

Suppression of charge-density formation in TiSe₂ by Cu doping

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The charge-density wave (CDW) state in TiSe₂ vanishes rapidly with Cu doping and is suppressed almost completely upon the onset of superconductivity. Since the CDW-related structural instability also disappears, it is suggested that the additional doped charge induces a redistribution of the density of states at the Fermi level, destroying the local double-well potential responsible for the CDW and the structural instability.

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TiSe₂ is a layered material which undergoes a charge-density wave (CDW) transition to a state with commensurate wave vector $(2a, 2a, 2c)$ around 200 K.¹⁻³ The weak interlayer coupling makes it easy to intercalate this compound with various guest atoms by means of which new properties can be tuned ranging from normal metallic states to antiferromagnetic and superconducting (SC) ground states.⁴⁻⁷ Mostly, intercalation with 3d metals causes a suppression of the CDW formation, but it has also been observed that the CDW state may reappear with large intercalant content.⁶ The CDW state itself has been investigated in detail since its origin was not shown to be due to Fermi-surface nesting.^{1,2} Instead, it was suggested that the combination of an indirect Jahn-Teller effect with strong electron-hole coupling⁸ could cause the instability. Also, the formation of an excitonic insulator⁹⁻¹¹ or a band-type Jahn-Teller effect^{12,13} has been considered to drive the CDW state. Since the CDW formation is accompanied by a pronounced zone-boundary phonon mode softening,^{1,14,15} an antiferroelectric instability could also cause the charge ordering.¹⁶ This origin has the advantage that charge redistribution takes place due to strong anharmonic electron-phonon interactions. In particular, the huge anomaly in the resistivity at the transition temperature T_{CDW} (Ref. 1) is naturally explained in this way.

The recent observation of superconductivity in Cu intercalated TiSe₂ (Ref. 7) has enormously renewed the interest in this material. In fact, in layered $MX_{2,3}$ compounds a superconducting instability frequently lies close to the charge ordered state.^{1,17-20} However, it is well known that both states are noncooperative and nearly mutually exclusive, even though electron-phonon interactions are driving both phenomena. Typically, the CDW state is suppressed in favor of the SC state upon applying pressure and/or doping. TiSe₂ is unique in this respect since Cu can be intercalated in a controlled manner and the crossover from CDW to SC studied systematically.⁷ With Cu intercalation, T_{CDW} decreases and seems to reach zero around $x=0.06$ in Cu_xTiSe_2 . Superconductivity sets in at $x=0.04$, has a maximum superconducting transition temperature T_c of 4.5 K at $x=0.08$, and decreases again for larger x .⁷ The doping dependence of T_c has a dome-like shape reminiscent of copper oxides. From the in-plane thermal conductivity, the absence of a residual linear term with temperature T approaching zero provides strong evidence that the order parameter in the superconducting samples is of simple s -wave symmetry.²¹ Together with the

loss of CDW order the structural instability is also suppressed. The CDW-related phonon mode energy systematically decreases, whereas its linewidth increases substantially.²² Since the Hall coefficient increases with Cu doping, it must be concluded that the carrier concentration also increases with doping.²³ In addition, in the superconducting regime an electronlike pocket near the L point starts growing, while the long-range coherence of the CDW state is lost.²⁴

All the above experimental results clearly reveal that with the loss of the structural instability and the correlated CDW state a redistribution of the electronic density takes place which is the origin of the SC state. The superstructure formation at T_{CDW} , the concomitant phonon mode softening, and the unknown origin of the CDW state have motivated us to relate its origin to the appearance of an antiferroelectric state which originates naturally from a zone-boundary mode instability.¹⁶ Such a phase transition is driven by strong p - d hybridization and nonlinearity which causes charge redistribution and localization as observed at T_{CDW} in TiSe₂.

