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Origin of the charge density wave in $1T$-TiSe$_2$

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All-electron *ab initio* calculations are used to study the microscopic origin of the charge density wave (CDW) in $1T$-TiSe$_2$. A purely electronic picture is ruled out as a possible scenario, indicating that the CDW transition in the present system is merely a structural phase transition. The CDW instability is the result of a symmetry lowering by electron correlations occurring with electron localization. Suppression of the CDW in pressurized and in Cu-intercalated $1T$-TiSe$_2$ is explained by a delocalization of the electrons, which weakens the correlations and counteracts the symmetry lowering.

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I. INTRODUCTION

A charge density wave (CDW) is a collective state that often appears in low-dimensional electronic systems. In many cases it is connected to superconductivity, another collective phenomenon.[1–7] One of the early discovered CDW materials is $1T$-TiSe$_2$,[8] which has seen a revival of interest with an intense debate about the origin of the CDW[9–21] and the recently discovered superconductivity.[18,22–29] $1T$-TiSe$_2$ is a layered compound, consisting of slabs in which Ti is octahedrally coordinated by six Se atoms. Successive Se-Ti-Se sandwiches with covalent ionic bonds are separated by a van der Waals gap, giving rise to a quasi-two-dimensional nature. Below 200 K, a commensurate CDW develops with a $2 \times 2 \times 2$ superstructure[8] [see Fig. 1(a)]. While lowering the temperature alone does not make $1T$-TiSe$_2$ superconducting, superconductivity is stabilized by either Cu intercalation[22] or pressure,[29] with a suppression of the CDW.

The origin of the CDW instability in $1T$-TiSe$_2$, though extensively studied both by experiment and theory, is not yet settled. Fermi surface nesting cannot be a possible scenario, since parallel Fermi surface sheets have neither been predicted nor observed.[6] One explanation is the band Jahn-Teller effect,[9,11,12,18,21] a lowering of the average energy of the valence and conduction bands around the Fermi surface as a result of lattice distortions. The most promising idea for the driving force, however, is exciton condensation,[10,13–15,17,19,20,30,31] which is a purely electronic effect. In $1T$-TiSe$_2$, electrons and holes appear at the Se $4p$ derived valence band maximum at the Γ point and the Ti $3d$ derived conduction band minimum at the L point, respectively. Due to a low free-carrier density, the weak screening of the electron-hole Coulomb interaction leads to the formation of stable electron-hole bound states (excitons).[30,31] When the exciton binding energy is larger than the energy gap, the formation of excitons makes the system unstable and yields the CDW transition. Both models are supported by a variety of experiments, including measurements of the electronic band structure by means of angle-resolved photoemission spectroscopy.

In this paper, we will explain the microscopic origin of the CDW transition in $1T$-TiSe$_2$ by first-principles calculations. We will show that electron correlations are the driving force. As a consequence, the localization of the valence electrons plays a crucial role, which allows us to understand the suppression of the CDW in pressurized and in Cu-intercalated $1T$-TiSe$_2$.

II. CRYSTAL STRUCTURE

In the normal state, $1T$-TiSe$_2$ crystallizes in the space group $P\bar{3}m1$ (No. 164). The Ti and Se atoms occupy $1a$ [(0, 0, 0)] and $2d$ [(1/3, 2/3, z_0)] sites, respectively, with experimental structure parameters of $a_0 = 3.54$ Å, $c_0 = 6.008$ Å, and $z_0 = 0.255\,04$. In the CDW state, on the contrary, the periodicity is doubled in all directions ($a = 2a_0$, $c = 2c_0$, and $z = 1/4 - z_0/2$), and atoms are displaced from their original position by small distances $\delta_{\mathrm{Ti}} = 0.012a$ and $\delta_{\mathrm{Se}} = 0.004a$. Thus, the space group changes to $P\bar{3}c1$ (No. 165) with the Ti atoms located at $2a$ [(0, 0, 1/4)] and $6f$ [($1/2 + \delta_{\mathrm{Ti}}$, 0, 1/4)] sites and the Se atoms at $4d$ [(1/3, 2/3, z)] and $12g$ [(1/3, $1/6 + \delta_{\mathrm{Se}}$, z)] sites.

III. TECHNICAL DETAILS

Full-potential linearized augmented plane wave calculations are performed using the WIEN2K package.[32] A threshold energy of -6.0 Ry is used to separate the valence from the core states. We employ a muffin-tin radius of $R_{\mathrm{mt}} = 2.2$ bohr, $R_{\mathrm{mt}}K_{\max} = 10$, $\ell_{\max} = 10$, and a $10 \times 10 \times 5$ Brillouin zone mesh. Three approximations to the exchange-correlation functionals are used: the local density approximation (LDA),[33] the generalized gradient approximation (GGA),[34] and a combination of the modified Becke-Johnson exchange potential and the LDA correlation potential (mBJ-LDA).[35] Spin-orbit coupling is included in all calculations using the second-variational method with a scalar relativistic basis, where states up to 10 Ry above the Fermi energy (E_F) are included in the basis expansion.

