nature portfolio

Peer Review File

Hund's coupling mediated multi-channel quantum phase transition of a single magnetic impurity in Fe(Se,Te)

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

Uldemolins et al. reported an STM study on the quantum phase transition of the YSR state on excess Fe impurities on Fe(Se,Te) superconducting surface. They discovered multiple YSR related peaks on Fe impurities with NDC, one of which moves across zero energy during tip approach while the others switch asymmetry without crossing zero energy. They formulated a theoretical model considering the Hund's coupling between two spin orbitals, attempting to explain such a phenomenon qualitatively. Their scientific method seems sound, and their observation is potentially interesting for specific audience.

Nevertheless, there are several major scientific issues both on the experimental and theoretical side which need to be properly addressed before this manuscript can be deemed suitable for publication anywhere. In addition, the paper is, in my view, only a small scientific increment regarding the quantum phase transition with limited broad interest. Moreover, the scientific writing (for example, how to place the current research in the context of previous studies) further diminishes the significance of the results. Consequently, I regrettably suggest rejection from Nature Comm, with detailed reasoning listed below:

Specific scientific questions and comments:

1. The general discussion of YSR states and how the current research is placed in the context of previous research are generally confusing and sometimes inappropriate. For example, in line 24-39, the logic for the main message is very confusing. The authors try to build up their arguments on the problem of the classical YSR model (which is well known and people already know the solution for long), then acknowledging the existence of a better model which is the Kondo/AIM with quantum spin, then going back saying that "these works did not invalidate the applicability of the YSR paradigm" which is incorrect (the universal scaling between YSR energy and Kondo temperature is exactly the crucial evidence of Kondo/AIM model and the breakdown of the classical YSR model), then implying that they can improve somehow (their model is just extending classical YSR model to two channels including a Hund's term between channels, it is not a fundamentally new paradigm). The authors keep comparing with the classical YSR and in line 253, they

claimed "where the YSR model fails", which is nothing new. Wherever the authors want to submit the paper to next, they should reformulate these discussions thoroughly to be scientifically precise and add more solid reasoning why their work is important at all.

2. The model the authors proposed is very suspicious to me because according to the authors themselves in the SI, "the lowest-lying excitation does not need to cross zero-bias energy at the transition" according to their model while experimentally they see "all examples show the crossing". They deliberately chose very special parameters to show consistency with the experiment (i.e. crossing of the lowest energy YSR peaks) in the main text, while Fig. S2 certainly raises many questions to the validity of the model because it gives so many unseen features compared to the experiment.

3. The authors assume that the QPT upon tip approach is due to the electric field effect on the impurity level rather than the more common belief of change of impurity substrate coupling \Gamma due to atomic forces. They never discuss how they rule out the change of \Gamma during tip approach (atomic force do exist for both molecule and atoms). Importantly, if it were due to electric field, then different YSR peaks will move very differently because they are measured at very different bias voltages (some close to 0, some close to 1mV, which results in different electric fields of several orders of magnitude apart), which is not observed in the experiment. Therefore, I suggest the authors to reconsider their choice of mechanism.

4. As for the NDC, have the authors considered the possibility of their tip already picking up some superconductor from the surface and being effectively (partially) superconducting? That would explain the NDC as well as the seemingly larger measured spectroscopy gap (which is around 2\Delta=4mV) compared with Ref. 23 (which is around 2\Delta=3mV) and Ref. 24 (which seems even smaller), and possibly also the multiple peaks observed in contrast to the earlier reported single peaks if the tip is only partially superconducting. Before a serious discussion about NDC, the authors should rule out this possibility with sufficient evidence. Can the authors give a value of the superconducting gap parameter and discuss its comparison with the previous reported values?

Some minor points:

4. line 14: it should be quasiparticle rather than electron which is gained or lost in superconductors

5. The choice of colorbar in Fig. 2 is confusing. Low is red and high is blue/purple, which is kind of counterintuitive.

6. Caption of figure 1: "setup resistance=100 MOhm" sounds confusing. The authors should derive and show the junction resistance or conductance instead.

Based on the above issues, I cannot recommend publication of the manuscript in its present form.

Reviewer #2 (Remarks to the Author):

REPORT ON “INTERACTION DRIVEN QUANTUM PHASE TRANSITION OF A SINGLE MAGNETIC IMPURITY IN Fe(Se, Te)” BY M. ULDEMOLINS ET AL.

The authors of this manuscript report a combined experimental and theoretical study of the tunneling spectra of excess Fe impurities on the Fe(Se,Te) superconductor. The spectra are acquired using a normal tip, and besides the existence of subgap excitations, one of which crosses zero bias, they also report the interesting observation of negative differential conductance (NDC) in spectra taken on top of the impurities at high (tunneling) junction resistance. These experimental observations are compared to the predictions of a minimal two-channel two-orbital Anderson impurity model in which the channels are treated in a zero bandwidth approximation. Some predictions extracted from this model appear to be in reasonable agreement with the experimental observations (see below). However, I find derivation of NDC from the model lacks much rigor and clarity. In my opinion, this fact and together with the way the results are presented (see below) undermine the broad interest of the work and make it more suitable for a more specialized publication.

1) The model proposed by the authors (Eqs. 4 to 8 in “Methods”) is able to account for the observation of 1) the switch in the intensity of the lowest in-gap states peaks from hole-like to particle like as soon as the lowest peak crosses zero bias 2) the discontinuity in the slope of the peak that crosses zero bias.

Intuitively I would agree that the switch in the intensity is caused by turning on some kind of a particle-hole symmetry-breaking perturbation which is controlled by the electric field of the STM tip. The derivation and explanation of the above two predictions from the Anderson model is relatively easy to follow. However, I have serious concerns about the way the authors explain the NDC observed in some of the spectra taken at large junction resistance.

In this regard, the mapping to the minimal interacting two-level model that is discussed in the supplementary information (SI) appears to be rather non-rigorous and obscure. The level of rigor in this part of the manuscript (besides being "hidden" in the SI) is not comparable to the rest of the work. And I fear that the ultimate reason for this is that there is no reasonable way to derive this result from a reasonable extension of the impurity model introduced in Eqs. 4 to 8 of the section on "Methods".

Furthermore, it is pointed out at various points by the authors that the NDC results from the asymmetry in the couplings (more on this below), but if one reads the assumptions made in Refs. 25 by Thielmann et al., another important requirement is a rapid relaxation rate from the excited states. The authors say nothing about how this is implemented in their calculations, presumably because they rely on some Lindblad equations for the model coupled to reservoirs that are never written down explicitly and whose solution is obtained using what I should call a "black box", namely the software package QmemQ 1.0. Therefore, it appears as if the interacting two-level model is just a poorly justified model that displays NDC as it is designed within the specifications of Ref. 25.

Regarding the justification of the key assumption of asymmetry in the couplings T_{1S}, T_{2S}, etc. The authors emphasize at various points in the SI that these

couplings are not to be understood as the couplings of the impurity orbitals to the substrate and tip. However, in order to justify their asymmetry, they invoke the symmetry properties of the impurity orbitals. This is justified by citing Ref. 2 and 3 in the SI, mentioning that the symmetry of the bound state wave function is the same as that of the impurity orbital. However, to be fully consistent the "bound state" is not a single particle state (as a solution to the BdG equations in the YSR paradigm) but it describes a transition between two complex many body states of different parity which can be approximated by the eigenstates of the model Hamiltonian introduced in the main text, section "Methods".

Thus, it is unclear how such complex many-body states inherit same symmetry properties as the impurity orbitals.

2) Another point of concern is that for such multichannel impurity model the authors provide no discussion of the single-ion anisotropy, which I believe should not be small in this system. If included in their model, could it at least account for the additional in-gap states?

Furthermore, the authors mention near the end that a multi-channel model of a high-spin impurity would be too fine tuned to explain the spectra, but could the authors show it explicitly? What would happen if the electric field of the tip were to tune D from positive to negative, for instance?

3) The abstract and introduction are misleading, contradictory and contain statements that misrepresent and/or ignore previous work:

In their effort to emphasize their own contribution, the discussion of the what the authors call the “YSR paradigm” mixes two different approximations: One is the approximation first used by Yu, Shiba, and Rusinov, which replaces the impurity spin operator by a classical vector. The other one is the assumption that the quantum impurity is the so-called “Kondo regime” and therefore the charge fluctuations can be neglected. The first approximation implies the second, but the second by itself does not conventionally fit into the “YSR paradigm” and the spin can be treated quantum mechanically.

The impurity model proposed by the authors does require to go beyond these two approximations, but I believe that an honest discussion of the ways in which it goes beyond the YSR paradigm is obscured by the authors’ desire to claim novelty.

In connection to this, it is interesting to notice the way Ref. 21 (von Oppen and Franke, Phys. Rev. B 103, 205424) is cited in the introduction using the sentence “Yet, these systems were interpreted by adding up several independent classical YSR channels [21]”. However, a careful reading of Ref. 21 reveals that it indeed provides a fully quantum

mechanical treatment of large-S impurities with single-ion anisotropy coupled to several channels in the Kondo regime. Surprisingly, near the end of the main text of the manuscript, the authors contradict themselves and cite Ref. 21 again (third paragraph before the section “Methods” beginning as “Despite the inability…”) providing a more accurate characterization of this work as dealign with “higher-spin quantum” impurities.

In the introduction the authors also use sentences such like “Only recently… “ but most of the works they cite (12-14) are rather old (the newest one, Ref. 13 is from 2011). Nevertheless, in addition to Ref. 21, there have been a few works going beyond the YSR paradigm in the STM and in the mesoscopic literature, which the authors failed to cite. These works describe analytical treatments of quantum impurities going beyond the standard “YSR paradigm”. Below I provide a non-exhaustive list, which I strongly urge the authors to read and properly cite:

Some early papers going beyond the “YSR paradigm”

1) A. V. Rozhkov and Daniel P. Arovas, Phys. Rev. B 62 6687 (2000)

(See section on the large \Delta limit for an effective single site model of the Anderson model coupled to superconducting leads)

2) E. Vecino, A. Martín-Rodero, and A. LevyYeyati, Phys. Rev. B 68, 035105 (2003).

