Extraordinary magnetoresistance in graphite: experimental evidence for the time-reversal symmetry breaking

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Abstract

We report a highly anisotropic in-plane magnetoresistance (MR) in graphite that possesses in-plane parallel line-like structural defects. In a current direction perpendicular to the line defects (LD), MR is negative and linear in low fields with a crossover to a positive MR at higher fields, while in a current direction parallel to LD, we observed a giant super-linear positive MR. These extraordinary MRs are respectively explained by a hopping magnetoresistance via non-zero angular momentum orbitals, and by the magnetoresistance of inhomogeneous media. The linear negative orbital MR is a unique signature of the broken time-reversal symmetry (TRS). We discuss the origin of the disorder-induced TRS-breaking in graphite.

(Some figures may appear in colour only in the online journal)

1. Introduction.

The transverse magnetoresistance (MR) in a magnetic field $B$ along the $z$-axis, defined as $\text{MR} = \sigma_{xx}(B)/\sigma_{xx}(0) - 1$ in terms of the conductivity tensor $\sigma_{ij}(B)$, is a sensitive probe of the electron transport mechanism in doped semiconductors, metals and semimetals, such as e.g. graphite. The question of the important role of mesoscopic length scale inhomogeneities in graphite on the anomalous (magneto) transport has been raised [1]. In an isotropic medium with Bloch electrons MR is positive and quadratic in $B$ [2], except for the open Fermi surfaces, where for some specific directions of $B$ the positive MR is linear in $B$ [3]. In the hopping regime with localized carriers, MR is caused by a strong magnetic field dependence of the exponential asymptotic of bound state wavefunctions at a remote distance from a donor (or an acceptor); in this case MR is also positive and quadratic at low magnetic fields [4]. One of the theoretical possibilities to account for the linear MR in graphite is the so-called quantum magnetoresistance originating from a massless (Dirac-type) nature of carriers that might be in the ultra-quantum limit at rather low magnetic fields [5].

On the other hand, nearly linear negative MR (NMR) has been observed in some hopping systems, such as amorphous germanium and silicon. It has been attributed to a magnetic field dependence of spin-flip transitions between sites when some fraction of them has a frozen spin [6], and/or to an increase of the density of localized states due to the Zeeman energy shift [7]. This NMR is rather small (much less than 1%) even in relatively high magnetic fields of about 1 T. More recently a linear NMR has been observed in the longitudinal $c$-axis inter-layer current direction in the normal state of cuprate superconductors and in graphite in high magnetic fields assigned to bipolarons in the former case [8] and to a growing population of the zero-energy Landau level of quasi-two-dimensional Dirac fermions with increasing magnetic field in the latter case [9]. Also a giant transverse NMR of nearly 100% was observed at low temperatures, with over 50% remaining at room temperature in graphene nanoribbons and attributed to some delocalization effect under the perpendicular magnetic field [10].
Here we report a low-field transverse MR in bulk quasi-two-dimensional graphite samples having in-plane parallel line-like structural defects. This MR is giant (1500% at 2 K and \( B = 200 \text{ mT} \), positive in current direction along the line defects (LD), and linear and negative (below 80 mT) in the perpendicular direction.

The observed MR is quantitatively understood in the framework of the magnetotransport of inhomogeneous low-carrier semiconductors [11] and of a hopping MR via non-zero angular momentum orbitals [12].

2. Experimental details and sample characterization.

We have performed magnetoresistance measurements on several HOPG (highly oriented pyrolytic graphite) samples with or without LD characterized by means of x-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM) measurements. The large scale LD (wrinkles, edge-plane steps or similar structures) occur as a result of cleaving graphite samples [13]. Figure 1 demonstrates nearly parallel LD as long as ~0.1 mm, separated by the distance ranging from a few nanometres to several microns, for two HOPG samples (S1 and S2) cleaved by means of Scotch Tape. X-ray diffraction measurements of pristine (without LD) samples revealed a characteristic hexagonal graphite structure in the Bernal (ABAB) stacking configuration, with no signature for other phases. The obtained crystal lattice parameters are \( a = 2.48 \text{ Å} \) and \( c = 6.71 \text{ Å} \). Raman spectroscopic measurements revealed the crystallite size in the basal plane \( L_b > 2 \mu \text{ m} \) [14]. The results presented below were obtained on the sample S1 from Union Carbide Co. with dimensions \( l \times w \times t = 2.5 \times 2.5 \times 0.5 \text{ mm}^3 \), the out-of-plane/in-plane room-temperature resistivity ratio \( \rho_c/\rho_b = 2 \times 10^5 \), \( \rho_b = 5 \mu\Omega \text{ cm} \), and FWHM \( = 0.7^\circ \) of x-ray rocking curve. Similar results were obtained on the sample S2 from Advanced Ceramics Co. that possesses similar resistivity ratio and FWHM \( = 0.8^\circ \). The magnetic field was applied parallel to the hexagonal c-axis (\( B \parallel c \parallel t \)), and in-plane resistances \( R_y(B, T), R_x(B, T) \) were recorded using the van der Pauw-type geometry (see insets in figure 2) sweeping the field between a target negative and positive values using Quantum Design and Janis 9 T-magnet He-4 cryostats. All resistance measurements were performed in the Ohmic regime.

