Ultrafast filling of an electronic pseudogap in photoexcited $(LaS)_{1.196}VS_2$

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We investigate by angle and time resolved photoemission spectroscopy the unusual insulating state of strongly distorted triangular V slabs in $(LaS)_{1.196}VS_2$. We show that the electronic structure is dominated by the lowest band of the V t_{2g} manifold, which disperses over 0.7 eV and is nearly filled. Hence, $(LaS)_{1.196}VS_2$ is not a Mott insulator. The spectra are strongly temperature dependent, shifting by 100 meV upon cooling to 50 K. The sudden photoexcitation at 50K induces a partial filling of the electronic pseudogap within less than 80 fs. The electronic energy flows into the lattice modes on a comparable timescale. We conclude that a very strong electron-phonon coupling makes this state extremely sensitive to small perturbations of the V clusters distortions.

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$(LaS)_{1.196}VS_2$ is a misfit compound, with the same VS_2 slabs as dichalcogenides $1T-MX_2$ (M=V, Ta, Ti... X=S, Se) [1] or the valence bond solid $LiVS_2$ [2]. However, these slabs are stacked with rock-salt planes LaS having an incommensurate periodicity in one direction. This induces a large modulation of the V-V atomic distance in the triangular plane, with a periodicity equal to the lattice mismatch q=1.1 $Å^{-1}$, and values ranging from 3 to 3.73 Å at room temperature [3–5]. One expects a charge transfer of one electron from each LaS unit to the VS_2 slabs, yielding ∼2.196 electrons per V atom. Band structure calculations are not possible in the truly incommensurate structure, but calculations in an approximate structure suggest that the compound should be a metal with a rather low density of states [6]. The occurrence of a Pauli-like susceptibility also supports a non vanishing density of the electronic states at the Fermi level [6]. Despite this, the conductivity of $(LaS)_{1.196}VS_2$ monotonously increases with temperature, thus rather following the behaviour of a semiconductor with small activation energy [6]. The existence of low energy electronic excitations despite the lack of metallicity is the first unusual property of $(LaS)_{1.196}VS_2$. It could be explained by the formation of a pseugogap at 300 K, as observed in angular integrated photoemission [7]. This was discussed in terms of strong correlations in the vicinity of a Mott insulator, possibly with important disorder effects associated with the incommensurate distortion [4, 6, 7]. The second difference between $(LaS)_{1.196}VS_2$ and a common band insulator is the non linear response arising for moderate electric fields. Upon the application of $\approx$ 50 V/cm, a current switching leads to a volatile increase of conductivity by 6 orders of magnitude [8]. Similar phenomena have been also observed in several insulating oxides [9, 10] or chalcogenides [11, 12] and are very interesting for potential applications [13]. This underlines an unusual proximity between the metallic and insulating states.

In this paper, we use Angle and Time Resolved Photoelectron Spectroscopy (ARPES and TRPES) to better understand the nature of this exotic insulating state. On one hand, ARPES gives a precise view of the background electronic structure. On the other hand, TRPES allows to probe the dynamic of this state. TRPES is often used with the idea of separating electronic and structural processes, the first ones being typically much faster than the second ones [14, 15]. In 1T-TaS_2, for example, the ultrafast collapse of the Mott gap in less than 50 fs [16–18] contrasts with the slower collapse of the Charge Density Wave (CDW) gap (∼200 fs) [19]. $(LaS)_{1.196}VS_2$ proposes a new situation, where the distortion is apparently purely structural in origin, due to the misfit stacking, and its coupling with the electronic degrees of freedom is largely unknown. We note that the shortest V-V distances become of the order of a true chemical bond, so that this compounds lies at the interesting frontier between quasi-molecular and solid states [20].