IV. RESULTS AND DISCUSSION

We first examine the possibility of a purely electronic CDW transition. This is important because a CDW and a structural phase transition both have a periodic lattice distortion as a macroscopic sign, being distinguished only by the origin of the transition.[36] In the purely electronic picture, the distortion is a secondary effect in response to an electronically driven charge density redistribution that occurs regardless of whether or not the ions shift off the symmetric positions.[36] One way to address

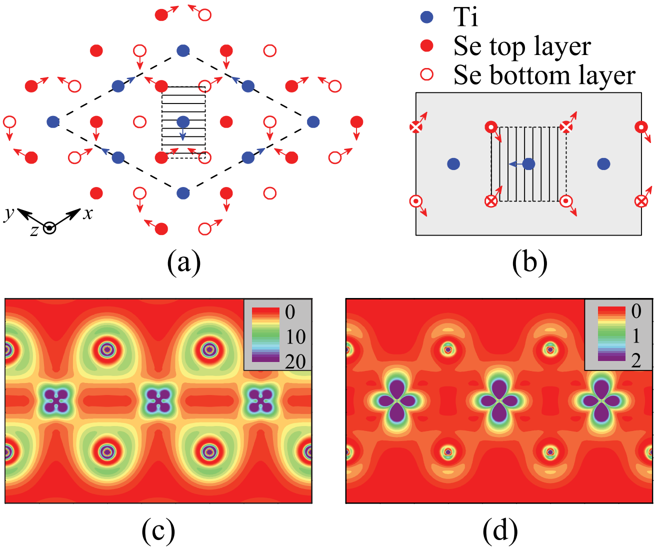


FIG. 1. (Color online) (a) Illustration of the CDW instability in one of the two Se-Ti-Se slabs in the $2 \times 2 \times 2$ $1T$-TiSe$_2$ superstructure. Arrows indicate the atomic displacements associated with the CDW distortion. (b) Se-Ti plane, containing the Se-Ti bonds. (c) Charge density distribution (e/a.u.^{3}) of valence electrons (Se $4p$ and Ti $3d$) in the Se-Ti plane defined in (b) in the undistorted structure. (d) Same as (c), but for electrons near the Fermi level ($E_F \pm 0.5$ eV).

