Room temperature multiferroicity in a 2D van der Waals material

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The coexistence of multiple ferroic order, i.e. multiferroicity, is a scarce property to be found in materials. However, the applications derived from this coexistence are promising in several fields, and motivates the search for new and better multiferroics. Historically, this state has been found mainly in 3-dimensional complex oxides and perovskites, or in heterostructures of ferroelectric/ferromagnetic thin-films, but so far this state has still been elusive for the most widely studied and characterized family of 2D compounds, the transition metal dichalcogenides (TMDs), in spite of numerous theoretical predictions in this respect. In this study, we report the first experimental realization of multiferroic states in TMDs, at room temperature, in bulk single crystals of Te-doped WSe$_2$. We observe the coexistence of ferromagnetism and ferroelectricity, evidenced in the presence of magnetization and piezoresponse force microscopy (PFM) hysteresis loops, resistive switching effects, and substantial piezoelectricity with higher effective coefficients than previously reported in any other TMD. These findings open the possibility of widening the use and study of Van der Waals-based multifunctional devices for new nanoelectronic and spintronic applications, and provide an affordable platform for the study of fundamental physics of ferroic orders on low-dimensional compounds.

**Introduction**

Multiferroics are materials that exhibit different coexisting ferroic orders such as ferroelectricity, ferromagnetism, or ferroelasticity$^1$. Due to the coupling among the different degrees of freedom leading to these ordered states, the order parameters of one state can be controlled by tuning parameters different from their conjugate variable. For example, magnetoelectric coupling allows the control of magnetization via an electric field, or conversely, the control of electric polarization via magnetic field, for the case of ferromagnetic/ferroelectric heterostructures and multiferroics$^{2,3}$. Multiple applications in spintronics$^4$, data storage$^5$, actuators$^6$, among others$^7$, have been envisaged and already realized. The search for new and better multiferroic materials is arduous: ferroelectrics tend to be insulators as a need to preserve electric polarization (free charges in metals screen this effect) while ferromagnets are metals in their majority$^8,9$. In this sense, a guiding strategy that has been used to attain profitable multiferroicity is chemical doping of either a ferroelectric host or conversely, a ferromagnetic host. For example, replacement of the transition-metal ion in ferroelectric LiNbO$_3$ or ZnO leads to magnetic order$^{10-13}$. On the other hand, chemical doping in complex oxides multiferroics has been effective in optimizing their properties$^{14}$.

Historically, these phenomena have been found mainly in 3-dimensional complex oxides and perovskites, such as Cr$_2$O$_3$,$^{15,16}$ YMnO$_3$,$^{17}$ BiFeO$_3$,$^{18,19}$ among others, or in heterostructures of ferroelectric/ferromagnetic thin-films$^{20-23}$. The 3D character of the crystal
structure of these compounds poses challenges in the fabrication of nanoscale multiferroic devices - highly desired for downsizing and integrating their associated applications - as their nanostructuring requires advanced fabrication techniques, as well as induces physical effects inherent to quantum confinement that typically weakens the multiferroic states 24,25. In this sense, the use of multiferroics with an intrinsic 2D-crystalline structure is highly desirable for obtaining affordable and robust multiferroic nanodevices.

Recent advancements in the realization and study of intrinsically 2D-multiferroics have been done 25,26, for example in the transition metal halide compounds such as NiI₂ 27,28 and CrI₃ 29, and in doped In₂As₃ 30. However, multiferroicity has been elusive, until now, for the most widely studied and characterized family of 2D compounds, the transition metal dichalcogenides (TMD’s), in spite of numerous theoretical works in this respect 31-34. In recent years, for this family of materials, individual ferroic orders have been experimentally observed at room temperature 35-40. Ferromagnetism has been attained in MoS₂ and WS₂ due to defects 37,46, and in WSe₂ via chemical doping in the transition metal site 38,39, among other examples. Ferroelectricity has been reported in bulk-WTe₂ 40, while for an odd number of layers, WSe₂ and MoS₂ are reported to be piezoelectric 31,42. Despite the presence of these individual ferroic orders, there is no experimental evidence for simultaneous ferromagnetism and ferroelectricity in TMDs to date.

