Exciton-phonon-driven charge density wave in $TiSe_2$

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In charge ordered materials such as the transition-metal dichalcogenides, the strong coupling between the lattice modes and the charges offers an excellent opportunity for novel phases and unconventional forms of superconductivity to arise. One such material, $TiSe_2$, has recently been found to superconduct under pressure [A. F. Kusmartseva, B. Sipos, H. Berger, L. Forró, and E. Tutiš, Phys. Rev. Lett. **103**, 236401 (2009)]. This finding cannot be explained simply as conventional superconductivity arising from an imbalance of charge carriers. To understand the nature of the fluctuations driving this superconducting phase, it is necessary to elucidate the driving mechanism of the charge ordered state from which it arises. Here we analyze the normal state of $TiSe_2$ starting from a tight-binding model to fit its band structure. The results of this procedure suggest that $TiSe_2$ is best viewed as a system of weakly linked quasi-one-dimensional chains. Building on these findings we propose a simplified quasi-one-dimensional model in which the interaction between the structural and excitonic charge fluctuations can be studied. The balance between competition and cooperation of these degrees of freedom is seen to have a large effect on the nature of the observed charge density wave transition. It is found that neither type of excitation can be held solely responsible for the transition and that it is rather the combined influence of both excitons and phonons that must underlie the observed properties of the charge density wave phase of $TiSe_2$. A qualitative description of experimental results based on the picture of hybrid exciton-phonon modes driving the transition is given and new experiments are proposed which may give quantitative insight into the extent to which each mode is involved.

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I. INTRODUCTION

$TiSe_2$ has been extensively studied for more than three decades but its electronic nature and the origin of its ordered phases remain a matter of debate to this day. The material is either a semiconductor[1–3] or a semimetal,[4–6] with many experimental and theoretical results supporting either view. The only consensus is that the gap separating the conduction band from the valence band is a small (positive or negative) indirect gap of order 150 meV or less and that the carrier density is of the order 5×10^{20} cm^{-3} (see, for example, Refs. 7–9). The predominantly Se $4p$ valence band is located at the center of the first Brillouin zone and the Ti $3d$ conduction band forms electron pockets at the zone boundaries.

Although the nesting between the central hole pocket and the outer electron pockets is poor at best,[3] $TiSe_2$ is observed to undergo a phase transition at 202 K in which a commensurate $(2\times2\times2)$ charge density wave (CDW) forms, accompanied by a periodic lattice distortion. One hypothesis is that a variant of the Jahn-Teller (JT) effect is driving the transition[3,10–13] in which a commensurate spatial reconstruction of the lattice lowers the average energy of both the conduction and the valence bands close to the Fermi surface by facilitating partial charge transfer between neighboring $4p$ and $3d$ orbitals. This could happen through either a lowering of the local bonding state energy, the so-called indirect JT effect described by Whangbo and Canadell[10] or by causing an alteration in the local crystal field around the Ti atoms, the band-type JT effect introduced by Hughes.[11]

The main competing hypothesis is that the transition is driven by exciton formation[5,6,9,14] and possibly condensation.[15,16] The exciton formation is made possible by the paucity of charge carriers in the system and the correspondingly poorly screened Coulomb interaction. With sufficient electron-hole coupling between the valence and conduction bands, the system is unstable to the formation of excitons and deforms with a periodicity governed by the wave vector connecting them,[17–21] which in the case of $TiSe_2$ leads to a doubling of the lattice spacing and backfolding of the conduction bands.

Both scenarios are supported by numerical as well as experimental results but neither can fully explain all the observed effects. For example, electronic band-structure calculations, which take into account JT effects,[13] predict the phonon involved in a JT driven transition to be the experimentally observed L_1^- mode. Holt *et al.*[22] have observed the softening of the L_1^- phonon mode in quasielastic x-ray scattering experiments, emphasizing its importance. In the exciton driven scenario it is much harder to understand why precisely this mode should become unstable because the nesting of electron and hole pockets in the Fermi surfaces of $TiSe_2$ is relatively poor. On the other hand, evidence that electron-hole coupling must also be an important effect comes, for example, from angle resolved photoemission spectroscopy (ARPES) measurements such as those by Cercellier *et al.*,[14] which show a large transfer of spectral weight to backfolded bands in the CDW phase. Such a large amount of charge transfer cannot be fully accounted for by the JT picture.[23]

It is notable that the transition itself is very robust across the range of experimental situations which support one picture or the other. ARPES measurements by Rossnagel *et al.*, for example, found a transition to a semiconducting state involving a continuous lowering of both p-band and d-band energies through the transition, strongly supporting a Jahn-Teller explanation.[3] This is in sharp contrast to the results of Li *et al.*[5] whose infrared measurements strongly support a

semimetal to semimetal transition, at the same critical temperature, driven by electron-hole coupling. Such robustness suggests that the physics driving the CDW might involve a combination of the different effects.

Indeed early work on the CDW state by Wilson *et al.*,[24,25] favoring the excitonic insulator mechanism, also stressed the importance of the strong electron-phonon coupling in $TiSe_2$ facilitating the formation of the periodic lattice distortion and CDW. More recent experimental evidence of the importance of a lattice distortion accompanying excitonic fluctuations in this system comes from ARPES results which examine the renormalization of the carrier mass in $TiSe_2$ at low temperatures.[26] The renormalization is strongly influenced by the anisotropy of the conduction-electron pockets and the resultant anisotropy in the bare effective masses along the two axial directions. The excitonic model of the CDW transition significantly underestimates this anisotropy and the lattice distortions are invoked as a possible source of the experimentally observed difference in effective masses.