The graphite samples that possess LD demonstrate qualitatively different temperature dependence of the in-plane zero-field resistance for the current in two perpendicular in-plane directions, see figure 2. In the direction parallel to LD (y) the resistance is metallic-like (\( dR_y/dT > 0 \)), while in the other direction (x), i.e. perpendicular to LD, \( R_x(T) \) is insulating-like (\( dR_y/dT < 0 \)), implying the insulating character of LD.

3. Giant positive and linear negative magnetoresistance

When a relatively weak magnetic field is applied perpendicular to the planes, MR along the metallic (y) direction appears to be huge and positive, see figure 3. The giant positive MR is expected in graphite since the parameter \( \beta = \omega_c \tau \) becomes large already in the mT-region of the field; here \( \omega_c \) and \( \tau \) are the Larmor frequency and the scattering time, respectively. However, it is neither quadratic as in the Boltzmann theory, nor linear in \( B \) as in the case of quantum magnetoresistance [5]. We suggest that the sample inhomogeneities are responsible for the strong departure from these regimes. The inhomogeneities lead to a radical rearrangement of the current flow pattern changing the magnetic field dependence of the transverse conductivity in the strong magnetic field, \( \beta > 1 \) [11]. Importantly, when
Figure 2. Normalized insulating-like, $R_x(T)$, and metallic-like, $R_y(T)$, zero-field in-plane resistances of graphite in two perpendicular current directions.

Figure 3. Magnetoresistance in the metallic (y) direction at various temperatures (symbols).

Figure 4. Upper panel: magnetoresistance (MR) in the insulating (x) direction at various temperatures. Lower panel demonstrates negative linear MR suggesting time-reversal symmetry breaking. Solid lines correspond to the equation $\text{MR}_x = -cB$ with $c = 0.0029 \text{ mT}^{-1} (T = 2 \text{ K}), c = 0.00115 \text{ mT}^{-1} (T = 20 \text{ K}), c = 0.00053 \text{ mT}^{-1} (T = 30 \text{ K}), c = 0.00028 \text{ mT}^{-1} (T = 40 \text{ K})$.

The magnetoresistance in the x direction can be expressed as

$$\text{MR}_x = \text{MR}_h \frac{1}{1 + r} + \frac{\text{MR}_b}{1 + 1/r}.$$  \hspace{1cm} (2)

where $r = R_h(0)/R_y(0)$ is the ratio of the zero-field resistances.

The textbook result [4] predicts the positive hopping MR $\text{MR}_h$. In the case of hopping via the orbitals with non-zero orbital momentum, $\text{MR}_b$ is negative and linear in relatively small $B$, if $m = 1, 2, 3, \ldots$. The linear NMR is caused by the

$\sigma_{xy} \gg \sigma_{yx}$, then even relatively small inhomogeneities in the carrier density lead to the MR proportional to $B^{4/3}$ [11]. In fact, $\text{MR}_x = (B/B_0)^{4/3}$ fits nicely the observed magnetic field dependence of the magnetoresistance in the metallic current direction (the inset of figure 5) with a single scaling parameter $B_0$ depending on the carrier density fluctuations [11].