With ARPES, we observe clearly dispersing bands, qualitatively similar to the ones calculated and observed [21, 22] in other VS_2 systems. However, they do not cross the Fermi level, forming instead a pseudogap near E_F, in agreement with ref. [7]. The electronic band approaching the Fermi level is the lowest of the t_{2g} manifold; it disperses over 0.7eV and is nearly filled. The large band dispersion and the fact that it is nearly filled makes it unlikely that the insulating nature of $(LaS)_{1.196}VS_2$ is due to a Mott localization of the electrons. Instead, the electronic pseudogap is likely stabilized by strong electron-phonon coupling and the incommensurate modulation of the V - V distance. This is further supported by the

strong evolution of the gaps and pseudogaps as a function of temperature, where the distortion increases [5]. We support the central role of the electron-phonon coupling by TRPES measurements of the photoexcited system. The data shows that excited electrons release their excess energy to the phonon modes within less than 80 fs. On the same timescale, the electronic pseudogap is partially filled by low energy excitations. Hence, $(LaS)_{1.196}VS_2$ provides the first example of a photoinduced gap filling that: a) occurs on an extremely short timescale and b) is driven by the electron-phonon coupling. Nonetheless, we do not observe any collective oscillations within experimental accuracy. We propose that such a strongly coupled case favours local and incoherent excitations, forming pseudogaps, rather than collective excitations typical of regular CDW materials.

Single crystals of $(LaS)_{1.196}VS_2$ have been synthesized using a self flux method. The ARPES experiments were carried out at the CASSIOPEE beamline of the SOLEIL synchrotron. Photoelectron spectra have been collected with a photon energy of 92 eV, energy resolution of 10 meV and angular resolution of 0.2 degrees. Reference band structure calculations for $LiVS_2$ were perfomed within the local density approximation, using the Wien2K package [23]. TRPES experiments were performed with the FemtoARPES setup, using a Ti:Sapphire laser that generates 35 fs pulses centered at 790 nm with repetition rate of 30 kHz. Part of the beam is employed to generate the fourth harmonic by a cascade of frequency mixing in BBO crystals (β-BaB_2O_4) [24]. The 197.5 nm probe and the 790 nm pump are focused on the sample with a spot diameter of 100 μm and 200 μm, respectively. Their cross-correlation in a BBO crystal has a full width at half maximum (FWHM) of 80 fs. The overall energy resolution of TRPES spectra is limited to 60 meV by the bandwidth of the 197.5 nm beam.

In Fig. 1, we present the room temperature electronic structure measured by conventional ARPES at 92eV. In Fig. 1A, the spectral weight is integrated in a 20meV window around -40meV. At first sight, its distribution exhibits 6-fold symmetry, as expected for a triangular lattice. The hexagonal Brillouin Zone (BZ) sketched in red corresponds to a triangular lattice of side a=3.41 Å, namely the mean V-V distance observed in the VS_2 slab. The highest spectral intensity is found near the zone center Γ and the points K. Deep minima (blue regions) are instead found inside large ellipses centered at each M point.

The band dispersions along different directions are displayed in Fig. 1B-D. In each case, one band is observed with a very clear dispersion, although the peaks are rather broad (about 0.35eV at half maximum). Such lineshapes are in fact typical of dichalcogenides [1], which might be due to intrinsic 3D character [25] and/or polaronic effects [26]. In any case, this shows that despite the 'disorder' introduced by the incommensurate modulation, the dispersions are still well defined. We do not clearly observe traces of the incommensurate modulation periodicity, probably because the new supercell zone boundaries are very ill-defined in this strongly incommensurate structure. The bands never cross the Fermi level and we indicate with black arrows the points where they get closest to it. In Fig. 2, we give examples of the spectral lineshapes at these points.