The question of the precise nature of the transition has lately attracted renewed attention because it was found that the transition can be tuned to zero temperature upon the intercalation of copper[27] or the application of pressure.[28] In both cases a "dome" of superconductivity arises around the expected location of the quantum critical point. The copper-doped $TiSe_2$ is believed to be a conventional BCS-type superconductor arising out of an imbalance of charge carriers. The pure compound under pressure on the other hand does not seem to easily fit that description. The mechanism driving its superconductivity is expected to be closely related to the nature of the parent CDW state, suggesting that the pairing in this state could be mediated by (Jahn-Teller) phonons, excitonic fluctuations, or a combination of both.

In this paper we argue that the observed strong interactions between excitons and JT distortions arise from the presence of a structure of weakly connected quasi-one-dimensional chains. In Sec. II we present a tight-binding approach to analyze the electronic structure of $TiSe_2$. The resulting values for the orbital overlap integrals show that the material consists of quasi-one-dimensional chains of Ti atoms, which are connected to each other only via the interspersed Se atoms. Excitons formed on such chains will be confined to them to first order of perturbation theory. Likewise, Jahn-Teller distortions will have a preference for aligning along these chains and they will strongly interact with any excitons that may be present.

Building on this observation, we present in Sec. III a simplified theoretical model in which the interacting tendencies toward exciton formation and lattice distortion can be studied. It is shown that the two effects can cooperate as well as compete, depending on the relative strength of the different coupling constants. Based on a comparison between the properties of the different phases of the model and the observed properties of the CDW state in $TiSe_2$, it is then argued that $TiSe_2$ should lie in the region of phase space in which excitons support phonon exchange and the combined action of both enforces the CDW order.

In Sec. IV we give a qualitative description, based on the findings of the earlier sections, of how excitons and electron-phonon coupling may effectively cooperate in $TiSe_2$ and give rise to the observed distortion pattern. In this combined scenario neither the Jahn-Teller effects nor the presence of excitons can be ignored. We conclude in Sec. V by suggesting some future experiments which may be able to disentangle the influences of excitons and phonons, and thus quantitatively probe the extent of the involvement of either mechanism in the formation of the CDW in $TiSe_2$.

II. TIGHT-BINDING MODEL

$TiSe_2$ is a layered material with hexagonal layers of Ti sandwiched by octahedrally coordinated Se atoms, the so-called 1T-polytype for transition-metal dichalcogenides. The layers are separated from each other by a van der Waals' gap, which allows us to neglect the effects of interlayer coupling to a first approximation. The octahedral coordination of the Ti atom splits its d-shell electrons into a set of high-energy e_g orbitals and low lying, degenerate t_{2_g} orbitals, all of which would be empty in a purely semiconducting ground state. Because the e_g orbitals are much higher in energy than the t_{2_g}, we will focus on the latter and only consider the effects of charge transfer between them and the surrounding Se $4p$ orbitals. The tight-binding Hamiltonian can then be written as[29]

$$\begin{aligned}\hat{H} = &\sum_{i,\alpha} \frac{\Delta}{2}(\hat{d}^{\dagger}_{i,\alpha}\hat{d}_{i,\alpha} - \hat{p}_{1i,\alpha}^{\dagger}\hat{p}_{1i,\alpha} - \hat{p}_{2i,\alpha}^{\dagger}\hat{p}_{2i,\alpha}) \\ &+ \sum_{\langle i,j\rangle,\alpha,\beta} \{t^{dd}_{\alpha,\beta,i-j}\hat{d}^{\dagger}_{i,\alpha}\hat{d}_{j,\beta} + t^{pp}_{\alpha,\beta,i-j}[\hat{p}_{1i,\alpha}^{\dagger}\hat{p}_{1j,\beta} + \hat{p}_{2i,\alpha}^{\dagger}\hat{p}_{2j,\beta}] \\ &+ t^{pd}_{\alpha,\beta,i-j}[\hat{d}^{\dagger}_{i,\alpha}\hat{p}_{1j,\beta} + \hat{d}^{\dagger}_{i,\alpha}\hat{p}_{2j,\beta} + \text{H.c.}] \\ &+ t^{pp}_{\alpha,\beta,i-j}[\hat{p}_{1i,\alpha}^{\dagger}\hat{p}_{2j,\beta} + \text{H.c.}]\}. \end{aligned} \quad (1)$$

Here $\hat{d}_i^{\dagger}$, $\hat{p}_{1i}^{\dagger}$, and $\hat{p}_{2i}^{\dagger}$ create electrons on the Ti, the upper Se, and the lower Se atom, respectively, in the unit cell centered at $\vec{R}_i$. The labels α and β run over all possible orientations of the Ti t_{2_g} and Se p orbitals and $\langle i,j\rangle$ denotes neighboring sites both within and between unit cells. The difference in chemical potential between the orbitals is given by Δ while all the different hopping pathways are included in the matrices t^{dd}, t^{pd}, and t^{pp}.

Many of the interactions between neighboring orbitals are (nearly) zero due to the symmetry of the crystal lattice. The remaining entries can be expressed in terms of Slater-Koster integrals.[30] Ignoring the weakest of these integrals,[31] there remain only seven different nonzero overlaps which are not equivalent under symmetry transformations (see Fig. 2). Writing these seven overlap integrals in terms of only five relevant Slater-Koster integrals and taking into account the chemical-potential difference between the Ti and Se sites, we can transform the Hamiltonian to momentum space and obtain the band structure for this model by diagonalizing the resulting 9×9 matrix. By adjusting the values of the Slater-Koster integrals the tight-binding bands can then be fit to the band structures obtained in earlier local-density approximation (LDA) calculations.[9,32,33] The resulting fits are shown in Fig. 1.

