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Superconductivity induced by gate-driven hydrogen intercalation in the charge-density-wave compound 1T-TiSe2

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

In the manuscript of E. Piatti et al., hydrogen doped 1T-TiSe2 has been characterized by various tools in details, and the doping effect on charge density wave and superconductivity was investigated. The experimental results are solid and conclusive; the conclusion will be useful to the community of superconductivity and two dimensional quantum materials. Thus I recommend its publication after clarifying several issues.

1. In Fig. 1c, the schematic guiding curve actually is not necessary, because in Fig. 1b there is already an experimental R-t curve. Why not use this real one? By the way, the derivation of error bar of the data points should be stated in the caption or main text.

2. In Fig. 1g, there is very broad peak around 3000 cm-1 for comparison, but not discussed in the main text.

3. Line 229: Raman spot size was used to estimate the length scale of inhomogeneity. Can the author confirm the size ~10 um? Usually the diameter is around 1 um for 100X objective.

4. From line 266 to line 289, the spin-lattice relaxation rate is discussed, trying to provide information of the evolution of Fermi surface. Can the authors state more clearly about the conclusion or speculation?

5. Line 368: Two-band superconductivity can be inferred from the upturn of Hc2(Tc). A recent study on monolayer WS2 provides coexistance of nonlinear Hall effect and the upturn in Hc2, due to the different characteristics of carriers. In this work, the Hall effect seems rather linear. The comparison should give the authors some information about the multibands.

6. Gating of 5 min is sufficiently long to induce superconductivity. The hydrogen doping level should be much less than H2TiSe2. Can the author estimate the minimum requirement of H concentration?

7. Gating voltage was kept as 3.5V. Can the authors discuss the effect of a large or smaller gating voltage? Say, at 3V, will the doping process be more controllable and the sample be more homogeneous?

Reviewer #2 (Remarks to the Author):

The authors present a systematical investigation of hydrogen intercalated TiSe2 crystals. Non-volatile H intercalation is realized by ionic liquid gating techniques. NMR measurements reveal a surprisingly high hydrogen concentration up to H:Se=1:1. Upon H intercalation, the CDW phase is suppressed and superconducting states are observed. Interestingly, both the CDW transition temperature and the onset temperature of the superconductivity are almost unchanged regardless of the H concentration. The theoretical calculation reveals a rigid band shift in the low H concentration regime, while a strong energy band deformation in the high H concentration regime.

These results are new and timely for publication in Communication Physics. They suggest that gate-induced H intercalation is a unique doping technique to engineer electronic states, and to engender new quantum phenomena.

The authors should address the following concerns before the acceptance of the manuscript.

In Fig 1b and c, the resistance of the sample decreases and then increases as a function of time,

despite the gating voltage remains unchanged. Is this behavior related to the deformation of the energy band? However, the Hall carrier is monotonic as a function of time.

In the high H concentration regime where the energy band deformation occurs, the HxTiSe2 transits from a single-band to a multi-band metal. Is there any evidence for such a transition from the transport measurements? Also, can the authors estimate the H concentration from the transport measurements?

In line 433, the authors claim that the band structure engineering, which seems to be related to the H-derived orbitals, is crucial for the development of SC order. I think this argument is inappropriate. As shown in Fig. 2b, as long as the superconductivity is observed, the Tc is almost a constant regardless of the H concentration. It indicates that in both the rigid-band regime and band deformation regime, the superconductivity has the same mechanism, which is not related to the H-derived orbitals.

Reviewer #3 (Remarks to the Author):

The paper by E. Piaati et al. entitled "Superconductivity induced by gate-driven hydrogen intercalation in the charge-density-wave compound 1T-TiSe2" is reporting hydrogen doped superconductivity in the title compound.
The authors made a rather comprehensive study on the superconductivity in H intercalated TiSe2, with a variety of experiments including electrical resistance, Hall effect, magnetization, x-ray diffraction, Raman scattering, and muSR. I was very impressed with the amount of experiments. However, I also found that some important information is missing, giving me an impression that this work is still incomplete. My concerns are listed below.
1) Regarding the gating experiment shown in Fig. 1a, what were the sizes of crystal and the device? What I mean by the size of device is the diameter of the container of ionic liquid. Did the author do the low temperature transport experiment with the device shown in Fig. 1a, or did they take out from the electrochemical cell?
2) Regarding Fig. 1e, was this measurement done on the single crystal or ground powders after protonation? If it is the former, was this measurement in-situ in ionic liquid, or did they removed all electrical leads from the device?
3) What is the size or weight of the samples used for muSR? According to the description, they mentioned a mosaic crystal. How did they know it is mosaic, and what does it mean?
4) How about the size of crystals for the magnetization? Is this case also mosaic?

The above concerns are rather technical or detailed, but such details are crucial to make the authors' claims reliable. The followings are more essential questions.
5) The DFT band calculations look to me that there is a direct band gap in undoped TiSe2. Is this consistent with the bunch of published results? I am afraid if the present theoretical result captures the intrinsic nature of TiSe2.
6) In the experiment, when the crystal quality of TiSe2 is high, the temperature dependence of resistivity has been always like the pristine one in Fig. 1f. This means that the undoped state looks like semimetallic with a finite overlap of valence and conductions bands. If there is a gap even though it is small, the R-T curves should be more insulating. Furthermore, T_CDW in published papers is always at around 200 K. If TiSe2 is intrinsically gapped, not only the R-T curves but also T_CDW should change dependent on samples or the intrinsically doped carrier density. Authors are encouraged to provide their interpretation of their experimental results and band calculations, taking the comments 5) and 6) into account.
7) As Fig. 2b shows, T_CDW and Tc is not changed against doping time or carrier density, while the

fraction of CDW keeps decreasing with increasing the gating time. The most straightforward or natural interpretation for me is the following.
There exist only two phases, one is undoped or very slightly doped CDW phase and the other is a rather heavily doped superconducting phase. With increasing the gating time, there is no continuous doping but the fraction of the above two phases changes.
I am afraid if the authors did not give a clear-cut picture on what is happening upon doping in the text. I believe this explanation is very important for this paper.
8) In Fig. 2e, the temperature dependence of R_H shows that R_H become positive above T_CDW for lightly doped samples. Why? Maybe this is also consistent with the literatures. Maybe the authors can repeat the already known interpretation, which will be very helpful for readers' understanding.
9) In H2TiSe2, what is the ratio of the electron density from The Hall measurement and the hydrogen density? I guess the ratio should be extremely small. Why doesn't proton supply full carriers?

These are my comments and questions that came to my mind. Without the authors' additional explanation, I am not able to recommend this paper published in Comms. Phys.