Incidentally, this article is probably the first to have used the zero bandwidth approximation for the single-impurity Anderson model coupled to superconductor(s) as used by the authors of this manuscript.

Some additional recent works employing analytical approaches going beyond the standard “YSR paradigm”

3) G. Kirsanskas,M. Goldstein, K. Flensberg, L. I. Glazman, and J. Paaske, Phys. Rev. B 92, 235422 (2015)

4) J. A. Andrade and A. M. Lobos, Phys. Rev. B 99, 054508 (2019).

5) E. Liebhaber, L. M. Rütten, G. Reecht, J. F. Steiner, S. Rohlf, K. Rossnagel, F. von Oppen, K. J. Franke, Nat. Comm. 13, 2160 (2022)

Finally, some papers where the “parity breaking” transition has been described using approaches that go beyond the “YSR paradigm¨

6) E. H. Lee, X. Jiang, M. Houzet, R. Aguado, C. M. Lieber, and S. de Franceschi, Nature Nanotech., 9 79-84 (2014)

7) S. Trivini, J. Ortuzar, K. Vaxevani, J. Li, F. S. Bergeret, M. A. Cazalilla, J. I. Pascual, Phys. Rev. Lett. 130 136004 (2023).

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4) As pointed out above, from the discussion provided by the authors below Eq. 1, It seems that the position of the tip, which controls the electric field acting on an excess Fe impurity, modifies the degree of particle-hole asymmetry. In the model, this is described by the average orbital energy (denoted by \bar{\epsilon} in Fig. 3). Strictly speaking, this is not an interaction parameter but single-particle potential. Thus, I find it misleading that the title contains the words “Interaction-driven…”. By using “Interaction-driven” is it suggested that the main effect of tip electric field is to control other interaction parameters such as Hubbard U or the Hund’s coupling J? This does not appear to be the case.

OTHER ISSUES:

1) In the abstract: “Parity Breaking” is rather unclear. Do the authors refer to spontaneous symmetry breaking? A clarification of why “breaking” is used would be welcome.

2) Could the experimental plots shown in e.g. Fig. 2 display the experimentally determined position of the superconducting gap?

3) To make reading easier, could the authors show the simulated in-gap LDOS shown in Fig. 3d side by side with the experimental spectra from Fig. 2?

4) I could not find a accurate estimate of the fraction of measured impurities that display NDC at large junction bias. On page 2, it is stated “a large fraction” but what is roughly the percentage of the probed 100 impurities?

5) Connected to this last question, is there a way to estimate some of the model parameters by comparing the spectra of different impurities? Wouldn’t the local environment affect the particle-hole symmetry-breaking terms in the Hamiltonian and drive some of these impurities sufficiently far from the mixed-valent regime so that no QPT can observed?

Reviewer #3 (Remarks to the Author):

Uldemolins et al. find evidence for intra-atomic electronic interactions reflected in the sub-gap excitations of magnetic excess Fe atoms on $Fe_{1+x}Se_{0.45}Te_{0.55}$. This is a very interesting finding, highlights the need for a theoretically advanced description of sub-gap states in superconductors and broadens our understanding of these systems. The study is timely, well done, and I would be happy to recommend publication after the authors have commented on my questions below:

- Please enhance the visibility of the substrate spectrum in Fig. 1b, I barely recognized it. Moreover: why is the conductance on the substrate finite all the way down to ±1meV even though the authors state that they "observe a fully gapped superconducting spectrum in between the impurities"? Is there a spatial structure to this sub-gap conductance?

- Previous results on sub-gap excitations in more conventional superconductors have found a clear correspondence between the d-orbital spatial structure of transition metal atoms and the sub-gap states' distribution (e.g. Refs. 18 & 27). Did the authors map the spatial distribution of their sub-gap states in the low-conductance regime? It would be interesting to see if the same similarities can be found. Would we expect to see d-orbital shapes like in these references for arbitrary ratios of JH vs. U or does this correspondence eventually break down for large JH?

- As the authors state, a simpler YSR description of multiple non-interacting classical channels has been applied successfully in previous studies. Can they comment a little more on why this description worked so well and what are the implications of their findings on the interpretation of previous works?

- I'm wondering if the relative intensity of the orbitals the tip is tunneling into could be changing with tip-sample distance. Then, new sub-gap peaks would rise in intensity while others would be suppressed. Can we tell from the data that this is not the case, e.g. by more clearly tracking the evolution of peak pairs through the phase transition? Showing additional examples in the SI might help.

- In Ruby et al., PRL 115, 087001 (2015), the authors observed an inversion of the relative sub-gap peak heights with junction conductance and interpreted it as an effect of different tunneling channels. Why can't this be the case here?

- On p. 7, line 169 the authors state that the mechanism tuning the sub-gap peaks in this experiment is related to the electric field in the junction but not to a tip-induced modification in the Fe-substrate coupling. Is there experimental evidence for this assumption?

- The observation of NDC at 100MΩ is interesting indeed. I remember that NDC has been observed in various systems just because of a bad (i.e. not well calibrated) STM tip. Did the authors see this effect with different tips? Did they calibrate the spectroscopic quality of their tips on another material like Au(111) or Cu(111)?

- The color schemes of the plots in Figs. 2b-e are highly nonlinear, especially for very high dI/dV values, and I would recommend choosing another one for clarity. At the very least, it

would be good to mark the color of zero conductance (instead of labeling dI/dV as “high/low”), which would make it much easier to visualize the NDC and its disappearance.

- Please provide some more information about the influence of a third orbital in the SI. So far it is only briefly mentioned on p. 7, line 186 but it sounds interesting.

- I am confused by the way that Ref. 21 is cited on p. 2, line 53 as being on independent classical channels, but on p. 9, line 231, it is referenced for the quantum case. I also feel like other references - including experimental ones - might be more suitable to make that point on line 53.

- The authors state on p. 3 that they studied up to 100 Fe atoms. It would be good if they could provide a few more examples of the conductance-dependent data on multiple atoms measured with multiple tips in the SI to prove the reproducibility of their results.

- Seeing some statistics on sub-gap states of various Fe atoms would also be interesting in terms of the claimed topological nature of Fe excess atoms on FeSe0.45Te0.55 (e.g. Nat. Comm. 12, 1348 (2021), Sci. Adv. 6, eaax7547(2020) or Nat. Phys. 11, 543–546 (2015)). Since this topic has been heavily debated recently: can the authors comment on a comparison between their results and the published data claiming a topological origin of low-energy sub-gap peaks in this material?

REVIEWER COMMENTS

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1. The general discussion of YSR states and how the current research is placed in the context of previous research are generally confusing and sometimes inappropriate. For example, in line 24-39, the logic for the main message is very confusing. The authors try to build up their arguments on the problem of the classical YSR model (which is well known and people already know the solution for long), then acknowledging the existence of a better model which is the Kondo/AIM with quantum spin, then going back saying that "these works did not invalidate the applicability of the YSR paradigm" which is incorrect (the universal scaling between YSR energy and Kondo temperature is exactly the crucial evidence of Kondo/AIM model and the breakdown of the classical YSR model), then implying that they can improve somehow (their model is just extending classical YSR model to two channels including a Hund's term between channels, it is not a fundamentally new paradigm). The authors keep comparing with the classical YSR and in line 253, they claimed "where the YSR model fails", which is nothing new. Wherever the authors want to submit the paper to next, they should reformulate these discussions thoroughly to be scientifically precise and add more solid reasoning why their work is important at all.

We thank the Reviewer for their careful reading. In view of the comments by all reviewers, we have completely rewritten the introduction of our manuscript and significantly modified the abstract: both aiming to more clearly state the significance and novelty of our findings, as well as to avoid confusion. We now focus more on our data which show a quantum phase transition involving several states (and therefore multiple orbitals) and the presence of interactions between them, i.e. Hund's coupling. To the best of our knowledge, this has not been observed before in STS experiments. We also emphasize that such a quantum phase transition involves a higher spin transition in contrast to the usual spin-1/2 transition where the single YSR state is either empty or filled with a quasiparticle.

2. The model the authors proposed is very suspicious to me because according to the authors themselves in the SI, "the lowest-lying excitation does not need to cross zero-bias energy at the transition" according to their model while experimentally they see "all examples show the crossing". They deliberately chose very special parameters to show consistency with the experiment (i.e. crossing

of the lowest energy YSR peaks) in the main text, while Fig. S2 certainly raises many questions to the validity of the model because it gives so many unseen features compared to the experiment.

The Reviewer is right to point out that there exists a range of parameters for which the model exhibits a phenomenology that is not observed experimentally. We show, however, that the degree of tuning is minimal, as there exists a large and physically-reasonable region in parameter space that describes the observed phenomenology, namely, the concurrent polarity flip with a zero-bias crossing within experimental resolution. Supplementary Note 1 details the parameter ranges. Given that all analysed impurities have the same nature (surface excess iron atoms), it is expected that they are described by sets of parameters that are close to each other in parameter space, and therefore it is not surprising that all impurities exhibiting a transition show an analogous behaviour (as it happens, an apparent crossing).

Further, we emphasize that a key property of the model is that the QPT involves a level crossing between two many-body states that are not connected by a single-particle excitation. While this implies that the QPT may occur without a zero-bias crossing of a single-particle excitation for a certain choice of parameters, it does imply as well that the slope of the single-particle excitation is discontinuous as the driving parameter varies across the QPT. This feature is observed in all the impurities we measured that undergo the QPT (see Supplementary Note 1).

We present these arguments in the revised manuscript.

3. The authors assume that the QPT upon tip approach is due to the electric field effect on the impurity level rather than the more common belief of change of impurity substrate coupling \Gamma due to atomic forces. They never discuss how they rule out the change of \Gamma during tip approach (atomic force do exist for both molecule and atoms). Importantly, if it were due to electric field, then different YSR peaks will move very differently because they are measured at very different bias voltages (some close to 0, some close to 1mV, which results in different electric fields of several orders of magnitude apart), which is not observed in the experiment. Therefore, I suggest the authors to reconsider their choice of mechanism.