In the following we use the same approach as already given in Ref. 16 to calculate the suppression of the CDW state with Cu doping in Cu_xTiSe_2 . In order to model an antiferroelectric instability, the nonlinear polarizability model²⁵ has been used, where a local double-well potential in the electron lattice interaction causes the zone-boundary phonon mode instability and the unit-cell doubling. The crucial quantity here is the configurational instability of the Se^{2-} ion. This is similar to the instability of the oxygen ion O^{2-} but less effective, namely, the p electrons have a stronger tendency toward delocalization.²⁶ This property can be modeled phenomenologically by introducing a polarizability coordinate w , which is the relative displacement between the Se ionic core and its surrounding shell.^{16,25} The Hamiltonian is then given by

$$H = \frac{1}{2} \sum_n \left[M_1 \dot{u}_{1n}^2 + m_2 \dot{u}_{2n}^2 + f'(u_{1n+1} - u_{1n})^2 + f(v_{1n} - u_{2n})^2 + f(v_{1n+1} - u_{2n})^2 + g_2 w_{1n}^2 + \frac{1}{2} g_4 w_{1n}^4 \right], \quad (1)$$

where M_1 refers to the Se ionic mass, m_2 is the Ti ionic mass, $u_{1n,2n}$ are their corresponding displacements at site n , and v_{1n}

is the displacement of the electronic shell surrounding the Se ion. The double-well potential is linked only to the relative displacement between the Se ionic core and its shell and is characterized by an attractive term g_2 which is a measure of the p - d hybridization stabilized by a fourth-order repulsive interaction g_4 . The Se ionic cores are coupled to each other through a harmonic coupling constant f' , which provides an additional stabilization against imaginary frequencies. The Se-Ti interaction is indirect through the Se shells and given by the harmonic coupling constant f . This latter term enhances in addition to g_2 the p - d hybridization. Since, opposite to ferroelectric systems, antiferroelectric compounds exhibit mode softening at the zone boundary,²⁷ i.e., the L point in TiSe_2 , back-folding of this mode has to be taken into account whereby the unit cell doubling at T_{CDW} is anticipated.¹⁶ The action of Cu doping is then to hinder the structural instability and diminish the Ti d -Se p hybridization, which within the above approach corresponds to a vanishing of the double-well potential through the decrease in the harmonic attractive term g_2 . In this way the related potential well height g_2/g_4 weakens and the charge localization is reduced. By using the self-consistent phonon approximation an effective temperature-dependent pseudoharmonic coupling constant is defined, namely, $g_T = -g_2 + 3g_4\langle w^2 \rangle_T$ with

$$\langle w^2 \rangle_T = |g_2| + 3g_4 \sum_{q,j} \frac{\hbar}{\omega(q,j)} w^2(q,j) \coth \frac{\hbar\omega(q,j)}{2kT}, \quad (2)$$

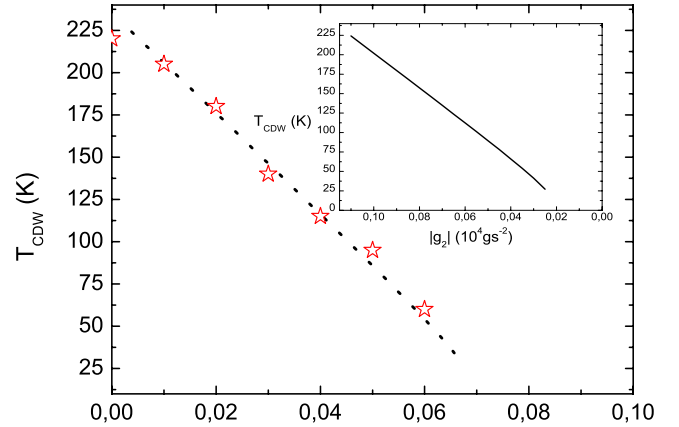
which is the thermal average of the polarizability coordinate.²⁵ The summation is over all phonon branches j and momentum q . By calculating self-consistently g_T, g_2, g_4 the temperature dependence of the antiferroelectric zone-boundary mode is obtained with its frequency being given by $\omega^2 = 2fg_T / [\mu(2f + g_T)]$, where μ is the reduced cell mass. The transition temperature T_{CDW} is defined by $\omega^2 = 0$ and is obtained through the implicit relation $|g_2|/3g_4 = \sum_{q,j} \frac{\hbar}{\omega(q,j)} w^2(q,j) \coth \frac{\hbar\omega(q,j)}{2kT_{\text{CDW}}}$. The connection to the CDW state is achieved through²⁸