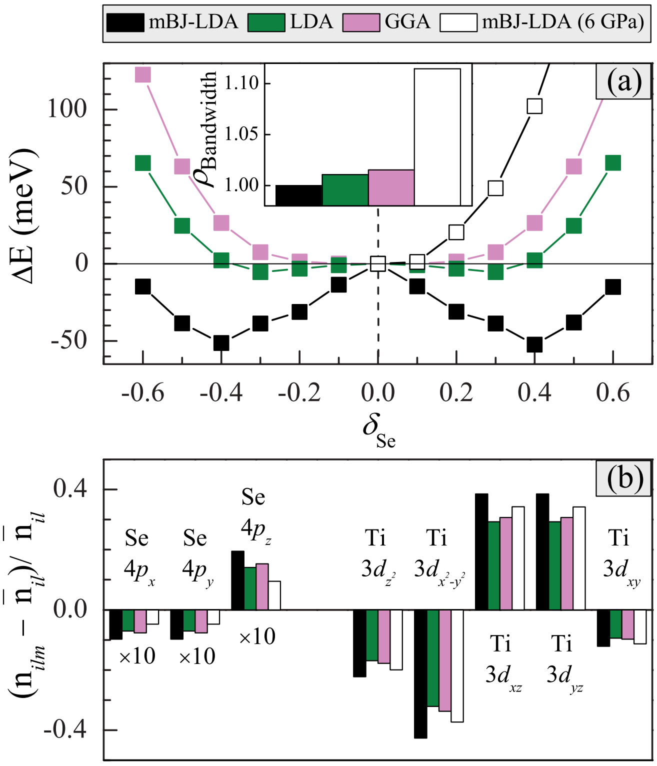


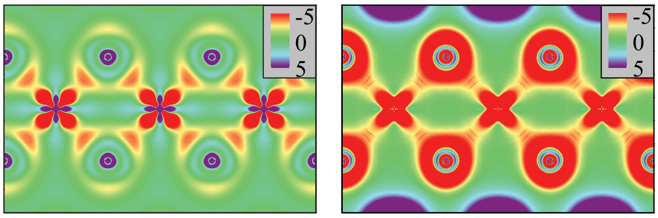
FIG. 2. (Color online) (a) Energy surface of the CDW distortion from the LDA, GGA, and mBJ-LDA calculations at ambient pressure and the mBJ-LDA calculation under a pressure of 6 GPa. The ratio of the valence bandwidths from the GGA, LDA, and mBJ-LDA calculations with respect to that from the mBJ-LDA calculation is addressed in the inset. (b) Orbital polarization $(n_{ilm} - \bar{n}_{il})/\bar{n}_{il}$ of the valence electrons. n_{ilm} is the occupation number of suborbital m of orbital l in atom i, and $\bar{n}_{il}$ is the average occupation number of orbital l in atom i. Note that occupation numbers refer to the muffin-tin spheres only.

this question is to check whether a charge density redistribution with doubled lattice periodicity in all three dimensions is possible in the artificially undistorted structure. The charge density distributions of the valence electrons (Se $4p$ and Ti $3d$) and the electrons around the Fermi level ($E_F \pm 0.5$ eV) in an undistorted $2 \times 2 \times 2$ supercell are presented in Figs. 1(c) and 1(d), respectively. Our LDA, GGA, and mBJ-LDA calculations yield no appreciable charge density redistribution with doubled lattice periodicity, ruling out a purely electronic instability as the driving force of the CDW transition. Only the mBJ-LDA results are shown in Fig. 1 as an example.

Furthermore, the valence electrons, see Fig. 1(c), and electronic states around E_F, see Fig. 1(d), show a very different spatial extension. While the former are mainly accumulated in the region where Se-Ti bonds are formed, the latter point to the interstitial areas. This means that the modifications of the Se-Ti bonds in the CDW transition will affect the valence electrons more significantly than the electronic states around E_F. In other words, the CDW instability is only slightly related to the latter. This also speaks against the purely electronic CDW transition as the promising excitonic picture of the transition is governed by the electronic states around E_F.[30,31] We therefore can conclude that the CDW transition in $1T$-TiSe$_2$ is merely a structural phase transition. This reasoning is in line with recent findings on NbSe$_2$, TaSe$_2$, and CeTe$_3$ showing that the lattice distortion is necessary for the CDW transition but not the other way round.[36]

A simulation of the CDW transition by a relaxation of the atomic forces is not possible in WIEN2K for spin-orbit coupling and/or the mBJ-LDA functional. Therefore, we search for the energy minimum by calculating the energy surface for a series of amplitudes of the CDW distortion, characterized by δ_{Ti} and δ_{Se}. For simplicity reasons, we fix the ratio $\delta_{\mathrm{Ti}}/\delta_{\mathrm{Se}} = 3$ to its experimental value. Results for the LDA, GGA, and mBJ-LDA approaches are shown in Fig. 2(a). We observe a strong dependence on the choice of the exchange-correlation functional. While the GGA calculation leads to no energy reduction when the structure is distorted toward the CDW, an energy minimum is found in the LDA calculation with an equilibrium value of $\delta_{\mathrm{Se}} = 0.3$ and an energy reduction of 5.4 meV. Although the LDA calculation successfully predicts the CDW instability, it misses a quantitative agreement with experiment. First, the theoretical equilibrium value of δ_{Se} deviates from the experimental value of 0.4. Second, at the experimental transition temperature of 200 K, the theoretical energy gain by the CDW distortion is smeared out by thermal vibrations and the CDW is not stable. On the other hand, a quantitative agreement is achieved in the mBJ-LDA calculation. The experimental equilibrium value of δ_{Se} here is perfectly reproduced and we obtain an energy gain of 51.2 meV, which is able to stabilize a CDW at 200 K.

The methodology dependence of the theoretical reproduction of the CDW transition provides an opportunity to gain insight into the microscopic origin of the CDW instability



(a) (b)

FIG. 3. (Color online) (a) Charge transfer ($10^{-3}\, e/\text{a.u.}^3$) in the Se-Ti plane defined in Fig. 1(b) associated with the alteration of the exchange-correlation functional from mBJ-LDA to GGA. (b) Charge transfer in the Se-Ti plane caused by a pressure of 6 GPa from mBJ-LDA calculations.

in $1T$-TiSe$_2$. The GGA, LDA, and mBJ-LDA approaches are approximate descriptions of the interacting electrons, all three favoring charge density inhomogeneity,[33–35] in particular orbital polarizations. For a partially filled orbital, a suborbital with smaller occupation is subject to a higher exchange-correlation potential and tends to donate electrons to a suborbital with higher occupation (smaller potential). For stronger correlations, this disproportionation is stronger. Moreover, an orbital polarization leads directly to a symmetry lowering. For sufficiently strong correlations, a symmetry breaking lattice distortion lowers the total energy because the gain in exchange-correlation energy overcompensates for the energy costs. Orbital polarization and symmetry lowering are found already for moderate correlations[37] and become prominent in strongly correlated systems.[38] In this regard, our results can be interpreted as a manifestation of a symmetry lowering due to electron correlations.