Reply to the Reviewers' report

We thank all the Reviewers for their comments and suggestions, that have allowed us to improve the clarity and the completeness of the paper. We have done our best to reply to all the points raised in their reports, by providing additional details and figure in the Main Text and/or in the Supplementary Information.

Below, we provide a point-by-point response to the comments of each Reviewer and a description of changes made. We include in the resubmission a marked-up version of the Main Text and of the Supplementary Information, with the changes to the text highlighted in blue font for the ease of the Reviewers.

We hope that, with these changes and amendments, the manuscript is suitable to publication in Communications Physics.

Yours sincerely,

The Authors

REPLY TO REVIEWER #1

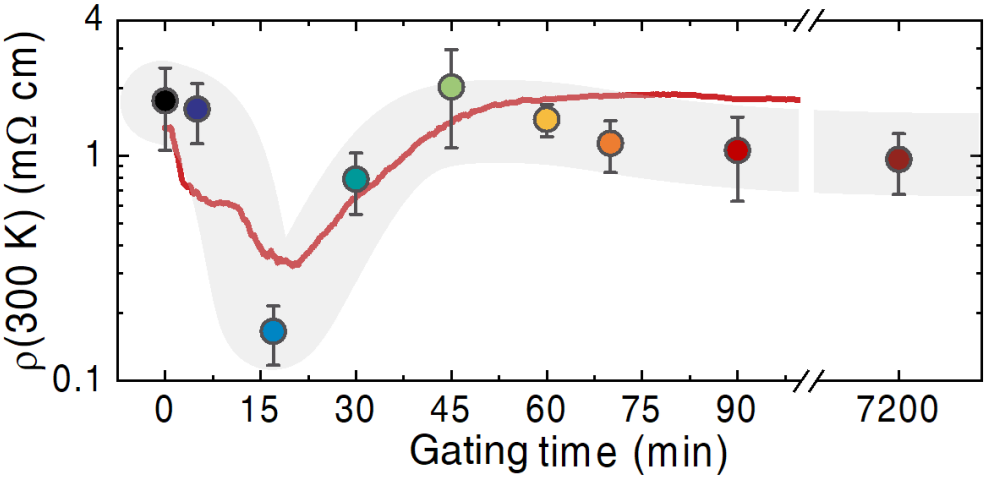
In the manuscript of E. Piatti et al., hydrogen doped 1T-TiSe2 has been characterized by various tools in details, and the doping effect on charge density wave and superconductivity was investigated. The experimental results are solid and conclusive; the conclusion will be useful to the community of superconductivity and two dimensional quantum materials. Thus I recommend its publication after clarifying several issues.

We thank the Reviewer finding our results to be solid, conclusive and useful to the community, and for recommending publication in Communications Physics.

1. In Fig. 1c, the schematic guiding curve actually is not necessary, because in Fig. 1b there is already an experimental R-t curve. Why not use this real one? By the way, the derivation of error bar of the data points should be stated in the caption or main text.

We thank the Reviewer for the suggestion. Indeed, we originally tried to use the experimental $\rho(t)$ curve measured in situ and shown in Fig. 1b as a guide to the eye for the ex situ data shown in Fig. 1c.

However, while the in-situ and ex-situ data sets exhibit the same qualitative behaviour, the quantitative details do not match perfectly, as shown in the plot below.



Here, note that to each of the data points of the in-situ curve (red line) is associated an uncertainty (of mostly geometrical origin) of the same order of those explicitly shown for the ex-situ data points. The difference between the two data sets can be ascribed to sample-to-sample variations: each of the filled circles measured ex situ refers to a different $TiSe_2$ crystal which was gated for a given amount of time, while the data measured in situ obviously pertains to one crystal only. As a consequence, the in-situ curves turn out not to be very suitable to act as guides to the eye for the ex-situ data points. This is the reason why we opted to show the two data sets separately in the Main Text: one representative in-situ curve in Fig. 1b, and the collection of ex-situ data points in Fig. 1c.

Concerning the derivation of the error bars, again they are almost entirely due to the geometrical uncertainties on the length and width of the measured channel, since the Ag paste electrical contacts were drop-casted by hand. We therefore included the error bar derivation by adding the following sentence to the revised caption of Fig. 1: "Error bars represent the uncertainties on the measurements, which almost entirely arise from non-ideal sample geometry".

2. In Fig. 1g, there is very broad peak around 3000 cm-1 for comparison, but not discussed in the main text.

We thank the Reviewer for their observation, which stimulates some further comment about our Raman spectroscopy measurements. We indeed already made extensive computational studies to interpret the broad band present in our Raman spectra around $\sim 2900\,\mathrm{cm}^{-1}$, concluding that the origin can most likely be attributed to the presence of molecular hydrogen in the samples. However, we refrained from explicitly discussing the observation because it is qualitatively irrelevant to explain the origin of

the superconducting phase (as evident from the band structures in the main text) and we could not have clear experimental evidence to support this conclusion.

However, stimulated by the Reviewer's comment, in the revised manuscript we opted to complete the discussion of the Raman spectra by including the following sentences in the revised Main Text (lines 205-218):

"...and a very broad band appears at high wavenumbers centered around $\sim 2900\,\mathrm{cm}^{-1}$. Our first-principle calculations (see Supplementary Section VII) indicate that the appearance of the peaks at $\sim 156\,\mathrm{cm}^{-1}$ and $\sim 260\,\mathrm{cm}^{-1}$ can be justified by the removal of symmetry of the $1T$-$TiSe_2$ system resulting from the incorporation of H atoms in both atomic (H_1TiSe_2) and molecular (H_2TiSe_2) forms. The broad band centered around $\sim 2900\,\mathrm{cm}^{-1}$ can instead be naturally interpreted as originating from H_2 molecules confined in the $TiSe_2$ matrix, with a renormalized phonon frequency [47, 48]. The simultaneous observation of these multiple peaks is therefore evidence of a strong disorder in the H concentration, phase and distribution in the $TiSe_2$ matrix."

and by adding the following discussion to Supplementary Section VII-B:

"From this analysis we can directly justify the appearance of the peaks at ~ 156 and $\sim 260\,\mathrm{cm}^{-1}$ in the experimental Raman spectra of H_2TiSe_2 (Main Fig. 1g). Specifically, the presence of the two peaks can be accounted in part by the configuration involving a single H atom in the "bridge position" modifying the Se vibrational properties, and in part by the configuration where two H atoms are included in the $TiSe_2$ structure, one in the VdW gap and the other one in the $TiSe_2$ trilayer.