$$H = \sum_p \varepsilon_p c_p^\dagger c_p + \sum_q \hbar\omega_q b_q^\dagger b_q + \frac{1}{\sqrt{N}} \sum_{p,q} g_T(q) c_{p+q}^\dagger c_p (b_q + b_{-q}^\dagger), \quad (3)$$

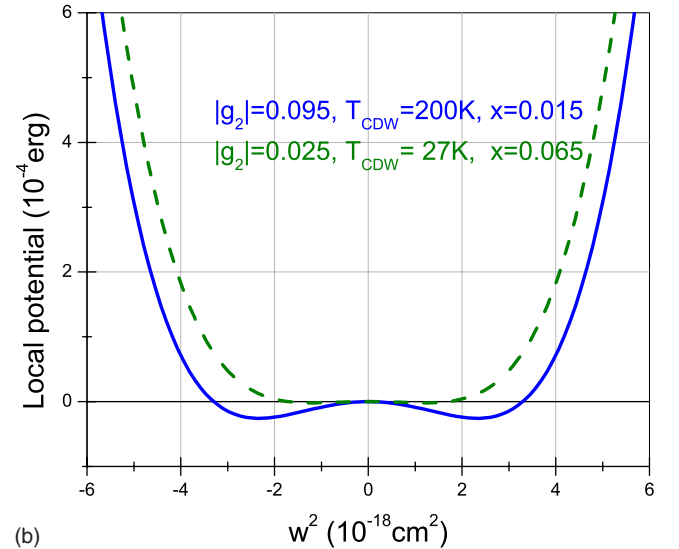
with c and b being annihilation operators for electrons with energy ε and phonons with frequency ω . Note that both ω and g_T are obtained self-consistently from the above lattice dynamics. It is also important to recognize that the double-well potential is a consequence of strong anharmonicity and thus explicitly enters the CDW state. Using standard notations, T_{CDW} is defined by $kT_{\text{CDW}} = 2.28\varepsilon_F \exp(-2\beta)$, where ε_F is the Fermi energy and 2β is the solution of²⁸

$$2\beta = \varepsilon_F \int_{\Delta}^{\sqrt{\varepsilon_F^2 + \Delta^2}} d\varepsilon \frac{\tanh(\varepsilon/2kT)}{(\varepsilon^2 - \Delta^2)^{1/2} (\varepsilon_F^2 + \Delta^2 - \varepsilon^2)^{1/2}}. \quad (4)$$

Here Δ is the soft phonon induced CDW gap and given by $\Delta = g_T \langle w^2 \rangle_T$. Within this model the CDW transition becomes a function of g_T , i.e., g_2 and g_4 . By varying the potential height the doping dependence of T_{CDW} is calculated and shown in Fig. 1(a) where experimental results are included.



(a)



(b)

FIG. 1. (Color online) (a) The CDW transition temperature T_{CDW} as a function of Cu doping x . The open stars are experimental data points which have been taken from Ref. 7. The dotted line corresponds to model calculations (the parameters are the same as in Ref. 16). The doping is linearly related to the double-well potential height via the relation $x = 0.0863 - 0.75g_2$ as suggested by the T_{CDW} dependence on g_2 which is shown in the inset of the figure. (b) The local double-well potential as a function of the polarizability coordinate w . The full line corresponds to a Cu doping level $x = 0.015$ while the dashed line corresponds to $x = 0.065$.

