

Varying Cu-Ti hybridization near the Fermi energy in Cu_xTiSe_2 : Results from supercell calculations

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The properties of Cu_xTiSe_2 are studied by band structure calculation based on the density functional theory for supercells. The density of states (DOS) for $x=0$ has a sharply raising shoulder in the neighborhood of the Fermi energy E_F , which can be favorable for spatial charge modulations. The Cu impurity adds electrons and brings the DOS shoulder below E_F . Hybridization makes the Ti d DOS at E_F , the electron-phonon coupling, and the Stoner factor very large. Strong pressure dependent properties are predicted from the calculations, since the DOS shoulder is pushed to higher energy at a reduced lattice constant. Effects of disorder are also expected to be important because of the rapidly varying DOS near E_F .

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The layered TiSe_2 compound is much studied because of the appearance of charge density waves (CDWs). The ground state is believed to be either a semimetal or a semiconductor with a small indirect gap.¹⁻³ From photoemission experiments, it is concluded that the CDW transition consists of a change in electronic structure from a small indirect gap into a state with a larger indirect gap at a slightly different location in the Brillouin zone.⁴ Recently, Morosan *et al.*⁵ reported that a continuous intercalation of TiSe_2 with Cu is possible, where the Cu atoms enter between the TiSe_2 layers to yield Cu_xTiSe_2 , with solubility of Cu up to $x \approx 0.11$. The CDW transition is continuously suppressed, and a superconducting state appears near $x=0.04$ with a maximum T_c of 4.15 K at $x=0.08$. A CDW superconductivity phase diagram as a function of doping is developed for Cu_xTiSe_2 , analogous to the antiferromagnetism-superconductivity phase diagram found for the high temperature superconductors.

In this work, we investigate the electronic structure of Cu_xTiSe_2 for $x=0$ and $x \approx 0.08$ based on the density functional theory applied to supercell calculations. As will be shown, one of the main results is that Cu doping introduces electronic charge carriers, leading to high density of states (DOS) properties, which partly confirms the interpretation of experimental results.⁵

TiSe_2 has the layered CdI_2 crystal structure. Planes of titanium atoms are surrounded by planes of selenium at $z = \pm \frac{1}{4}$. The TiSe_2 layers are stacked directly above each other and bound by van der Waals interaction. Inserted Cu atoms occupy positions within the open spaces between the TiSe_2 layers, and the unit cell expands with increasing Cu content. The experimental lattice constants are $a=6.7$ a.u. and $c=11.35$ a.u. when x is near 0.08.⁵

The self-consistent linear muffin-tin orbital (LMTO) method^{6,7} is applied in the local density approximation⁸ (LDA) to a 48-site supercell, $\text{CuTi}_{12}\text{Se}_{24}$, in which one Cu atom is intercalated between two Se layers. The cell contains also 11 empty spheres in the open space between the TiSe_2 layers, as is common in LMTO calculations for open structures. The repeat distance between Cu atoms is two unit cells in the two plane directions and three cells along \hat{z} . This minimizes the Cu-to-Cu interactions for a Cu concentration x of 0.0833, which is close to the concentration for optimal T_c .

The self-consistent iterations are terminated using 75 k points in the irreducible Brillouin zone. The Wigner-Seitz sphere radii are 2.88 a.u. for Ti and 3.17 a.u. for Se, respectively. The ℓ basis for the atoms includes d states in the direct basis and f states as tail contribution, while for empty spheres the ℓ 's are one unit smaller. The bands are calculated at the experimental lattice constant, and at two smaller volumes. It should be recalled that LDA typically underestimates the lattice constant by 1%–3% for $3d$ metals. In addition, calculations show that the c/a ratio is overestimated for TiSe_2 .⁹

The supercell is repeated periodically. Effects of random disorder, of distortion around the impurity, or of higher order periodicities among the Cu atoms are omitted. It should be noted that any disorder (structural or substitutional) within the supercell will introduce band broadening in general, since degenerate bands of the perfectly repeated supercell will be split. Such effects are likely to be more important for this particular system, because of the very sharp DOS structures near E_F .