Accounting for the broad band at $\sim 2900\,\mathrm{cm}^{-1}$ on the other hand is more complex. In general, molecular hydrogen shows a high-frequency stretching mode which falls around $\sim 4000\,\mathrm{cm}^{-1}$ and strongly depends on the structural environment in which H_2 is hosted [14]. Our calculations indicate that the H_2 vibrational frequency lies at $\sim 4100\,\mathrm{cm}^{-1}$ when the molecule is isolated; but when the H_2 is intercalated in the $TiSe_2$ matrix (i.e, the H_2TiSe_2 phase where the H_2 molecule lies in the VdW gap with the H–H bond parallel to the $TiSe_2$ plane) its vibrational frequency softens down to $\sim 3700\,\mathrm{cm}^{-1}$, due to the structural and metallic electronic environment. This result is in line with what observed for other systems containing molecular hydrogen, in which the interstitial H_2 molecule shows a strongly renormalized frequency down to $\sim 3000\,\mathrm{cm}^{-1}$ [14, 15]. Based on this result, the very broad band roughly centered at $\sim$2900 cm^{-1} in the experimental spectrum can be naturally interpreted as originating from H_2 molecules confined in the $TiSe_2$ matrix, with renormalized phonon frequency. Considering that our estimation of the frequency shift was obtained for H_2 in the most stable site found in $TiSe_2$, disorder effects related to multiple-site intercalation, interaction with other molecules due to inhomogeneities, temperature effects and/or interactions with free atomic hydrogens will result in a

broad feature statistically including different frequency shifts (depending on structural environment and electronic doping). Overall, the experimental observation of the additional low-frequency peaks and of the broad band at high frequencies in the Raman spectrum is therefore a further indication of the presence of disorder in the hydrogen concentration, phase and distribution in the intercalated $TiSe_2$ samples."

3. Line 229: Raman spot size was used to estimate the length scale of inhomogeneity. Can the author confirm the size 10 um? Usually the diameter is around 1 um for 100X objective.

We thank the Reviewer for spotting this typo. The laser spot with the 100X objective was indeed around 1 μm wide in our experimental setup, not 10 μm wide. The Main Text has been amended accordingly.

4. From line 266 to line 289, the spin-lattice relaxation rate is discussed, trying to provide information of the evolution of Fermi surface. Can the authors state more clearly about the conclusion or speculation?

We thank the Reviewer for this request of clarification. A linear dependence of the spin-lattice relaxation rate on temperature (i.e., the so-called Korringa relaxation) has been reported for several transition-metal dichalcogenides within the CDW state (see the new bibliographic references [55-57] added in the revised Main Text). The Korringa relaxation is induced by itinerant electrons and, in the ideal case of a Fermi gas, it can be shown that $(T_1 T)^{-1} \propto \varrho(E_F)$ – i.e., the density of states at the Fermi energy. We observe a linear-in-temperature trend of the spin-lattice relaxation rate in hydrogenated $TiSe_2$ within the CDW state for $80\,\mathrm{K} \lesssim T \lesssim 170\,\mathrm{K}$ and, remarkably, the major deviations from this behaviour at high temperatures correlate with the critical temperature to the CDW state. Based on this, we argue that the onset of the CDW state induces a change in the density of states at the Fermi energy and, more in general, a reconstruction of the Fermi surface. However, we also stress that the onset of the CDW transition in other transition-metal dichalcogenides has a markedly different effect on the spin-lattice relaxation rate, making our results highly specific of hydrogenated $TiSe_2$. All these aspects are reported in the main text alongisde a citation to a new paper – currently under preparation – that will deal exclusively with the results of the NMR spin-lattice relaxation rate.

We clarified this point in the revised manuscript by adding the following sentences to the Results section (lines 303-327):

"...strong indications of a reconstruction of the Fermi surface around $T \sim 200\,\mathrm{K}$ are also obtained from NMR measurements of the ^{1}H spin-lattice relaxation rate T_1^{-1} in H_2TiSe_2 samples at $\mu_0 H \simeq 3.5\,\mathrm{T}$ (Methods). As shown in the inset to Fig. 2c, T_1^{-1} exhibits a linear dependence on T for $80\,\mathrm{K} \lesssim T \lesssim 170\,\mathrm{K}$

consistent with the so-called Korringa behaviour proper of relaxation processes mediated by itinerant electrons [54]. This is in agreement with the results of NMR measurements in other TMDs such as VSe_2, VS_2, and $IrTe_2$ within the CDW phase [55-57]. Higher temperatures $T \gtrsim 170\,\mathrm{K}$ mark a clear departure from the linear-in-temperature trend. In particular, a plateau of T_1^{-1} between 170 K and 210 K is followed by a suppression of T_1^{-1} upon increasing T. The crossover between the two different behaviours is even clearer in the T dependence of $(T_1T)^{-1}$ (main panel of Fig. 2c) and, remarkably, it seemingly correlates with the onset of the CDW phase. In the ideal case of a Fermi gas, it is well-known that $(T_1T)^{-1} \propto \varrho(E_F)$ – i.e., the density of states at the Fermi energy [54]. The observed drop of $(T_1T)^{-1}$ for $T \gtrsim 170\,\mathrm{K}$ is then strongly indicative of a progressive decrease of $\varrho(E_F)$ upon increasing temperature above the critical temperature of the CDW phase, at variance with what is observed in VSe_2, VS_2, and $IrTe_2$ [55-57]. This peculiar behaviour will be discussed in detail elsewhere [58]. Finally, we stress that..."

5. Line 368: Two-band superconductivity can be inferred from the upturn of Hc2(Tc). A recent study on monolayer WS2 provides coexistance of nonlinear Hall effect and the upturn in Hc2, due to the different characteristics of carriers. In this work, the Hall effect seems rather linear. The comparison should give the authors some information about the multibands.

We thank the Reviewer for bringing this point to our attention. Indeed, the Hall effect in multi-band systems is in general non-linear. However, the detectability of this non-linearity hinges on the different bands exhibiting different carrier mobilities. The ideal conditions for observing a non-linear Hall effect in a two-band system is for the first band to exhibit a large carrier density with a low mobility, and conversely the second band to exhibit a low carrier density with a high mobility. This is precisely the case occurring in the manuscript by Ding et al. on WS_2 [Nano Lett. 22, 7919 (2022)], where the fit of the experimental data to the two-carrier model resulted in a first band with a carrier density of $\sim 10^{14}\,\mathrm{cm}^{-2}$ and a mobility of $\sim 10^{2}\,\mathrm{cm}^{2}\mathrm{V}^{-1}\mathrm{s}^{-1}$, and a second band with a carrier density of $\sim 10^{12}\,\mathrm{cm}^{-2}$ and a mobility of $\sim 10^{3}\,\mathrm{cm}^{2}\mathrm{V}^{-1}\mathrm{s}^{-1}$. If these conditions are not met, however, the nonlinearity of the Hall effect quickly vanishes even in multiband systems. In particular, the Hall effect remains linear at any magnetic field if the two bands exhibit comparable mobilities; whereas the slope change remains detectable but is shifted to extremely large magnetic fields if the mobilities are different but the carrier densities become comparable.