As can be seen from the figures, the shapes of the bands in our tight-binding calculations are in good qualitative

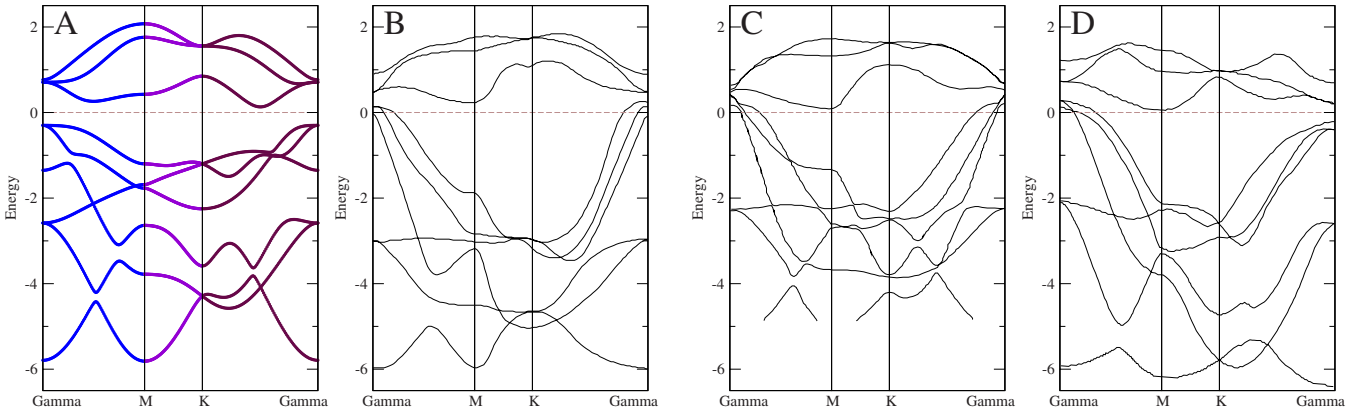

FIG. 1. (Color online) Comparison of the tight-binding band structures with earlier calculations. (A) shows the results of our calculations with parameters which give the best overall agreement with all of the previous results. (B) compares the result to the LDA calculations of Zunger and Freeman (Ref. 9), (C) to the DFT results of Jishi *et al.* (Ref. 32), and (D) to the 23-parameter tight-binding calculations of Yoshida *et al.* (Ref. 33). The values for the three most important Slater-Koster integrals used in these fits are $(dd\sigma)=-0.75$, $(pp\sigma)=0.6$, and $(pd\pi)=1.1$ while $\Delta=1.5$ eV.

agreement with the earlier results. The values of the parameters that give the optimal fit suggest that three Slater-Koster integrals, in particular, dominate the behavior of the bands. In fact, setting the other overlap integrals identical to zero and repeating the fitting procedure with only Δ, $(dd\sigma)$, $(pp\sigma)$, and $(pd\pi)$ as fitting parameters results in fits which are very similar to the ones shown in Fig. 1 both in appearance and in their closeness to the LDA results. This observation leads us to the conclusion that only three hopping pathways contribute significantly to the behavior of charges close to the Fermi energy in $TiSe_2$. These three pathways are marked t_1^{dd}, t^{dp}, and t_2^{pp} in Fig. 2, from which it becomes clear that they constitute a network of one-dimensional chains of Ti $3d$ orbitals, connected to other chains only via the Se p orbitals.[29]

To see the effect of the quasi-one dimensionality on the properties of the charge fluctuations in $TiSe_2$, focus on a single unoccupied Ti $3d$ orbital, and the occupied Se $4p$ orbitals surrounding it. By forming a bonding state along one of the available Ti-Se links, the indirect Jahn-Teller effect described by Whangbo and Canadell[10] is realized and the total energy is lowered due to a gain in kinetic energy. Further energy can be gained by shortening the corresponding bond length. Alternatively, the transfer of an electron charge to the Ti site and the creation of a hole on the Se site it leaves behind can lead to the formation of an exciton (a bound particle-hole pair with a finite lifetime) in which case the total energy is found to be lowered by the binding energy of this exciton.[6] The excitonic radii in semiconductors closely related to $TiSe_2$ are approximately 5–20 Å due to the low Thomas-Fermi screening length (see Ref. 25, and references therein). This radius is further reduced by the high polarizability of the Se atoms and so is likely to be of order the lattice constant.[25,34]

It is thus clear that any charge transferred toward a Ti site, whether stabilized by the exciton binding energy or Jahn-Teller physics, will be constrained to remain adjacent to the Se hole. The combined excitation is free to move only along the one-dimensional chain associated with the particular Ti $3d$ orbital that it occupies. To jump to any of the neighboring or crossing chains, the existing Ti charge would have to be transferred back to a Se atom before it could be given to any other Ti orbital. Such processes only show up in second order in perturbation theory and to a first approximation we can therefore consider $TiSe_2$ to consist of weakly coupled one-dimensional Ti chains and their surrounding Se environment.[29]

Because both of the possible charge-transfer excitations are bound to the one-dimensional chains, a strong interaction between excitonic modes and Jahn-Teller modes within each chain will be unavoidable. These modes however do not necessarily compete: both of them favor a shortening of the bond length connecting the central Ti atom to the Se atoms from which charge has been transferred. It thus seems very well possible that the excitonic mode is reinforced by the presence of Jahn-Teller distortions and vice versa.

