Ultrafast filling of an electronic pseudogap in [LaS]$_{1.2}$VS$_2$

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Sample synthesis

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Optical measurements
Outline

[LaS]_{1.2}VS_{2} : a « strange » insulator

⇒ Resistive switching under applied electric pulses

ARPES investigation of the electronic structure

⇒ A very strong temperature dependence of the Fermi level « pseudogap »

Manipulating the pseudogap by pump-probe experiments

⇒ Ultrafast filling of the pseudogap
⇒ Evidence for very strong electron-phonon coupling

[LaS]_{1.2}VS_{2} appears to be at the frontier between cluster and solid behaviors
[LaS]_{1.2}VS_2: a « misfit » structure

LaS and VS_2 are incommensurate along a.

=> approximate supercell:

$$3a_{LaS} = 5a_{VS_2} = 17\text{Å}$$

Distorted triangular V planes

Modulation of V position with:

$$q = \frac{a_{VS_2}}{a_{LaS}}a_{VS_2}^* = 1.1\text{Å}^{-1}$$

=> V-V (min) = 2.92Å

V-V (max) = 3.73Å

L. Cario et al., Mat Res Bul 2005
A « strange » insulator?

- 2.2 electrons in the V 3d $t_{2g}$ orbitals

Resistivity

$\sim$ semiconducting-like?

Susceptibility

$\sim$ Pauli-like?

L. Cario et al., Synthetic Metals 1999
A « strange » insulator?

- 2.2 electrons in the V 3d $t_{2g}$ orbitals

Resistivity

~ semiconducting-like?

Optical conductivity

Unexpectedly strong T dependence!

V. Ta Phuoc et al., submitted
Resistive switching under applied electric pulses

Resistivity can change up by 5 order of magnitudes!

ARPES view of the electronic structure

\[ E_{kin} = h\nu - W - |E_B| \]

\[ \hbar k_{||} = \sqrt{2mE_{kin}} \sin \theta \]

CASSIOPEE beamline, SOLEIL synchrotron

=> 10-1000eV

=> high energy and angular resolution
Fermi Surface (300K, 96eV)

Calculated FS in LiVS$_2$ ($d^2$)

→ 6-fold symmetry expected for a triangular lattice
Fermi Surface & band structure

Calculation for LiVS$_2$
Pseudogaps along the FS (300K)
Evolution with temperature (at $\Gamma$)

ARPES spectra as a function of $T$

Gaps and spectral weight at $E_F$

First angle integrated study:
Ino, Fujimori et al., PRB 2004
Direct connection between $n(E_F)$ and structure

ARPES and optic spectral weight scale with the distortion.

The modulation amplitude increases with decreasing $T$.

ARPES pseudogap scales with the distortion.

V. Ta Phuoc et al., submitted
Probing the dynamic of the pseudogap formation

How are structural and electronic degrees of freedom linked in this system?

FemtoARPES setup

Sample

- pump: 1.57 eV, 35 fs
- probe: 6.28 eV, 50 fs

Laser ARPES of $[\text{LaS}]_{1.2}\text{VS}_2$ (6.28eV)

Opening of the pseudogap between 300 and 40 K observed at 6eV

FS measured at 100eV

Heating due to laser pumping

=> Cut down repetition rate
Ultrafast filling of the pseudogap

Sample at 40K excited by laser pulse of 2.3 mJ/cm² fluence

The pseudogap fills up in less than 80fs, close to the experiment temporal resolution
Ultrafast filling of the pseudogap

Sample at 40K excited by laser pulse of 2.3 mJ/cm² fluence

Comparaison of hot electron decay rate in different systems

Hot electrons release their energy to phonon modes in less than 80fs.
=> very strong electron-phonon coupling
Ultrafast filling of the pseudogap

Sample at 40K excited by laser pulse of 2.3 mJ/cm² fluence

After closing the gap, the system is still far from thermal equilibrium.
Why is $[\text{LaS}]_{1.2}$VS$_{2}$ insulating?

- **Band gap**
  
  *Incommensurate structure: it’s hard to make a band insulator!*
  Why such a fast relaxation?

- **Mott, electronic correlations…**
  
  Not close to half-filling, no strong renormalization $\Rightarrow$ *unlikely*

- **Disorder**
  
  Clear dispersion in ARPES, clear modulation in x-ray $\Rightarrow$ *unlikely*
Change of electronic structure with T

There is no gap opening at low T but a complete change of electronic structure.

⇒ The distortion brings atoms close to chemical bonding in V clusters.

⇒ Very strong electron-phonon coupling!
Strong coupling between distortion and electronic properties

⇒ No collective excitation
⇒ Filling of the gap by local and incoherent excitations
Conclusion: nature of the instability in $[\text{LaS}]_{1.2}\text{VS}_2$?

Origin of the instability

- « purely electronic »
- « purely structural »
- Mott insulator
- Charge Density Waves
- Band insulator
- Excitonic insulator

el-ph coupling

weak → strong
On the origin of charge-density waves in select layered transition-metal dichalcogenides

Table 1. Qualitative comparison of weak-coupling and strong-coupling CDWs.

<table>
<thead>
<tr>
<th></th>
<th>Weak-coupling CDW</th>
<th>Strong-coupling CDW</th>
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</thead>
<tbody>
<tr>
<td>PLD/CDW amplitude</td>
<td>Small</td>
<td>Large</td>
</tr>
<tr>
<td>Energy gap</td>
<td>Small ($\Delta / E_F \ll 1$)</td>
<td>Large ($\Delta / E_F \lesssim 1$)</td>
</tr>
<tr>
<td>Coherence length</td>
<td>Large ($\xi / a \gg 1$)</td>
<td>Small ($\xi / a \gtrsim 1$)</td>
</tr>
<tr>
<td>Electronic energy gain</td>
<td>Arising mostly near $k_F$ ($\propto \Delta^2 \ln \Delta$)</td>
<td>Spread over Brillouin zone ($\propto \Delta$)</td>
</tr>
<tr>
<td>CDW periodicity w.r.t. original lattice</td>
<td>Incommensurate ($\lambda_0 = \pi / k_F$)</td>
<td>Tends to be commensurate</td>
</tr>
<tr>
<td>Thermal disordering</td>
<td>Due to electronic entropy</td>
<td>Due to lattice entropy</td>
</tr>
<tr>
<td>Electron–hole pairing above $T_0$</td>
<td>No</td>
<td>Yes, but pairs are incoherent</td>
</tr>
<tr>
<td>Qualitative picture</td>
<td>Fermi surface instability</td>
<td>Local chemical bonding</td>
</tr>
</tbody>
</table>

K. Rossnagel et al., J. Phys Cond Mat 2011
Conclusion: nature of the instability in $[\text{LaS}]_{1.2}\text{VS}_2$?

« purely electronic » coupled « purely structural »

Origin of the instability

- Mott insulator
- Charge Density Waves
- Band insulator
- Excitonic insulator
- $[\text{LaS}]_{1.2}\text{VS}_2$?

⇒ Such « hidden » chemical bonding could play a role in many « CDW » systems or valence bond solids (LiVS$_2$)

⇒ High sensitivity to perturbations: resistive switching
GK dispersion
Band structure for $a=3.4\text{Å}$ and $3.5\text{Å}$