In this study we report the first experimental realization of multiferroic states in TMDs, specifically in Te-doped WSe₂. The multiferroic state is observed at room temperature and in bulk single crystals, for Te-doping above 7%. The multiferroic states are revealed in the observation of ferromagnetic hysteresis loops in the magnetization, and ferroelectric hysteresis loops in the phase and amplitude of piezoresponse force microscopy (PFM) measurements. In addition, the highest Te-doping samples studied (15%) show very large effective piezoelectric coefficients, comparable to the commercially used 3D-piezoelectric LiNbO₃ 43, and one order of magnitude higher than in WSe₂ and other pure TMD’s nanolayers 41,44-46. Our results are accompanied by Density functional theory (DFT) calculations, which support our experimental findings and provide insights about the possible mechanisms leading to the multiferroic state. These findings open the possibility of widening the use and study of vdW-based multifunctional devices for new nanoelectronic and spintronic applications, and provide an affordable platform for the study of fundamental physics of ferroic orders on low-dimensional compounds.

**Experimental Results:**

**Raman spectroscopy and X-rays techniques**

Figure 1(a) shows a picture of representative single crystals of Te-doped WSe₂, with typical lateral sizes around 1mm, and a hexagonal morphology. A level of chalcogen vacancies is naturally developed during the crystal growth process 47, and crystals with a general stoichiometry W(Sₑₓ₋ₓTeₓ)ₓ(1₋ₓ) are produced, where x represents the fraction of Se atoms that were replaced by Te atoms, and δ is the fraction of chalcogen sites that are not occupied by neither a Se nor a Te. The values of x and δ for the different crystals studied were determined through X-ray fluorescence spectroscopy (see methods, and SI Table S1 for values). Samples with four different Te-doping values, up to a maximum of x=15%, plus undoped samples (x=0) with three different levels of chalcogen vacancies were characterized in this study. Two different types of X-ray diffraction measurements (powder diffraction, presented in Figs. 1(d-f) and Fig. S2; and single crystal diffraction, presented in table S2 and crystallographic
information file - CIF - available in supporting data) reveal that the crystalline structure of all the pure and Te-doped compounds is the 2H-structure (space group P6₃/mmc, #194)⁴⁸. The most intense diffraction peaks in Fig. 1(d) come from the {0 0 1} family of planes, given that the a-b plane of the crystals tend to align parallel to the sample holder (see methods). Few peaks corresponding to different families of planes can still be recognized. Close inspection to the {0 0 1} diffraction peaks (Fig. 1(e) for the (0 0 2) peak) reveals a continuous shift to the left, and therefore, an increase of interplanar c-lattice parameter with increasing Te-doping. Single-crystal diffraction confirms the increase in c-lattice parameter, and in addition reveals an increase in-plane a-lattice parameter with Te-doping. SI Table 2 shows a summary of a and c lattice-constants found by X-ray diffraction.

Figure 1. (a) Representative single crystals of W(Se₁₋ₓTeₓ)₂(1-δ) (this case, for x=15% and δ=21%) synthesized by chemical vapor transport, and characterized in this work. Scale bar is 1 mm long. (b) Crystal structure of a 2H-polytype of Te doped WSe₂ with space group P6₃/mmc (#194). (c) Raman spectroscopy measurements for W(Se₁₋ₓTeₓ)₂(1-δ) single-crystals of the compositions studied in this work. Data shows a close up look to the Raman shift around the characteristic E₂g and A₁g peaks of the 2H phase, which shift to lower values with increasing doping. Dashed gray lines indicate the peak positions for the pure x=0 compound. (d) Powder X-ray diffraction data for a collection of undoped (x=0, δ=4%), and highest Te-doped (x=15%, δ=21%) samples. Diffraction peaks are consistent with the 2H-polytype, as compared with the reported peak positions of pure 2H-WSe₂, shown by the blue vertical lines. (e, f) Close-up look to the (0 0 2) and (1 0 3) peaks, which reveal a shift to the left for the Te-doped samples, indicative of an increase of 2.5% in the c-lattice parameter.