III. EXCITON FORMATION AND ELECTRON-PHONON COUPLING

To describe a material like $TiSe_2$ in which excitons as well as lattice deformations are present, we should consider a model Hamiltonian of the general form

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{exc}} + \hat{H}_{\text{e-p}}. \tag{2}$$

This includes the bands of noninteracting electrons H_0, the Coulomb interaction between electrons and holes responsible

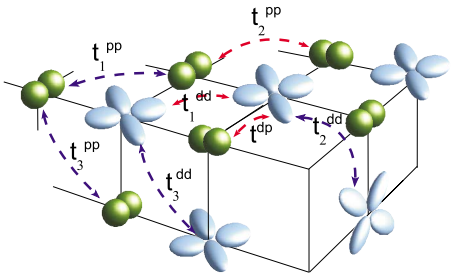

FIG. 2. (Color online) The seven inequivalent hopping pathways used in the tight-binding description. All other overlap integrals are either zero by symmetry or expected to be negligibly small.

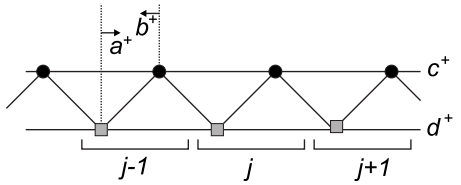

FIG. 3. The quasi-one-dimensional double chain used as a model to study the interplay of electron-phonon coupling and exciton formation. Hoppings between sites on the upper and lower chains are described by combinations of the electronic c and d operators while lattice deformations are included through the a and b phonon operators.

for creating excitons H_{exc}, and the electron-phonon interaction $H_{\text{e-p}}$. The tight-binding description of the previous section gives us an idea of the form of H_0 but it does not include the effects of the other two terms. The precise strengths of the effective electron-phonon coupling arising from JT effects and the exciton binding energy in $TiSe_2$ are difficult to estimate from first principles. The balance between these two influences however is precisely what determines the driving force behind its mysterious CDW transition, and it is thus important to understand how they interact, and whether they will compete, coexist, or indeed cooperate. To study the interplay between electron-phonon interactions and exciton formation we introduce a greatly simplified model, based on the presence of quasi-one-dimensional chains in $TiSe_2$. The model system consists of two coupled chains, schematically shown in Fig. 3. The c sites represent the Se $4p$ orbitals while the $d^\dagger$ operators create electrons in the Ti $3d$ orbitals. Multiple copies of these double chains may be put together to form a larger, three-dimensional structure but if the coupling between different double chains is weak it can be taken to be a higher order effect and we will thus neglect it here.

The Hamiltonian governing the model will take the form of Eq. (2). The noninteracting part includes the chemical potential, the bare dispersions along the c and d chains, and the hopping between c and d sites, taken directly from the tight-binding results. Together with the phonon energy (whose value is taken from experiment), they constitute the bare potential and kinetic-energy terms of the model,

$$\hat{H}_0 = \hbar\omega\sum_i (\hat{a}_i^\dagger\hat{a}_i + \hat{b}_i^\dagger\hat{b}_i) + \frac{\Delta}{2}\sum_i (\hat{d}_i^\dagger\hat{d}_i - \hat{c}_i^\dagger\hat{c}_i) + \frac{t}{2}\sum_i (\hat{d}_i^\dagger\hat{d}_{i+1} + \hat{c}_i^\dagger\hat{c}_{i+1} + \text{H.c.}) + t'\sum_i (\hat{d}_i^\dagger\hat{c}_i + \hat{d}_{i+1}^\dagger\hat{c}_i + \text{H.c.}). \quad (3)$$

The exciton binding energy is approximated as a purely local term which favors electrons and holes to be no further than one lattice spacing apart

$$\hat{H}_{\text{exc}} = -V\sum_i [\hat{d}_i^\dagger\hat{d}_i(1-\hat{c}_i^\dagger\hat{c}_i) + \hat{d}_i^\dagger\hat{d}_i(1-\hat{c}_{i-1}^\dagger\hat{c}_{i-1})]. \quad (4)$$

Notice that this term does not describe the bare Coulomb interaction but rather the effective attraction between electrons and holes that is left over after the repulsive interaction between bare electrons has been taken into account in the band structure. Jahn-Teller effects can be encoded in the electron-phonon term, which couples the c and d orbitals to the phonon operators $\hat{a}^\dagger$ and $\hat{b}^\dagger$, and their associated dimensionless distortions, $\hat{X}^a = (\hat{a}^\dagger + \hat{a})/\sqrt{2m\omega a^2}$ and $\hat{X}^b = (\hat{b}^\dagger + \hat{b})/\sqrt{2m\omega a^2}$,

$$\hat{H}_{\text{e-p}} = \alpha\sum_i [(\hat{X}_i^a + \hat{X}_i^b)(\hat{d}_i^\dagger\hat{c}_i + \hat{c}_i^\dagger\hat{d}_i) - (\hat{X}_{i+1}^a + \hat{X}_i^b)(\hat{d}_{i+1}^\dagger\hat{c}_i + \hat{c}_i^\dagger\hat{d}_{i+1})]. \quad (5)$$

