers of graphene on the valleys K_1 and K_2' (right panel), with two states of wave vector $|k\rangle$ and $|-k\rangle$, which are coherent superpositions of the sublattice pseudospin states $|A_{1,2}\rangle$ and $|B_{1,2}\rangle$. The interlayer pairing between $|\pm k\rangle$ is asymmetrically partial, since only $|A_1\rangle$ and $|B_2\rangle$ components are paired. (b) The mean field phase diagram of the chiral superconductivity showing dependence on the interlayer hopping energy $t_\perp$ and the temperature T for a pure bilayer graphene ($\mu = 0$). The line of transition from N to S phases is shown in which dashed and solid parts indicate the first- and the second-order transitions, respectively. A color plot of the PG is also presented. (c) The resulting gapless S band structure along k_y for undoped bilayer graphene and for $t_\perp = 0.13t$.

its momentum. Each momentum state in Dirac cones of layers 1 and 2, $|k_{1,2}\rangle$, is a coherent superposition of the two sublattice pseudospin states $|A_{1,2}\rangle$ and $|B_{1,2}\rangle$ as $|k_{1,2}\rangle = |A_{1,2}\rangle + \exp(i\varphi_{k_{1,2}})|B_{1,2}\rangle$, with the angles $\varphi_{k1,2}$ determining the directions of the wave vectors $k_{1,2}$. The interlayer superconductivity will pair electrons in $A1$ and $B2$ sublattices but not those in $A2$ and $B1$ sublattices, which implies that the pairing between the states $|k_1\rangle$ and $|k_2\rangle$ is asymmetrically partial with respect to the pseudospin degree of freedom. Taking into account the chirality, together with the requirement that the paired electrons have equal but opposite momentum on the valleys K_1 and K_2', we obtain a rough qualitative picture of N and S state configuration in the momentum space. In each valley, only electrons of one sublattice becomes S, and the other sublattice remains in the N state. This simultaneous existence of N and S phases can give rise to the gapless property of the chiral superconductivity for an undoped bilayer. Having a partial pairing at zero temperature $T = 0$, a thermal excitation can redistribute electrons in the N component of wave vector states in new momentum states of coherent superposition of A and B states, where they have potential for a partial pairing again. This corresponds to a temperature-induced condensation process in which two primarily normal electrons are thermally excited to the coherent states, where they can now be partially paired and absorbed into the chiral superconducting condensate. By this process, the pair amplitude can increase with increasing temperature.

The above described qualitative picture can be supported by a mean field calculation based on the tight-binding theory of π electrons in graphene. In the absence of superconductivity, we consider the following Hamiltonian [13] for bilayer graphene:

$$H_0 = -\mu \sum_{\ell,\sigma,i} n_{\ell,i,\sigma} - t \sum_{\ell,\sigma,\langle i,j\rangle} (a^+_{\ell,i,\sigma} b_{\ell,j,\sigma} + \text{H.c.}) - t_\perp \sum_{i,\sigma} (a^+_{1,i,\sigma} b_{2,i,\sigma} + \text{H.c.}), \quad (1)$$

where $a_{\ell,i,\sigma}$ ($b_{\ell,i,\sigma}$) and $a^\dagger_{\ell,i,\sigma}$ ($b^\dagger_{\ell,i,\sigma}$) are the annihilation and creation operators of an electron in the ith unit cell in sublattice $A(B)$ and layer $\ell(= 1, 2)$; $\sigma = \pm$ denotes the spin state of the electron; $n_{\ell,i,\sigma}$ is the corresponding on-site particle density operator. The intralayer nearest neighbor hopping energy $t \approx 3$ eV determines the Fermi velocity in graphene as $v_F \approx 10^6$ m/s, and $t_\perp \approx 0.4$ eV ($t_\perp/t \approx 0.13$) is the dominant interlayer hopping energy between the nearest neighbors $A1$ and $B2$; the chemical potential μ can be controlled by gate voltages. The interlayer superconductivity can be introduced by adding the following potential to H_0:

$$V_\perp = -g_\perp \sum_i \sum_{\sigma,\sigma'} a^\dagger_{1,i,\sigma} a_{1,i,\sigma} b^\dagger_{2,i,\sigma'} b_{2,i,\sigma'}, \quad (2)$$

where $g_\perp$ is the S coupling energy [14,15]. Below, we will discuss the origin of this attractive potential. The interlayer Coulomb repulsion, competing with this attractive potential, is expected to be rather weak because of the interlayer spacing between the electrons. We note that the potential (2) presents an on-site local interaction in the 2D plane of the bilayer, which requires the pairing to have an isotropic s-wave orbital symmetry. On the other hand, the pairing is antisymmetric with respect to the pseudospin (i.e., sublattice) degree of freedom. The Pauli exclusion principle requires that the total wave function, composed of the product of the orbital, spin, and pseudospin components, should be antisymmetric under the exchange of electrons. Therefore we conclude that the interaction (2) allows only a spin-triplet pairing. We find that the interacting Hamiltonian $H = H_0 + V_\perp$ can be decoupled by the following spin-triplet order parameter:

$$\Delta_{i,\perp} = -g_\perp \langle a_{1,i,\downarrow} b_{2,i,\uparrow} + a_{1,i,\uparrow} b_{2,i,\downarrow} \rangle, \quad (3)$$

which describes the interlayer pairing of electrons with the sublattices $A_1 - B_2$, the valleys $K_1 - K_2'$ (and $K_1' - K_2$), and the spins $\uparrow - \downarrow$ (and $\downarrow - \uparrow$). It is worth noting that, while the unconventional s-wave spin-triplet pairing is expected to exhibit an odd-frequency superconductivity [16], we have found that the order parameter (3) has an even parity in the frequency space. This is the result of an odd-pseudospin parity, as described above. We obtain the excitation spectrum by replacing the mean field order parameter (3) in $H = H_0 + V_\perp$ and performing the Fourier transformation of the Hamiltonian in the space of 2D wave vector $\mathbf{k}$ of electrons. For zero doping $\mu = 0$, we obtain a simple expression for the spectrum $E_{\mathbf{k}}^{sl}$, which reads

$$\alpha E_{\mathbf{k}}^{sl} = \frac{\alpha}{2}[\sqrt{(\Delta_\perp + st_\perp)^2 + 4\epsilon_{\mathbf{k}}^2} + l(\Delta_\perp + st_\perp)], \quad (4)$$

where $l, s, \alpha = \pm$ indicate different branches of the spectrum. Here $\epsilon_{\mathbf{k}} = \pm t|\gamma_{\mathbf{k}}|$ with $\gamma_{\mathbf{k}}^\star = \sum_\delta \exp -i\mathbf{k}.\delta$, with δ indicating the nearest neighbor position vectors of graphene. The spectrum (4) represents a gapless superconductivity as can be seen in Fig. 1(c), in which different branches of $E_{\mathbf{k}}^{sl}$ versus k_y are plotted when $\mu = 0$. Now, having the excitation spectrum and using the standard many-body Green's function method, we can obtain the self-consistent equation for the PG $\Delta_\perp$, as follows:

$$\Delta_\perp = \frac{g_\perp}{2}\sum_{\mathbf{k},s,l}\frac{lE_{\mathbf{k}}^{sl}}{\sqrt{(\Delta_\perp + st_\perp)^2 + 4\epsilon_{\mathbf{k}}^2}}\tanh\left(\frac{\beta E_{\mathbf{k}}^{sl}}{2}\right). \quad (5)$$