The 2H-polytype is also confirmed by Raman spectroscopy. Fig. 1(c) shows the Raman spectra for the different Te concentrations studied (x=0-15%), around the E₂g and A₁g modes for 2H-WSe₂⁴⁹. A continuous decrease...
in the Raman shifts of both modes as tellurium concentration increases is observed, which also reveals a 2H-structure with a continuously increasing $a$- and $c$-lattice parameters (to first order, larger lattice parameters lead to weaker ‘spring constants’ which leads to smaller frequencies of oscillation of the vibrational modes). Raman peaks associated with the 1T$_{d}$-polytype, which for pure WTe$_{2}$ appear around 150 cm$^{-1}$ and 200 cm$^{-1}$, are not present, implying that there is no presence of secondary phase domains with this structure. Our results of the crystallographic structure align with a previous study in W(Se$_{x}$,Te$_{y}$)$_{2}$, which reports a pure 2H-structure for compositions $x < 0.5$.

**Magnetic response**

Magnetization measurements as a function of magnetic field at room temperature are shown in Fig. 2(a) (see Fig. S3 for measurements at 80K) and reveal two contributions to the magnetic signal: a diamagnetic component (subtracted in fig. 2a, and similar to what has been reported by other groups in WSe$_{2}$ and other TMDs), and a paramagnetic or ferromagnetic component (states which have been theoretically predicted and experimentally realized in different TMDs). Measurements of samples with different times of exposure to ambient conditions suggests that the diamagnetic component is highly dependent to the level of oxidation of the samples. For instance, freshly synthesized samples showed no or minimum diamagnetic contribution, whereas the same samples after being stored in soft vacuum for a couple of days showed a marked diamagnetic contribution (see SI Fig. S4). The paramagnetic or ferromagnetic contribution appears to be more robust to sample oxidation (see SI section S3, and SI Fig. S4). Samples with no Te-doping and low number of chalcogen vacancies (see black curve in the inset to Fig. 2(a)) show a paramagnetic behavior, with a saturating magnetization above fields of the order of 150 Oe. Te-free samples with an increased number of Se-vacancies showed weak hysteresis loops with small coercive fields, indicating weak ferromagnetism (see red curve in the inset to Fig. 2(a), and SI Fig. S4(a-c) for other vacancy levels). For all the Te-doped samples studied, the ferromagnetic hysteresis loops became more notorious, reaching a maximum coercive field of 700 Oe for the sample with $x = 7.6\%$ and $\delta = 38\%$. Figs. 2(b,c) plot the coercive field for the different samples studied, as a function of Te-doping ($x$) and chalcogen vacancies ($\delta$), respectively. The coercive field as a function of chalcogen vacancies grows monotonically, in contrast to its behavior as a function of Te-doping. This suggests that magnetism is strongly affected by the amount of chalcogen vacancies. Nevertheless, the apparent strengthening of the ferromagnetism in the Te-doped samples, in contrast to the undoped samples, suggests some role of the Te-atoms. We argue that this is due to the fact that the presence of Te in the synthesis promotes the formation of chalcogen vacancies (see SI Table S1). For instance, all the Te-free synthesis reached maximum vacancy levels of 12%, even though for some of them nominal vacancy-values of 50% were aimed. Whereas for the Te-doped synthesis, measured vacancy-levels above 12% could be easily reached, with a maximum obtained vacancy-level of 38%.