We have added the following paragraph to revised Supplementary Section III to discuss this point:

"Additionally, all $B-\rho_{xy}$ curves exhibit good linear behaviour up to 9 T. This indicates that, if H_xTiSe_2 is a multi-band superconductor as suggested by the observed upturn in the temperature-dependence of

the critical magnetic field, its electronic structure does not support the ideal conditions for the observation of a non-linear Hall effect, namely a first band with high carrier density and low mobility and a second band with low density and high mobility [5]. This is consistent with existing data in undoped $TiSe_2$ [6]. However, the limited range of magnetic fields accessible in our cryostat do not allow us to discern whether the possible multi-band superconductivity would be supported by two bands of comparable mobility and different density, or two bands of comparable density and different mobility, or a first band with high density and high mobility and a second band with low density and low mobility."

The work by Ding et al. has also been included as Ref. 5 in the revised Supplementary Information and Ref. 63 in the revised Main Text.

6. Gating of 5 min is sufficiently long to induce superconductivity. The hydrogen doping level should be much less than H2TiSe2. Can the author estimate the minimum requirement of H concentration?

The Reviewer raises a very interesting point. In general, a reliable estimation of the minimum H concentration required to induce superconductivity in H_xTiSe_2 is made extremely challenging due to two main factors. The first issue is that the only experimental technique at our disposal able to accurately assess the H concentration is nuclear magnetic resonance, and due to their time-consuming nature NMR measurements were performed only on the $TiSe_2$ crystals with maximum H loading.

The second issue is that nearly all experimental techniques suggest H intercalation to be very inhomogeneous even in the samples at maximum H loading, with a significant amount of H being incorporated in forms that do not provide electron doping at all (such as H_2 molecules). We expect this issue to be particularly exacerbated in samples at reduced H loading, likely leading to a percolating filamentary network of highly-doped regions embedded in a nearly undoped matrix. In such a sample, the average sample doping would of course be very different from the actual critical doping required for the onset of superconductivity in the highly-doped regions.

Keeping in mind all these caveats, a rough estimate of the *average* H loading corresponding to the 5 min gating time can be obtained by ignoring the issue of sample homogeneity, and by assuming that the H loading in the samples follows the same qualitative behaviour of the Hall carrier density as a function of the gating time. This *rough* estimate corresponds to ~ 0.4 H atoms per $TiSe_2$ formula unit, which we have included in the revised Main Text (lines 188-193):

"Assuming the H concentration to be linearly proportional to n_H at $T = 4.2$ K, this then allows estimating an average x $\sim$ 0.4 for intercalated $TiSe_2$ to exhibit an incomplete resistive transition with reduced T_c^{on} (gating time of $\sim$ 5 min), and an average x $\sim$ 1 for a complete resistive transition to develop (gating time of $\sim$ 17 min)."

7. Gating voltage was kept as 3.5V. Can the authors discuss the effect of a large or smaller gating voltage? Say, at 3V, will the doping process be more controllable and the sample be more homogeneous?

We thank the Reviewer for highlighting this point where we can better elucidate our choice of gating parameters. As we wrote at the beginning of the Results section of the original manuscript, the field-driven H intercalation was performed by sweeping the gate voltage from 0 V to +3.0 V and then keeping it constant for a selected amount of time. As shown in Fig. 1b, +3.0 V is the minimum gate voltage value required to attain H intercalation. We decided not to investigate the application of larger gate voltages since the surface of $TiSe_2$ is notoriously environment-sensitive and we did not want to risk activating gate-driven etching processes that could damage the samples [see for example Shiogai et al. Nat. Phys. 12, 42 (2016)], nor the intercalation of the organic cations of the ionic liquid itself [see for example our related work on MoS_2, Piatti et al. Nanomaterials 12, 1842 (2022)]. According to Refs. 10-11, improved homogeneity could potentially be attained by gating at a higher temperature; this however also runs the risk of triggering additional undesired electrochemical reactions between the sample and the electrolyte, and we therefore preferred to avoid increasing the gating temperature in the present work.

We added the following sentence to the revised Methods to clarify our choice of maximum applied gate voltage (lines 633-636):

"The applied V_G was always limited to a maximum value of +3 V and the gating temperature to 300 K so as to avoid undesired electrochemical reactions between the sample and the ionic liquid such as sample etching [78] or organic-ion intercalation [79]."

REPLY TO REVIEWER #2

The authors present a systematical investigation of hydrogen intercalated TiSe2 crystals. Non-volatile H intercalation is realized by ionic liquid gating techniques. NMR measurements reveal a surprisingly high hydrogen concentration up to H:Se=1:1. Upon H intercalation, the CDW phase is suppressed and superconducting states are observed. Interestingly, both the CDW transition temperature and the onset temperature of the superconductivity are almost unchanged regardless of the H concentration. The theoretical calculation reveals a rigid band shift in the low H concentration regime, while a strong energy band deformation in the high H concentration regime. These results are new and timely for publication in Communication Physics. They suggest that gate-induced H intercalation is a unique doping technique to engineer electronic states,

and to engender new quantum phenomena. The authors should address the following concerns before the acceptance of the manuscript.

We thank the Reviewer for finding our results to be new, timely and suitable for publication in Communications Physics.

In Fig 1b and c, the resistance of the sample decreases and then increases as a function of time, despite the gating voltage remains unchanged. Is this behavior related to the deformation of the energy band? However, the Hall carrier is monotonic as a function of time.

We thank the Reviewer for this request of clarification. The non-monotonic behaviour of the resistivity with increasing gating time coupled with the monotonic increase in Hall carrier density indicates a reduction in the charge carrier mobility. In general, this could be partially ascribed to the changes in the electronic bandstructure leading to a reduction in the Fermi velocity and/or to an increase of the effective mass; in addition, differences in the electron-phonon scattering as a function of doping can easily determine a different qualitative behaviour of the mobility. However, in most instances where electron doping is introduced by means of intercalation and/or substitution, the mobility is suppressed simply because the dopants act as sources of extrinsic disorder.

In our system, the calculated band structure of the hydrogenated samples clearly disclosed an important band structure modification as a function of the H doping, from a rigid band shift in the low doping regime to a band redistribution in the high doping regime. This peculiar effect *could* be qualitatively related to the change in mobility as a function of doping, but a reliable first-principles prediction (even at a qualitative level) would require including multiple effects that go well beyond the scope of the present work. Furthermore, in our samples a direct quantitative determination of the room-temperature mobility is problematic because most of the values of Hall density are determined at low temperatures only, but the Hall coefficient itself is strongly temperature-dependent (as shown in Fig. 2e).

