Ordered Defects: A Roadmap towards room temperature Superconductivity and Magnetic Order

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(Dated: February 21, 2019)

Defects in the atomic lattice of solids are sometimes desired. For example, atomic vacancies, single ones or more elaborated defective structures, can generate localized magnetic moments in a non magnetic crystalline lattice. Increasing their density to a few percent magnetic order can appear. Furthermore, certain two dimensional interfaces can give rise to localized superconductivity with a broad range of critical temperatures. Old and new experimental facts emphasize the need to join efforts to start using systematically “ordered defects” in solids to achieve room temperature superconductivity and magnetic order.

Magnetic and superconducting orders at room temperature are highly desirable due to the large number of possibilities to apply these phenomena in devices at normal life conditions, apart from the huge basic research interest. Although magnetic order is found at 300 K in a not so large list of materials, superconductivity at room temperature appeared to be much more difficult to find [1]. Here, we would like to emphasize that ordered defects in some lattice structures can provide us a path to reach both phenomena at very high temperatures in materials that do not show them in their defect free state. We would like to pay attention here on two cases of lattice defects in solids. Namely, a single or a group of vacancies and two dimensional (2D) well defined interfaces in some specific atomic lattices.

Vacancies can trigger a magnetic moment around its position in the atomic lattice. A large number of experimental and theoretical work has been done in this respect. For example, STM local measurements revealed that C-vacancies, produced by low energy ion irradiation at the surface of graphite, have a local magnetic moment [2]. Having a large enough density (\(\sim 5\%\)) of hydrogen (or protons) or C-vacancies at certain positions [3, 4], one can show experimentally that magnetic order at room temperature appears in graphite bulk samples. Several studies with techniques like element specific X-ray magnetic circular dichroism (XMCD) [5, 6], NMR [7], magnetization and transport (see [8] and refs. therein) indicate that the magnetic order triggered by defects is intrinsic and with Curie temperatures clearly above 300 K. In the case of graphite [6] or ZnO [9, 10], XMCD results indicate that the valence band is spin polarized in a relative large energy range, an apparently general feature in materials that show defect induced magnetism (DIM).

Due to the rather simple way to trigger in non-magnetic materials, room temperature magnetic order by low energy ion irradiation, we may ask whether some kind of devices have been already proposed. Two recent examples are worth mentioning. The first is the spin filter that occurs at the interface between magnetic and non magnetic regions of the same material, ZnO:Li in the reported case [11]. Whereas the magnetic path of the oxide micro- or nanostructure is produced by an inexpensive \(\sim 300\) eV proton irradiation plasma chamber, the protected non-magnetic semiconducting regions act as a potential well for the thermally activated conduction electrons. The interfaces between magnetic and non-magnetic regions do produce a giant positive magnetoresistance, in contrast to the small and negative magnetoresistance of the magnetic paths alone. This characteristic and other details of the homo-junctions open up a new and simple way to use the spin splitting created in the irradiated oxide for spintronic devices.

Other unexpected result was obtained recently by low-energy ion irradiation on TiO$_2$ films. After a gentle ion irradiation fluence, the originally non-magnetic film becomes magnetic at room temperature due to Ti-divacancies (which are stable at room temperature) and with the magnetization vector normal to the main area of the film [12]. The rather large magnetic anisotropy is related apparently to the fact that the magnetic layer resides at the very near surface region. Further increase of the amount of defects by subsequent ion irradiation, vanishes the magnetic anisotropy. Recently obtained results [13] indicate that should be possible to produce nanostructured areas of TiO$_2$ with perpendicular magnetic anisotropy. Low energy ion irradiation and the existence of DIM in several oxides may open up a new method to reach perpendicular magnetic anisotropy by far more simple and economically advantageous than several others used nowadays [14].

Let us now discuss the other order phenomenon that appears at a specially ordered lattice defect, namely at certain 2D interfaces. Systematically done STM studies of graphene bilayers showed the existence of Van Hove singularities in the electronic density of states that shift to lower bias voltages the smaller the twist angle between the graphene layers [17]. As emphasized recently by Volovik (see [18] and refs. therein) the Van Hove singularities are related to the flattening of the electronic energy band at well defined regions related to the mea-

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moiré pattern in the electronic spectrum. This appears to be the reason for the existence of superconductivity found recently in bilayer graphene with critical temperatures around 1 K [16, 19].

We may ask now, whether well ordered bulk graphite samples have similar 2D interfaces. The answer is yes, indeed, and the experimental evidence is overwhelming. Moiré patterns in the electronic spectrum measured by STM due to misoriented graphene layers of the graphite structure were found already in 1990, at the surface of a highly oriented pyrolytic graphite (HOPG) bulk sample [20], see also [21]. Their influence on the measured conductivity was not, however, realized till 2008 (for a review see [22] and also [23]). There are two more 2D interfaces that can appear parallel to the graphene planes in real graphite samples, namely: (a) The one between regions with Bernal and rhombohedral (RH) stacking orders, twisted or untwisted, and (b) between twisted RH regions. The existence of the minority RH stacking phase was confirmed in a large number of graphite bulk samples by XRD studies [15] and its influence in the conductivity was recently reported [24].