The electron-phonon coupling λ is calculated using the rigid-ion approximation¹⁰ and experimental information of the phonon moment $\langle \omega^2 \rangle$. As the Debye temperature for TiSe_2 is not known to us, we use average Debye temperatures of NbSe_2 [280 K (Ref. 11)] and TiS_2 [235 K (Ref. 12)]. The modification of the pure phonon contribution to λ due to the additions of Cu is probably not very important. Since the DOS is large on Ti, it is expected that the electronic contribution will be dominated by these sites. The pressure variation of the phonon moment is scaled through the calculated variation of the Bulk modulus in TiSe_2 . These approximate procedures should be sufficient for getting insight of the contributions to λ .¹³

The Stoner factor \bar{S} is calculated from the paramagnetic band results in the standard way, by assuming a finite rigid-band splitting due to exchange of all bands.¹⁴ If there is only one band contributing to $N(E_F)$, one can write $\bar{S}=NI$, where I is an exchange integral for that band. The DOS is dominated by the Ti d band and the Stoner factor is mainly because of Ti d electrons. Hybridization with other bands, and the induced exchange splitting on other sites, is likely to reduce the effective Stoner enhancement.

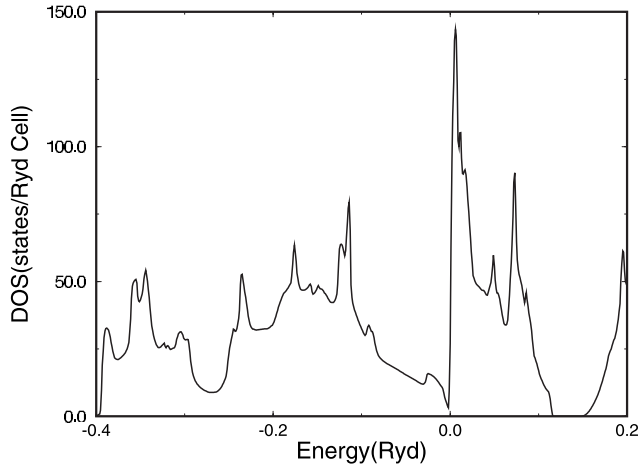


FIG. 1. The total density of states of TiSe_2 . The energy is relative to E_F .

The DOS for the primitive cell of undoped TiSe_2 is shown in Fig. 1. A calculation using the full potential local orbital¹⁵ method, using a potential based on the gradient corrected density functional,¹⁶ gives the same qualitative band features. In particular, the DOS increases rapidly just above E_F , although with a slower pace than for LMTO. The band results indicate that the pure material is a semimetal, where E_F is in a valley in the DOS, with a low value of $N(E_F)$ of 10–20 states/Ryd per TiSe_2 . The uncertainty is due to the fact that E_F falls slightly on the right hand side of the minimum of the DOS (see Fig. 1), on the steep shoulder, where the DOS increases rapidly with energy. This is for the perfect structure without disorder or CDW.

A simple rigid-band model for a potential (or charge) modulation in a material with an increasing DOS near E_F (as for pure TiSe_2) can be shown to favor CDW. Shifts of the local DOS functions relative to E_F suggest that some regions of the material should get a high local $N(E_F)$ because of the large DOS just above E_F . On the other hand, other regions where the potential is repulsive will have E_F closer to the local “gap” with minimum DOS. A similar reasoning as for a Peierls transition show that the total kinetic energy will be lowered by such a splitting of local states. Namely, since the DOS is sharply rising at E_F and the number of states is conserved, we find that an upward shift δ_u of the DOS relative to E_F within the regions that lose electrons will be larger than the downward shift δ_d of the DOS within the region that gains electrons. If the average DOS to the left and right sides are N_u and N_d , respectively, and Δn is the number of transferred electrons, we have $\Delta n = \delta_u N_u = \delta_d N_d$. However, the kinetic energy will be $\frac{1}{2} \Delta n (\delta_d - \delta_u)$, i.e., negative, or, equivalently, the total (kinetic) energy will be lower for the CDW state. If, by electron doping, E_F moves to higher energy on a linearly increasing DOS, then the relative difference between N_u and N_d will be smaller, and the gain in kinetic energy and the tendency for CDW formation will diminish.