The calculated T_{CDW} vanishes abruptly for values of $|g_2| < 0.025$ and is finite for all larger values with the smallest value of T_{CDW} being 27 K [see inset of Fig. 1(a)]. Since the transport properties of Cu_xTiSe_2 vary linearly with x , and also the c -axis lattice constant does so,²³ the harmonic p - d hybridization term, given by g_2 , should be affected by Cu doping in the same way, namely, it should vary linearly with x . This assumption is in addition supported by the fact that Cu doping counteracts the Se p -Ti d hybridization since the p states at the L point weaken significantly with doping in agreement with data from angle-resolved photoemission experiments.²⁹ Thus we can establish a phenomenological relation between g_2 and doping x by comparing the experimental data [open stars in Fig. 1(a)] to the calculated dependence of T_{CDW} on g_2 [see inset of Fig. 1(a)]. From this we

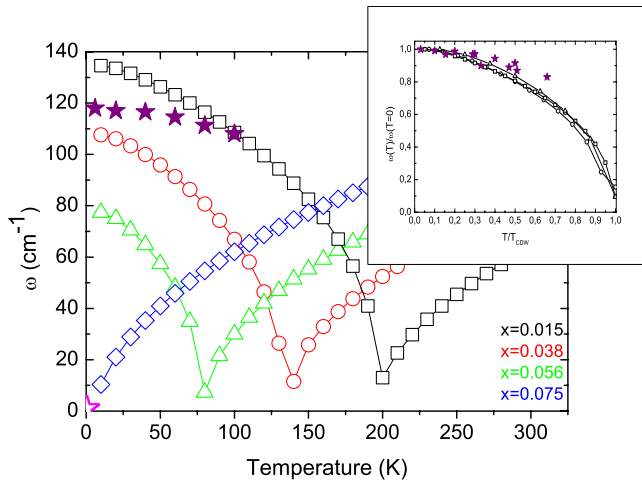


FIG. 2. (Color online) Temperature dependence of the soft zone-boundary mode which is folded back to the zone center for different Cu doping levels. Squares: $x=0.015$; circles: $x=0.038$; triangles: $x=0.056$; and diamonds: $x=0.075$. The full stars are experimental results from Ref. 22. The inset shows the normalized frequency versus normalized temperature for $x=0.015$ (squares), $x=0.038$ (circles), and $x=0.056$ (triangles) in comparison to experimental data (full stars) from Ref. 22.

obtain the linear relation between doping x and g_2 , i.e., $x = 0.0863 - 0.75g_2$ which yields good agreement between theory and experiment. Our lowest T_{CDW} value of 27 K is thus obtained for $x=0.06$ which seems to be slightly larger than observed experimentally. It is important to note that the abrupt vanishing of the CDW transition excludes the existence of a quantum critical point.

The doping-related double-well potential changes substantially with x as can be seen in Fig. 1(b). While in the undoped case the potential clearly exhibits two minima, these have almost vanished for the case of $x=0.06$ and merged together to a broad single minimum where an instability can no longer occur and unit-cell doubling is excluded. Simultaneously charge ordering is inhibited. Together with the change in the double-well potential the zone-boundary soft mode frequency moves to smaller values in the high-temperature phase, whereas in the low-temperature phase its frequency is increased as the potential well deepens (Fig. 2). This agrees with recent Raman data taken in the low-temperature phase only.²²

Also in agreement with the experimental data²² is the shift of the soft mode with decreasing T_{CDW} in the CDW state, such that the same scaling relations are obeyed at any x (see inset of Fig. 2). For $x=0.015$, where no CDW transition occurs, a substantial mode softening is still present reminiscent of an incipient instability as observed in quantum paraelectrics. This should be observable by photoemission spectroscopy since it is a signature of temperature-dependent charge redistribution. An interesting change with temperature is observed in the squared polarizability coordinate $\langle w^2 \rangle_T$, which is an indicator for the charge redistribution. This is shown in Fig. 3 as a function of temperature.

