Strong dopant dependence of electric transport in ion-gated MoS$_2$

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We report modifications of the temperature-dependent transport properties of MoS$_2$ thin flakes via field-driven ion intercalation in an electric double layer transistor. We find that intercalation with Li$^+$ ions induces the onset of an inhomogeneous superconducting state. Intercalation with K$^+$ leads instead to a disorder-induced incipient metal-to-insulator transition. These findings suggest that similar ionic species can provide access to different electronic phases in the same material.

Transition metal dichalcogenides are a fascinating class of layered materials, where different orders - such as superconductivity and charge-density waves - compete with each other and give rise to complex phase diagrams reminiscent of those of cuprates and iron pnictides. Intercalation by means of a wide range of compounds, both organic and inorganic, is a particularly powerful tool to tune the properties of these materials, resulting in superconducting compounds characterized by sharp transition temperatures and well-defined upper critical fields.

In recent years, ionic gating has been utilized to control the transport properties of a wide range of materials, including oxides, metal chalcogenides, graphene, and other 2-dimensional materials, resulting in superconducting compounds characterized by sharp transition temperatures and well-defined upper critical fields.

We prepared few-layer MoS$_2$ flakes by micromechanical exfoliation of their bulk crystals (2H polytype, SPI supplies) via the well-known scotch-tape method and transferred them on SiO$_2$(300 nm)/Si substrates. We inspected the flakes with an optical microscope, and selected samples with the number of layers between ~5 and 10 by analyzing their reflection contrast. We realized the electrical contacts (Ti(5 nm)/Au(35 nm)) in Hall bar configuration, together with a co-planar side gate electrode, by standard microfabrication techniques. We patterned and deposited a solid oxide mask (Al$_2$O$_3$ thickness ~40 nm) on the metallic leads only to reduce their interaction with the electrolyte during the experiments. Reactive Ion Etching (Ar gas, RF Power 100 W, exposure time 2 min) was used to pattern the flakes into a rectangular shape, in order to achieve a well-defined aspect ratio for sheet resistance measurements. Fig. 1 presents the optical micrograph of a completed device before drop-casting the polymer electrolyte prepared by dissolving ~ 25 wt% of either K$^+$ or Li$^+$-based salts in polyethylene glycol (PEG, $M_w$ ~ 600). We tested both ClO$_4^-$ and bis(trifluoromethane)sulfonimide (TFSI$^-$)-based salts, and observed no significant dependence of the gating efficiency on the anion choice. Both Li$^+$ and K$^+$ electrolytes were liquid at room temperature and underwent a glass transition below ~ 250 K. Transport measurements were performed as a function of the temperature $T$ via the standard lock-in technique in a Quantum Design Physical Properties Measurement System with minimal exposure to ambient condition.

We accessed the intercalated state in our MoS$_2$ de-
voltage

toring their conductivity for sharp increases in its value

 comparable with those of a few-nanometer-thick metal

Hall carrier density

can more reliably be detected as a large increase in the

1c). However, intercalation allows the ions in the elec-

ular to the surface of the active channel. At this point,

accumulation

FIG. 1. (a) Ball-and-stick model of the MoS

2

intercalated K

σ

2

conductivity

FIG. 1. (a) Ball-and-stick model of the MoS

2

ion intercalation. The four values of densities correspond to

indicate the corresponding threshold voltages for the onset of

intercalation process: each step corresponds to a different doping state, and these states are sample-dependent. Moreover, the behavior of K

+ and Li

+-gated devices is clearly different.

We first consider the behavior of a K

+-gated device (device A): in this case, the gate voltage was ramped up to a maximum of +3.1 V, and \( R_G \) was measured twice: first at \( V_G = +2.8 \) V, and then at \( V_G = +3.1 \) V. The corresponding values of \( n_H \) show that the carrier density at \( V_G = +2.8 \) V (\( n_H \approx 4.4 \times 10^{14} \text{ cm}^{-2} \)) is about six times smaller than the one at \( V_G = +3.1 \) V (\( n_H \approx 2.6 \times 10^{15} \text{ cm}^{-2} \)). This strongly suggests that the device is still mainly in the electrostatic accumulation regime at \( V_G = +2.8 \) V, and is instead intercalated at \( V_G = +3.1 \) V. It is worth noting that this large increase in \( n_H \) does not lead to a significant increase in \( \sigma \), indicating that doping with K

+ ions, while inducing carriers, severely reduces the carrier mobility (at \( T = 300 \text{ K} \), \( \mu_H \approx 12 \pm 3 \) and \( 2.5 \pm 0.2 \text{ cm}^2/\text{Vs} \) for \( V_G = +2.8 \) and +3.1 V, respectively). We can also roughly estimate the nominal doping level \( x \) in the K\(_3\)MoS\(_2\) stoichiometry at \( V_G = +3.1 \) V (K\(_{0.45}\)MoS\(_2\)), assuming a uniform distribution of the dopants in all the layers (five for this specific sample). This estimation indicates that the sample at \( V_G = +3.1 \) V should be completely in the metallic state, and in the correct doping range to show superconductivity at low temperature. Inducing larger doping levels in K

+-gated devices by applying gate voltages in excess of \( V_G = +3.5 \) V always leads to device failure.