Superconductivity at these interfaces is expected to appear at very high temperatures due to the existence of a dispersionless electron band, a so-called flat band [18]. This flat band has been predicted to exist at, e.g., the surface of graphite with RH stacking order [18, 26] or at the 2D interface between Bernal and RH stacking orders [27]. Its existence was confirmed experimentally at the surface of small and thin RH patches surrounded by regions with Bernal stacking order [28].

It is interesting to compare the superconducting transitions identified in the temperature dependence of the electrical resistance at constant applied fields in a bilayer graphene [16] and the one reported two years before in several bulk samples with internal interfaces [15]. Figure 1 shows the two sets of normalized resistance data for a better comparison. As discussed in [15] the background resistance in Fig. 1(a) is simply because the voltage electrodes do not touch the interface(s) of interest. Both transitions show some similarities worth mentioning, in spite of the two orders of magnitude difference in temperature. Namely, there is not a simple shift of the transition to lower temperatures with magnetic field, but a small applied field already prevents a complete superconducting path between the voltage electrodes. Although in the case of the bulk graphite sample (Fig. 1(a)) one would tend to explain this fact by an extra magnetoresistance coming from the background resistance, this does not seem to be the reason for the bilayer device.

Whereas in the case of the bulk graphite sample the
transition hardly shifts to lower temperatures under an applied magnetic field (in the measured field region), the broadness of the transitions in the bilayer prevents a clear determination of a temperature dependent upper critical field $B_{c2}(T)$. The overall results suggest the existence of granular superconductivity in both samples. In other words, neither in the bilayer nor in the internal interface(s) of the bulk sample a homogeneous superconducting region between the voltage electrodes exists but superconducting patches. A magnetic field influences the (Josephson) coupling between those patches and therefore no zero resistance path between the electrodes remains. In spite of granular superconductivity, at low enough fields permanent current paths can exist, the reason for flux trapping [29] and the remanent resistance observed after removing the applied field [15]. Future studies should clarify whether the granular superconductivity is intrinsic or extrinsic due to defects (or inhomogeneous doping) at the interfaces or in the bilayer graphene. The Josephson response between superconducting patches that exist within the embedded interfaces in bulk graphite samples, can be measured by depositing electrodes directly at the edges of the interfaces, as has been done using TEM lamellae in [25]. Let us compare the results published in 2013 of one of those TEM lamellae with one of the bilayer graphene devices published recently. Figure 2(a) shows the temperature dependence of the resistance of device M2, see Fig.1(b) and (e) in [16], and of the voltage (measured at constant current) of the lamella L3, see Fig.3(c) and (f) in [25]. Note first that the transition observed in the lamella does not represent necessarily the critical temperature of the superconducting patches but the temperature where the Josephson coupling gets robust enough to influence the measured voltage. The Josephson response was identified by measuring current-voltage characteristics in both samples shown in Figure 2(b) at two temperatures. The Josephson characteristics curves measured in sample L3 at higher temperatures [25] are also similar to those measured in the M2 device [16] and can be very well understood following the Ambegaokar and Halperin model [30]. Furthermore, transport measurements on different thin graphite samples revealed that under a large enough applied electric field near surface regions undergo a superconducting-like transition at $T \sim 17$ K [31]. The similarities between the reported measurements in [16, 25] make any further comment superfluous. Recently, using point contact spectroscopy at the surface of a graphite sample, local superconductivity was found [32]. The BCS-like features reveal a magnetic field dependent energy gap with a critical temperature of $14$ K [32]. Already in 1992 similar BCS-like features were found by STM measurements at low temperatures, localized at certain unknown regions at the surface of HOPG sample, without attracting the attention of the scientific community [33]. Future experiments should try to localize and characterize the interfaces in bulk graphite samples, which show high critical temperatures in order to hopefully start their difficult but necessary production.

Finally, apart from the interesting cases of superconductivity found in oxides films, semiflons, semiconductor superlattices and ultra thin films (see, for example, [34–36] and refs. therein), there are some examples in literature on the existence of superconductivity at certain interfaces that we would like to note. Superconductivity has been found at the interfaces of pure Bi (a material with some similarities to graphite) and BiSb bicrystals up to critical temperatures $\lesssim 21$ K [37–40]. Moreover, dislocations at certain interfaces of semiconductor superlattices are thought to trigger superconductivity up to 6 K [41, 42], an idea that has been also proposed for graphite [43]. Also strain-induced superconductivity at interfaces of semiconducting layers has been treated theoretically based on the influence of partial flat-bands [44].

Acknowledgements: We are grateful to A. Ballestar, M. Stiller and J. Barzola-Quichua for discussions and for share their unpublished magnetic force microscopy data on TiO$_2$ films are gratefully acknowledge. We acknowledge the help of C. Precker for digitalizing the data of Fig.1(b).

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