We thank the Reviewer for pointing out the need for clarification on this subject, for which we both strengthen the arguments about the electric field effect and perform new calculations with varying Γ.

Indeed, quantum phase transitions in literature have been established by tuning the impurity-substrate coupling using the atomic force between tip and impurity. Specifically, MnPc molecules were used, which are relatively large objects that are deposited on top of the surface. In our case, however, such tuning is less likely to be important. First of all, the excess Fe impurities we focus on are relatively strongly bound to the substrate: unlike MnPc we cannot push them around or pick them up with the tip. Secondly, for subsurface impurities in Fe(Se,Te), where the force between the tip and impurity is even smaller, sub-gap states have been seen to shift with tip-sample distance (see Ref. 22). Therefore, as put forth in Ref. 22, a tip gating effect is more likely causing the level shifts. Importantly, the energy scale of such gating is very different to the scale of the measurements. Similar to band-bending in semiconductors, the gating depends on the relative work functions, which are in the eV range - orders of magnitude larger than the voltage variations in our measurements. Changing the tip-sample distance in this case will thus to a good approximation shift all levels equally, hence $\bar{\varepsilon}$ is the key driving parameter. We present these arguments in the Supplementary Note 4.

To fully address the modelling of the driving mechanism, in Supplementary Note 5 we present new calculations (Fig. S10) in which the impurity levels (and hence $\bar{\varepsilon}$) are fixed, while instead we drive the impurity-substrate coupling Γ. The MCQPT phenomenology is fully exhibited in this scenario too. The

physical reason is that in our model the impurity is in the mixed-valence regime, and the charge fluctuations can be driven through the MCQPT either by $\bar{\varepsilon}$ or by Γ. The key role is played by the Hund's coupling, which ties together the occupation and spin changes of the two orbitals through the MCQPT.

We note that both in the added Fig. S10 and in main text Fig. 3d,e and Fig. S2 we use the same slightly modified colour scale (with respect to the initial submission), following feedback regarding the poor visibility of faint features (in particular, the bottom-right section of Fig. 3d).

4. As for the NDC, have the authors considered the possibility of their tip already picking up some superconductor from the surface and being effectively (partially) superconducting? That would explain the NDC as well as the seemingly larger measured spectroscopy gap (which is around 2\Delta=4mV) compared with Ref. 23 (which is around 2\Delta=3mV) and Ref. 24 (which seems even smaller), and possibly also the multiple peaks observed in contrast to the earlier reported single peaks if the tip is only partially superconducting. Before a serious discussion about NDC, the authors should rule out this possibility with sufficient evidence. Can the authors give a value of the superconducting gap parameter and discuss its comparison with the previous reported values?

Indeed, NDC is readily observed with a superconducting tip. This is because instead of a flat tip DOS, the superconducting coherence peaks of the tip act as filter leading to a strong increase in the current upon aligning one of the coherence peaks with a sub-gap state, and subsequent drop in current upon passing the sub-gap state.

However, we can rule out that our tip is superconducting. Firstly, a superconducting tip would lead to much sharper features in spectroscopy. We stress that our data are taken at 0.3K, whereas those of e.g. Ref. 5 were taken at 1.1K: with a superconducting tip our resonances would have been near delta peaks (assuming the intrinsic lifetime of the states is much less than kT, as is typically the case). Secondly, a superconducting tip leading to negative differential conductance would need to have coherence peaks and thus a non-zero gap. In this case one would never observe a zero crossing of a sub-gap state, as the superconducting gap of the tip will always be present. Additionally, NDC would be seen on all (sufficiently isolated) sub-gap states, and be particle-hole symmetric, both of which is not the case for us.

Regarding the position of the coherence peaks, we stress that there is a considerable spatial variation in peak-to-peak distance, and that there are multiple coherence peaks, as also detailed in Ref. 24. Our spectrum in Fig. 1 falls on the larger end of this variation.

We have added discussion of all these points to the Supplementary Note 4.

Some minor points:

4. line 14: it should be quasiparticle rather than electron which is gained or lost in superconductors

We have changed 'electron' to 'quasiparticle'.

5. The choice of colorbar in Fig. 2 is confusing. Low is red and high is blue/purple, which is kind of counterintuitive.

We acknowledge that the color scale is not the simplest. It is however a standard scale that in our view best highlights two important features at once, namely, the evolution of both the in-gap excitations and the NDC, which have different absolute magnitudes. We note that the scale more or less follows the colour pattern of a flame: red (low temperature) to blue (high temperature). We further refer the Reviewer to our answer to a related comment by Reviewer 3.

6. Caption of figure 1: "setup resistance=100 MOhm" sounds confusing. The authors should derive and show the junction resistance or conductance instead.

We are not sure what the Reviewer means. A tunnelling spectrum recorded with an STM is defined by the voltage and current at which the tip-sample distance is fixed: these two parameters define the setup resistance. The y-scale of each spectrum we present is furthermore in Siemens, which directly shows the dynamical conductance.

Based on the above issues, I cannot recommend publication of the manuscript in its present form.

We hope our replies and changes to the manuscript have changed the Reviewer's mind.

Reviewer #2 (Remarks to the Author):

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In this regard, the mapping to the minimal interacting two-level model that is discussed in the supplementary information (SI) appears to be rather non-rigorous and obscure. The level of rigor in this part of the manuscript (besides being "hidden" in the SI) is not comparable to the rest of the work. And I fear that the ultimate reason for this is that there is no reasonable way to derive this result from a reasonable extension of the impurity model introduced in Eqs. 4 to 8 of the section on "Methods".

Furthermore, it is pointed out at various points by the authors that the NDC results from the asymmetry in the couplings (more on this below), but if one reads the assumptions made in Refs. 25 by Thielmann et al., another important requirement is a rapid relaxation rate from the excited states. The authors say nothing about how this is implemented in their calculations, presumably because they rely on some Lindblad equations for the model coupled to reservoirs that are never written down explicitly and whose solution is obtained using what I should call a "black box", namely the software package QmemQ

1.0. Therefore, it appears as if the interacting two-level model is just a poorly justified model that displays NDC as it is designed within the specifications of Ref. 25.

Regarding the justification of the key assumption of asymmetry in the couplings T_{1S}, T_{2S}, etc. The authors emphasize at various points in the SI that these couplings are not to be understood as the couplings of the impurity orbitals to the substrate and tip. However, in order to justify their asymmetry, they invoke the symmetry properties of the impurity orbitals. This is justified by citing Ref. 2 and 3 in the SI, mentioning that the symmetry of the bound state wave function is the same as that of the impurity orbital. However, to be fully consistent the "bound state" is not a single particle state (as a solution to the BdG equations in the YSR paradigm) but it describes a transition between two complex many body states of different parity which can be approximated by the eigenstates of the model Hamiltonian introduced in the main text, section "Methods". Thus, it is unclear how such complex many-body states inherit same symmetry properties as the impurity orbitals.

We thank the Reviewer for their careful reading of the manuscript and insightful comments. As summarized by the Reviewer, the 2-orbital Anderson impurity model we use is able to account for the most salient spectroscopic features observed in the experiments and prove that the particle-to-hole spectral switch involves correlations (i.e. Hund's coupling) between orbitals. However, to account for NDC, we would need to incorporate the tip in the model and perform a transport calculation within this model. As the Reviewer certainly may have anticipated, a proper treatment, within the Keldysh formalism, would involve the calculation of the current in terms of the retarded and lesser impurity Green's function for the 2-orbital AIM connected to a superconducting lead and a normal lead (and the tunnelling matrix elements) and more importantly the numerical calculation of such Green's functions. Even with the numerical renormalization group (NRG), this is a highly non-trivial task and some approximation or Ansatz would be necessary. Even if possible, this kind of an approach is clearly beyond the scope of the present paper.

In view of these difficulties that we are fully aware of, we decided to opt for a different and more phenomenological strategy and a model which, we think, is reasonable. We have partially rewritten Supplementary Note 2 to clarify our phenomenological model and the underlying assumptions that justify it, as well as its relation with the model we used in the main text. The main assumptions are:

(i) the thermal broadening is larger than the intrinsic linewidth of the in-gap quasiparticle states, (ii) there is an interaction between the quasiparticle states and (iii) there is an asymmetry of the coupling between the tip and the in-gap quasiparticle states. The first two are experimentally justified (see the Supplementary Notes) while the last one is a relatively weak and reasonable assumption. We hope the rewriting of this Supplementary Note clarifies our approach to negative differential conductance.

2) Another point of concern is that for such multichannel impurity model the authors provide no discussion of the single-ion anisotropy, which I believe should not be small in this system. If included in their model, could it at least account for the additional in-gap states?

Furthermore, the authors mention near the end that a multi-channel model of a high-spin impurity would be too fine tuned to explain the spectra, but could the authors show it explicitly? What would happen if the electric field of the tip were to tune D from positive to negative, for instance?

We have considered the simplest model that captures the essential spectroscopic features shown in the data. Single ion-anisotropy may be certainly present in this system. However we think that the key ingredient is the inter-orbital interaction (Hund's coupling) which leads to the correlated transfer of spectral weight from the hole to the particle sector.

Concerning the second point of the Reviewer, we cannot exclude some alternative explanation. Again we chose the simplest ingredients to capture the salient experimental features. A model such as the one the Reviewer has in mind (i.e. à la Franke-von Oppen) would involve many more parameters and therefore demands more fine-tuning. Furthermore, we do not see how it could, and hence we doubt that it would, explain negative differential conductance. Therefore, we did not pursue such an alternative explanation. We would like to stress that the key result is that our relatively simple model is able to reproduce the experimental data.

3) The abstract and introduction are misleading, contradictory and contain statements that misrepresent and/or ignore previous work:

In their effort to emphasize their own contribution, the discussion of the what the authors call the "YSR paradigm" mixes two different approximations: One is the approximation first used by Yu, Shiba, and Rusinov, which replaces the impurity spin operator by a classical vector. The other one is the assumption that the quantum impurity is the so-called "Kondo regime" and therefore the charge fluctuations can be neglected. The first approximation implies the second, but the second by itself does not conventionally fit into the "YSR paradigm" and the spin can be treated quantum mechanically.