Nevertheless, the fact that H loading introduces a strong degree of structural disorder is independently confirmed by our X-ray diffraction measurements, which show a pronounced peak broadening in the protonated samples with respect to the pristine ones (as shown in Fig. 1e). This increase is also mirrored in the sharp reduction of another parameter commonly employed as a proxy for the structural disorder in metallic samples, i.e. the ratio between the room-temperature resistivity and its value immediately above the superconducting transition (residual resistivity ratio, RRR): in our protonated samples, RRR strongly decreases from ≈ 32 at a gating time of 30 min to ≈ 8 at a gating time of 5 days. It is therefore our interpretation that the re-entrant behaviour of the resistivity with increasing gating time and H loading can be chiefly ascribed to the increase in structural disorder, and only marginally

to band reconstruction effects.

We further stress the importance of intercalation-driven disorder in the revised manuscript by updating the following sentence in the Results section (lines 135-140):

"The pronounced broadening of the XRD peaks however indicates that the protonation introduces a large degree of structural disorder in the samples, which is likely responsible for the re-entrant behaviour of $\rho(300\,\mathrm{K})$ upon gating times in excess of those associated to the local minimum shown in Fig. 1b,c."

by adding the following sentence discussing the reduction in RRR (lines 172-177):

"Consistent with the XRD results, a large degree of structural disorder in these highly-doped samples is evidenced by the four-fold reduction in their residual resistivity ratio (Methods), from its maximum value ~ 32 attained at a gating time of ~ 30 min, to a final value ~ 8 at a gating time of 5 days."

and by suitably updating the Methods (lines 676-678):

"the residual resistivity ratio was determined as $\rho(300\,\mathrm{K})/\rho_0$, where ρ_0 is the resistivity value in the normal state immediately above the superconducting transition".

In the high H concentration regime where the energy band deformation occurs, the HxTiSe2 transits from a single-band to a multi-band metal. Is there any evidence for such a transition from the transport measurements? Also, can the authors estimate the H concentration from the transport measurements?

We thank the Reviewer for the question. As also discussed in our answer to Question 5 of Reviewer #1, multi-band metals can present non-linearities in the Hall effect if a significant difference exists in the mobility of the two bands. Our transport data, however, rule out such a scenario, and unfortunately cannot be of use in discriminating the issue one way or the other.

We have added the following paragraph to revised Supplementary Section III to discuss this point:

"Additionally, all $B-\rho_{xy}$ curves exhibit good linear behaviour up to 9 T. This indicates that, if H_xTiSe_2 is a multi-band superconductor as suggested by the observed upturn in the temperature-dependence of the critical magnetic field, its electronic structure does not support the ideal conditions for the observation of a non-linear Hall effect, namely a first band with high carrier density and low mobility and a second band with low density and high mobility [5]. This is consistent with existing data in undoped $TiSe_2$ [6]. However, the limited range of magnetic fields accessible in our cryostat do not allow us to discern whether the possible multi-band superconductivity would be supported by two bands of comparable mobility and different density, or two bands of comparable density and different mobility, or a first band with high density and high mobility and a second band with low density and low mobility."

Similarly, the transport data are only sensitive to the density of free charge carriers introduced by the

H dopants via the Hall effect, not to the H density directly, and as such Hall effect data cannot be safely used as a reliable proxy for the H concentration. This mismatch is the main reason why we employed nuclear magnetic resonance to accurately assess the H concentration in our protonated crystals.

In line 433, the authors claim that the band structure engineering, which seems to be related to the H-derived orbitals, is crucial for the development of SC order. I think this argument is inappropriate. As shown in Fig. 2b, as long as the superconductivity is observed, the Tc is almost a constant regardless of the H concentration. It indicates that in both the rigid-band regime and band deformation regime, the superconductivity has the same mechanism, which is not related to the H-derived orbitals.

We thank the Reviewer for highlighting this point where the clarity of our manuscript can be improved. The critical temperature in our samples is indeed nearly independent on the H concentration. However, our quantitative NMR results clearly demonstrate that ionic gating is extremely efficient in introducing H dopants in the $TiSe_2$ crystals (2 H atoms per $TiSe_2$ formula unit for gating times $\gtrsim 45$ min). As also discussed in our response to Question 6 of Reviewer #1, a rough estimate of the *average* H loading corresponding to the gating times smaller than those necessary to obtain the H_2TiSe_2 stoichiometry can be obtained assuming the H loading in the samples to be proportional to the Hall carrier density as a function of the gating time: this gives an estimate of ~ 0.4 H atoms per $TiSe_2$ formula unit in the *least* doped samples (gating time ~ 5 min). This makes it so that even the samples at the lowest H concentrations fall beyond the limits of applicability of the rigid-band regime, which predicts the critical temperature to become rapidly suppressed as the doping increases beyond 0.2 electrons per unit cell (therefore making it more suited to describe the effects of electron doping in Cu and Li-doped $TiSe_2$). Furthermore, nearly all experimental techniques suggest H intercalation to be inhomogeneous even in the samples at maximum H loading, and we expect this issue to be particularly exacerbated in samples at reduced H loading, likely leading to a percolating filamentary network of highly-doped regions (where the rigid-band regime is even less applicable) embedded in a nearly undoped matrix.

We have discussed the issue of the doping level in the least-doped $TiSe_2$ crystals by including this rough estimation of their H concentration in the revised Main Text (lines 188-193):

"Assuming the H concentration to be linearly proportional to n_H at $T = 4.2$ K, this then allows estimating an average x ~ 0.4 for intercalated $TiSe_2$ to exhibit an incomplete resistive transition with reduced T_c^{on} (gating time of ~ 5 min), and an average x ~ 1 for a complete resistive transition to develop (gating time of ~ 17 min)."

and we have clarified how the large H doping introduced even at short gating times makes the rigid-band regime not applicable to our samples by adding the following sentences in Supplementary Section

VII-C:

"Furthermore, the large H concentration levels estimated even in the least-doped samples (average x $\sim$ 0.4 at the shortest gating time of $\sim$ 5 min) indicate that the jellium approximation does not correctly describe the superconducting properties of our H_xTiSe_2 crystals at any gating time, and would be more suited to describe superconducting Cu- and Li-doped $TiSe_2$. This lack of applicability is particularly relevant in the likely case that, in samples at reduced H loading, the inhomogeneity in the H concentration leads to samples characterized by a percolating filamentary network of highly-doped regions embedded in a nearly undoped matrix."