To understand the basic interplay between exciton formation and electron-phonon coupling in this model, we solve it on the mean-field level. The mean fields are given by the average electron density on the different sites, $\langle\hat{d}_i^\dagger\hat{d}_i\rangle$ and $\langle\hat{c}_i^\dagger\hat{c}_i\rangle$; the charge transfer between Ti and Se sites both within and between unit cells, $\langle\hat{c}_i^\dagger\hat{d}_i\rangle$ and $\langle\hat{c}_i^\dagger\hat{d}_{i+1}\rangle$; and the displacements of the Ti and Se atoms within each unit cell, $\langle\hat{X}_i^a\rangle$ and $\langle\hat{X}_i^b\rangle$. If we name these mean-field expectation values ρ_D, ρ_C, τ_{in}, τ_{out}, u_a, and u_b, respectively, then the fully decoupled Hamiltonian describing the charge density wave formation is given by

$$\begin{aligned}\hat{H} = {} & \sum_k \{\hbar\omega(\hat{a}_k^\dagger\hat{a}_k + \hat{b}_k^\dagger\hat{b}_k)\} + 2\alpha\tau\sqrt{N}[\hat{a}_{k=0}^\dagger + \hat{a}_{k=0} + \hat{b}_{k=0}^\dagger \\ & + \hat{b}_{k=0}]\sum_k \left\{\hat{c}_k^\dagger\hat{c}_k\left[t\cos(ka) - \frac{\Delta}{2} + 2V\rho_d\right]\right. \\ & + \hat{d}_k^\dagger\hat{d}_k\left[t\cos(ka) + \frac{\Delta}{2} + 2V(\rho_c - 1)\right] + \hat{d}_k^\dagger\hat{c}_k[t'(1+e^{ika}) \\ & + \alpha(u_a+u_b)(1-e^{ika}) - V(\tau_{in} + e^{ika}\tau_{out})] + \hat{c}_k^\dagger\hat{d}_k[t'(1 \\ & \left. + e^{-ika}) + \alpha(u_a+u_b)(1-e^{-ika}) - V(\tau_{in}^* + e^{-ika}\tau_{out}^*)]\right\},\end{aligned} \quad (6)$$

where $\tau = \text{Re}(\tau_{in} - \tau_{out})$. Notice that in the bosonic part of this Hamiltonian, only the $k=0$ components of the displacement operators show up because we require the mean-field solution to be translationally invariant. This form of the Hamiltonian can be straightforwardly diagonalized by introducing shifted operators for the phonon modes and employing a Bogoliubov transformation to solve the Fermionic part. Physically, this corresponds to a renormalization of the phonon spectrum (at $k=0$) due to the charge transfer from c to d sites caused by exciton formation and the formation of valence bonds while simultaneously the electronic spectrum is renormalized due to both the presence of lattice distortions, and the interplay between exciton formation and valence bonding.

The phase diagram found by self-consistently solving for the values of the mean fields is shown in Figs. 4 and 5. Figure 4 shows the phase transitions between the different zero-temperature states for different values of the exciton binding energy V and the electron-phonon coupling α (both normalized with respect to the unperturbed bandwidth t_0). The CDW state is characterized by a nonzero mean-field lattice distortion as well by a nonzero value of the parameter τ, which measures the amount of mixing between the c and d

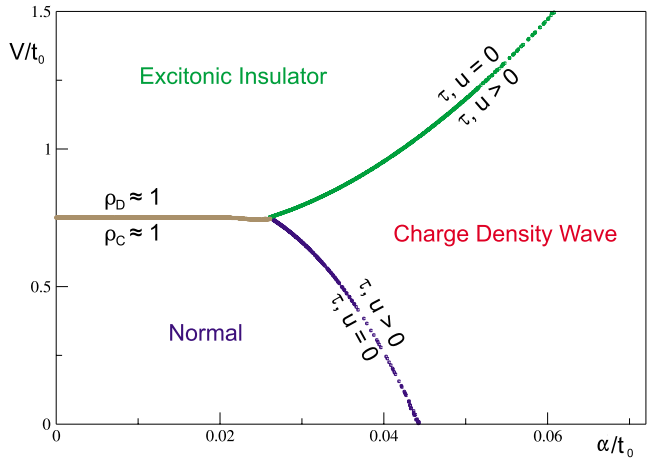

FIG. 4. (Color online) The zero-temperature phase diagram in the mean-field treatment of Eq. (6). Both electron-phonon coupling (Jahn-Teller effects) and exciton formation can be seen to play a role in the transition to the CDW phase.

wave functions. The excitonic insulator signifies the state in which all available charge carriers are bound up into excitons. As one would expect, increasing the strength of the electron-phonon coupling drives the system into a CDW state. There is also a clear initial enhancement of the CDW order with increasing exciton binding energy. At higher binding energies, however, the system is driven into an insulating state in which there is a local exciton on every site. Because there is no direct exciton-phonon coupling in the model on the mean-field level, the lattice distortion disappears completely in the excitonic insulator.

This behavior is shown in more detail in Fig. 5 which displays the variation in the charge transfer ρ_C-ρ_D in the various phases.[35] The normal state has a (nearly) full occupation of the c sites ($\rho_C \simeq 1$) and empty d orbitals ($\rho_D \simeq 0$). Upon increasing the electron-hole coupling while keeping