MR in the insulating (x) direction is even more intriguing: it is linear and negative at low fields and positive and super-linear at higher fields (figure 4). Because virgin (without LD) HOPG sample demonstrated isotropic metallic in-plane resistance, the insulating-like temperature dependence of the resistance (figure 2) implies the insulating behaviour of LD. In inorganic and organic insulators lattice defects, such as e.g. vacancies or interstitials, often localize carriers with a finite momentum rather than in the zero-momentum s-states [15]. To model the observed insulating-like resistance, we apply a recent extension of the conventional theory of hopping MR to the hopping via non-zero orbital momentum states [12]. Quite remarkably this renders a large negative low-field hopping magnetoresistance $\text{MR}_h$. The theory [12] has accounted for the unconventional MRs in some organic insulators (dubbed OMAR) observed in about the same range of the magnetic field [16] as in our graphite samples. Moreover, if the orbital degeneracy is lifted due to broken time-reversal symmetry with or without net magnetization, the negative $\text{MR}_h$ is linear in $B$ [12]:

$$\text{MR}_h = \exp[-m \kappa r b + \kappa^3 \rho^2 r^2 b^2/48] - 1.$$ \hspace{1cm} (1)

Here $m$ is the magnetic quantum number of the localized state, $\kappa$ is the inverse zero-field localization length, $r$ and $\rho$ are an average hopping range and its projection on the plane perpendicular to the magnetic field, respectively, and $b = B/B_0$ is the reduced magnetic field with $B_0 = \hbar \kappa^2/2e$. Thus, the magnetoresistance in the x direction can be expressed as

$\text{MR}_x = \frac{\text{MR}_h}{1 + r} + \frac{\text{MR}_b}{1 + 1/r}.$ \hspace{1cm} (2)
expansion of the localized states with the positive $m$ due to a linear magnetic lowering of their ionization energy by $\hbar \omega_c m/2$. It dominates in the wide range of realistic impurity densities for any non-zero $m$ because of the small numerical factor ($1/48$) in the quadratic term in the exponent in equation (1). With $MR_h \approx \exp(-B/B_h) - 1$, equation (2) fits remarkably well the low-temperature MR in the insulating current direction with a single scaling parameter $B_h$ which is proportional to the localized-state ionization energy, figure 5. The same equation (2) describes reasonably well the negative to positive MR crossover even at temperatures as high as 50 K. With increasing temperature, deeper localized states with a higher ionization energy become accessible for the hopping conductance, so that the slope $c = 1/B_h$ of the linear negative MR drops, as observed (figure 4).

4. **Time-reversal symmetry breaking**

While the outlined model with one or two scaling parameters agrees well with our experimental observations, there are other mechanisms for NMR. Importantly, there is no NMR and virtually no MR in the same range of the magnetic fields parallel to the planes, which rules out a spin origin of the observed MR. Also, the lack of quantum oscillations at high temperatures, where NMR is still observed, see figures 3 and 4, excludes the effect of Landau quantization. The weak localization gives NMR which is often almost linear in a certain field range. But such NMR smoothly evolves from sub-linear magnetic field dependence at lower temperatures to a super-linear one at higher temperatures. However, we observe a perfectly linear NMR at low $B$ in a wide temperature range, figure 4. A strong NMR exists in the classical two-dimensional electron gas due to freely circling electrons, which are not taken into account by the Boltzmann approach. But it is parabolic rather than linear at low fields [17]. The parabolic orbital NMR has been also predicted by the gauge theory in two-dimensional strongly correlated doped Mott insulators [18].

On the other hand, in the absence of time-reversal symmetry (TRS) breaking, the states with the opposite direction of the orbital angular momentum, $m$ and $-m$, are degenerate, so that the linear term in $MR_h$, equation (1), cancels, and MR is parabolic, in agreement with the basic properties of the conductivity tensor [19]. To get the linear MR at $B \to 0$ one has to break TRS, if the conductivity is an analytical function of the magnetic field. For instance, magnetic moments break the TRS, and hence split $m$ and $-m$ states. Such zero-field splitting gives preference to the hopping via orbitals with a lower ionization energy (positive $m$) providing the negative linear MR [12].

It has been demonstrated that graphitic edges with a zig-zag topology [20] and/or carbon vacancies possess magnetic moments leading to enhanced paramagnetism [21] or ferro-(ferri-) magnetism [22, 23] in graphene (a single layer of graphite) and graphite. An enhanced density of states has been observed near steps on the surface of cleaved graphite [24, 25]. These localized states suggest the occurrence of magnetic moments. On the other hand, insulating-type resistance behaviour across the kink- or ripple-like LD is expected due to opening of the transport (semiconducting) gap for the electronic transport [26, 27]. Besides, the LD harbour graphitic edges [24]. The in-plane crystallite size $L_b > 2 \mu m$ and the carrier mean free path as large as $\sim 1–3 \mu m$ [28] imply that LD can be the main source of the electron (hole) scattering when current predominantly flows across the LD. Thus, graphitic surfaces with LD that harbour localized magnetic moments appear to be suitable objects to test the hopping magnetoresistance via non-zero angular momentum orbitals [12].