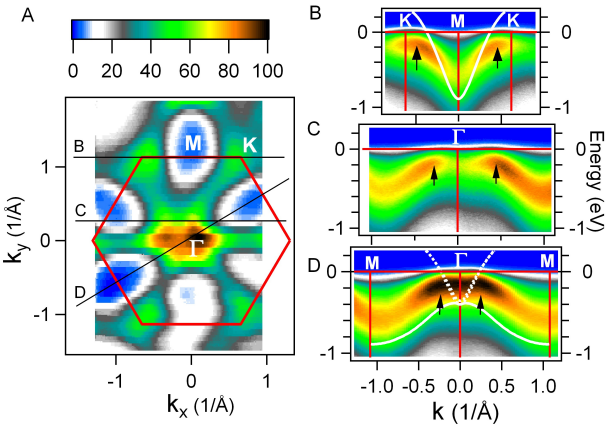

FIG. 1: A): ARPES spectral weight distribution in k-space and integrated at -40meV in a 20meV window. The temperature is 300K and the beam was linearly polarized in xz plane, with a photon energy of 92eV. Red lines indicate BZ boundaries for a triangular lattice with a=3.41Å. Black lines labelled B, C and D correspond to the sections of the k space for which the dispersions B-D are represented. B-D): Corresponding dispersion along KMK (B), a direction parallel to ΓK at k_y=0.2Å^{-1} (C) and ΓM (D). The white lines are the dispersions calculated for the t_{2g} levels calculated for $LiVS_2$, the solid line has a dominant d_{z^2} character, the two other bands (dotted lines) are degenerate along ΓM and above E_F along MKM.

To fix ideas, we plot on top of the dispersions the band structure calculated in $LiVS_2$, a system with undistorted VS_2 slabs and 2 electrons in the V 3d orbitals, close to the filling expected for $(LaS)_{1.196}VS_2$ (2.196). There is a qualitative agreement, if bands are pushed to higher energy along the Γ-M direction and down at K. These shifts could be a consequence of the crystal field splittings induced by the distortion in the VS_6 octahedra and/or gap openings due to the distortion. There may also be correlation-induced redistribution of spectral weight between the different bands. We do not clearly observe the upper two t_{2g} bands (dotted lines), although they could still form small electron pockets at Γ. The clearest dispersions comes from the lowest band, which is of dominant d_{z^2} character [1]. It is nearly filled, although one could speculate that there would be small hole pockets around Γ and K [approximately delimited by the arrows of Fig. 1B-D], if there were no gaps. The 0.7eV dispersion of this d_{z^2} band along ΓM is close to that expected in the calculation. This large bandwidth and the large filling factor appear incompatible with the simple picture of a Mott insulating phase arising in the degenerate t_{2g}

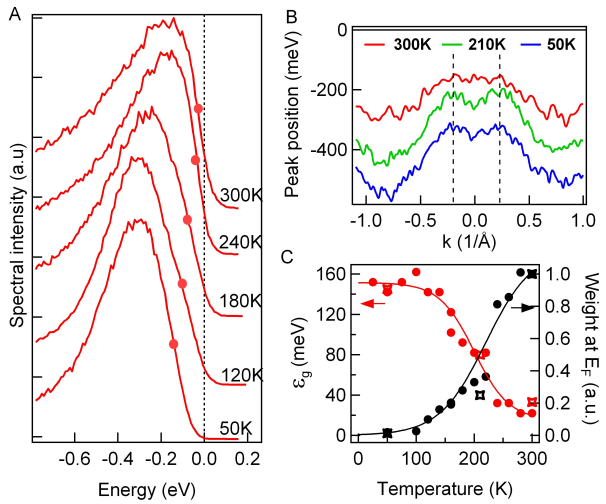

FIG. 2: A): Photoelectron spectra at k=0.2Å^{-1} for the indicated temperatures. B): Dispersion of the band along ΓK at 3 different temperatures. Dotted lines indicate the location of the pseudogap minimum (arrows in Fig. 1). C): Temperature evolution of the leading edge pseudogap ϵ_g (red point in A) and spectral weight at the Fermi level. Filled and open symbols correspond to 2 different samples. All these data were acquired at 92eV.

manyfold.