We can also obtain the thermodynamic potential Ω_S and the entropy S_S of S state from the following formulas, respectively:

$$\Omega_S = \frac{\Delta_\perp^2}{g_\perp} - \frac{1}{\beta}\sum_{\mathbf{k},s,l,\alpha}\ln(1 + \exp^{-\beta\alpha E_{\mathbf{k}}^{sl}}), \quad (6)$$

$$S_S = -2k_B\sum_{\mathbf{k},s,l}[f_{\mathbf{k}}^{sl}\ln f_{\mathbf{k}}^{sl} + (1 - f_{\mathbf{k}}^{sl})\ln(1 - f_{\mathbf{k}}^{sl})], \quad (7)$$

where $f_{\mathbf{k}}^{sl} = [1 + \exp(\beta E_{\mathbf{k}}^{sl})]^{-1}$ is the Fermi-Dirac occupation factor with $\beta = 1/k_BT$ (k_B being the Boltzmann constant). The expressions for the thermodynamic potential and entropy in the N state follow from Eqs. (6) and (7) by taking $\Delta_\perp = 0$.

The temperature dependence of PG for different values of the interlayer hopping energy can be obtained from a numerical solution of Eq. (5). We have examined the stability of the resulting S states by ensuring that any solution of (5) presents indeed a global minimum of Ω_S (see Fig. 3). The resulting phase diagram and $\Delta_\perp(T)$ are surprisingly anomalous, as is presented in Figs. 1(b) and 2(a), respectively, for an undoped bilayer ($\mu = 0$). For $t_\perp = 0$, the gap increases from its zero temperature value with increasing temperature and reaches a maximum

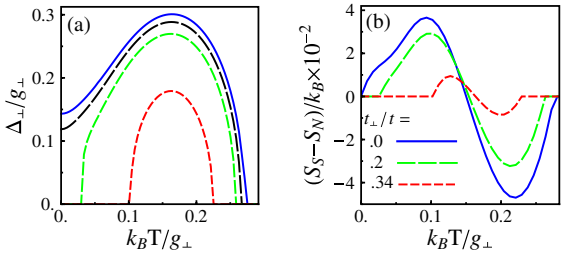

FIG. 2 (color online). Exotic thermodynamic properties of the chiral superconductivity. (a) Pairing gap versus T for $t_\perp/t = 0.0$, 0.13, 0.2, and 0.34 (from top to bottom). (c) Difference in entropies of N and S states versus T for the same values of parameters as in (a).

before showing a BCS-like decrease with T. As described above, this is the result of thermal excitations of electrons from a N valence band into a S conduction band, where they can form a condensate and contribute to the PG. An interlayer hoping $t_\perp$ introduces a normal coupling between the $A1$ and $B2$ sublattices and will weaken the superconducting correlation and hence the interlayer PG. The interplay between this effect and the temperature-induced increase of the chiral condensation leads to the most amazing behavior of PG. As is seen in Figs. 1(b) and 2(a), it appears that, for $t_\perp$ exceeding some critical value, PG vanishes at a temperature range starting from $T = 0$, while it takes a sizable value at higher temperatures.

In the phase diagram of the chiral superconductivity in the $t_\perp - T$ plane [Fig. 1(b)], the color plot of PG is also shown. The normal-superconducting (NS) transition is first order at lower temperatures (the dashed part of a NS boundary) and second order at higher temperatures (the solid part). This can be seen from Fig. 3, in which the potential difference $\Omega_S - \Omega_N$ in N and S states is plotted versus $\Delta_\perp$ for $\mu = 0$ and two values of $t_\perp/t = 0.1$ and 0.18. While for $t_\perp/t = 0.1$ the low temperature NS transition is continuous, for $t_\perp/t = 0.18$ it happens discontinuously, as the stable solution $\Delta_\perp$ undergoes a jump from zero to a finite value at the transition.