The impurity model proposed by the authors does require to go beyond these two approximations, but I believe that an honest discussion of the ways in which it goes beyond the YSR paradigm is obscured by the authors' desire to claim novelty.

We refer to our reply to a similar critique by Reviewer 1. We have completely rewritten the introduction of our manuscript and significantly modified the abstract in order to more clearly state the significance and novelty of our findings, as well as to avoid confusion.

In connection to this, it is interesting to notice the way Ref. 21 (von Oppen and Franke, Phys. Rev. B 103, 205424) is cited in the introduction using the sentence "Yet, these systems were interpreted by adding up several independent classical YSR channels [21]". However, a careful reading of Ref. 21 reveals that it indeed provides a fully quantum mechanical treatment of large-S impurities with single-ion anisotropy coupled to several channels in the Kondo regime. Surprisingly, near the end of the main text of the manuscript, the authors contradict themselves and cite Ref. 21 again (third paragraph before the section "Methods" beginning as "Despite the inability…") providing a more accurate characterization of this work as dealign with "higher-spin quantum" impurities.

We thank the Reviewer for pointing out this issue, which was also pointed out by Reviewer 3. Our new introduction no longer discusses different models in detail as we decided, based on the comments of all Reviewers, that a more experimental motivation to our findings would be more suitable to highlight the significance and novelty of our work. This also solves the citing of Ref. 21.

In the introduction the authors also use sentences such like "Only recently… " but most of the works they cite (12-14) are rather old (the newest one, Ref. 13 is from 2011). Nevertheless, in addition to Ref. 21, there have been a few works going beyond the YSR paradigm in the STM and in the mesoscopic literature, which the authors failed to cite. These works describe analytical treatments of quantum impurities going beyond the standard "YSR paradigm". Below I provide a non-exhaustive list, which I strongly urge the authors to read and properly cite:

Some early papers going beyond the "YSR paradigm"

1) A. V. Rozhkov and Daniel P. Arovas, Phys. Rev. B 62 6687 (2000)

(See section on the large \Delta limit for an effective single site model of the Anderson model coupled to superconducting leads)

2) E. Vecino, A. Martín-Rodero, and A. LevyYeyati, Phys. Rev. B 68, 035105 (2003).

Incidentally, this article is probably the first to have used the zero bandwidth approximation for the single-impurity Anderson model coupled to superconductor(s) as used by the authors of this manuscript.

Some additional recent works employing analytical approaches going beyond the standard "YSR paradigm"

3) G. Kirsanskas, M. Goldstein, K. Flensberg, L. I. Glazman, and J. Paaske, Phys. Rev. B 92, 235422 (2015)

4) J. A. Andrade and A. M. Lobos, Phys. Rev. B 99, 054508 (2019).

5) E. Liebhaber, L. M. Rütten, G. Reecht, J. F. Steiner, S. Rohlf, K. Rossnagel, F. von Oppen, K. J. Franke, Nat. Comm. 13, 2160 (2022)

Finally, some papers where the "parity breaking" transition has been described using approaches that go beyond the "YSR paradigm¨

6) E. H. Lee, X. Jiang, M. Houzet, R. Aguado, C. M. Lieber, and S. de Franceschi, Nature Nanotech., 9 79-84 (2014)

7) S. Trivini, J. Ortuzar, K. Vaxevani, J. Li, F. S. Bergeret, M. A. Cazalilla, J. I. Pascual, Phys. Rev. Lett. 130 136004 (2023).

Following the valuable criticisms of the Reviewer, which are also corroborated by the ones of Reviewer 1, we have decided to fully rewrite the abstract and introduction of our manuscript. We have also tried to improve where and how we cite previous works, and how these works relate to our findings, aiming to alleviate ambiguities and/or inconsistencies. In this process, we have added new references including some of the ones that were suggested by the Reviewer.

4) As pointed out above, from the discussion provided by the authors below Eq. 1, It seems that the position of the tip, which controls the electric field acting on an excess Fe impurity, modifies the degree of particle-hole asymmetry. In the model, this is described by the average orbital energy (denoted by \bar{\epsilon} in Fig. 3). Strictly speaking, this is not an interaction parameter but single-particle potential. Thus, I find it misleading that the title contains the words "Interaction-driven…". By using "Interaction-driven" is it suggested that the main effect of tip electric field is to control other interaction parameters such as Hubbard U or the Hund's coupling J? This does not appear to be the case.

We agree with the Reviewer that our title was not sufficiently clear. We have decided to changed the title to "Hund's coupling mediated multi-channel quantum phase transition in Fe(Se,Te)", which more clearly states which interaction is crucial for our observed phenomenology, and it's role.

OTHER ISSUES:

1) In the abstract: "Parity Breaking" is rather unclear. Do the authors refer to spontaneous symmetry breaking? A clarification of why "breaking" is used would be welcome.

We agree with the Reviewer that the word "breaking" is unclear. We should have used "parity changing" (i.e. from S to S-1/2) and have resolved this issue in our modified manuscript.

2) Could the experimental plots shown in e.g. Fig. 2 display the experimentally determined position of the superconducting gap?

We now indicate the superconducting gap in Fig. 2.

3) To make reading easier, could the authors show the simulated in-gap LDOS shown in Fig. 3d side by side with the experimental spectra from Fig. 2?

We agree that having experimental and theoretical LDOS (Fig. 2e and Fig. 3d) side-by-side would perhaps make it easier to appreciate the correspondence between the two. However, we think that a separate figure for theory and experiment is warranted in this case: the experimental Fig. 2e can only be properly understood with Figs. 2a-d next to it. Similarly, Fig. 3d requires Figs. 3a-c to be understood. Combining everything into one figure would make it too cumbersome. Additionally, since the theory is not a fit to the data, but a minimal model describing the salient features of the experiment, and since the comparison between $J_H \gg \delta\bar{\varepsilon}$ (Fig. 3d) and $J_H = 0$ (Fig. 3e) is essential to have side-by-side, we chose (and prefer to keep) our initial arrangement of figures.

4) I could not find a accurate estimate of the fraction of measured impurities that display NDC at large junction bias. On page 2, it is stated “a large fraction” but what is roughly the percentage of the probed 100 impurities?

In the main text and Supplementary Note 4 we have added a rough estimate of the occurrence of NDC in our experiments, which we find to be well over 50% of impurities we have measured. Since the appearance of NDC depends on the junction resistance, it may actually be possible that all impurities have some regime where NDC occurs.

5) Connected to this last question, is there a way to estimate some of the model parameters by comparing the spectra of different impurities? Wouldn’t the local environment affect the particle-hole symmetry-breaking terms in the Hamiltonian and drive some of these impurities sufficiently far from the mixed-valent regime so that no QPT can observed?

This is an interesting point. It is true that we do not observe the QPT in some impurities, which are indeed likely far away from the mixed-valence regime. We have added a few examples in Fig. S9 for completeness. We agree that it would be nice to extract model parameter values directly from a measurement, but unfortunately we are not aware of methods by which our setup could do that, nor did we found a way to compare impurities to extract a quantity that would be reasonable to compare with our simple model. Perhaps it is worth mentioning that a rough theoretical estimate in Ref.8 indicates that electric-field induced changes of orbital energies in this material could be of order meV, which is consistent with our modelled parameter range.

Reviewer #3 (Remarks to the Author):

Uldemolins et al. find evidence for intra-atomic electronic interactions reflected in the sub-gap excitations of magnetic excess Fe atoms on Fe1+xSe0.45Te0.55. This is a very interesting finding, highlights the need for a theoretically advanced description of sub-gap states in superconductors and broadens our understanding of these systems. The study is timely, well done, and I would be happy to recommend publication after the authors have commented on my questions below:

We thank the Reviewer for their insightful comments and positive evaluation of our work.

- Please enhance the visibility of the substrate spectrum in Fig. 1b, I barely recognized it. Moreover: why is the conductance on the substrate finite all the way down to ±1meV even though the authors state that they "observe a fully gapped superconducting spectrum in between the impurities"? Is there a spatial structure to this sub-gap conductance?

We have adjusted the contrast of the substrate spectrum. It is true that there is a very small signal inside the gap. This is due to our finite concentration of excess Fe atoms and reflects remnant signal from nearby impurity states. We have modified the text to reflect that the sub-gap dI/dV is not perfectly zero.

- Previous results on sub-gap excitations in more conventional superconductors have found a clear correspondence between the d-orbital spatial structure of transition metal atoms and the sub-gap states' distribution (e.g. Refs. 18 & 27). Did the authors map the spatial distribution of their sub-gap states in the low-conductance regime? It would be interesting to see if the same similarities can be found. Would we expect to see d-orbital shapes like in these references for arbitrary ratios of JH vs. U or does this correspondence eventually break down for large JH?

The Reviewer raises an interesting point. Trying to identify the orbital character of the different states was one of the first things we did. Unfortunately, this proved impossible: unlike earlier work, our data show no clear orbital character, but are instead strongly varying as function of energy and position, and spatially asymmetric.

One of the reasons for this absence could be the spatially inhomogeneous character of Fe(Se,Te): there is a strong spatial variation in the superconducting gap, as well as Se/Te inhomogeneity, both of which may influence the spatially resolved sub-gap density of states. Another complicating factor is that the tuning of the sub-gap states by the tip depends on the location of the tip with respect to the impurity as e.g. Fig. 2b-d show. For most junction resistances this means that any possible orbital character in dI/dV will easily be obscured.

Additionally, interactions between the various levels may wash out or alter the orbital character. One clear example of inter-level interactions is the NDC, which, however, also does not have a clear orbital signature. Given the absence of a clear orbital character in our data, we have not studied this in more detail theoretically, but it may indeed be possible that J_H lifts the orbital character.

We now mention this in the Supplementary Note 2.

- As the authors state, a simpler YSR description of multiple non-interacting classical channels has been applied successfully in previous studies. Can they comment a little more on why this description worked so well and what are the implications of their findings on the interpretation of previous works?