To confirm our idea, we need to establish a relationship between the strength of the electron correlations and the choice of the exchange-correlation functional in our calculations. The strength of the correlations is related to the degree of electron localization, which can be characterized by the bandwidth. The relative change of the valence bandwidth in the LDA and GGA calculations with respect to the mBJ-LDA calculation is addressed in the inset of Fig. 2(a). Indeed, the valence band widens in the order mBJ-LDA, LDA, and GGA, reflecting an enhanced delocalization of the electrons and a weakening of the correlations. As a result, the dependence of the theoretical reproduction of the CDW transition on the exchange-correlation functional [recall Fig. 2(a)] is well explained by reduced correlation effects along the series mBJ-LDA, LDA, and GGA, and thus a reduced tendency to symmetry lowering. We emphasize that the exact reproduction of the CDW by the mBJ-LDA approach is not a simple coincidence. In contrast to the LDA and the GGA, the mBJ-LDA approach mimics the behavior of orbital-dependent potentials. Thus, electron correlations are treated with high accuracy, similar to involved hybrid functional and Gutzwiller calculations.

The orbital polarization effect, which depends on the strength of the electron correlations and determines the symmetry lowering, is also reflected by the charge density distributions for different exchange-correlation functionals. In Fig. 3(a), we analyze the modification of the valence charge density distribution in the Se-Ti plane of the undistorted structure when the exchange-correlation functional is switched from mBJ-LDA to GGA. Going to the GGA leads to a shift of charge from the bonding area with high electron density to the interstitial area with low density. This means that the weaker electron correlations in the GGA calculation come along with less orbital polarization. A reduced orbital polarization in the LDA and GGA calculations, as compared to the mBJ-LDA, is also seen in Fig. 2(b), although the occupation numbers refer only to the interior of the muffin-tin spheres, ignoring the interstitial area. If we switch from mBJ-LDA to LDA or GGA, the occupation numbers of the Se $4p_z$, Ti $3d_{xz}$, and Ti $3d_{yz}$ orbitals, which contribute to the Se-Ti bonding, are reduced. However, the occupation numbers of the Se $4p_x$, Se $4p_y$, Ti $3d_{z^2}$, Ti $3d_{x^2-y^2}$, and Ti $3d_{xy}$ orbitals, which point to the interstitial area, are increased.

To support the picture of a CDW transition driven by electron correlations, we next investigate the suppression of the CDW both in pressurized and in Cu-intercalated $1T$-TiSe$_2$.[22,29] Because the symmetry lowering effect that occurs along with the correlations is determined by the electron localization, the suppression of the CDW under Cu intercalation is fully explained by the delocalization of the electronic states due to hybridization between the TiSe$_2$ valence electrons and the itinerant Cu $4s$ electrons. Similarly, the disappearance of the CDW under pressure traces back to the electron delocalization induced by the enhanced orbital overlap due to smaller atomic distances. As an example, results for $1T$-TiSe$_2$ under a pressure of 6 GPa are shown in Figs. 2 and 3(b). A widening of the valence band by 10% signals an electron delocalization and therefore a weakening of electron correlations in the pressurized compound. The consequent reduction of the orbital polarization is confirmed by the modifications of the charge density distribution [see Fig. 3(b)] and occupation numbers of relevant suborbitals [see Fig. 2(b)]. As a result, the CDW vanishes in pressurized $1T$-TiSe$_2$.

V. CONCLUSION

In conclusion, we have used all-electron *ab initio* calculations to investigate the microscopic origin of the CDW in $1T$-TiSe$_2$. No charge density redistribution with doubled lattice periodicity is found as long as the atoms are kept at their original positions. This prevents the CDW from being of a purely electronic origin. No distinction can be made between the CDW and a structural phase transition. The theoretical reproduction of the CDW depends strongly on the choice of the exchange-correlation functional, indicating a crucial role of electron correlations. Symmetry lowering along with the correlations is found to be responsible for the CDW instability. Electron localization, determining the strength of the correlations and thus the symmetry lowering, is shown to be crucial. Our conclusion is strongly supported by the suppression of the CDW in pressurized as well as in Cu-intercalated $1T$-TiSe$_2$. Both phenomena can be attributed to the delocalization of valence electrons caused by enhanced hybridization under pressure and additional hybridization with itinerant Cu $4s$ electrons, respectively.

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