5. **Conclusions**

In conclusion, we reported the highly anisotropic in-plane MR in HOPG samples governed by large scale (macroscopic) linear defects (LD). The measured negative linear MR has been accounted for by the electron hopping via non-zero angular momentum orbitals. This observation provides an unambiguous experimental evidence for the time-reversal symmetry breaking that can be attributed to the magnetic moments harboured by LD. Our results are also in agreement with recent reports on semiconducting character of kinked or rippled graphene.

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References

[1] Dusari S, Barzola-Quicia J, Esquinazi P and Garcia N 2011 Phys. Rev. B 83 125402
[2] Anselm A I 1978 Introduction to Semiconductors Theory (Moscow: Nauka)
[3] Lifshitz I M and Peschanskii V G 1959 Sov. Phys.—JETP 8 875
[4] Shklovskii B I and Efros A L 1984 Electronic Properties of Doped Semiconductors (Berlin: Springer)
[5] Abrikosov A A 2000 Europhys. Lett. 49 789
[6] Movaghar B and Schweitzer L 1978 J. Phys. C: Solid State Phys. 11 125
[7] Kurobe A and Kamimura H 1983 J. Non-Cryst. Solids 59/60 41
[8] Zavaritsky V N, Vanacken J, Moshchalkov V V and Alexandrov A S 2004 Physica C 404 444
[9] Kopelevich Y, da Silva R R, Pantoja J C M and Bratkovsky A M 2010 Phys. Lett. A 374 4629
[10] Bai J, Cheng R, Xu F, Liao L, Wang M, Shailos A, Wang K L, Huang Yu and Duan X 2010 Nature Nanotechnol. 5 655
[11] Dreizin Yu A and Dykhne A M 1973 Sov. Phys.—JETP 36 127
[12] Alexandrov A S, Dediu V A and Kabanov V V 2012 Phys. Rev. Lett. 108 186601
[13] Makarova T L and Han K-H 2007 Phys. Status Solidi b 244 4138
[14] Goers D, Buga H, Hardwick L, Würsig A and Novák P 2003 Ionics 9 258
[15] Zunger A, Lany S and Raebiger H 2010 Physics 3 53
[16] Mermer O, Veeraraghavan G, Francis T L, Sheng Y, Nguyen D T, Wohlgemann M, Kohler A, Al-Suti M K and Khan M S 2005 Phys. Rev. B 72 205202
[17] Dmitriev A, Dyakonov M and Jullien R 2001 Phys. Rev. B 64 233321
[18] Ioffe L B and Wiegmann P 1992 Phys. Rev. B 45 519
[19] Lifshitz E M and Pitaevskii L P 1981 Physical Kinetics (Course of Theoretical Physics) vol 10, ed L D Landau and E M Lifshitz (Oxford: Pergamon)
[20] Nakada K, Fujita M, Dresselhaus G and Dresselhaus M S 1996 Phys. Rev. B 54 17954
[21] Wakabayashi K, Fujita M, Ajiki H and Sigrist M 1999 Phys. Rev. B 59 8271
[22] Wakabayashi K, Sigrist M and Fujita M 1998 J. Phys. Soc. Japan 67 2089
[23] Ugeda M M, Brihuega I, Guinea F and Gomez-Rodriguez J M 2010 Phys. Rev. Lett. 104 096804
[24] Esquinazi P, Setzer A, Höhne R, Semmelhack C, Kopelevich Y, Spemann D, Butz T, Kohlstrunk B and Lüsche M 2002 Phys. Rev. B 65 241101
[25] Niimi Y, Matsui M, Kambura H, Tagami K, Tsukada M and Fukuyama H 2006 Phys. Rev. B 73 085421
[26] Hicks J et al 2013 Nature Phys. 9 49
[27] Rasmussen J T, Gunst T, Boggild P, Jauho A P and Brandbyge M 2013 Beilstein J. Nanotechnol. 4 103
[28] Esquinazi P, Barzola-Quicia J, Dusari S and Garcia N 2012 J. Appl. Phys. 111 033709