Indeed, the simple YSR model seems to work well in most cases. The crucial point is that it cannot explain the quantum phase transition we observe. Away from the quantum phase transition, the two models we show (Fig. 3d and e) are rather similar in behaviour and either would have worked to describe the phenomenology. The underlying physics of the transition, however, is much richer than the simple YSR model suggests. In previous works, this may also have been the case, but the more complex physics would have likely been observed only upon tuning the system (i.e. the in-gap states) further than has been done to date - assuming these studies had enough energy resolution to distinguish multiple states and the amplitude of their electron and hole parts. We have tried to clarify this point in the revised manuscript.

- I'm wondering if the relative intensity of the orbitals the tip is tunneling into could be changing with tip-sample distance. Then, new sub-gap peaks would rise in intensity while others would be

suppressed. Can we tell from the data that this is not the case, e.g. by more clearly tracking the evolution of peak pairs through the phase transition? Showing additional examples in the SI might help.

The Reviewer raises an excellent point. We take that the essential question is: what happens to the relative intensities of the sub-gap states if there is no crossing – is this a smooth evolution, or can there be jumps in those cases as well? To address this question we have added Figure S9 to the Supplementary Note showing the junction resistance dependence for two excess Fe atoms where none of the levels cross. As these data show, there are nonzero changes in the amplitude of the peaks. These changes, however, are very gradual and never lead to a switch in intensity between polarities. Interestingly, particularly the NDC appears sensitive in Fig. S9, which is consistent with the notion that NDC occurs due to blocking by a weakly coupled level: for lower junction resistances the level will become more strongly coupled, lifting the NDC. We have added discussion of these points to the Supplementary Note 4.

- In Ruby et al., PRL 115, 087001 (2015), the authors observed an inversion of the relative sub-gap peak heights with junction conductance and interpreted it as an effect of different tunneling channels. Why can't this be the case here?

We thank the Reviewer for raising this point. Indeed, the Ruby et al. paper shows an interesting inversion of peak height with junction resistance, not dissimilar to what we observe. However, the underlying reason is their use of a superconducting tip. With a normal tip, the contribution of Andreev reflection increases upon decreasing the tip-sample distance, reducing the particle-hole asymmetry of the sub-gap peak heights of a single state. For pure Andreev reflection, both peaks will become identical in height. For a superconducting tip, though, the situation is different, in particular, Ruby et al. write: "Unlike for normal-metal tips [18,28], the Andreev contribution to the main peaks is asymmetric for a superconducting tip, but with the asymmetry reversed relative to single-electron tunnelling. ... Indeed, an inversion of the peak heights is seen in Fig. 3(a), as pointed out above." Since we have a normal tip (see also our reply to Reviewer 1), this scenario is not applicable. We now mention and discuss this point in the main text and Supplementary Note 4.

- On p. 7, line 169 the authors state that the mechanism tuning the sub-gap peaks in this experiment is related to the electric field in the junction but not to a tip-induced modification in the Fe-substrate coupling. Is there experimental evidence for this assumption?

We refer to our reply to Reviewer 1. We have added discussion of this point to the Supplementary Note.

- The observation of NDC at 100MΩ is interesting indeed. I remember that NDC has been observed in various systems just because of a bad (i.e. not well calibrated) STM tip. Did the authors see this effect with different tips? Did they calibrate the spectroscopic quality of their tips on another material like Au(111) or Cu(111)?

We would be very interested in reading more about the studies that the Reviewer mentions. We calibrate our tips before each measurement run on a Pt sample, but given the complexity of changing tips, we have not used different tips for this study. Without more information on the work the Reviewer refers to, we cannot argue in more detail on whether a 'bad' tip scenario is (un)likely for our case where only a subset of peaks shows NDC, which moreover can (reproducibly) appear or disappear as function of junction resistance.

- The color schemes of the plots in Figs. 2b-e are highly nonlinear, especially for very high dI/dV values, and I would recommend choosing another one for clarity. At the very least, it would be good to mark

the color of zero conductance (instead of labeling dI/dV as “high/low”), which would make it much easier to visualize the NDC and its disappearance.

Marking zero dI/dV on the colour scales is an excellent suggestion, which we implemented. To a reasonable approximation, the NDC in main text Fig. 2 is black, which was why we had chosen this colour scale. Given the relatively large variation in sub-gap peak amplitudes, it is rather difficult to find a scale that highlights both the switch of all peak intensities vividly, as well as the disappearance of negative differential conductance, hence the rather non-linear scale.

- Please provide some more information about the influence of a third orbital in the SI. So far it is only briefly mentioned on p. 7, line 186 but it sounds interesting.

We appreciate the Reviewer's interest in this point. By adding a third orbital *c* coupled to a scattering channel *C* in the superconductor the situation becomes more complicated, but the essence remains the same. In particular, for a similar set of parameters, upon varying the mean impurity energy level, the ground state of the system changes from |0,+,+,+> to |3/2,-,-,->, with three in-gap states that correspond to excitations into |1,-,-,+>, |1,-,+,->, and |1,+,-,->, where the third quantum number indicates the parity in channel *c*,*C*. As in the minimal scenario discussed in the text, the system evolves from a higher-occupation/small-spin state into a lower-occupation/high-spin state due to the effect of the Hund's coupling. This transition also manifests as a concurrent flip of the polarity of the in-gap states. We have included this analysis in the Supplementary Note 6.

- I am confused by the way that Ref. 21 is cited on p. 2, line 53 as being on independent classical channels, but on p. 9, line 231, it is referenced for the quantum case. I also feel like other references - including experimental ones - might be more suitable to make that point on line 53.

This issue was rightfully also pointed out by Reviewer 2. Our new introduction no longer discusses different models in detail as we decided, based on the comments of all Reviewers, that a more experimental motivation to our findings would be more suitable to highlight the significance and novelty of our work. This also solves the citing of Ref. 21.

- The authors state on p. 3 that they studied up to 100 Fe atoms. It would be good if they could provide a few more examples of the conductance-dependent data on multiple atoms measured with multiple tips in the SI to prove the reproducibility of their results.

We have taken (relatively simple) point spectra on close to 100 Fe atoms, a large portion of which have negative dI/dV. The detailed junction resistance dependence, however, is a much more complicated measurement as the atomic (xy) position needs to be identical throughout the measurement and several preparatory measurements need to be taken to find the most suitable location for an Rj dependent measurement. We have therefore done this type of measurement for only 8 impurities of which 4 had a zero crossing. Two of the four that cross zero energy are shown in Fig. S3, and one of the four that does not cross is shown in Fig. 1d. For completeness, we have added Figure S8 to the Supplementary Note 4 with the two additional Fe impurities with a zero crossing, which show the same characteristics as the other data where a zero crossing occurs. Additionally, we have added an overview of 18 different excess Fe sites as Figure S7 in Supplementary Note 4, showing the reproducibility of our observation of multiple in-gap states as well as negative differential conductance.

- Seeing some statistics on sub-gap states of various Fe atoms would also be interesting in terms of the claimed topological nature of Fe excess atoms on FeSe0.45Te0.55 (e.g. Nat. Comm. 12, 1348 (2021), Sci. Adv. 6, eaax7547(2020) or Nat. Phys. 11, 543–546 (2015)). Since this topic has been heavily debated

recently: can the authors comment on a comparison between their results and the published data claiming a topological origin of low-energy sub-gap peaks in this material?

This is a very good point. We chose not to stress this issue as it would distract from our main results, but among all our impurities, none show a state at zero bias that does not move off-zero with changing tip-sample distance. We therefore have no signatures in our data that requires us to invoke unconventional topology. We have added this point to the caption of the new Supplemental Figure S7 with point spectra of 18 different excess Fe atoms.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have made major revision to the original manuscript according to the suggestions from all referees and the current version has undoubtedly improved substantially. The rewritten introduction now is much more convincing and the validity of the alternative explanation of varying hybridization strengthens the argument a lot. I thank the authors for making substantial and valuable effort in improving the manuscript.

Nevertheless, my major concern still remains unfortunately, which is basically whether the model which the authors used can explain the phenomena they observed. In addition, the novelty of the QPT seems not enough to me for publication in Nat. Comm., and thus I could not recommend publication still, and I will elaborate in the following part.

The authors used a 2-orbital Anderson impurity model with inter-orbital coupling term, and as far as I understand, they solved the model on the mean-field level (otherwise NRG is necessary if correlation is fully incorporated).

1. About zero crossing: my original question was that the model does not predict any protected zero crossing, while in the experiment they always saw clear zero crossing. The authors then added a 2D plot to show the parameter space of approximate zero crossing within experimental resolution in Figure S1, which is very informative. However, firstly, the energy resolution should be around 3.5kB*T for metallic tip corresponding to about 120 uV for 0.4K, while the authors chose a much larger value \delta E = 1.5mV*0.13 ~ 200 uV such that the region looks much wider than it should be (also, the FWHM of the sharpest Shiba peak in Figure 2e seems to be around 0.13mV, consistent with my estimation rather than the over-estimation from the authors). In addition, as can be seen in Figure S7 in the supplementary material, the Fe atoms show a wide variety of YSR states on the surface, indicating that they are at various very different adsorption sites, which suggests that the parameters for the Anderson model for the actual experimental system span a wide range in the experiment. I am therefore not convinced that the experimental system is so lucky that it lies on the narrow window showing in Figure S1 (narrower than shown there). My

intuition is that their mean field model is too primitive to capture important physics, or there are some topological features special to the system important to the Shiba physics, which might change the interpretation completely.

2. About the jump of YSR peak heights across the QPT: across a conventional QPT, the peak heights of positive and negative voltage YSR peaks just switch with each other. In the case of MCQPT, the spectral weights jump, but in general the values will be all new (meaning that if the YSR peak heights are x1, x2, x3, x4 just before the MCQPT, the four peak heights just after the MCQPT would not be a simple shuffle of x1, x2, x3, x4. Also, for the peaks crossing zero, the height will not be continuous across zero). One can easily see that in Figure 3 (d,e). This is because vertical arrows connect different lines across MCQPT (Figure S2 (c,e), by the way, there are two panel c in this figure by mistake). The above is a natural result of the model proposed by the authors. I would suggest that the authors plot the YSR peak heights as a function of conductance for all datasets they showed and investigate whether this is consistent with their experimental observation.