In the computational modeling section we will present our DFT calculations, which provide more insight about the role of chalcogen vacancies in the magnetic properties.
**Figure 2.** (a) Magnetization hysteresis loops at 300K for samples of W(Se\textsubscript{1-x}Te\textsubscript{x})\textsubscript{2(1-δ)} with different x and δ values. For all curves, the diamagnetic components were subtracted, and their values normalized by the saturation magnetization, M\textsubscript{s}. Inset in (a) shows the hysteresis loops for undoped (x=0) WSe\textsubscript{2(1-δ)} samples with different amounts of chalcogen vacancies, δ. (b) and (c) Show coercive fields H\textsubscript{c} for all samples presented in (a), as a function of (b) Te-doping, x, and (c) chalcogen vacancies, δ.

**Piezo- and ferro-electric response**

Piezoelectricity in these compounds was investigated using an atomic force microscope (AFM) through the Dual AC Resonance Tracking (DART) piezo force microscopy (PFM) technique (see methods for further details), in freshly-cleaved samples under an inert argon atmosphere in order to prevent surface oxidation and minimize electrostatic effects. This technique measures the amplitude of elongation for a given applied AC bias, and therefore it is a direct measurement of the piezoelectric response. Figs. 3(a-c) show DART piezoresponse maps for different values of the AC bias voltage, in single crystals with three different doping levels. The color in each plot represents the amplitude of out-of-plane deformation, which spatial average increases with the AC applied bias. The spatially-averaged piezoresponse as a function of AC bias, presented in Fig. 3(d), is linear for all samples, and the slope of the curves allows the determination of the effective piezoelectric constant d\textsubscript{33}. This method was examined in Periodically Poled Lithium Niobate (PPLN) and demonstrated a high degree of accuracy for quantifying its d\textsubscript{33} (see SI section S4 for details). The effective d\textsubscript{33} for the two lowest Te concentration samples are comparable, and of the order of 4 pm/V. This value is similar to the piezoelectric constants previously reported for TMD monolayers \cite{61,62}, and even higher than the d\textsubscript{11} coefficient reported for a WSe\textsubscript{2} monolayer or bilayer in a non-centrosymmetric configuration \cite{41,46}. For the highest Te-doped sample, with x=15% and δ=21%, d\textsubscript{33} = 26±4 pm/V. This remarkably high value is comparable to the d\textsubscript{33} of PPLN - a device based on LiNbO\textsubscript{3}, a widely used piezoelectric material \cite{43} - and it is the highest reported or predicted d\textsubscript{33} value among the TMDs, in any configuration \cite{44,63,64}. It is important to mention that previously reported piezoelectric properties in the TMD’s have
been measured in nanostructures of these compounds, generally in single layers in which centrosymmetry is broken, and recently, in thin films of TMD alloys\textsuperscript{65}. Our measurements are performed in macroscopic bulk single crystals, and as such, constitute, to the best of our knowledge, the first report of piezoelectricity in the bulk of TMDs, with piezoelectric coefficients that are comparable to the materials used in commercial piezoelectric devices.

Figure 3. DART-PFM piezoresponse amplitude normalized by SHO model as function of the AC applied bias for W(Se\textsubscript{1-x}Te\textsubscript{x})\textsubscript{2(1-δ)} samples with (a) x=1.4%, δ=9%; (b) x=7.6%, δ=38%; and (c) x=15%, δ=21%. Scale bars of all three figures are 200 nm long. (d) Spatial average of the DART-PFM piezoresponse values from (a), (b) and (c) versus AC applied bias. The effective $d_{33}$ piezoelectric coefficient is obtained from the slope of these curves. The curve for a sample of PPLN is included for comparison purposes. SS-PFM piezoresponse phase and amplitude for samples with (e-f) x=1.4%, δ=9%; (g-h) x=7.6%, δ=38%; and (i-j) x=15%, δ=21%. Insets to all phase curves show topography images indicating the exact locations at which the SS-PFM piezoresponse curves were performed.