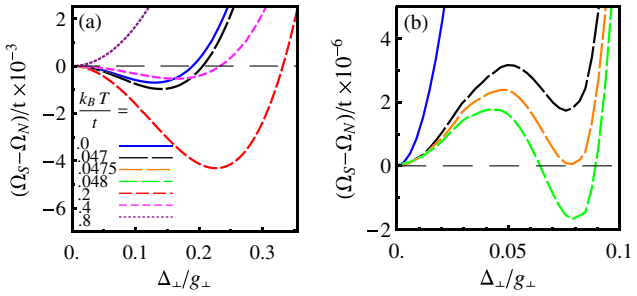

FIG. 3 (color online). Stability of the exotic chiral superconducting states. Difference in thermodynamic potentials of N and S states versus the pairing gap calculated at different temperatures for interlayer hopping energies $0.1t$ (a) and $0.18t$ (b).

The anomalous behavior of $\Delta_\perp(T)$ is associated with a very unusual behavior of the entropy, as is presented in Fig. 2(b) by plotting the entropy difference $S_S - S_N$ in N and S states as a function of T for different values of $t_\perp$. The entropy difference undergoes a change of sign at the temperature of maximum PG, which implies that the entropy of the S state is higher than that of the N state, in the temperature interval where PG increases with T. This unusual finding can also be understood in terms of the above described temperature-induced condensation process. Similar to the above found exotic behavior of PG and the entropy are also predicted to exist in the pairing state of asymmetric nuclear matter [6], and the gapless color superconducting phase of dense quark matter in which correlations between quarks with three different colors and three different flavors results in a variety of pairing patterns [5,17]. A similar to colored pairing of quarks can be simulated by the interlayer chiral superconductivity in trilayer graphene with two different *ABA* and *ABC* stackings [18], which provides pairing between electrons whose states lie in three distinct Dirac cones with opposite sublattice pseudospins.

Finally, let us comment on the experimental realization of our predicted exotic superconductivity. The possibility of an intrinsic superconductivity, with plasmon or phonon mediated pairing interactions, has been proposed in graphene coated with a metal [15]. For a coated bilayer graphene, the formation of the S state is expected to be closely similar to that of the graphite intercalated with alkaline metals, for which a critical temperature up to 11.5 K has been reported (see, e.g., [19]). This can serve as an estimation of the critical temperature (and essentially the coupling energy $g_\perp$) for the interlayer coupling. Alternatively, the superconductivity can be induced by the proximity to a metallic superconductor. Already, significant progress has been made in fabricating highly transparent contacts between a graphene monolayer and a superconductor; the TiAl bilayer has proved to be a suitable material because of good electrical contact of Ti to graphene (see, e.g., [20]). For the proximity-induced superconductivity, T_c is determined by that of the contacted superconductor (for the TiAl bilayer, it is about 1.3 K). A superconductor-bilayer-graphene-superconductor setup [21], with several S electrodes contacting independently to the top and bottom layers, can provide the possibility for an induction of controllable interlayer superconducting correlations. We anticipate that a hybrid system (like a *SNS* Josephson junction) made of chiral superconductors will exhibit peculiar properties due to the exotic order parameter and thermodynamic characteristics of these type of superconductors. This can be used for the experimental observation of chiral superconductivity, which may also provide potential for new applications. It is worth noting that, in both of the above proposed methods, measurements sensitive to interlayer pairing, similar to those of the intrinsic Josephson effect in layered high-T_c superconductors (see, e.g., [22]), are required.

In conclusion, we have predicted a new type of gapless superconductivity which can be realized by an interlayer pairing of relativisticlike chiral electrons in graphene materials. This chiral superconductivity possesses an exotic s-wave spin-triplet order parameter with anomalous thermodynamic properties. We have found that the pairing gap can increase with an increasing of temperature, with the possibility of vanishing at a lower temperature range including $T = 0$, while having a finite value at higher temperatures. The entropy of these anomalous stable superconducting states is found to be higher than that of the normal state.

We acknowledge fruitful discussions with R. Asgari and M. R. Kolahchi. We also gratefully acknowledge support by the Institute for Advanced Studies in Basic Sciences (IASBS) Research Council under Grant No. G2010IASBS110. M. Z. thanks MPIPKS in Dresden and ICTP in Trieste for the hospitality and support during his visit to these institutes.