3. About the YSR energy as a function of conductance: it seems that all YSR peaks move in parallel in Figure 2. Is this more consistent with the assumption of electric field gating effect rather than the changing hybridization effect shown in Figure S10a?

4. About the novelty: there have been so many papers about YSR across QPT upon tip approach for some time. This paper shows an interesting observation that only one pair of YSR peaks crosses zero while the others not and the system of Fe defect on iron-based superconductor is certainly interesting, but the model turns out quite trivial (nothing new, just straightforward mean field with a coupling between the two channels). Therefore, I find the paper more suitable for more specialized journals like PR series or Comm. Physics.

Reviewer #3 (Remarks to the Author):

I really appreciate the fact that the authors have put quite some effort in answering most of my questions and revising the manuscript. However, in some places I feel that their changes did not improve the work. For instance, the revised title makes it sound as if they found a phase transition of the entire material FST instead of a local impurity study. I would recommend revising this again. Some more comments:

- YSR states tunable with tip-sample distance have been observed in various systems. I'm not entirely getting the connection of these studies to this manuscript. Mostly, I got confused by the relation of this work to Ref. 8 (Nat. Commun. 8, 298 (2021)). They also observe multiple YSR states in the very same material, some of which are tunable across the QPT, but the higher-lying YSR states do not show a reversal in intensity (Fig. 3 of Ref. 8). What is the reason these two experiments are so different? Couldn't this mean that this mechanism isn't all that robust?

- The authors say that if their tip was superconducting, they would see much sharper features. That might be true for perfect bulk SC tips, but it can vary a lot when you just pick up some small clusters! In fact, I have even seen tips with imperfect SC gaps that made the actual energy resolution worse (because you're convoluting the LDOS with something that is not flat but not ultrasharp either). There should not be a zero-crossing with a perfect SC tip gap, but if the gap of a small cluster on the tip does not go to zero, you will get a mixture of SIS and SIN tunneling (I have seen this before). Also, the particle-hole symmetry can be very complex in these highly convoluted spectra. Thus, I am not fully convinced by that interpretation. How many different microtips did the authors use?

- Concerning their question on NDC with different STM tips: I can recommend the paper by Heinrich et al., PRL 107, 246801 (2011) and the references therein. Again: How many different microtips were used and showed the NDC? (to be clear: when I say microtips, I'm talking about minor tip modifications, e.g. on platinum, not to take the whole tip out of the STM)

- I think the question on magnetic anisotropy raised by Reviewer #2 is important. In their reply, the authors basically say that it should be relevant in this system, but the Hund's coupling is more relevant (without explaining why in great detail). Anisotropy is known to split the YSR peaks into multiplets (Hatter et al., Nat. Commun. 6, 8988 (2015)). Wouldn't that mean that if one peak crosses the QPT, the others will change as well since they are related to the same orbital?

- This is just a minor point and I don't want to get into arguments about basic stuff like this but: please really reconsider the color scale of Fig. 2. This point has been raised by multiple

reviewers and I think it’s solvable (maybe even by saturating some of the extremal data points), but it’s very hard to understand what’s going on this way. If it doesn’t work at all, maybe even consider replacing it by a waterfall plot like in Fig. 1.

Also in the light of the other two reviews (that raise some important questions), I cannot recommend publication until these points have been clarified.

Reviewer #4 (Remarks to the Author):

The authors report interesting Scanning Tunneling Microscopy (STM) experiments on excess Fe impurities on the Fe(Se,Te) superconductor. These experiments show evidence of Hund-correlated subgap states induced by the impurities.

By exploiting the tunability of these subgap states with the STM tip's electric field, the authors were able to tune the energy of the state closest to zero energy through the Fermi energy, thereby inducing a quantum phase transition (QPT) in the system.

This QPT is peculiar because only one state crosses the Fermi energy, while all other subgap states abruptly change their particle-hole asymmetry. Additionally, the authors report the appearance of Negative Differential Conductance (NDC) depending on the tip-impurity distance. Interestingly, the observed phenomena cannot be explained within the usual scenario of independent scattering channels (i.e., independent d-levels in the Fe atom). The authors interpret their findings in terms of a two-level Anderson model in the zero-bandwidth approximation, with a dominant Hund's coupling between the atomic d-levels.

This model predicts, under certain circumstances, a multi-channel QPT dominated by Hund-coupled many-body impurity states, rather than independent impurity d-states.

A key point in the authors' interpretation is that the QPT involves a level crossing between two many-body states not connected by a single-particle excitation. The fact that only one peak (the closest to zero) crosses the Fermi level, along with the change of slope of the peaks and the existence of NDC,

is indeed suggestive of a correlated multichannel QPT. As the authors mention, in an independent channel scenario, the other peaks should continue shifting their energies.

The authors have significantly improved their manuscript by addressing all the comments from previous reviewers (1, 2, and 3). Notably, they clarified the general description of YSR and Kondo-screened impurities on superconductors in the abstract and introduction, citing known relevant articles. Additionally, they convincingly argued that the observed NDC is not an artifact of superconducting impurities contaminating the normal tip,

and that the STM tip remains in the normal state (i.e., subgap states crossing zero energy cannot occur in an S-S junction).

In this revised version, the authors have reasonably defended their main experimental findings and general interpretation.

The mechanism underlying this multi-channel QPT is certainly different from other known mechanisms (YSR model, Kondo or Anderson model with SC substrate) in impurity-induced subgap systems, making it an interesting experimental finding which will trigger new research. The results are timely, interesting, and relevant for the fundamental understanding of magnetic impurities on superconductors. I would be happy to recommend this manuscript once the following points are addressed:

1) Perhaps the most critical point concerns the interpretation of the results using the two-level Anderson model. As raised by previous reviewers, the requirement of a specific parameter regime (encoded in Eqs. 2 and 3) to justify the experimental phenomenology is questionable considering the variability of the local environment at the Fe(Se,Te) uperconductor surface.

The authors argue that the only essential requirements in the phenomenological model are:

a) Fe impurities are in the mixed valence regime.

b) Inter-orbital Hund's coupling must be the dominant energy scale.

While this regime is certainly plausible, the requirement $J_H > U$ is somewhat unusual, as the opposite is generally true in correlated d-level systems

(see, e.g., A. Georges et al., Annual Reviews of Condensed Matter Physics 4, 137-178 (2013)). Can the authors explain or justify why this is the case in this experiment?

In particular, if the superfluid density is low (a crucial fact that justifies the electric field-driven tunability of subgap states), then the local interaction should be poorly screened, and the Hubbard parameter U should likely be large.

2) Even if the observed MCQPT deviates from the paradigm of a transition due to impurity screening by the substrate,

the Kondo effect (or screening) should still be expected after the transition, i.e., when a high-spin configuration is favored.

Are the authors implicitly assuming that the Kondo temperature (T_K) is very small in this experiment (e.g., smaller than the measurement temperature)? While their phenomenological model cannot capture Kondo physics, estimating the Kondo temperature in the parameter regime proposed in Eqs. 2 and 3 would help to analyze the consistency of the proposed scenario.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have made major revision to the original manuscript according to the suggestions from all referees and the current version has undoubtedly improved substantially. The rewritten introduction now is much more convincing and the validity of the alternative explanation of varying hybridization strengthens the argument a lot. I thank the authors for making substantial and valuable effort in improving the manuscript.

Nevertheless, my major concern still remains unfortunately, which is basically whether the model which the authors used can explain the phenomena they observed. In addition, the novelty of the QPT seems not enough to me for publication in Nat. Comm., and thus I could not recommend publication still, and I will elaborate in the following part.

The authors used a 2-orbital Anderson impurity model with inter-orbital coupling term, and as far as I understand, they solved the model on the mean-field level (otherwise NRG is necessary if correlation is fully incorporated).

1. About zero crossing: my original question was that the model does not predict any protected zero crossing, while in the experiment they always saw clear zero crossing. The authors then added a 2D plot to show the parameter space of approximate zero crossing within experimental resolution in Figure S1, which is very informative. However, firstly, the energy resolution should be around 3.5kB*T for metallic tip corresponding to about 120 uV for 0.4K, while the authors chose a much larger value \delta E = 1.5mV*0.13 ~ 200 uV such that the region looks much wider than it should be (also, the FWHM of the sharpest Shiba peak in Figure 2e seems to be around 0.13mV, consistent with my estimation rather than the over-estimation from the authors). In addition, as can be seen in Figure S7 in the supplementary material, the Fe atoms show a wide variety of YSR states on the surface, indicating that they are at various very different adsorption sites, which suggests that the parameters for the Anderson model for the actual experimental system span a wide range in the experiment. I am therefore not convinced that the experimental system is so lucky that it lies on the narrow window showing in Figure S1 (narrower than shown there). My intuition is that their mean field model is too primitive to capture important physics, or there are some topological features special to the system important to the Shiba physics, which might change the interpretation completely.

We agree that the energy broadening we used was slightly too large given our electron temperature of ~0.4 K. We now use a broadening in all figures in line with the Reviewer's estimation.

Regarding the different local environments of Fe atoms: indeed there is a variety in the spectra for different Fe atoms. This likely reflects a different Se/Te configuration underneath the excess Fe impurity. Unfortunately, since the contrast is dominated by the Fe impurity, we cannot clearly distinguish the different underlying Se/Te configurations from each other. What is crucial, though, is that a crossing is observed only for those impurities that have a sub-gap state already close to 0 meV for large junction resistances, a requirement that is met by a relatively small subset of impurities. It is not unlikely that the impurities in this subset all have a very similar local environment and can therefore all be described by a similar parameter range in theory. Since our experimentally accessible junction resistance range was not sufficient to effect a MCQPT for impurities with resonances further from zero, we could not directly examine whether crossings for impurities in a different environment are also zero crossings.

Future studies may be able to go beyond our experimental range in which case they may indeed observe a non-crossing MCQPT as allowed by theory.