In order to further characterize the electro-mechanical properties in these compounds, Switching Spectroscopy (SS) PFM measurements were performed (see SI section S4 for SS-PFM analyses of the PPLN, and SI section S5 and methods for experimental details). The phase (Figs. 3(e,g,i)) and amplitude (Figs. 3(f,h,j)) of the SS-PFM piezoresponse was recorded, as a function of the DC bias voltage at different random locations over the surface of the samples, as indicated in the insets to Figs. 3(e,g,i). The (x=1.4%, δ=9%) Te-doped crystal (Figs. 3(e,f)) reveals a piezoelectric response without hysteresis. Interestingly, the amplitude tends to saturate for $|V_{DC}|>1$V, suggesting a possible saturation of the electric dipole moment response. The (x=7.6%, δ=38%) and (x=15%, δ=21%) Te-doped samples show clear hysteresis loops both in the amplitude and phase of the SS-PFM piezoresponse (Figs. 3(g,h) and 3(i,j), respectively), with shapes
equivalent to the ones shown in prototypical ferroelectric materials such as BaTiO$_3$ and PZT. These loops indicate the presence of domains of electric polarization that can be aligned, with a coercive voltage of 0.2 V and 0.5V for the x=7.6% and 15% Te-doped bulk samples, respectively, and therefore reveal that these materials are ferroelectric.

In addition, electrical current vs voltage (IV) measurements taken in the Te-doped samples reveal asymmetric and hysteretic curves (see SI Figs. S8), with similar characteristics to those measured in the prototypical ferroelectric BaTiO$_3$ and multiferroics such as BiFeO$_3$. This makes Te-doped WSe$_2$ suitable for a variety of multifunctional applications in electronic devices.

As presented in a previous section, the crystalline structure of our samples is the centrosymmetric 2H-polytype. Previous reports of piezoelectric behavior in monolayer TDM’s, and ferroelectric behavior in WTe$_2$ have attributed the non-centrosymmetric structures in those systems as the underlying mechanism for the existence of electric dipole moments. Therefore, these results invite us to search for alternative mechanisms for ferroelectricity in the TMD’s, as will be presented in the computational modeling and discussion sections.

\[ W(W\text{Se}_{1-x}\text{Te}_x)_{2(1-\delta)} \text{ for } x=0.07733 \text{ and } \delta=0.390625. \]

W-W and W-Te bonds are drawn if the interatomic distances are less than 2.74 Å and 2.81 Å, respectively (see text). Top views of the superior (a) and inferior (b) unit cell monolayers and perspective view of the optimized structure (c). Arrows indicate resulting atomic magnetic moments more than 0.02 $\mu_B$ in magnitude. (d) Spin density plotted on planes containing atoms W1, W5 and W24. To facilitate visualization, atom W24 from a neighboring unit cell is depicted. (e) Total spin up (red) and spin down (blue) density of states. (f) Projected density of states on p orbitals of Se and Te atoms, and on d orbitals of W.
**Computational Modeling results**

In order to gain further insight into the mechanisms that can lead to the multiferroic properties of W(Se$_{1-x}$Te$_x$)$_{2(1-\delta)}$, first principles calculations were performed using Density Functional Theory (DFT)\(^2\) (see methods for computational details). Starting with the simulation of pure WSe$_2$, its unit cell composed of 2 W and 4 Se atoms, ionic positions and unit cell lattice parameters were optimized. Resulting structural parameters are in good agreement with the measured ones and with previously reported DFT calculations\(^3\), as can be seen in the table S4 of SI section S7. Inclusion of both, chalcogen vacancies and Te-doping, was achieved in a 4x4x1 supercell, which allowed the simulation of systems with Te-doping and chalcogen vacancy levels similar to the measured single crystals. The effect of vacancies and Te-doping on the magnetic behavior was analyzed by performing spin-polarized calculations with and without spin-orbit coupling. For each concentration random configurations were selected to perform the calculations. Resulting total magnetizations for different levels of Te-doping and chalcogen vacancies can be found in table S4, for one particular realizations of each composition. The system with the highest magnetic moment corresponds to the one with the highest value of chalcogen vacancies, $\delta$, independent of the value of Te-doping, $x$.