Total energy contributions from the Coulomb interaction and hybridization are neglected here, but the model gives a hint that a sufficiently rising DOS near E_F is favorable for CDW. From qualitative arguments, it is expected that long

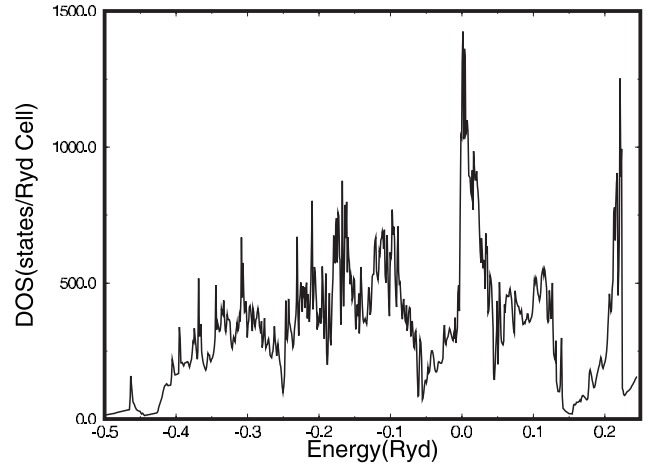


FIG. 2. The total density of states of $\text{CuTi}_{12}\text{Se}_{24}$ at the lattice constant of 6.7 a.u. The energy is relative to E_F .

wavelength modulations are more probable, because of low costs in hybridization energy. Also irregular regions of up- and down-shifted potentials, as for long-range disorder, will be favored through the same mechanism. It is generally believed that Fermi surface nesting is not determining for the \mathbf{k} vector of the CDW.⁴

When Cu is inserted it acts as an electron dopant. It brings along d states near E_F , which hybridize with the Ti d band, and the total $N(E_F)$ increases very much (see Fig. 2). From an inspection of the local Ti DOS functions, it can be verified that the Ti close to the Cu site has the highest $N(E_F)$ values. The total Cu d and the sum of all Ti d DOS functions are shown in Fig. 3.

The DOS peak near E_F is high and narrow. This makes any calculation of $N(E_F)$ dependent properties very sensitive to small shifts of E_F (nonstoichiometry) and to band broadening (disorder effects). The energy derivative of $N(E_F)$ is high, by shifting E_F 2 mRyd to lower energies, N can be reduced by a factor of 2.

Nevertheless, by using the unshifted unbroadened band results, we obtain a very large Stoner enhancement, S

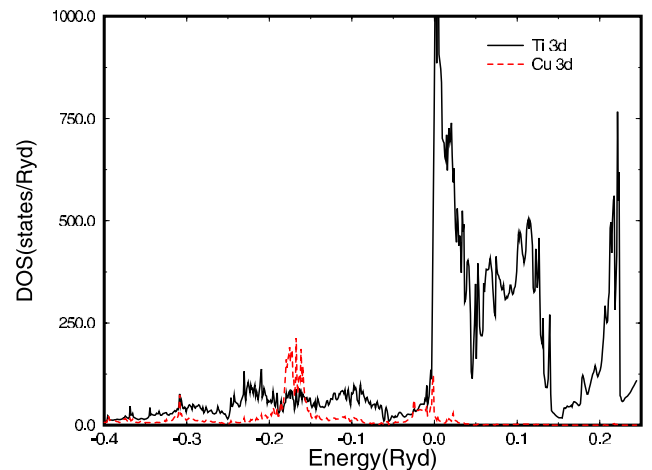


FIG. 3. (Color online) The projected Ti 3d and Cu 3d parts of the total DOS shown in Fig. 2.