The gap openings evidence deviations from the undistorted VS_2 band structure. It is natural to attribute them to the incommensurate modulation. In Fig. 2A, we show spectra at k=0.2 Å^{-1}, corresponding to the black arrow in Fig. 1D. At 300K, the leading edge of the spectra ϵ_g is shifted from E_F by about 20meV. As this shift is smaller than the temperature (∼25meV), it is likely that any coupling with low energy excitations will create states in the gap. This explains the residual density of states we observe at E_F and we will refer to this situation as pseudogap. Note that the pseudogap is larger at other points in k-space (it is for example 80meV near K points).

When the temperature is lowered, the main peak shifts to higher binding energy by about 100meV, pushing clearly the compound into the insulating limit. More precisely, the whole band shifts down quite uniformly, as detailed in Fig. 2B for the ΓK direction. As the compound becomes quite insulating in the process [8], we checked at each temperature that there was no shift due to charging effects. We ruled this out because reducing the photon flux by a factor 3 does not induce any shifts (we only observed charging problems below 30K). It is known that the distortion amplitude increases by 0.05 Å between 300K and 100K [5]. We believe this is enough to induce the observed shifts, as our calculations in $LiVS_2$ (not shown) indicate that a uniform increase of the lattice parameter by 0.1Å induces band shifts of the order of 100meV.

In Fig. 2C, we finally plot the shift of the leading edge point (left) and the vanishing of the spectral density at E_F (right), as a function of temperature. There is no unique definition for the absolute value of a pseudogap, a similar shift would be obtained from the peak position (-0.17 to -0.35eV) or the center of gravity (-0.3 to -0.4eV). We choose ϵ_g (red points in Fig. 2A), which is well defined, but the absolute value somewhat depends on the lineshape.

To better understand the relevance of electron-phonon coupling on the charge gap we investigate next the temporal evolution of the electronic states after photoexcitation by an intense laser pulse. Figure 3A displays a photoelectron intensity map acquired at 40 K as a function of pump-probe delay. The photoelectrons generated by the 6.3 eV probe beam are detected in a small angular window centred around normal emission. Pump pulses with incident fluence of 2.3 mJ/cm^2 induce an excitation density of roughly 0.065 electrons per $(LaS)_{1.196}VS_2$ unit. Upon photoexcitation, the electronic spectrum experiences a redistribution of spectral weight on a large energy scale. As shown by Fig. 3A, the pump pulse increases the photoelectron signal in the energy window between -250 meV and the Fermi level. In this spectral range, the partial filling of the electronic pseudogap overwhelms the photoinduced change of the electronic occupation factor. Nonetheless, the non-equilibrium distribution of the electrons is still visible in the counts above the Fermi level.

We show in Fig. 3B, the photoelectron spectra, extracted from the intensity map of Fig. 3A, 100 fs after the arrival of the pump beam (green curve). As a term of comparison we also plot the photoelectron spectra in thermal equilibrium at 40K (blue curve) and 300 K (violet curve). When the sample is at 40 K and the pump beam is off, the value of the leading edge is $\epsilon_g = -95$ meV. This is somewhat smaller than the pseudogap observed at 92eV, which might be due to the different integration window and cross section at 6eV. As shown in Fig. 3C, the presence of the pump beam slightly reduces the magnitude of ϵ_g at negative pump-probe delay. This accumulative effect is due to the local heating of the sample and does not exceed the maximum value of 15 meV. We find that a laser repetition rate of 30 kHz is the optimal compromise between the accumulative heating and good statistics. Upon the arrival of the pump pulse, the leading edge suddenly approaches the Fermi level. This reduction of the electronic pseudogap is proportional to the incident fluence and therefore to the internal energy deposited into the system. We fit the early dynamics of ϵ_g by the convolution of $\theta(t-t_0)e^{-t/\tau}$ with a gaussian function. The width of the gaussian function is 100 fs and turns out to be only 20 fs larger than the cross correlation between pump and probe pulse. The parameter t_0 is 30 fs larger than zero only for the curve obtained with incident fluence of 2.3 mJ/cm^2. We conclude that the pseudogap filling arises on a very short timescale, comparable to or shorter than the temporal resolution of

