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Varying Cu-Ti hybridization near the Fermi energy in Cu\textsubscript{x}TiSe\textsubscript{2}: Results from supercell calculations

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The properties of Cu\textsubscript{x}TiSe\textsubscript{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 \textit{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\textsubscript{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.\textsuperscript{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.\textsuperscript{4} Recently, Morosan et al.\textsuperscript{5} reported that a continuous intercalation of TiSe\textsubscript{2} with Cu is possible, where the Cu atoms enter between the TiSe\textsubscript{2} layers to yield Cu\textsubscript{1}\textsubscript{x}TiSe\textsubscript{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\textsubscript{1}\textsubscript{x}TiSe\textsubscript{2}, analogous to the antiferromagnetism-superconductivity phase diagram found for the high temperature superconductors.

In this work, we investigate the electronic structure of Cu\textsubscript{1}\textsubscript{x}TiSe\textsubscript{2} for \(x=0\) and \(x=0.08\) 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.\textsuperscript{5}

TiSe\textsubscript{2} has the layered Cd\textsubscript{2} crystal structure. Planes of titanium atoms are surrounded by planes of selenium at \(z = \pm \frac{1}{4}\). The TiSe\textsubscript{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\textsubscript{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.\textsuperscript{3}

The self-consistent linear muffin-tin orbital (LMTO) method\textsuperscript{6,7} is applied in the local density approximation\textsuperscript{8} (LDA) to a 48-site supercell, CuTi\textsubscript{2}Se\textsubscript{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\textsubscript{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 \(z\). 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 \(\ell\) basis for the atoms includes \(d\) states in the direct basis and \(f\) states as tail contribution, while for empty spheres the \(\ell\)'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\textsubscript{2}.\textsuperscript{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 \(\lambda\) is calculated using the rigid-ion approximation\textsuperscript{10} and experimental information of the phonon moment \(\langle \omega^2 \rangle\). As the Debye temperature for TiSe\textsubscript{2} is not known to us, we use average Debye temperatures of NbSe\textsubscript{2} [280 K (Ref. 11)] and TiS\textsubscript{2} [235 K (Ref. 12)]. The modification of the pure phonon contribution to \(\lambda\) 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\textsubscript{2}. These approximate procedures should be sufficient for getting insight of the contributions to \(\lambda\).\textsuperscript{13}

The Stoner factor \(\tilde{S}\) is calculated from the paramagnetic band results in the standard way, by assuming a finite rigid-band splitting due to exchange of all bands.\textsuperscript{14} If there is only one band contributing to \(N(E_F)\), one can write \(\tilde{S}=NI\), where \(I\) is an exchange integral for that band. The DOS is dominated by the Ti \textit{d} band and the Stoner factor is mainly because of Ti \textit{d} electrons. Hybridization with other bands, and the induced exchange splitting on other sites, is likely to reduce the effective Stoner enhancement.
The DOS for the primitive cell of undoped TiSe$_2$ is shown in Fig. 1. A calculation using the full potential local orbital method, using a potential based on the gradient corrected density functional, 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 $\delta_\uparrow$ of the DOS relative to $E_F$ within the regions that lose electrons will be larger than the downward shift $\delta_\downarrow$ of the DOS within the region that gains electrons. If the average DOS to the left and right sides are $N_\uparrow$ and $N_\downarrow$, respectively, and $\Delta n$ is the number of transferred electrons, we have $\Delta n = \delta_\uparrow - \delta_\downarrow$. However, the kinetic energy will be $\frac{1}{2}\Delta n (\delta_\uparrow - \delta_\downarrow)$, 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 $N_\uparrow$ and $N_\downarrow$ 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 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 $k$ vector of the CDW.

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 mRy 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, $S$.
TABLE I. The calculated parameters of CuTi12Se24. The Debye temperature $\theta_D$ is from experiment and scaled through the calculated volume dependence. The units of $\gamma$ is (mJ/mol K²), and $N(E_F)$ is in units of states/(Ry cell).

<table>
<thead>
<tr>
<th>$a_0$ (a.u.)</th>
<th>$\lambda$</th>
<th>$T_c$ (K)</th>
<th>$\bar{S}$</th>
<th>$\gamma$</th>
<th>$\theta_D$ (K)</th>
<th>$N(E_F)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7</td>
<td>1.52</td>
<td>20.2</td>
<td>1.31</td>
<td>11.13</td>
<td>240</td>
<td>1220</td>
</tr>
<tr>
<td>6.67</td>
<td>0.37</td>
<td>0.11</td>
<td>1.09</td>
<td>4.75</td>
<td>250</td>
<td>960</td>
</tr>
<tr>
<td>6.53</td>
<td>0.21</td>
<td>0.01</td>
<td>0.49</td>
<td>1.26</td>
<td>290</td>
<td>290</td>
</tr>
</tbody>
</table>

FIG. 4. (Color online) The total density of states of CuTi12Se24 near $E_F$ (at zero energy in each case) at three different lattice constants.

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

<table>
<thead>
<tr>
<th>$a_0$ (a.u.)</th>
<th>Cu $d$ $N(E_F)$</th>
<th>TiCu $d$ $N(E_F)$</th>
<th>Ti $d$ $N(E_F)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7</td>
<td>22.1</td>
<td>127</td>
<td>63.0</td>
</tr>
<tr>
<td>6.67</td>
<td>19</td>
<td>72</td>
<td>41</td>
</tr>
<tr>
<td>6.53</td>
<td>0.85</td>
<td>28.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>
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 $\lambda$. By reducing the lattice constant, it is possible to increase the hybridization and the electronic contribution to $\lambda$, 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 1). However, some reduction is expected from spin fluctuations, especially since the calculations indicate large exchange enhancement. The calculated electronic specific heat constants includes the enhancement for electron-phonon coupling but not from possible spin fluctuations. At the largest lattice constant, $\gamma$ is considerably larger than the measured value, about 4.5 mJ/mol K$^2$. The calculated result for $\gamma$ 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 TiSe$_2$ 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 TiSe$_2$. 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 TiSe$_2$ 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 TiSe$_2$ and the supercell. It depends certainly on the volume and probably also on Cu ordering. The estimation of $\lambda$ 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 TiSe$_2$ to a high-DOS material at high Cu doping, it is the Ti state that makes $\lambda$ 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 $\lambda$ 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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