Fig. 4 shows different views of two layers of a simulated crystal structure with $x=7.7\%$ and $\delta=39\%$, very close to the values of one of our experimentally characterized samples that shows the strongest ferromagnetism and intermediate ferroelectricity. Arrows in Fig. 4(c) represent the magnetic moment contribution per atom for the atoms that contribute the most magnetic moment in this configuration. In this figure, bonds between W atoms are drawn if the interatomic distance is equal or less than the bond distance in crystalline tungsten (2.74 Å). In order to facilitate visualization, bonds between W and chalcogen atoms are drawn if the interatomic distance is less than 2.72 Å and 2.747 Å for W-Se and W-Te bonds respectively. The W atoms that are not bonded to a chalcogen element in the figure (labeled as W24 in Fig. 4(a), and W1 and W5 in Fig. 4(b)) are the ones that contribute the most magnetization of all atoms in the structure (as represented by the length of the gray arrows in Fig. 4(c)). The next-higher contributions come from W atoms that have a reduced number of bonds with chalcogen atoms (this is, W atoms labeled as 17, 21, 23, 25, 28 and 29 in Fig. 4(a), and 4, 6 and 16 in Fig. 4(b), displayed as red arrows in Fig. 4(c)). The magnitude of the contributions seems to be unaffected by whether the W is bonded to Te or Se atoms. Therefore, the relevant parameter that drives the magnitude of the magnetic moment is the number of bonds of each W with neighboring chalcogen atoms. Although the criteria for drawing a bond in fig. 4 is rather arbitrary, a different number of bonds for each W-ion is an indication of a different local environment for each. Therefore, our calculations indicate that the magnitude of the W magnetic moment in this system is driven by the local environment of the W atoms, and the strength of its hybridization to chalcogen atoms (or alternatively, its bonding to a chalcogen vacancy). Localization of the magnetization $n_r(r)=n_u(r)\cdot n_d(r)$, where $n_u$ ($n_d$) is the density of spin-down (up), on W atoms which are not bonded to chalcogens in Fig. 4(a-c) is evidenced in Fig. 4(d), where the spin density is plotted on two planes containing W1, W5 and W24 (atoms without bonds to chalcogen atoms). It is important to notice that throughout the unit cell the spin density keeps low values $\approx 5\times 10^{-4}\mu_B$ (pink) while on these 3 atoms the spin density peaks at $\approx 8.8\times 10^{-3}\mu_B$ (violet). For the atoms notbonded to a chalcogen element in Fig. 4(a-c), atomic magnetization (the integral of the spin density
up to the covalent radius) takes values as high as 0.56 $\mu_B$. Indeed, the overall ferromagnetic character of the system is corroborated by means of the total density of states (DOS) for spin up and down (Fig. 4(e)), which shows that at the Fermi energy there is a larger contribution from the spin-up channel (red) than from the spin-down channel (blue). The projection of the DOS on atomic orbitals allows for the identification of tungsten d-orbitals as the electronic states associated with the found magnetic order, as shown in Figs. 4(f) and S9(a).

In order to corroborate if magnetic order is dependent on the positions of chalcogen vacancies and/or Te substitutions, calculations were performed for a different configuration keeping the same concentration of vacancies and Te-doping. In this second configuration (shown in SI Fig. S9(b)) there is a more homogeneous distribution of vacancies which causes that all W-atoms are bonded to at least one chalcogen-atom, either Se or Te. The resulting supercell magnetization is null in this case, with almost negligible atomic magnetizations (around $10^{-4} \mu_B$) with opposite directions uniformly distributed throughout the cell.