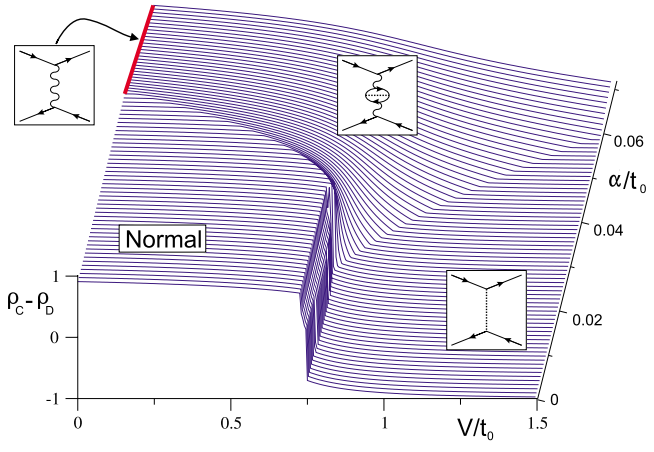

FIG. 5. (Color online) The zero-temperature charge transfer $\rho_C - \rho_D$ in the mean-field treatment of Eq. (6), as a function of the exciton binding energy V and the electron-phonon coupling strength α. The Feynman diagrams indicate the different instabilities of the normal (low V, low α) state. From left to right, they are driven purely by electron-phonon coupling, by a mixture of phonons and excitons, and purely by the excitonic binding energy.

the excitonic binding energy equal to zero, a structural instability is encountered which displaces the atomic positions but only indirectly causes charge to be transferred. The order parameter for this phase is τ, which is of the form $\langle \hat{c}^\dagger \hat{d} + \hat{d}^\dagger \hat{c} \rangle$. The transition thus gives rise to a kink in the evolution of ρ_C-ρ_D rather than a direct discontinuity. Within this state, an increase in the exciton binding energy leads to a continuous enhancement of the charge-transfer effect.

For low enough α however, a different kind of behavior is observed. In this case, the exciton binding energy does not induce much charge transfer until an instability is reached and at zero temperature all of the fully occupied d sites form locally bound excitons with the adjacent empty c orbitals, thus creating an excitonic insulator. The transition into this phase is sharp and characterized by the sudden inversion of ρ_C-ρ_D, without inducing lattice distortions or mixing between wave functions (i.e., τ=0 in this phase).

For α and V both finite, an intermediate type of transition can occur in which an increase in V leads to the renormalization and softening of the phonon spectrum which in turn causes the structural instability. In this case both τ and ρ_C-ρ_D form part of the order parameter and the CDW is mediated by hybridized exciton phonons. To obtain significant amounts of both charge transfer and lattice distortions, it is thus clear that in this model one requires significant values for both the exciton binding energy and the electron-phonon coupling.

Before extrapolating these results to the case of $TiSe_2$, it should be noted that the band structure of $TiSe_2$ is such that there are three symmetry-equivalent conduction bands which couple to the valence band. It has been argued that in this case, for a purely exciton driven transition, the resulting state is not necessarily insulating.[15] The complexity involved in having three symmetry-equivalent conduction bands is not captured in the present simplified model nor does it account for the possible existence of direct exciton-phonon coupling, which could cause a structural transition to accompany the onset of the excitonic insulator phase. On the other hand it is also well known that any purely excitonic CDW transition on a lattice will be rendered first order by the presence of Umklapp processes,[36] in agreement with the results presented in Fig. 5. We therefore suggest that the observed second-order transition in $TiSe_2$ into a state characterized by large structural deformations as well as a large amount of spectral weight transfer is most straightforwardly accounted for in a picture in which both electron-phonon coupling and exciton binding energy have a significant role to play.

This statement is further supported by examining the influence of excitons on the ordered state in closer detail.[35] Figure 6 shows the mean-field phase diagram as a function of exciton binding energy and temperature. With increasing temperature, the model is driven into the normal state with zero CDW order parameter. An increase in exciton binding energy initially dramatically enhances the transition temperature and then cuts off the CDW as the system is driven insulating. Slices through the phase diagram at fixed temperatures elucidate the amount of charge transfer induced by increasing the exciton binding energy and are shown on the right-hand side of Fig. 6. As the exciton binding energy

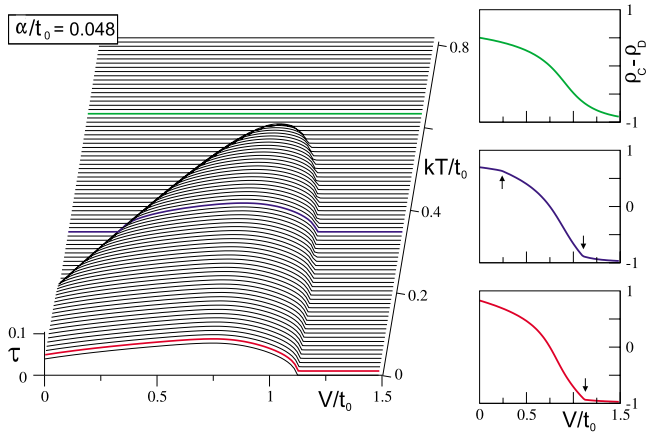

FIG. 6. (Color online) Left: the CDW order parameter τ in the mean-field treatment of Eq. (6), as a function of temperature and the exciton binding energy (normalized with respect to the unperturbed bandwidth) for a constant value of the electron-phonon coupling strength. Right: the charge transfer ρ_C-ρ_D as a function of the exciton binding energy for selected temperatures, corresponding to the thick lines in the diagram on the left. The arrows indicate the transition to the ordered CDW state. Increasing the exciton binding energy leads to an increase in charge transfer, even in the absence of CDW order.

drives the system into, and out of, the CDW phase, kinks appear in the charge transfer vs binding-energy diagrams. Above the critical temperature, the kinks have disappeared but the behavior remains very similar; there is a significant amount of charge transfer due to the exciton binding energy, even in the normal phase of the system. In fact, the exciton formation does not seem much affected at all by the temperature increase shown in Fig. 6 and excitons remain stable to temperatures far beyond the structural transition temperature. By comparison with Fig. 5 we can attribute the kink in charge transfer upon entering the CDW phase to the effects of electron-phonon coupling. It thus appears that although the charge transfer associated with exciton formation strongly modifies the transition temperature of the phonon mediated CDW phase, the excitons by themselves cannot be held responsible for its onset.

