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Strong dopant dependence of electric transport in ion-gated MoS₂

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We report modifications of the temperature-dependent transport properties of MoS₂ 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.

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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.¹,² 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.²⁻⁴ 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,⁵⁻¹¹ metal chalcogenides,¹²⁻²² graphene²³⁻²⁶ and other 2-dimensional materials,²⁷⁻²⁹ and even metals.³⁰⁻³⁵ Most of these results have been obtained within the electrostatic limit, i.e., by only accumulating ions at the material surface and exploiting the ultrahigh electric field that develops in the electric double layer (EDL).³⁶ However, ionic gating of layered materials allows for a further degree of freedom in the technique, by exploiting the electric field to intercalate the ions between the van der Waals-bonded layers, thus allowing control over the properties of the entire bulk. This technique has already showcased its possibilities by allowing a robust control of the electronic ground state in TaS₂,¹⁵ MoTe₂,¹⁶ WSe₂,¹⁶ and FeSe.¹⁷ These studies mainly focused on the modulation of the bulk carrier density achieved via ion intercalation, without analyzing in detail the effects of different ionic species on the same ion-gated material. In principle, however, the choice of the dopant ion may severely affect the properties of the intercalated phase, leading to ion-specific device behavior and possibly entirely different phase diagrams for the field-induced intercalated state.

Here, we tackle this issue by performing ionic gating experiments on archetypal layered semiconductor MoS₂ using K⁺ and Li⁺ as dopant ions. MoS₂ is known to undergo a series of insulator-to-metal-to-superconductor phase transitions upon both surface electrostatic carrier accumulation¹² and chemical intercalation with different ionic species.³⁷,³⁸ We find that, for field-driven intercalation, this is the case only for the smaller Li⁺ ion [see the lower panel of Fig. 1(a)]. The larger K⁺ ion (upper panel) leads instead to an incipient metal-to-insulator transition for large doping levels due to the introduction of disorder during the intercalation process. This disorder may originate from simple lattice distortions or a more complex coexistence of different incommensurate doped structures, such as those reported in superconducting intercalated TaS₂.¹⁹ and Bi₂Se₃.⁴⁰ These results demonstrate the critical importance of the specific ionic type on the properties of the intercalated phase.
ionic species and size in ion-gated devices and indicate that different electrolytes can be used to explore different phase diagrams within the same material and device architecture.

We prepared few-layer MoS2 flakes by micromechanical exfoliation of their bulk crystals (2H polytype, SPI supplies) via the well-known scotch-tape method41–43 and transferred them on SiO2(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.44 We realized the electrical contacts [Ti(5 nm)/Au(35 nm)] in the Hall bar configuration, together with a co-planar side gate electrode, by standard microfabrication techniques. We patterned and deposited a solid oxide mask (Al2O3 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. Figure 1(b) presents a rectangular shape, in order to achieve a well-defined aspect ratio for sheet resistance measurements. Figure 1(b) presents the 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, Mw ~ 600). We tested both ClO4- 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 MoS2 devices by slowly (dVG/dt ~ 2 mV/s) ramping the gate voltage VG to a target value at T = 300 K and monitoring their conductivity for sharp increases in its value as the signature of the onset of intercalation4,5 [see Fig. 1(c)]. However, intercalation allows the ions in the electrolyte to migrate across the entire thickness of the device, and the increase in conductivity may potentially be suppressed by an increase in disorder. Hence, its onset can more reliably be detected as a large increase in the Hall carrier density nH = 1/eRH of the device to values comparable with those of a few-nanometer-thick metal (~10^15 cm^-2). These values are one order of magnitude larger than those achievable on MoS2 upon pure surface accumulation12,14,16,45 and are thus a reliable signature for the onset of bulk doping.

Thus, when the target VG was reached, we waited for ~30 min as sufficient time allowing the full relaxation of ion dynamics to improve doping homogeneity. We then cooled the sample to T ~ 240 K (below the glass transition of the electrolyte) and measured the Hall coefficient RH by sweeping the magnetic field perpendicular to the surface of the active channel (see supplementary material). At this point, we either performed a full T-dependent characterization of the transport properties of the device by cooling the system down to 2 K or warmed the sample up to 300 K and increased VG 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.