REPLY TO REVIEWER #3

The paper by E. Piaati et al. entitled "Superconductivity induced by gate-driven hydrogen intercalation in the charge-density-wave compound 1T-TiSe2" is reporting hydrogen doped superconductivity in the title compound. The authors made a rather comprehensive study on the superconductivity in H intercalated TiSe2, with a variety of experiments including electrical resistance, Hall effect, magnetization, x-ray diffraction, Raman scattering, and muSR. I was very impressed with the amount of experiments. However, I also found that some important information is missing, giving me an impression that this work is still incomplete. My concerns are listed below.

We thank the Reviewer for praising the comprehensiveness of our experimental investigation.

1) Regarding the gating experiment shown in Fig. 1a, what were the sizes of crystal and the device? What I mean by the size of device is the diameter of the container of ionic liquid. Did the author do the low temperature transport experiment with the device shown in Fig. 1a, or did they take out from the electrochemical cell?

We thank the Reviewer for this request of clarification. We have added the requested information on the size of the samples and of the ionic liquid container in the revised Methods (lines 626-629):

"Freshly-cleaved 1T-$TiSe_2$ crystals (HQ Graphene; typical size 1.0×0.5×0.05 mm^3) were electrically contacted by drop-casting small droplets of silver paste (RS Components) to thin gold wires and immersed in a Duran crucible (40 mm diameter)..."

Concerning the low temperature transport measurements, they were all performed *ex situ*, which is now explicitly stated in the revised Methods (lines 650-651):

"All protonated $TiSe_2$ crystals discussed in this work were characterized via *ex-situ* temperature-

dependent resistivity measurements..."

2) Regarding Fig. 1e, was this measurement done on the single crystal or ground powders after protonation? If it is the former, was this measurement in-situ in ionic liquid, or did they removed all electrical leads from the device?

We have amended the revised Methods to answer the Reviewer's question (lines 686-688):

"X-ray powder diffraction patterns of the $TiSe_2$ samples were collected *ex situ* on selected single crystals after thorough removal of the ionic liquid residues and of the electrical leads using a 114.6 mm Gandolfi camera, with Ni-filtered Cu K-α radiation source and an exposure time of 48 hours."

3) What is the size or weight of the samples used for muSR? According to the description, they mentioned a mosaic crystal. How did they know it is mosaic, and what does it mean?

The overall sample surface for the μSR measurements is approximately $\sim 20\ mm^2$. As now discussed in the revised Supplementary Section V and shown in the new Supplementary Fig. 6, the sample was composed of a collection of oriented flake-like single-crystals – hence the use of the term "mosaic". The following paragraph has also been added to the corresponding section:

"A set of H_2TiSe_2 single crystals belonging to the same batch was glued using cryogenic heat-sinking varnish (GE 7031) on a thin (25-μm) Cu foil, so as to realize a mosaic (surface exposed to the muon beam $\sim 20\ mm^2$ – see Supplementary Fig. 6). The resulting sample consisted of crystals with aligned *c* axes, but with random orientation of the in-plane *a* and *b* axes. A few layers of crystals were necessary in order to achieve a minimum thickness of about 0.2 mm. Such average sample thickness and the presence of a 100-μm-thick high-purity silver degrader on the sample surface ensure that muons are implanted in the sample (and do not pass through it)."

4) How about the size of crystals for the magnetization? Is this case also mosaic?

The mosaic of single crystals was required to attain a measurable signal in the μSR measurements only. The magnetization was measured on one single flake-like crystal with approximate surface $\sim 1\ mm^2$, as now explicitly stated in the revised Methods (lines 717-720):

"Systematic measurements of the magnetic moment as a function of temperature and magnetic field were carried out on a small H_2TiSe_2 single crystal with approximate surface $\sim 1\ mm^2$..."

The above concerns are rather technical or detailed, but such details are crucial to make the authors' claims reliable. The followings are more essential questions.

We thank the Reviewer for helping us improve the reliability of our results.

5) The DFT band calculations look to me that there is a direct band gap in undoped TiSe2. Is this consistent with the bunch of published results? I am afraid if the present theoretical result captures the intrinsic nature of TiSe2.

We thank the Reviewer for their comment, because we think that is an important point, frequently understated in the literature: the correct description of the electronic properties of $1T$-$TiSe_2$ is a very delicate and crucial issue. Although the exact ground state of undoped $1T$-$TiSe_2$ is still debated in the literature, it is now accepted that its band structure is characterized by the presence of a very small indirect band gap between Se-4p and Ti-3d states, of the order of $\simeq$ 0.01-0.2 eV [see Refs. 85, 86, 89, and 90; and also Stoffel et al., Phys. Rev. B 31, 8049 (1985); Pillo et al., Phys. Rev. B 61, 16213 (2000); Kidd et al., Phys. Rev. Lett. 88, 226402 (2002)]. As demonstrated by Bianco *et al.* in their seminal work on the description of physical properties of $TiSe_2$ (Ref. 85), the opening of the gap is related to the relatively high electronic correlation effects of localized *d* orbitals of Ti atoms. These effects, underestimated by local exchange-correlation potentials, were accounted for by including a Hubbard-like correction for Ti-*d* orbitals within the GGA+U framework, with U parameter, determined from first principles (as discussed in Ref. 85). This aspect is sometimes ignored in the literature, in which $TiSe_2$ is predicted metallic, using local functionals without Hubbard corrections.

For the present work, we obviously adopted the right computational framework, using the appropriate value for the Hubbard U parameter, $U = 3.9$ eV, which guarantees the proper description of the normal (undoped) phase. Thus, as shown in Fig. 5b (gray lines) of the main paper and in Supplementary Fig. 9a-d (gray lines), we reproduce the $1T$-$TiSe_2$ electronic properties, predicting a small indirect gap. We also wish to point out that these same corrections are not (strictly) necessary to describe the doped phases which are the focus of our work, these being metallic. Indeed, one can show that removing the Hubbard corrections does not qualitatively alter the band structures of the metallic phases shown in the present manuscript.

We further clarify that our choice of employing Hubbard corrections and of the value of the U parameter was taken in order to correctly reproduce the experimentally-measured electronic bandstructure by adding the following sentence to the revised Methods (lines 794-796):

"The U parameter, determined from first principles [85, 88], was set to $U = 3.9$ eV, allowing to reproduce the Fermi surface experimentally determined via angle-resolved photoemission spectroscopy [86, 89, 90]."

6) In the experiment, when the crystal quality of TiSe2 is high, the temperature dependence of resistivity has been always like the pristine one in Fig. 1f. This means that the undoped state looks like semimetallic with a finite overlap of valence and conductions bands. If there is a gap even though it is small, the R-T curves should be more insulating. Furthermore, T_CDW in published papers is always at around 200 K. If TiSe2 is intrinsically gapped, not only the R-T curves but also T_CDW should change dependent on samples or the intrinsically doped carrier density. Authors are encouraged to provide their interpretation of their experimental results and band calculations, taking the comments 5) and 6) into account.