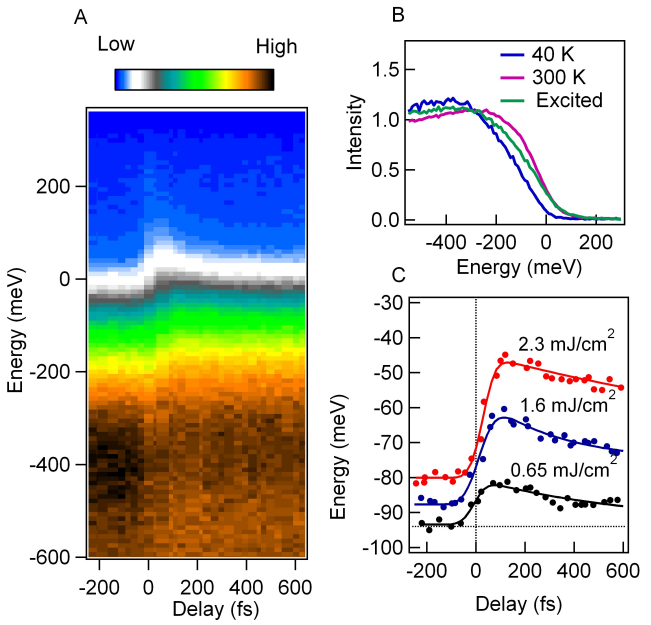

FIG. 3: A): Intensity map of photoelectrons emitted normal to the sample surface as a function of pump probe delay. The sample is excited by a laser pulse with incident fluence of 2.3 mJ/cm^2. B): Photoelectron spectra acquired in equilibrium at 40 K (blue curve) and 300 K (violet) are compared to the spectrum acquired at the base temperature of 40 K and 100 fs after the arrival of the pump beam (green curve). C: Sudden reduction and subsequent recovery of the electronic pseudogap for several fluences of the incident pump beam.

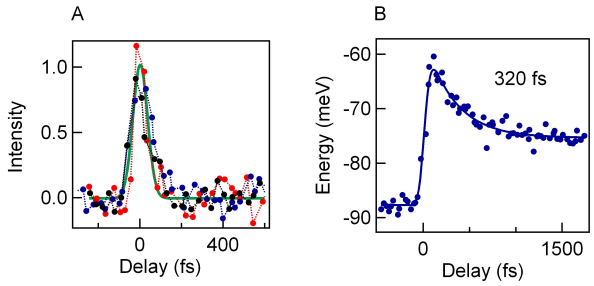

FIG. 4: A): Temporal evolution of the photoelectron current acquired at energy $\epsilon = 220$ meV above the Fermi level. The red, blue and black dots stands for measurements with incident pump fluence of 2.3 mJ/cm^2, 1.6 mJ/cm^2 and 0.6 mJ/cm^2, respectively. The green line superimposed to the data is the measured cross correlation between our pump and probe pulse. B): Evolution of the electronic pseudogap as a function of pump probe delay. The initial recovery displays an exponential dynamics with time constant of 320 fs.

our experiment.

The depopulation of the electronic states above the Fermi level confirms the occurrence of an abrupt energy flow in lattice modes. We show in Fig. 4A the temporal evolution of the renormalized photoelectron signal acquired for $\epsilon = 220$ meV. The transient electronic occupation displays a gaussian shape which is comparable to the cross-correlation between pump and probe pulse. We deduce that heat is transferred from electrons to the phonons on a timescale shorter than Δt=80 fs. As a term of comparison, the decay rate is about 250fs in 1T-TaS_2 in similar conditions. As a consequence of such strong coupling, it is impossible to separate the electronic and nuclear variables within the probing time. We note that such timescale corresponds to an energy width $\Delta\epsilon \approx h/\Delta t = 55$ meV. Since $h/\Delta t$ is already comparable to the size of the electronic pseudogap, any analysis of the $(LaS)_{1.196}VS_2$ within the Born-Oppenheimer approximation is somehow called into question.