Figure 1(c) shows a comparison between the VG dependence of the sheet conductivity σx of four devices, two gated with the KClO4/PEG electrolyte (devices A and B) and the other two with the LiTFSI/PEG electrolyte (devices C and D). While the details of these bias ramps vary between different samples, the same choice of electrolyte results in similar curves across multiple devices. We attribute the random appearance of step features in σx to the dynamics of the 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 RH was measured twice: first at VG = +2.8 V and then at VG = +3.1 V. The corresponding values of nH show that the carrier density at VG = +2.8 V (nH ~ 4.4 × 10^14 cm^-2) is about six times smaller than the one at VG = +3.1 V (nH ~ 2.6 × 10^15 cm^-2). This strongly suggests that the device is still mainly in the electrostatic accumulation regime at VG = +2.8 V and is instead intercalated at VG = +3.1 V. It is worth noting that this large increase in nH does not lead to a significant increase in σx, indicating that doping with K+ ions, while inducing carriers, severely reduces the carrier mobility (at T = 300 K, μH ~ 12 ± 3 and 2.5 ± 0.2 cm^2/V s for VG = +2.8 and +3.1 V, respectively). We can also roughly estimate the nominal doping level x in the K,MoS2 stoichiometry at VG = +3.1 V (K0.45MoS2), assuming a uniform distribution of the dopants in all the layers (five for this specific sample). This estimation indicates that the sample at VG = +3.1 V should be completely in the metallic state and in the correct doping range to show superconductivity at low temperature.37

Inducing larger doping levels in K+-gated devices by applying gate voltages in excess of VG = +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 σx with increasing gate voltage up to VG ≈ +3.6 V. Larger voltage values caused a peculiar behavior to emerge, where σx appeared to randomly “jump” between high- and low-conductivity states as VG increased. This behavior, which may be associated with an unstable incorporation of the Li+ ions between the MoS2 layers, continued up to VG ≈ +6.1 V. Even larger gate voltages up to VG ≈ +7.0 V featured a second stable region of monotonically increasing σx, which was about 4 times larger than that for VG ≈ +3.6 V. The corresponding values of carrier density, as measured by the Hall effect at T = 220 K, were nH(+3.6 V) ~ 2.8 × 10^14 cm^-2 and nH(+7.0 V) ~ 7.1 × 10^14 cm^-2 (Li0.12MoS2), with a Hall mobility μH ~ 12±2 and 9.2 ± 1.8 cm^2/V s in the two cases, respectively. The significant increase in both σx and nH indicates that the high-conductivity state at VG ≈ +7.0 V may be associated with Li+- intercalation. The corresponding nominal doping x ~ 0.12 achieved in our sample is still below the onset of superconductivity in chemically intercalated samples, which emerges only for x ≥ 0.4.37
Overall, the following main differences emerge when comparing K$^+$ and Li$^+$ intercalation at the same operating temperature ($T = 300$ K): first, the decrease in mobility is much less pronounced in the case of Li$^+$ doping, indicating a much less prevalent introduction of extra defects in the system; second, while the thickness of the two samples was comparable, the final $n_H$ is significantly smaller in the Li$^+$-doped one, indicating that K$^+$ ions are able to more efficiently penetrate between the MoS$_2$ layers. Furthermore, the onset of K$^+$ doping requires smaller gate voltages but leads to device degradation for smaller $V_G$ values as well.

We now consider the $T$-dependent transport properties of our devices down to 2 K in both K$^+$ and Li$^+$-doped samples. We characterize our devices first in the electrostatic regime and again after the electric field has driven the ions to intercalate the material.

Figure 2(a) shows the $T$-dependence of the square resistance $R_s$ of device A, gated with the KClO$_3$/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$_{0.35}$MoS$_2$ determined at 240 K, we would also expect the emergence of a superconducting transition at $T \approx 6$ 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 $T \geq 150$ K and the other for $T \approx 20$ 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. 2(b)]. 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. Figure 2(c) 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 $n_H \approx 2.9 \times 10^{14}$ cm$^{-2}$ and an Arrhenius-like term $n(T) \approx e^{-E_a / k_BT}$, 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$^2$/V s 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(a) 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 the 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 $T \leq 150$ 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, $n_H \approx 3.9 \times 10^{14}$ cm$^{-2}$, was significantly larger than the one for K$^+$ doping, even though its nominal doping level $x$ was nearly 3 times smaller. This
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. Figure 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 ($T_{on} \approx 3.7$ K) agrees well with that of chemically doped Li$_x$MoS$_2$ for $x \geq 0.4$. Moreover, superconductivity does not appear in chemically doped Li$_x$MoS$_2$ for $x \leq 0.4$. 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 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, for both electrostatic carrier accumulation and field-driven ion intercalation.

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

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