Let us focus now on the behavior of a Li

+-gated device (device C). Interestingly, Li

+-gated devices did not show significant signs of intercalation in the same voltage range for which intercalation occurred in the K

+-gated devices. Instead, we observed an electrostatic increase of \( \sigma \) with increasing gate voltage up to \( V_G \approx +3.6 \) V. Larger voltage values caused a peculiar behavior to emerge, where \( \sigma \) appeared to randomly “jump” between high- and low-conductivity states as \( V_G \) was increased. This behavior, which may be associated with an unstable incorporation of the Li

+ ions between the MoS\(_2\) layers, continued up to \( V_G \approx +6.1 \) V. Even larger gate voltages up to \( V_G \approx +7.0 \) V featured a second stable region of monotonically increasing \( \sigma \), which was about 4 times larger than that for \( V_G \approx +3.6 \) V. The corresponding values of carrier density, as measured by Hall

system down to 2 K, or we warmed the sample up to 300 K and increased \( V_G \) even further. We performed the \( T \)-dependent characterization both before (ionic-gating regime) and after (ionic-doping regime) the onset of intercalation on our devices.
The corresponding nominal doping $V_G$ of device A, gated with the KClO$_4$/PEG electrolyte, for both ionic gating ($V_G = +2.8$ V, green curve) and ionic doping ($V_G = +3.1$ V, blue curve). When the ions only accumulate at the surface of MoS$_2$ (low $V_G$), the device shows a clear metallic behavior, with a smaller low-$T$ value of $R_s$ than that typically displayed by ionic-liquid-gated MoS$_2$. This is consistent with the larger doping level induced in the sample. Moreover, this suggests that K$^+$ gating is able to bring MoS$_2$ beyond the field-induced superconducting dome.

When the ions are able to intercalate the sample, we would also expect a metallic behavior and a further reduction of $R_s$ at low-$T$. Moreover, given that the doping level $K_0.45$MoS$_2$ determined at 240 K, we would also expect the emergence of a superconducting transition at $T \sim 6$ K. However, the $T$-dependence of $R_s$ in the intercalated state does not show any of these features. Instead, it shows a clear non-monotonic behavior and two regions where $R_s$ decreases for increasing $T$: one for $T \gtrsim 150$ K and one for $T \lesssim 20$ K. The second one, the low-temperature upturn, is insensitive to the applied magnetic field, ruling out a possible contribution from weak localization. For intermediate temperatures, $R_s$ increases as $e^{-A/T}$, $A \approx 107$ K (see Fig. 2b). This type of behavior is reminiscent of a two-dimensional system very close to a metal-to-insulator transition.

These results indicate the peculiar condition of a system being close to becoming an insulator, while at the same time presenting a metal-like density of charge carriers at high $T$. Thus, we investigated whether $n_H$ was metallic at low-$T$ as well. Fig. 2k shows the $T$-dependence of $n_H$ obtained from Hall effect measurements. It is apparent that $n_H$ in the bulk doped state (blue dots) strongly decreases at the reduction of $T$. Indeed, the $T$-dependence of $n_H$ can be separated into two contributions: a relatively small constant value $n_0 \approx 2.9 \times 10^{14}$ cm$^{-2}$ and an Arrhenius-like term $n(T) \propto e^{-E_a/k_BT}$, where $E_a \approx 0.03$ eV is an activation energy and $k_B$ is the Boltzmann constant. For comparison, the carrier density induced by surface ionic gating (green dots) is much less $T$-dependent, while at the same time reaching nearly the same low-$T$ value. The resulting low-$T$ mobilities are $\mu_H \approx 110 \pm 33$ and $50 \pm 12$ cm$^2$/Vs for K$^+$ accumulation and intercalation respectively. Thus, it is natural to assume that the quasi-constant term arises from ionic gating at the sample surface, while the thermally-activated one is associated with bulk ion doping.

We thus suggest that the electrochemically intercalated K$^+$ ions are behaving as thermally-activated electron donors and reside in shallow trap states in the bulk MoS$_2$ energy gap: the material thus behaves more like a highly-doped but highly-defective semiconductor with a field-induced metallic channel at its surface, instead of showing a proper metallic character across its entire thickness. Moreover, this very defective character of the K$^+$-doped regime is able to account for both...
the sharp reduction in carrier mobility, and the emergence of an Anderson-like localization regime at low $T$. A disorder-induced metal-to-insulator transition was recently reported in ion-gated monolayer ReS$_2$, but not in any ion-gated multilayer transition metal dichalcogenide.