It is interesting to note that strong charge-transfer fluctuations above the CDW transition temperature have recently been observed in $TiSe_2$ and attributed to short-range fluctuations in an excitonic condensate order parameter, analogous to the pseudogap in high T_C superconductors.[14,35,37] The "order parameter" above T_C, thus interpreted, has a magnitude of more than half that of the ordered state and changes little up to 288 K. It is difficult to explain why such strong, quasitemperature-independent fluctuations in charge transfer can persist while the CDW phonon frequency smoothly increases with temperature away from the transition if the CDW is purely excitonic in origin.[22] The comparison to Fig. 6 instead suggests that this result could be interpreted as showing the CDW transition to be driven by phonons which are strongly influenced by the presence of excitons. The CDW is destroyed as the phonons are overwhelmed by temperature but the excitons remain stable and show up in the measurement as high-temperature charge fluctuations.

IV. A QUALITATIVE PICTURE

Based on the findings of the previous sections, one can straightforwardly obtain a *qualitative* understanding of how the combined influence of excitons and electron-phonon coupling in $TiSe_2$ can give rise to the observed distortion and charge-transfer patterns, in a way which draws together the competing JT and excitonic scenarios into a coherent picture consistent with all experimental findings.

Because all experiments agree that the overlap between the valence and conduction bands is very small at best, we start our considerations from the state in which all Se 4*p* orbitals are fully occupied while the Ti 3*d* orbitals are empty. We then consider the effect of a single electron temporarily hopping from an occupied Se to an empty Ti orbital. We can describe the resulting state of the electron with a delocalized wave function of the form $|p>+|d>$, which realizes the bonding state described by Whangbo and Canadell,[10] and lowers the total energy due to a gain in kinetic energy. Alternatively, the Ti electron and the Se hole it leaves behind can be said to form an exciton (a bound state with a finite lifetime) in which case the total energy is found to be lowered by the binding energy of this exciton.[6] As argued extensively in the previous section, it should be expected that in practice, both effects simultaneously contribute to charge being delocalized and transferred from Se to Ti, thus lowering the total energy of the system.

The energy of both the exciton and the bonding state can be further lowered by a shortening of the relevant Ti-Se bond, which results in increased orbital overlap (beneficial to the bonding state) as well as an increase in the excitonic binding energy. Focusing on the former influence this effect could be called an indirect JT effect[10] while using the latter it should be described as exciton-phonon coupling.[6] Further energy can be gained by also transferring some charge from other Se atoms into the partially occupied Ti 3*d* orbital, as in Fig. 7(a). This process produces an excitonic object spread over two different Se 4*p* orbitals but sharing the same Ti 3*d* orbital. Alternatively it could be described as a resonating valence bond state occupying these sites.

Next, we consider a single one-dimensional chain of similar Ti 3*d* orbitals and their surrounding Se sites. This is justified by the findings of Sec. II, which were based on both tight-binding calculations of the band structure of $TiSe_2$ and the observation that with the minimal screening and high polarizability in $TiSe_2$, excitons will be tightly bound objects. The electron on the Ti 3*d* orbital therefore cannot escape its one-dimensional hopping path along similar neighboring Ti orbitals without first recombining with a hole on one of the Se 4*p* orbitals. To first order then, both excitons and bonding states are confined to quasi-one-dimensional ribbons in the two-dimensional lattice and give rise to a charge distribution along the chain indicated in Fig. 7(b). Simple electrostatic considerations taking into account the generated dipole moments are sufficient to determine that several of these parallel ribbons will orient themselves as shown in Fig. 7(c). This pattern corresponds exactly to the single-*q* pattern found by Motizuki *et al.*[12] to be a mode to which the undistorted $TiSe_2$ is unstable. They also found that the triple-*q* or L_1^- mode, observed experimentally, was even

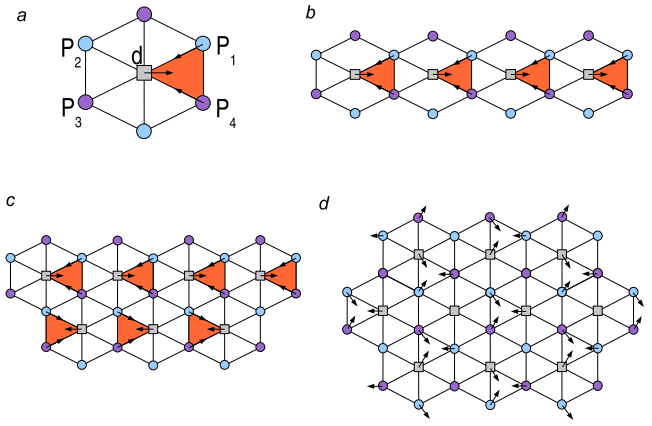

FIG. 7. (Color online) Mechanism for the observed distortion in $TiSe_2$, shown using a c-axis projection of one $TiSe_2$ layer to illustrate the hopping between Se p orbitals (light and dark circles) and Ti d orbitals (gray squares). (a) Hopping between adjacent Se and Ti atoms leading to charge transfer and exciton formation. (b) Deformation pattern along a 1D ribbon caused by the delocalization of the charge-transfer objects in (a). (c) Deformation pattern for adjacent 1D ribbons in the charge density wave state in $TiSe_2$. (d) The deformation pattern that results from the superposition of the distortion pattern in **c** with its two directional equivalents, a distortion found experimentally in $TiSe_2$.