**Figure 5.** (a) Different views of a (0 1 0) plane of a W(Se$_{1-x}$Te$_x$)$_{2(1-\delta)}$ simulated structure with $x=0.0625$ and $\delta=0.390625$. The top view is a 3D-perspective view of the atoms around a chalcogen vacancy located in the upper side of the top-layer of the unit cell. The bottom view shows both layers of the unit cell (marked in the dashed square), and the color scale represents a slice of the total charge density. Arrows indicate the direction of the electric dipole moment around the vacancy, in the c-direction. (b) Same representations as in (a), but now with the chalcogen vacancy located in the bottom side of the top layer of the unit cell. The direction of the electric dipole moment is flipped in this case, as indicated by the arrow.

In order to find possible sources for the ferroelectric state, electric polarization and ferroelectric behavior were analyzed in the framework of the modern theory of polarization $^{74,75}$, which allows to obtain the unit cell polarization from the Berry phase of
the system. The electric polarization vector was calculated in the same systems for which magnetization was studied. Results show a dependency on vacancies concentration and Te-doping as can be seen in Table S5. Additionally, Hirshfeld charge analysis was carried out in order to identify both the atoms responsible for polarization and the possible mechanism of ferroelectricity.

In the case of pristine WSe$_2$ it is found that chalcogen atoms have positive Hirshfeld charges while W atoms gain a negative charge which is approximately equal to twice the charge of the chalcogens. This is expected from the coordination numbers of Se and W, three and six respectively (see table S5). This distribution of charge makes WSe$_2$ monolayers non-polar due to its centrosymmetry, which is broken by the presence of vacancies. As can be seen in figure 5, the absence of a Se atom develops electric polarization directed from the negative W plane towards the remaining Se atom below or above the vacancy. Since the sign of the polarization depends on the position of the chalcogen atom, this results suggest that polarization could be reverted by moving the chalcogen atom from one face of the monolayer to the other one passing through the triangular space defined by the neighboring W atoms, in this case W27, W28 and W32, as labeled in fig. 5. This system corresponds to the same configuration of fig. 4. Even though there is a high concentration of vacancies ($\delta=0.390625$), there is only one place with an uncompensated vacancy, located at the top monolayer. The remaining vacancies sites are located on both sides of the monolayers, therefore not breaking its centrosymmetry, as can be seen in the bottom layers of the unit cell in fig 5.

To study the effect of Te-doping on polarization, Se5 was exchanged by a Te atom. The resulting Hirshfeld charge of this Te is $\sim 2.61$ times larger than that of Se5 and the total polarization of the supercell presents a $\sim 20$ times enhancement if compared to the previous system. The larger separation of charge seen with Te can be ascribed to the difference in its electronegativity with respect to both Tungsten and Selenium, in Pauling units $\chi_{Se}=2.55$, $\chi_{W}=2.36$ and $\chi_{Te}=2.1$ which accounts for the larger migration of charge from Te to W atoms. An additional configuration with a higher concentration of Te and less vacancies was studied ($x=0.125$ and $\delta=0.2187$). In this case there are 13 non-compensated vacancies, and chalcogen atoms are distributed on both faces of the two monolayers of the unit cell, 9 on the superior face and 4 in the inferior face. In general, Hirshfeld charges of Te range from 2 to 3 times the charges of Se, which gives larger local electric dipole moments.