In Fig. 3, instead we present the $R_s$ vs. $T$ behavior of device C, gated with the LiTFSI/PEG electrolyte. The yellow and red curves refer to Li$^+$-gating ($V_G = +3.6$ V) and doping ($V_G = +7.0$ V) respectively. The inset shows the corresponding $T$-dependence of their sheet carrier density $n_H$ as measured by Hall effect. Unlike the K$^+$ ion, the Li$^+$ ion allows the system to retain a full metallic behavior also in the bulk doping regime, without evidences of non-monotonicity or low-$T$ upturns. The $T$-dependence of $n_H$ is also less pronounced, being nearly constant for $T \lesssim 150$ K in the case of ionic gating and losing less than half of its high-$T$ value in the case of ionic doping. Indeed, the low-$T$ carrier density in the Li$^+$-doped state, $n_H \simeq 3.9 \times 10^{14}$ cm$^{-2}$, was significantly larger than the one for K$^+$ doping, even though its nominal doping level $x$ was nearly 3 times smaller. This indicates that, in the case of Li$^+$ doping, the smaller density of defects acting as shallow trap states allows for a higher fraction of charge carriers to participate in conduction at low $T$. This reduced density of defects is also apparent in the low-$T$ mobilities $\mu_H \simeq 800 \pm 160$ and $300 \pm 94$ cm$^2$/Vs for Li$^+$ gating and doping respectively, several times larger than the ones we observed in the case of the K$^+$ ion.

The most likely explanation of these results is that the size of the K$^+$ ion is too large to be able to intercalate the MoS$_2$ lattice without introducing significant distortions and defects in its entire volume. These defects would then act as shallow trap states, capturing most of the transferred electrons at low $T$ and suppressing the metallic behavior except in the thin layer at the surface due to electrostatic accumulation. We note that a similar disruptive effect of large intercalating species was also observed in ion-gated TaS$_2$, where it leads to abrupt device failure. It is interesting then to consider why the larger K$^+$ ion shows an enhanced doping efficiency with respect to the smaller Li$^+$. We suggest that this behavior may arise from the lattice distortions introduced during the intercalation process allowing the K$^+$ ions still dissolved in the electrolyte to diffuse more easily through the damaged regions. On the other hand, the lattice remains relatively unaffected during the intercalation by the smaller Li$^+$ ions, thus requiring larger driving voltages to intercalate the bulk of the sample. However, further investigations - such as disorder studies by means of x-ray diffraction - are needed to clarify this issue.

Further evidence of the importance of dopant size on the behavior of ion-gated devices lies in the fact that we were able to observe a clear downturn in the $R_s$ vs. $T$ curve in the Li$^+$-doped state below 4 K. Fig. 3(b) shows its response to the application of a magnetic field perpendicular to the active channel of the device. While the downturn never reaches a zero-resistance state, its suppression by a magnetic field is precisely the behavior expected from a superconducting transition. We point out that while the nominal doping level at $V_G = +7.0$ V was estimated to be Li$_{0.12}$MoS$_2$, the onset temperature of the downturn ($T_{on} \simeq 3.7$ K) agrees well with that of chemically doped Li$_{x}$MoS$_2$ for $x \geq 0.42$. Moreover, superconductivity does not appear in chemically doped Li$_{x}$MoS$_2$ for $x \leq 0.42$. Since we observe a superconducting onset, the doping level in the intercalated state must be strongly inhomogeneous. This is supported by the behavior of the superconducting transition: the $R_s$ vs. $T$ profile is not the sharp drop associated with homogeneous bulk superconductivity. Instead, the transition is broad and strongly suggestive of multiple phases. This kind of behavior is typical of granular superconductors: in the Li$^+$-doped state only a handful of regions are able to reach a doping level large enough to induce a superconducting state, while most of the active channel remains metallic and prevents the realization of homogeneous 3D superconductivity. The slowly vanishing resistance tail is due to Josephson tunneling between the superconducting regions (weak-link superconductivity).

In conclusion, we employed polymer electrolyte gating to intercalate MoS$_2$ thin flakes with different ionic species. We unveiled the critical role of ionic size in the determination of the electric transport properties of the
intercalated devices. The larger $\text{K}^+$ ions were found to strongly damage the MoS$_2$ lattice leading to an incipient metal-to-insulator transition at high doping levels. The smaller Li$^+$ ions preserved the metallic character of the devices and allowed the emergence of an inhomogeneous bulk superconducting phase. These findings highlight the critical role of the ionic medium in electrochemically gated devices, both for electrostatic carrier accumulation and field-driven ion intercalation.

**SUPPLEMENTARY MATERIAL**

See Supplementary Material for further details on the measurement setup, Hall effect measurements, and optical characterization of the intercalation process.

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