TABLE I. The calculated parameters of $\text{CuTi}_{12}\text{Se}_{24}$. The Debye temperature θ_D is from experiment and scaled through the calculated volume dependence. The units of γ is (mJ/mol K²), and $N(E_F)$ is in units of states/(Ry cell).

a_0 (a.u.)	λ	T_c (K)	\bar{S}	γ	$\theta_D(K)$	$N(E_F)$
6.7	1.52	20.2	1.31	11.13	240	1220
6.67	0.37	0.11	1.09	4.75	250	960
6.53	0.21	0.01	0.49	1.26	290	290

$= 1/(1-\bar{S})$ (see Table I). Ferromagnetism is expected when \bar{S} is larger than 1. Nonstoichiometry and disorder may reduce the large Ti d DOS near the Cu site and \bar{S} . Moreover, as was indicated above, the Stoner model assumes equal exchange splitting on all sites. However, Cu and Se have low DOS and are expected to have a small exchange splitting, which could modify the true Stoner criterion. A spin-polarized calculation would give a better answer, but it has not been attempted at this stage because of the very slow convergence for the supercell.

The calculated values of λ are reasonable and not as extreme as could be expected from the large DOS and \bar{S} . The main contribution to λ comes from the Ti atoms. The Ti DOS is large, but there is only a moderate dipole scattering contribution to the electronic part of λ , because the total DOS is dominated (about 98%) by the d character.

A surprising effect is the large variation of $N(E_F)$ with pressure P . It has been shown earlier that the band structure of TiSe_2 is sensitive to changes of the a and c lattice constants.¹⁷ Two calculations at smaller volumes clearly show that the narrow peak of the Cu d state is displaced. Calculations for undoped TiSe_2 show that the overlap between Ti d and Se p bands increases near E_F for increasing volume, but the effect on the DOS at E_F is enhanced by the presence of Cu. Hybridization between Cu and Ti states makes also the Ti d DOS at E_F to vary much with volume. A downward shift of this peak by about 5 mRy is found when

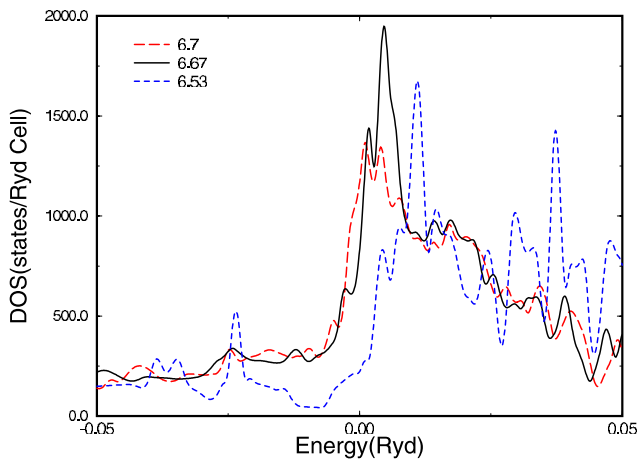


FIG. 4. (Color online) The total density of states of $\text{CuTi}_{12}\text{Se}_{24}$ near E_F (at zero energy in each case) at three different lattice constants.

the lattice constant is increased from 6.67 to 6.7 a.u. (Fig. 4). If the lattice constant is reduced to 6.53 a.u., there will be an upward shift of the DOS edge to a location above E_F and the total $N(E_F)$ is not much larger than for pure TiSe_2 . The charges on Cu and Ti increases with P at the expense of charge on Se. The effect is that the Cu d band becomes more filled for a uniform reduction of volume. The peak in the DOS 20 mRy below E_F for the smallest lattice constant is mainly a Cu d state. The Ti d DOS is too far away in energy to hybridize with this state, and at E_F there will be less Cu d to Ti d hybridization. This will result in a reduction of $N(E_F)$. An inspection of the local Ti DOS for the smallest lattice constant reveals an important proximity effect near the Cu site (see Table II) The Ti d DOS at E_F is of the order 28 states/(Ry atom) on each of the eight Ti on the layers closest to Cu. However, in the more distant Ti layer, where there are four Ti atoms, the local Ti d DOS at E_F is only of the order of 1–2 states/(Ry atom), which is like the case for pure TiSe_2 . The reason is that the local Ti d DOS is pushed just above E_F for these sites. In the calculations for the two larger lattice constants, the local Ti d DOS values at E_F are comparable between all Ti sites, also within the most distant layer. This shows that the properties of Cu doped TiSe_2 will be very sensitive because of the exact position of the DOS shoulder relative to E_F .