At T_{CDW} a peak is observed which decreases and becomes less pronounced with decreasing T_{CDW} to vanish for x

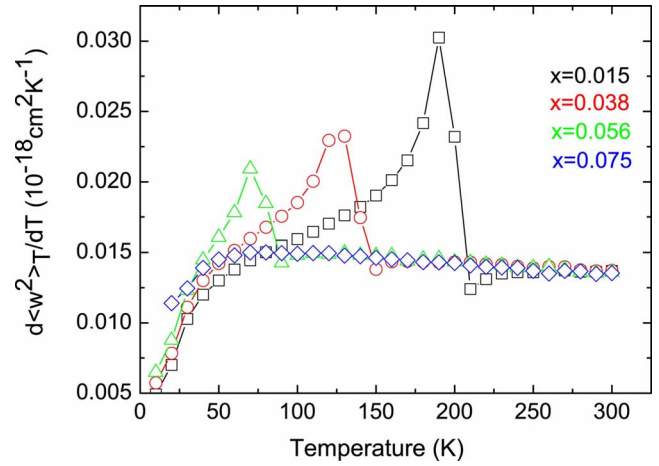


FIG. 3. (Color online) Derivative of the squared polarizability coordinate with respect to temperature as a function of temperature and different Cu doping levels. Squares: $x=0.015$; circles: $x=0.038$; triangles: $x=0.056$; and diamonds: $x=0.075$.

$=0.075$ where no CDW transition takes place. The anomaly at T_{CDW} is suggested to be the origin of the resistivity anomaly which shows similar trends with Cu doping.²³ While above T_{CDW} the polarizability is almost constant for all values of x , it is strongly temperature dependent below T_{CDW} and decreases rapidly as T_{CDW} decreases. Since large values of $\langle w^2 \rangle_T$ correspond to the ionization limit and small ones to complete localization, the derivative of $\langle w^2 \rangle_T$ with respect to T indicates that at T_{CDW} enormous charge redistributions occur and a rapid localization with decreasing temperature takes place. In the case of the $x=0.075$ sample these features are not observed. There are almost no changes in the temperature derivative of $\langle w^2 \rangle_T$. At temperatures below 25 K, a reorganization of the charge distribution begins which is, however, much less distinct than in the true CDW phases.

Soft phonon modes have also been observed in the A15 and transition metal dichalcogenide compounds which exhibit both CDW and SC phases.^{30,31} In these systems the soft mode appears in the acoustic branch at finite wave vector and mostly does not freeze out. These phonon anomalies have been related to superconductivity since their small energies suggest large electron phonon couplings which can explain the rather high values of T_c .³² In TiSe_2 a real instability takes place which changes the Fermi-surface topology²⁴ and suppresses superconductivity. With Cu doping, states at the L point are filled,^{24,29} suppressing the formation of the double-well potential but removing the pronounced anharmonicity and the large electron-phonon coupling. Correspondingly, the tendency toward localization vanishes and provides opportunity for a superconducting instability. That the transition temperature remains moderately small can be ascribed to the stabilization of the lattice mode frequencies which, in turn, gives rise to small values of the electron-phonon coupling and thus limit T_c . An enhancement of T_c under pressure is predicted here since pressure suppresses the double-well potential and simultaneously the CDW state.

To conclude, we suggest that the Cu doping induced

charge redistribution of the CDW state in TiSe_2 can be understood in terms of strong nonlinearity and anharmonic electron-phonon interactions related to an incipient antiferroelectric phase transition. The tendency toward charge localization can be suppressed by doping. This stabilizes the lat-

tice and removes the double-well potential but limits T_c since the electron-phonon coupling decreases in the SC state as compared to the CDW state. It is predicted that pressure can substantially enhance T_c since this suppresses the CDW formation.

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