We thank the Reviewer for highlighting this subtle issue in the interpretation of the temperature-dependent resistivity data of undoped $TiSe_2$. Again, we stress that whether the ground state of undoped $TiSe_2$ is semimetallic or semiconducting is a long-standing issue in the literature, with electric transport (see e.g. Refs. 36-37) and optical conductivity measurements [see e.g. Li et al., Phys. Rev. Lett. 99, 027404 (2007); Velebit et al., Phys. Rev. B 94, 075105 (2016)] most often – although not always, see Refs. 38-39 – depicting a semimetallic picture, whereas ARPES experiments systematically report the presence of a semiconducting energy gap [see Refs. 85, 86, 89, and 90; and also Stoffel et al., Phys. Rev. B 31, 8049 (1985); Pillo et al., Phys. Rev. B 61, 16213 (2000); Kidd et al., Phys. Rev. Lett. 88, 226402 (2002)]. The issue is extremely hard to solve because, in both pictures, either the semimetallic band overlap or the semiconducting energy gap are of the order of few tens of meV, being therefore comparable to the thermal energy in most of the temperature range. Additionally, even the highest-quality $TiSe_2$ crystals exhibit small but non-negligible amounts of excess Ti and/or Se vacancies, which act as electron donors (see Refs. 37 and 38 respectively). As such, "self-doping" and thermal population of the bands can easily mask the presence of a small semiconducting gap in transport and optical measurements, and indeed the temperature-dependence of the resistivity of undoped $TiSe_2$ has been reproduced on a semi-quantitative level by explicitly assuming the material to be a narrow-gap semiconductor with small extrinsic electron doping (see Ref. 40). Another consequence of the narrowness of the proposed band gap is that it easily allows for valence band states to hybridize with conduction band states, transforming the material from being semiconducting in a single-particle picture into being semimetallic from a many-particle perspective (see Refs. 86 and 90). Overall, the question of which exactly is the intrinsic ground state of undoped $TiSe_2$ is a very complicated issue which has puzzled physicists for several decades, and our manuscript is not aiming at providing a definitive solution to it – indeed, our results are largely agnostic on the matter. Rather, our work is focused on unveiling the properties of the hydrogen-rich phase at large electron doping, where the bandstructure becomes heavily distorted and largely independent on whether the parent compound exhibited a small band overlap or a narrow band gap.

We have clarified the still debated nature of the metallic-like conductivity of $TiSe_2$ at low temperatures in the revised manuscript by adding the following sentence to the Results section where we discuss the temperature dependence of the resistivity of our undoped crystals (lines 156-161):

"The monotonically-increasing $\rho(T)$ dependence up to T_{CDW} is also commonly observed in high-quality 1T-$TiSe_2$ crystals, but whether it originates from a semimetallic band overlap [36,37] or from a narrow semiconducting gap in the presence of a small extrinsic electron doping [38-40] remains currently uncertain."

and added the new Refs. 37-40 to the revised Bibliography.

7) As Fig. 2b shows, T_CDW and Tc is not changed against doping time or carrier density, while the fraction of CDW keeps decreasing with increasing the gating time. The most straightforward or natural interpretation for me is the following. There exist only two phases, one is undoped or very slightly doped CDW phase and the other is a rather heavily doped superconducting phase. With increasing the gating time, there is no continuous doping but the fraction of the above two phases changes. I am afraid if the authors did not give a clear-cut picture on what is happening upon doping in the text. I believe this explanation is very important for this paper.

We thank the Reviewer for the suggestion. Indeed, we concur that the existence of phase separation between phases with different H content is crucial in reconciling all the experimental evidences with the theoretical results, as was also proposed in the case of Li-doped $TiSe_2$ in Ref. 33. This crucial role played by phase separation was already explicitly acknowledged in several instances throughout the original manuscript, including:

Lines 249-256: "The insensitivity of T_{CDW} to increasing doping was interpreted, in the case of Li_xTiSe_2, as a lack of full in-plane percolation of the dopants, leading to a spatial separation between SC Li-rich regions and CDW-ordered pristine regions [33]. The pronounced increase in structural disorder detected by both XRD and Raman spectroscopy in our samples suggests that a similar picture may hold also in the case of H_xTiSe_2."

Lines 414-419: "We find a lower limit for the SC volume fraction $f_{sc} = 44 \pm 1\%$, thus confirming the bulk nature of H_xTiSe_2 superconductivity, leaving however open the possibility that some sample regions may still be normal, as expected in case of an inhomogeneous distribution of H dopants."

Lines 488-490: "The actual H_xTiSe_2 samples are likely to be characterized by a strong disorder in the distribution of H atoms, and will thus exhibit a mixture of different single phases..."

We have however refrained from directly calling for the existence of only two phases, one (nearly) undoped and CDW ordered, the second highly doped and superconducting, for several reasons. The

first reason is that we cannot currently rule out some other kind of coexistence between the two orders (as proposed instead for Cu_xTiSe_2 [50,51]) since we currently lack direct evidence of phase separation from nanoscale-resolved techniques such as STM. It is possible that, even in the SC phase, CDW order survives as a small gap in the bandstructure that gets (at least partially) shifted below the Fermi level, or fragments into short-range-ordered domains lacking long-range coherence. The second reason is that our results actually suggest that this phase separation occurs over multiple possible configurations for the occupied H intercalation sites, rather than over a simple separation between an H-deficient CDW phase and an H-rich SC phase. The main evidence for this arises from the apparent conflict between the experimental evidence of metallic behaviour and bulk superconductivity in the samples at maximum H loading (H_2TiSe_2) with the theoretical prediction for that same stoichiometry not to exhibit metallic behavior at all. Indeed, the allowed structures for H_2TiSe_2 result in electronic bandstructures that are either pristine-like (see Supplementary Fig. 9b) or completely insulating (see Supplementary Fig. 9d) depending on the specific intercalation sites, whereas the superconducting phase is predicted for a significantly lower stoichiometry (H_1TiSe_2).

It is our opinion that the best option to reconcile these conflicting observations is to admit that phase separation occurs over: i) superconducting regions with H_1TiSe_2 stoichiometry, that fill at least 44% of the sample volume and that might (or might not) still exhibit vestigial traces of CDW order; ii) insulating regions with H_2TiSe_2 stoichiometry, with one H atom intercalated in the vdW gap and another one embedded within the $TiSe_2$ trilayer; iii) pristine-like regions rich in intercalated H_2 molecules; iv) residual, if any, pristine regions with little to no H intercalants.