Regarding the model, we indeed use a 2-orbital Anderson impurity model with inter-orbital coupling term to capture essential spectroscopic features of the data. However, we want to stress that we do not use any mean field calculations (local electronic correlations are in fact the corner stone of our modelling). Instead, we solve the 2-orbital Anderson Impurity Model exactly in the zero-bandwidth limit approximation. The only assumptions we have to make to describe the particle-hole switch of the spectral weight are that the impurity is in the mixed-valence regime and that the strength of the Hund's coupling exceeds the crystal-field splitting of the impurity energy levels, both of which are largely plausible in transition-metal impurity atoms. In addition, even though we put special care in being consistent with previous works of iron impurities on FeSe [see our reply to Reviewer 4's first question], we would like to emphasize that the minimal nature of our model makes it difficult to extract realistic estimates for the numerical values of its parameters from *ab initio* calculations that go beyond the hierarchy of energy scales discussed in the manuscript. This is especially evident for the tunnelling rates $\Gamma_{A,a}$, $\Gamma_{B,b}$ which, owing to the zero-bandwidth approximation, have units of energy squared instead of energy as in the case of an impurity coupled to an extended bath. The impression of fine-tuning in the $\Gamma_{A,a}$, $\Gamma_{B,b}$- parameter space that Fig. S1 conveys depends largely on the chosen parameter range in the plot, which is impossible to assess precisely. We stress, nevertheless, that our theory does not seek to provide a detailed description of the impurity (which would require high throughput numerical simulations), but rather, to pinpoint the relevant physical mechanisms that explain the distinguishing features of the experimental data.

For further clarity, we have added the remark concerning the choice of parameter range to the caption of Fig. S1.

2. About the jump of YSR peak heights across the QPT: across a conventional QPT, the peak heights of positive and negative voltage YSR peaks just switch with each other. In the case of MCQPT, the spectral weights jump, but in general the values will be all new (meaning that if the YSR peak heights are x1, x2, x3, x4 just before the MCQPT, the four peak heights just after the MCQPT would not be a simple shuffle of x1, x2, x3, x4. Also, for the peaks crossing zero, the height will not be continuous across zero). One can easily see that in Figure 3 (d,e). This is because vertical arrows connect different lines across MCQPT (Figure S2 (c,e), by the way, there are two panel c in this figure by mistake). The above is a natural result of the model proposed by the authors. I would suggest that the authors plot the YSR peak heights as a function of conductance for all datasets they showed and investigate whether this is consistent with their experimental observation.

We thank the Reviewer for raising this interesting point. Indeed, for the MCQPT one would not only expect the slope to change upon crossing, but also the intensity. This is exactly what we observe in our data as the new colour scale (see below) clearly shows. Conversely, the peak height for Fe impurities where there is no MCQPT remains almost perfectly constant for all Rj, showing that the difference in peak height is intimately linked to the MCQPT, exactly as the model suggests, and not resulting from the change in Rj.

We now discuss this observation in Fig. S3, where we also plot the height of the peak that crosses zero energy as function of junction resistance for the two measurements shown.

3. About the YSR energy as a function of conductance: it seems that all YSR peaks move in parallel in Figure 2. Is this more consistent with the assumption of electric field gating effect rather than the changing hybridization effect shown in Figure S10a?

It would indeed be interesting if there are specific signatures in the trajectory of the sub-gap states that may distinguish the two scenarios from each other. Unfortunately, in both cases, the sub-gap states move roughly in parallel (see Fig. S2 and S10), so there does not seem to be an easy way to distinguish the two scenarios on these grounds. We stress that the model describes the data in either case.

4. About the novelty: there have been so many papers about YSR across QPT upon tip approach for some time. This paper shows an interesting observation that only one pair of YSR peaks crosses zero while the others not and the system of Fe defect on iron-based superconductor is certainly interesting, but the model turns out quite trivial (nothing new, just straightforward mean field with a coupling between the two channels). Therefore, I find the paper more suitable for more specialized journals like PR series or Comm. Physics.

We respectfully disagree with the Reviewers' assessment. We first would like to emphasize that our experiment shows completely unexpected and new features: YSR or Kondo do not predict the simultaneous switching of intensity we observe to happen at all. Secondly, the model we introduce to explain these surprising observations is not mean field contrary to the Reviewer's statement. One could discuss to which extent a model needs to be radically different from previous ones to merit a 'novelty' label or be called non-trivial. We would argue that despite "so many papers about YSR across QPT upon tip approach for some time" none of them considers Hund's coupling to be relevant, whereas in this work we show it is a crucial parameter. Deeming the inclusion of Hund's coupling to be "trivial" thus ignores the fact that nobody previously considered it. Once again, we stress that this insight is based on completely unexpected experimental observations, which our minimal model accurately captures. We strongly believe that this harmonious combination of experiment and theory, that provides new insights into quantum phase transitions, makes this work ideally suited for Nature Communications.

Reviewer #3 (Remarks to the Author):

I really appreciate the fact that the authors have put quite some effort in answering most of my questions and revising the manuscript. However, in some places I feel that their changes did not improve the work. For instance, the revised title makes it sound as if they found a phase transition of the entire material FST instead of a local impurity study. I would recommend revising this again. Some more comments:

We have reintroduced 'a single magnetic impurity' to the title to avoid this possible misunderstanding.

- YSR states tunable with tip-sample distance have been observed in various systems. I'm not entirely getting the connection of these studies to this manuscript. Mostly, I got confused by the relation of this work to Ref. 8 (Nat. Commun. 8, 298 (2021)). They also observe multiple YSR states in the very same material, some of which are tunable across the QPT, but the higher-lying YSR states do not show a reversal in intensity (Fig. 3 of Ref. 8). What is the reason these two experiments are so different? Couldn't this mean that this mechanism isn't all that robust?

This is an interesting point. Indeed, as the Reviewer points out, in addition to a single dispersing YSR state, Fig. 3 also contains a faint non-dispersing sub-gap signal at higher energy. Although this is not discussed in Ref. 8, the presence of such a non-dispersive signal is actually quite surprising within the framework of electric field induced shifting of levels. Since the signal does not seem to appear in any of the other figures, it is not clear, though, whether this is a second sub-gap state of the impurity in question, or has a different origin.

Crucially, while we study excess Fe atoms on top of the surface, Ref. 8 studies a sub-surface impurity of unknown origin. The fact that we see many more sub-gap states is thus not surprising or contradictory,

nor that, unlike Ref. 8, we observe a multi-channel quantum phase transition. The impurity in Ref. 8 is not necessarily a high-spin Fe and may very well be an object for which Hund's coupling is not a relevant parameter.

- The authors say that if their tip was superconducting, they would see much sharper features. That might be true for perfect bulk SC tips, but it can vary a lot when you just pick up some small clusters! In fact, I have even seen tips with imperfect SC gaps that made the actual energy resolution worse (because you're convoluting the LDOS with something that is not flat but not ultrasharp either). There should not be a zero-crossing with a perfect SC tip gap, but if the gap of a small cluster on the tip does not go to zero, you will get a mixture of SIS and SIN tunneling (I have seen this before). Also, the particle-hole symmetry can be very complex in these highly convoluted spectra. Thus, I am not fully convinced by that interpretation. How many different microtips did the authors use?

Please see our response to the next comment.

- Concerning their question on NDC with different STM tips: I can recommend the paper by Heinrich et al., PRL 107, 246801 (2011) and the references therein. Again: How many different microtips were used and showed the NDC? (to be clear: when I say microtips, I'm talking about minor tip modifications, e.g. on platinum, not to take the whole tip out of the STM)

We thank the Reviewer for pointing out this reference. We indeed did not consider more exotic scenarios where the tip is partially superconducting as suggested in the previous comment, or picked up some unusual molecule or atomic cluster like in the PRL reference. Although unlikely, it may perhaps be possible to have a tip with excellent atomic resolution and high quality dI/dV that has a sharp feature leading to NDC, yet no full gap. On Pt this would likely clearly show up, so it would have had to have been picked up after tip preparation. Such a tip, however, would show NDC for all sufficiently isolated states, regardless of the bias polarity, both of which is not the case for us - except if there is some form of orbital selectiveness as is the case for the PRL paper. To dispel all doubts, we went back through all our measurements on Fe(Se,Te), also of runs prior to the one we report on in this work which we previously did not discuss. Among these prior runs we also found multiple instances of NDC on excess Fe impurities in Fe(Se,Te) - even on a different sample using a completely different tungsten tip during a different cool-down cycle. Additionally, minor tip changes on Fe(Se,Te) itself did not affect the observation of NDC. All combined, we can safely conclude that the tip is not responsible for NDC.

We have added this information to the section in the SI and modified its text to reflect the above discussion.

- I think the question on magnetic anisotropy raised by Reviewer #2 is important. In their reply, the authors basically say that it should be relevant in this system, but the Hund's coupling is more relevant (without explaining why in great detail). Anisotropy is known to split the YSR peaks into multiplets (Hatter et al., Nat. Commun. 6, 8988 (2015)). Wouldn't that mean that if one peak crosses the QPT, the others will change as well since they are related to the same orbital?

The Reviewer is correct that if all peaks originate from the same orbital due to anisotropy, they may indeed all switch simultaneously. However, the fact that we observe negative differential conductance (NDC) means that at least two orbitals are present instead of only one. If we would only consider a spin model with spin anisotropy like in the reference quoted by the Reviewer, we do not see how it would ever lead to NDC and explain our data, as we mention in the discussion section of the main text. Therefore, we think anisotropy is not the crucial parameter at play here.

- This is just a minor point and I don't want to get into arguments about basic stuff like this but: please really reconsider the color scale of Fig. 2. This point has been raised by multiple reviewers and I think it's solvable (maybe even by saturating some of the extremal data points), but it's very hard to understand what's going on this way. If it doesn't work at all, maybe even consider replacing it by a waterfall plot like in Fig. 1.

We thank the Reviewer for stressing this point. Upon re-examining our colour scale for the second time, we noticed that it is indeed difficult to interpret if printed in black and white, or in case of certain colour vision impairments. To make the images more accessible to all readers we have now made a composite of two colour scales: one for the positive values and one for the negative values, with zero being black for both scales (zero is still marked in the colour legends of all figures). This scale has the advantage of clearly distinguishing positive from negative values, as well as resolving the important features of both polarities, which remain reasonably clear when viewed in black and white. To balance the new colour scale, we have also replaced the colour scale of all topographic images from a blue to an orange one (Fig. 2 would otherwise have become very dark).