**Discussion**

Ferromagnetic states have been predicted theoretically and experimentally realized in TMD through defects formation, vacancies formation, proton irradiation, nanostructuration, and doping with magnetic impurities. In the case of this study, the dependence of the coercive fields on Te-doping and chalcogen vacancies suggests that the magnetic properties of bulk W(Se$_{1-x}$Te$_x$)$_2$(1-\delta), are strongly influenced by the amount of chalcogen vacancies. This result aligns with the mechanism for ferromagnetic order derived from our DFT calculations, which reveals that the spin density is strongly localized onto the d-orbitals of the W-atoms less bonded with chalcogen atoms (or equivalently, more bonded to chalcogen vacancies), as presented in Figs. 4(f) and S9. This suggests that unpaired/localized d-electrons in W are responsible for the observed magnetic behavior. The key role of chalcogen vacancies in the magnetic order of TMD systems has been previously predicted and experimentally observed in systems such as MoS$_2^{37}$, WS$_2^{38}$, and monolayer V-doped WSe$_2^{39}$. For instance, the presence of
vacancies in 2H-MoS₂ nanosheets has been shown to transform the crystalline structure around the vacancies into a 1T-structure, in which the Mo⁴⁺ ions have a net magnetic moment, in contrast to stoichiometric 2H-MoS₂ in which the Mo⁴⁺ ions are non-magnetic. Data suggests that the origin of the measured ferromagnetism in this system is intimately connected to an enhanced Mo⁴⁺-S-vacancy exchange interaction. Similar conclusions have been recently reached in monolayer V-doped WSe₂, in which ferromagnetic properties are significantly enhanced by promoting Se-vacancies in the structure. In the case of W(Se₁₋ₓTeₓ)₂(1₋ₓ), the role of chalcogen vacancies can be completely analogous to their TMD’s counterparts. This is, a local magnetic moment is generated in the d-orbitals of transition metal atoms surrounded by vacancies due to their modified local environment, with a possible strengthening in the exchange interaction through their coupling with chalcogen vacancies, leading to the ferromagnetic states.

On the other hand, ferroelectric states have been commonly associated with the non-centrosymmetry inherent to certain crystal-structures. Among the TMD’s, piezoelectric and ferroelectric properties have been previously reported in crystals with the non-centrosymmetric 1Tc-phase, like the case of pure WTe₂, or in nanostructures of the 2H-polytype with an odd number of layers, for which centrosymmetry is broken. However, alternative mechanisms, other than the underlying crystalline symmetry, have been proposed for the appearance of electric polarizations in ferroelectric materials. For example, in type-II multiferroics such as TbMnO₃, Ca₃CoMnO₅ and the 2D material NiI₂ local electric polarization is proposed to be induced by strong the spin-orbit coupling in magnetic materials, which can lead to inversion symmetry breaking, and to a ferroelectric state. In addition, and for the specific case of TMD’s, inequivalent Te-W distances in adjacent 1T-WTe₂ layers has been theoretically shown to induce a charge imbalance, leading to an out-of-plane electric polarization. In the case of this work, our DFT calculations identify a feasible mechanism for the existence of electric dipole moments in the 2H- unit cell that can lead to a non-zero total dipole moment in the crystal. In our model, the electric dipoles are originated in the charge imbalance created by a chalcogen vacancy aligned with a chalcogen atom in the c-direction. Our calculations indicate that such imbalance is a order of magnitude stronger if the chalcogen is a Te-atom, which is consistent with our experimental results: no ferroelectric state is found in the pure WSe₂(1₋ₓ), in which, although the charge imbalance mechanism due to vacancies is also present, it is possibly not strong enough to result in a ferroelectric state; whereas ferroelectricity grows stronger with Te-doping, being well established for the largest Te-doping crystals.

For both states, ferromagnetism and ferroelectricity, the role of chalcogen vacancies seem to be crucial. However, each of these states can be individually present, as WSe₂(1₋ₓ) is ferromagnetic and WTe₂ is ferroelectric. This, together with the fact that multiferroicity in W(Se₁₋ₓTeₓ)₂(1₋ₓ) is observed at room temperature, suggests that, although part of the origin of both ferroic orders can be common, this material is not a type-II multiferroic (for which the mechanisms for both ferroic orders are highly intertwined through spin-orbit coupling, and generally show cryogenic critical temperatures). Interestingly, the strong influence of chalcogen vacancies on both ferroic orders in W(Se₁₋ₓTeₓ)₂(1₋ₓ) makes possible, not only the simultaneous presence of these states, but also their magnetoelectric coupling - a crucial ingredient in several envisaged applications of multiferroic materials. These ingredients, combined in an intrinsically 2D vdW layered material, and at room temperature, opens the
door to a wide use of nanostructured multiferroic devices.

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