These calculations are made for perfect scaling of the supercell lattice. Thus, no effects of possible rearrangement of the Cu occupations, different c/a ratio, or disorder are taken into account. If such effects are small, one can expect strong P variations of the properties. According to our calculations, the system would pass from ferromagnetism, toward exchange enhanced paramagnetism, through a region with superconductivity and large electron-phonon coupling, and finally, to a fairly low DOS material when the volume is reduced by about 8% only. However, this unusual sensitivity is caused by a sharp DOS shoulder which passes through E_F , and therefore, one can also expect large error bars. As men-

TABLE II. d DOS at E_F on Cu and Ti near (Ti_{Cu}) and far from (Ti) the Cu impurity. The units of $N(E_F)$ are states/(Ry atom).

a_0 (a.u.)	Cu d $N(E_F)$	Ti_{Cu} d $N(E_F)$	Ti d $N(E_F)$
6.7	22.1	127	63.0
6.67	19	72	41
6.53	0.85	28.1	1.0

tioned before, disorder and different Cu impurity distributions can be important and have a moderating effect on the P dependence.

More hybridization with the Ti p and f bands is needed for a larger λ . By reducing the lattice constant, it is possible to increase the hybridization and the electronic contribution to λ , but the effect is masked by the changes in total $N(E_F)$, which decreases much at large pressure. In addition, fine structures in the peaked DOS add some noise to the evolution of $N(E_F)$ with pressure.

An estimation of the superconducting T_C from the calculated electron-phonon coupling via the McMillan equation gives reasonable values in line with observations (see Table I). However, some reduction is expected from spin fluctuations, especially since the calculations indicate large exchange enhancement. The calculated electronic specific heat constant γ includes the enhancement for electron-phonon coupling but not from possible spin fluctuations. At the largest lattice constant, γ is considerably larger than the measured value,⁵ about 4.5 mJ/mol K². The calculated result for γ at the intermediate volume agrees best with experiment, but the electron-phonon coupling is rather low at the same volume. Again, this is an indication that disorder in the real material will reduce the effective DOS at E_F and increase hybridization.

In conclusion, we find that undoped TiSe₂ is a low-DOS material with semimetallic properties, but the DOS rapidly increases near E_F . The latter fact is probably important for

the properties of pure and doped TiSe₂. For instance, the kinetic contribution to the total energy will be lowered by spatial modulations of the potential as produced by a CDW or disorder. Electron doping, accompanied by disorder, will put E_F closer to the broadened DOS peak. This should weaken the mechanism for CDW formation, while the material soon becomes a high-DOS material. The local Ti d DOS at E_F for a supercell of Cu doped TiSe₂ is increased very much through hybridization with the Cu impurity and its d band. The exact value of $N(E_F)$ is uncertain because of the sharp structure of the DOS near E_F , which is found both for pure TiSe₂ and the supercell. It depends certainly on the volume and probably also on Cu ordering. The estimation of λ shows that conventional superconductivity based on electron-phonon coupling is probable, with a T_C of the order of a few kelvins. Despite the changes in electronic structure, from a low-DOS semimetal in pure TiSe₂ to a high-DOS material at high Cu doping, it is the Ti state that makes λ large. Some results, like the large Stoner factor, indicate that disorder in the real material is important to moderate the very large $N(E_F)$. Effects of disorder will increase hybridization and can make λ larger even if the total DOS is lowered. The particular situation with E_F near a shoulder in the DOS, and electron doping via Cu impurities, turns out to give strong volume dependence of $N(E_F)$ in addition to the dependence on x .

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