more unstable. This L_1^- mode corresponds to the superposition of a finite density of all three possible single-q modes (the three ribbon orientations) as shown in Fig. 7(d). It can be easily understood that indeed the L_1^- pattern is energetically favored over the single-q pattern, by noticing that the environment of a third of the Ti atoms in the L_1^- distorted lattice is made more prismatic, lowering the energy of the lowest Ti 3d orbitals. This is precisely the band-type JT effect of Hughes.[11]

Thus all three existing hypotheses are combined into a single JT-exciton driven scenario. The specific orbital configuration of $TiSe_2$ gives rise to a network of weakly linked chains, which allows the exciton formation and indirect JT effects to effectively combine and cause charge transfer and CDW formation within each quasi-one-dimensional Ti chain. These chains then align themselves in an L_1^- pattern to make full use of the band JT effect and further lower the overall energy. Like its constituent mechanisms, the combined scenario opens up a gap between Ti 3d and Se 4p bands in the CDW phase of $TiSe_2$.

It is interesting to note in this context that very recent scanning tunneling microscope (STM) measurements on $TiSe_2$ have shown the presence of a phase difference between the different single-q modes making up the triple-q pattern.[38] This results in a helical three-dimensional charge density wave pattern in which the orientation of the dominant single-q mode rotates as one traverses the Se and Ti layers in the material along the direction of its c axis. Within each single layer this implies a slightly more one-dimensional character of the charge distribution than in the case of a triple-q pattern without phase differences. In the above qualitative picture this added one dimensionality may be accounted for as a result of balancing the contributions of the band-type and indirect Jahn-Teller effects.

V. CONCLUSIONS

We have argued in this paper that excitons, orbitals, and phonons are all necessary ingredients in a description of the observed CDW transition in 1T-$TiSe_2$. A tight-binding calculation of the band structure close to the Fermi energy indicates that $TiSe_2$ should be considered a network of weakly coupled one-dimensional chains of Ti 3d orbitals, which interact only via the surrounding Se 4p orbitals. This quasi-one-dimensional character enhances the interaction between excitons and Jahn-Teller distortions in the chains, prompting the need for a more detailed understanding of the possible cooperative and competitive effects arising from their interplay.

The mean-field solutions of a simplified model in which these interactions can be studied by independently varying the strength of the electron-phonon coupling and the exciton binding energy show that the presence of excitons can significantly enhance the CDW order induced by electron-phonon coupling. The softening of the phonons by the excitons allows the CDW phase to occur at lower values of the electron-phonon coupling strength and persist to higher temperatures. Once the exciton binding energy gets too large however, all the available charge carriers are bound up in electron-hole pairs and an excitonic insulator is formed instead. Combined with the experimental observations that the transition in $TiSe_2$ is a second-order transition characterized by large amounts of charge transfer as well as large lattice distortions, this suggests that $TiSe_2$ lies in the region of phase space where both electron-phonon coupling and exciton formation are significant. The CDW transition in that case is caused by hybrid objects consisting of phonons which are strongly renormalized due to the presence of excitons.

From these observations a qualitative understanding of the CDW transition in $TiSe_2$ is easily obtained. The resulting picture of a combined Jahn-Teller/exciton driven scenario combines all of the previously prevailing hypotheses into a single, consistent description, explaining how the observed L_1^- CDW pattern in $TiSe_2$ is formed, why both the displacements and the charge transfer are substantial, and why one should expect the presence of excitons to persist even above the CDW transition temperature.

To get a more quantitative handle on the relative importance of the exciton binding energy and the electron-phonon coupling in $TiSe_2$, several experimental pathways are available. First of all, a comparison can be made between the shape of the gap observed in high-precision ARPES measurements and a more quantitative model of $TiSe_2$, taking into account its full three-dimensional band structure as well as the presence of both Jahn-Teller effects and an excitonic binding energy. Such a comparison is complicated however by the limited portion of available band structure close to the Fermi energy, as well as by the difficulty of fully incorporating all Coulombic and structural terms in the model Hamiltonian.

It may be more useful therefore to look for a way of directly measuring the strength of each contribution to the

observed CDW transition. One way in which this could be done is using time-resolved electron spectroscopy in which the material is heated through the transition by an intense ultrashort infrared pulse and the spectrum is analyzed in a pump-probe setup as the material relaxes back toward the ordered state. This results in a real time picture of the evolving electronic band structure during the transition.[39] Comparison of the observed relaxation rates with the time scales on which excitonic and phononic effects are expected to set in can then reveal the importance of either contribution.

Finally, it has been pointed out that the excitonic binding energy in a material with very small (positive or negative) band overlap can be increased by applying a strong external magnetic field.[40] Using this effect as a way of tuning the relative importance of the electron-phonon coupling and the exciton binding energy and combining it with the spectroscopic techniques mentioned before, one can begin to explore the phase space spanned by the independent influences of exciton formation and electron-phonon coupling. Depending on the parameter values realized in $TiSe_2$ it may even be possible to drive it from a combined phonon-exciton driven CDW phase into a purely excitonic insulator.

Establishing the importance of both the electron-phonon coupling and the presence of exciton formation in $TiSe_2$ in this way provides a platform for describing not only the CDW phase itself but also the nature of the superconductivity which appears as CDW order is suppressed by pressure. The physics in this region of phase space will strongly depend on the nature of the critical fluctuations arising from the suppressed CDW phase and again there is the possibility of competition, coexistence, and even cooperation between excitons and (Jahn-Teller) phonons in the formation of the ordered state.

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