Also in the light of the other two reviews (that raise some important questions), I cannot recommend publication until these points have been clarified.

Reviewer #4 (Remarks to the Author):

The authors report interesting Scanning Tunneling Microscopy (STM) experiments on excess Fe impurities on the Fe(Se,Te) superconductor. These experiments show evidence of Hund-correlated subgap states induced by the impurities.

By exploiting the tunability of these subgap states with the STM tip's electric field, the authors were able to tune the energy of the state closest to zero energy through the Fermi energy, thereby inducing a quantum phase transition (QPT) in the system.

This QPT is peculiar because only one state crosses the Fermi energy, while all other subgap states abruptly change their particle-hole asymmetry. Additionally, the authors report the appearance of Negative Differential Conductance (NDC) depending on the tip-impurity distance. Interestingly, the observed phenomena cannot be explained within the usual scenario of independent scattering channels (i.e., independent d-levels in the Fe atom). The authors interpret their findings in terms of a two-level Anderson model in the zero-bandwidth approximation, with a dominant Hund's coupling between the atomic d-levels. This model predicts, under certain circumstances, a multi-channel QPT dominated by Hund-coupled many-body impurity states, rather than independent impurity d-states.

A key point in the authors' interpretation is that the QPT involves a level crossing between two many-body states not connected by a single-particle excitation. The fact that only one peak (the closest to zero) crosses the Fermi level, along with the change of slope of the peaks and the existence of NDC, is indeed suggestive of a correlated multichannel QPT. As the authors mention, in an independent channel scenario, the other peaks should continue shifting their energies.

The authors have significantly improved their manuscript by addressing all the comments from previous reviewers (1, 2, and 3). Notably, they clarified the general description of YSR and Kondo-screened impurities on superconductors in the abstract and introduction, citing known relevant articles. Additionally, they convincingly argued that the observed NDC is not an artifact of superconducting impurities contaminating the normal tip, and that the STM tip remains in the normal state (i.e., subgap states crossing zero energy cannot occur in an S-S junction).

In this revised version, the authors have reasonably defended their main experimental findings and general interpretation. The mechanism underlying this multi-channel QPT is certainly different from other known mechanisms (YSR model, Kondo or Anderson model with SC substrate) in impurity-induced subgap systems, making it an interesting experimental finding which will trigger new research. The results are timely, interesting, and relevant for the fundamental understanding of magnetic impurities on superconductors. I would be happy to recommend this manuscript once the following points are addressed:

We thank the Reviewer for their positive evaluation of our work.

1) Perhaps the most critical point concerns the interpretation of the results using the two-level Anderson model. As raised by previous reviewers, the requirement of a specific parameter regime (encoded in Eqs. 2 and 3) to justify the experimental phenomenology is questionable considering the variability of the local environment at the Fe(Se,Te) uperconductor surface.

The authors argue that the only essential requirements in the phenomenological model are:

a) Fe impurities are in the mixed valence regime.

b) Inter-orbital Hund's coupling must be the dominant energy scale.

While this regime is certainly plausible, the requirement J_H > U is somewhat unusual, as the opposite is generally true in correlated d-level systems

(see, e.g., A. Georges et al., Annual Reviews of Condensed Matter Physics 4, 137-178 (2013)). Can the authors explain or justify why this is the case in this experiment?

In particular, if the superfluid density is low (a crucial fact that justifies the electric field-driven tunability of subgap states), then the local interaction should be poorly screened, and the Hubbard parameter U should likely be large.

We thank the Reviewer for raising this important point concerning the relationship between the magnitude of the Hund's coupling and the intra-orbital Coulomb interaction. Indeed, our model relies on two assumptions:

a) Fe impurities are in the mixed-valence regime, which imposes that $U \sim |\bar{\varepsilon}|$.

b) Inter-orbital Hund's coupling exceeds the orbital energy splitting (i.e. $J_H > |\delta\varepsilon|$).

These assumptions are in fact independent from each other, therefore, the phenomenology of the MCQPT can be observed for any U/J_H ratio, including the more realistic scenario $U/J_H > 1$.

We have updated Eq. (3) in the main text which was somewhat misleading as the Reviewer pointed out, and we have set $U = 2J_H = 60\Delta$ in all the simulations in the manuscript. We have included Supplementary Note 7 where we discuss the independence of the MCQPT on the U/J_H ratio. Additionally, we note that our new choice of parameters is consistent with previous studies of iron impurities on FeSe systems [Martiny et al. PRB 99, 014509 (2019)], which now we explicitly mention after Eq. (3) in the main text.

2) Even if the observed MCQPT deviates from the paradigm of a transition due to impurity screening by the substrate, the Kondo effect (or screening) should still be expected after the transition, i.e., when a high-spin configuration is favored. Are the authors implicitly assuming that the Kondo temperature (T_K) is very small in this experiment (e.g., smaller than the measurement temperature)? While their phenomenological model cannot capture Kondo physics, estimating the Kondo temperature in the

parameter regime proposed in Eqs. 2 and 3 would help to analyze the consistency of the proposed scenario.

The Reviewer is perfectly right that our model cannot capture Kondo physics. We indeed implicitly assumed that in the large-spin configuration (therefore far from the quantum transition which supposes a mixed-valence regime), the Kondo temperature(s) is (are) smaller than the superconducting gap.

On the experimental side, we have no data to verify any signatures of Kondo physics. A possible way would be to add a magnetic field to suppress superconductivity and measure a zero-bias anomaly in the local density of states. Unfortunately, our experiment does not allow us to add a large enough magnetic field to do so. Alternatively, to see if $T_K > T_c$, one could increase the temperature beyond T_c and look for a Kondo signature. While we have not performed such measurements, there are previous reports showing data at excess Fe impurities above T_c, for example Ref. 18 and PRB 80, 180507(R) (2009). Given the large T_c of 15 K, however, thermal broadening ($\Delta E = 3.5\, k_B T$) becomes significant and it is difficult to distinguish a possible Kondo signature from e.g. band structure effects. Additionally, in absence of a clear Kondo signature it will still not be clear whether $T_K < 0.3$ K or not.

At the theoretical level, the hybridization between the orbitals and the substrate is unknown, which makes an accurate estimation of the Kondo temperature rather speculative. However, by noting that the density of states at the Fermi level for this compound is $\rho_0 \sim 2.5$ eV^{-1} (or $\rho_0\, \Delta \sim 5\text{x}10^{-3}$) [Tsurkan et al. Eur. Phys. J. B 79 (2011)], one finds $\rho_0\, |J_K| \sim 5\text{x}10^{-3}$ for the choice of parameters in the main text, which in turns yields a negligibly small Kondo temperature, $T_K \sim e^{-1/(\rho_0 |J_K|)}$. Therefore, assuming the Kondo temperature much smaller than the gap is theoretically consistent in our model. In addition, while this rough estimate does not take into account the multichannel nature of the model, we may argue that a large Hund's coupling tends to decrease T_K as explained in the review quoted by the Reviewer [A. Georges et al., Annu. Rev. Cond. Matt. Phys. 4, 137-178 (2013)].

We now discuss this point at the end of Supplementary Note 3.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

Uldemolins et. al. answered questions from all referees and made substantial improvements to the manuscript. I am glad to see that the manuscript, as it is now, becomes much better thanks to the authors' several rounds of effort.

I have to admit that my major concern still stands (although the authors made very good arguments regarding this) that the model might not be the proper one explaining the experimental observation, especially about the zero crossing and the validity of the simple zero band-width approximation. The authors listed now the non-crossing cases in Fig. S9 wanting to show that not every case feature zero crossing, but there are no QPT at all in those cases shown, not what I talked about previously about the non-zero crossing at QPT as predicted by the model. About the approximation used in the model, a mixed-valence regime and much smaller Kondo temperature compared to the superconducting gap is kind of unusual for Shiba states deep in the gap. I would even say that the existence of Shiba state in mixed-valence regime is a very important observation itself, if confirmed.

My other major concern about the novelty and the meaningfulness of the result also stands: why is this two orbital Hund's coupling induced QPT important and what is the impact of this paper other than adding more and more Hamiltonian terms in the Shiba model and see different crossing behavior?

Nevertheless, I do understand that Fe(Se,Te) system is complicated and such a simplistic model will have caveats and will not cover all aspects, so as long as the experimental part is correct guaranteed, it is fine on my side. As for the novelty part, I refrain from taking a strong stand against the paper and leave it for the editor to decide. So I do not have any objection to publishing this paper in Nature Communications at the point, given that the authors can revise further, discuss 1. the limitation of the model and possible future improvements/alternatives to the model 2. compare the model in the context of standard full bandwidth Anderson model which can be solved by NRG numerically and show that the result is similar in the mixed valence regime 3. why is this paper important and 4. questions from other referees.

Reviewer #3 (Remarks to the Author):

The authors have convincingly answered my questions and I am happy to recommend the manuscript for publication now.

Reviewer #4 (Remarks to the Author):

I appreciate the effort made by the authors in answering my previous questions and updating the manuscript accordingly. The authors have convincingly responded to my (and other referees') questions in favor of their 2-level Anderson model interpretation of the experimental data.

In particular, regarding my concerns about the hierarchy of U vs J_H, in their reply they have shown numerical evidence of a wide range of parameters where their MCQPT can take place.

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We thank the Reviewer for lifting their objections to publication of our work. To satisfy the remaining points, we have added a sentence about the generality of the multi-orbital Anderson model and our zero-bandwidth approximation of the substrate which is the main limitation of our model. We have also added relevant references for this approximation, including a reference that explicitly compares the zero-bandwidth approximation to a full numerical renormalization group (NRG) treatment for the (single orbital) impurity Anderson model. It turns out that the zero-bandwidth approximation qualitatively captures the parameter phase diagram. We stress that a full NRG calculation for the multi-orbital Anderson model with a proper description of the superconducting substrate (including surface anisotropy) is well beyond the scope of our present work.

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