[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[2] F. Wilczek, Mod. Phys. Lett. A **25**, 3169 (2010).
[3] M. Tinkham, *Introduction to Superconductivity* (Dover, New York, 2004).
[4] W. V. Liu and F. Wilczek, Phys. Rev. Lett. **90**, 047002 (2003); E. Gubankova, W. V. Liu, and F. Wilczek, Phys. Rev. Lett. **91**, 032001 (2003).
[5] M. Alford, K. Rajagopal, and F. Wilczek, Nucl. Phys. **B537**, 443 (1999); Mark G. Alford, Krishna Rajagopal, Thomas Schaefer, and Andreas Schmitt, Rev. Mod. Phys. **80**, 1455 (2008).
[6] A. Sedrakian and U. Lombardo, Phys. Rev. Lett. **84**, 602 (2000); for a review, see *Pairing in Fermionic Systems: Basic Concepts and Modern Applications* (World Scientific, Singapore, 2006).
[7] M. W. Zwierlein, A. Schirotzek, C. H. Schunck, and W. Ketterle, Science **311**, 492 (2006); G. B. Partridge, W. Li, R. I. Kamar, Y. Liao, and R. G. Hulet, Science **311**, 503 (2006); for a review, see Nature (London) **416**, 205 (2002).
[8] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, Nature (London) **438**, 197 (2005); Y. Zhang, Y.-W. Tan, H. L. Stormer, and P. Kim, Nature (London) **438**, 201 (2005).
[9] A. K. G. M. I. Katsnelson and K. S. Novoselov, Nature Phys. **2**, 620 (2006); A. F. Young and P. Kim, Nature Phys. **5**, 222 (2009).
[10] M. Katsnelson, Eur. Phys. J. B **51**, 157 (2006); T. M. Rusin and W. Zawadzki, Phys. Rev. B **80**, 045416 (2009).
[11] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, and A. K. Geim, Science **320**, 1308 (2008).

[12] C. W. J. Beenakker, Rev. Mod. Phys. **80**, 1337 (2008); A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, Rev. Mod. Phys. **81**, 109 (2009).
[13] E. McCann and V. I. Falko, Phys. Rev. Lett. **96**, 086805 (2006).
[14] G. Baskaran, Phys. Rev. B **65**, 212505 (2002).
[15] Bruno Uchoa and A. H. Castro Neto, Phys. Rev. Lett. **98**, 146801 (2007).
[16] F. S. Bergeret, A. F. Volkov, and K. B. Efetov, Rev. Mod. Phys. **77**, 1321 (2005).
[17] M. Huang and I. Shovkovy, Nucl. Phys. **A729**, 835 (2003).
[18] F. Zhang, B. Sahu, H. Min, and A. H. MacDonald, Phys. Rev. B **82**, 035409 (2010).
[19] T. Valla and Z. Pan, in *Physics and Applications of Graphene—Experiment*, edited by Sergey Mikhailov (InTech, Rijeka, Croatia, 2011), ISBN: 978-953-307-217-3.
[20] H. B. Heersche, P. Jarillo-Herrero, J. B. Oostinga, L. M. K. Vandersypen, and A. F. Morpurgo, Nature (London) **446**, 56 (2007); F. Miao, S. Wijeratne, Y. Zhang, U. C. Coskun, W. Bao, and C. N. Lau, Science **317**, 1530 (2007).
[21] F. Dolcini, D. Rainis, F. Taddei, M. Polini, R. Fazio, and A. H. MacDonald, Phys. Rev. Lett. **104**, 027004 (2010).
[22] P. Muller, in *Intrinsic Josephson Effects in Layered Superconductors*, edited by R. Helbig, Festkorper probleme/Advances in Solid State Physics Vol. 34 (Vieweg, Braunschweig, 1994); Yu. I. Latyshev, J. E. Nevelskaya, and P. Monceau, Phys. Rev. Lett. **77**, 932 (1996).