The temporal evolution of Fig. 4B indicates that electron-phonon system at 100 fs is still far from equilibrium conditions. Only the strongly coupled modes are efficiently populated, whereas the others can be considered as still frozen. Such selective heating has already been reported in copper oxides [27] and other layered systems [28]. The warming up process is followed by the reduction of free energy via the anharmonic scattering between highly excited modes and colder ones. In agreement with this mechanism, Fig. 4B shows that the electronic pseudogap partially recovers with time constant of 320 fs.

Next, we discuss how non-equilibrium phonons affect the electronic structure. Qualitatively speaking, two complementary effects lead to the collapse of the electronic pseudogap. First, when photoexcited electrons transfer their energy to some phonon modes, the mean standard deviation of the atomic displacements becomes much larger than in the unpumped system. It follows the emergence of intragap electronic excitations that are likely localized on a rather short lengthscale. Second, the photoinduced change of the free energy suddenly switches on a force on the atomic lattice. Therefore, the resulting atomic displacement should oscillate at the characteristic frequency of the related mode [29]. In this case, the coupling between the lattice and the electronic system would modulate the electronic pseudogap [19].

Concerning $(LaS)_{1.196}VS_2$, both mechanisms are in principle possible. However, we show in Fig. 3 that the photoelectron map does not display any periodic modulation of the spectral density. It is not excluded that coherent phonons of small amplitude lie below the noise threshold of our measurement. Moreover, the 80 fs temporal duration of our probe pulse would hinder the detection of oscillations with frequency higher than 5 THz (20meV). The phonon cut-off is not known for $(LaS)_{1.196}VS_2$, but it is as high as 80meV in 1T-VSe_2 [30], so that we may average in time the effects due to fast modes. Nonetheless, the fact that the spectral shape is different in the photoexcited and high temperature cases (see. Fig. 3B) also suggest that photoexcitation fills the electronic pseudogap rather than closes it and that this process is dom-

inated by incoherent lattice motion instead of a coherent one. In this respect, time resolved electron and X-ray diffraction could be a valuable approach to discriminate the first (which would affect the Debye waller factor) from the second (which changes the structure factor) [31].

In conclusion, our data reveal that $(LaS)_{1.196}VS_2$ is an original example of a strongly coupled electron and phonon system. We have shown that despite the incommensurate structure intrinsic to this compound, the electronic structure is rather simple and follows that of a triangular system. The filling and bandwidth of the d_{z^2} are not compatible with a Mott scenario of the insulating phase. Instead, strong electron-phonon coupling, possibly cooperating with electronic correlations, gives rise to a charge pseudogap with strong temperature dependence. This unusal sensitivity of the electronic system to the lattice distortion makes it highly tunable by external parameter such as temperature, electric field or laser pulses. We report the collapse of the electronic pseudogap on photoexcitation by intense fs laser pulses at 50K and the rapid flow of the electronic energy to the phonon modes on time scales shorter than 80fs. Interestingly, the transient pseudogap displays an initial relaxation due to the redistribution of energy within the different phonon modes. This is a much faster thermalization timescale for the electron-phonon system than that observed in related dichalcogenide Mott or Peierls systems of the order of 300fs [17, 19]. This could be partly due to higher phonon frequency and electron-phonon coupling. However, with such a coupling, we also likely reach the limit where a description in terms of local interactions, akin to chemical bonding, becomes more relevant than a weak coupling approach of extended electronic states [32]. This is supported by the fact that the type of excitations we induce by laser pulses seem to be predominantly incoherent excitations created in the soft pseudogap, rather than collective excitations expected for a regular CDW. In this sense, $(LaS)_{1.196}VS_2$ brings interesting new insight about the diversity of electron-phonon couplings in complex systems, as well as on the limits between quasi-molecular and solid states.

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