We now further stress the importance played by the mixture of different intercalation configurations in the H-rich $TiSe_2$ compound by adding the following sentence to the revised Results (lines 215-223):

"The simultaneous observation of these multiple peaks is therefore evidence of a strong disorder in the H concentration, phase and distribution in the $TiSe_2$ matrix. In this case, the observation of consistent Raman spectra across different spots in the H_2TiSe_2 crystals could be interpreted as the phase separation between regions with different H concentration to occur over length scales smaller than the laser spot size (~ 1 μm)."

and to the Revised Discussion (lines 549-556):

"Still, vestigial traces of the charge-density wave ordering, observed even in H_2TiSe_2 – a stoichiometry unattainable via Li or Cu intercalation – hint at the coexistence of both phases in a wide doping range. This coexistence is likely enabled by the strongly disordered nature of the hydrogen-rich compound, which hosts a mixture of different phases with distinct electronic structures determined by the several possible hydrogen intercalation configurations."

8) In Fig. 2e, the temperature dependence of R_H shows that R_H become positive above T_CDW for lightly doped samples. Why? Maybe this is also consistent with the literatures. Maybe the authors can repeat the already known interpretation, which will be very helpful for readers' understanding.

We thank the Reviewer for the comment. Indeed, the sign change in the Hall coefficient of $TiSe_2$ in correspondence of the CDW transition temperature is well documented in the literature, and is caused by the opening of a partial gap on the Fermi surface due to the onset of CDW order. In turn, the opening of this partial gap makes it so that the character of the dominant charge carriers evolves from being holonic above T_{CDW} (with a positive Hall coefficient), to electronic below it (with a negative Hall coefficient). Introducing electron dopants in the system obviously suppresses this sign change, since it promotes electronic quasiparticles to be dominant also above T_{CDW}.

We clarify this point in the revised manuscript by adding the following sentence to the Main Text (lines 271-279):

"In agreement with the established literature [33,35,36,53], pristine $TiSe_2$ exhibits both a strong CDW peak in $\rho(T)$ (black curve in Fig. 2d, $I_{CDW} \approx 0.9$) and a change of sign in R_H around $T \approx 215\,K$ (black curve in Fig. 2e). This occurs when the onset of CDW order opens a gap at the Fermi level in part of the band structure, causing a reconstruction in the Fermi surface which changes the dominant character of the charge carriers from holonic for $T \gtrsim T_{CDW}$ to electronic for $T \lesssim T_{CDW}$ [33,35,36,53]."

9) In H2TiSe2, what is the ratio of the electron density from The Hall measurement and the hydrogen density? I guess the ratio should be extremely small. Why doesn't proton supply full carriers?

We thank the Reviewer for highlighting this very interesting point. In our interpretation, a first reason as to why the electron doping is not efficient is that large amounts of H dopants are incorporated in intercalation sites which do not supply free charge carriers to the system. This interpretation was already discussed in the Results section of the original manuscript (lines 480-490):

"...a further increase in doping level, to the concentration determined in fully-doped H_xTiSe_2 samples by NMR ($x \approx 2$), leads to the emergence of two possible phases. One is characterized by the formation of H_2 molecules in the van der Waals gap and a band structure akin to that of intrinsic 1T-$TiSe_2$ (Supplementary Fig. 9b). The other is an insulating phase, achieved when the stoichiometry is exactly 2 H atoms per unit cell (Supplementary Fig. 9c). The actual H_xTiSe_2 samples are likely to be characterized by a strong disorder in the distribution of H atoms, and will thus exhibit a mixture of different single phases..."

A more subtle but equally crucial ingredient in explaining the mismatch may be gleaned from the

temperature dependence of the Hall coefficient shown in Fig. 2e. Even in the sample at maximum H loading, characterized by a very low intensity of the CDW anomaly in the resistivity ($I_{CDW} \approx 0.016$), the Hall coefficient is strongly temperature dependent and its magnitude decreases by about ten times as the temperature is raised from 4 K to 300 K. Since the Hall density increases by the same factor, one obtains a ten-fold increase in the electron doping efficiency per H atom, from ≈ 1.7% at 4 K to ≈ 17% at 300 K. Pinpoiting the origin of this temperature dependence is not trivial, but we can tentatively ascribe it to two main factors: i) the significant structural disorder – evidenced by X-ray diffraction measurements – may act as a source of trap states, effectively freezing out a subset of the free charge carriers donated by the H intercalants; ii) if a weakened CDW order still exists in the samples at maximum H loading, as independently suggested by the small but finite intensity of the resistivity anomaly and – most relevantly – by the temperature dependence of the NMR ^{1}H spin-lattice relaxation rate, it could still be able to partially gap the doped Fermi surface, thereby reducing the density of free carriers as the temperature is reduced below T_{CDW}.

We have added the following sentences to the Results section of the revised Main Text (lines 284-302) to discuss the strong temperature dependence of the Hall coefficient in the $TiSe_2$ sample at maximum H loading:

"H_2TiSe_2 alone (red curve in Fig. 2d,e) exhibits no sign change in R_H up to ∼ 300 K, and a CDW peak in $\rho(T)$ reduced to a slope change ($I_{CDW} \approx 0.016$). However, the Hall coefficient remains strongly T-dependent, resulting in a tenfold reduction in n_H as the sample is cooled from 300 K to 4 K. This freeze-out of the free charge carriers can be ascribed to the presence of trap states introduced by structural disorder, but could also be assisted by a residual partial gapping of the Fermi surface if a weakened CDW order survives in the H-rich regions. The absence of a sign change in R_H could indicate either that the CDW gap still opens around ∼ 200 K in H_2TiSe_2 but is partially shifted below the Fermi level by the increasing electron doping (similar to the case of Cu_xTiSe_2 [50, 51]), or that the disorder introduced by the H intercalation suppresses long-range CDW order in the H-rich regions and allows only short-range CDW order to survive (as in the case of irradiated $NbSe_2$ [52]). A combination of the two effects is of course also possible."

These are my comments and questions that came to my mind. Without the authors' additional explanation, I am not able to recommend this paper published in Comms. Phys.

We hope that, after having addressed their questions and concerns, the Reviewer will now consider our manuscript to be suitable for publication in Communications Physics.

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

I read through the revised manuscript and the response letter. The authors fully addressed my comments. I thus recommend its publication.

Reviewer #2 (Remarks to the Author):

The authors have addressed all my concerns. Now I agree with the publication of the manuscript.

Reviewer #3 (Remarks to the Author):

I think the authors fully addressed my concerns raised in the previous report. I recommend this paper published in Communications Physics.