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Polarization dependence of sub-micro ARPES reveals emerging one-dimensionality of electrons in NbSe₃

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In materials with nearly commensurate band filling the electron liquid may spontaneously separate into components with distinct properties, yielding complex intra- and inter-unit cell ordering patterns and a reduced dimensionality. Polarization-dependent angle-resolved photoemission data with sub-micron spatial resolution demonstrate such an electronic *self-organization* in NbSe₃, a compound considered to be a paradigm of charge order. The new data indicate the emergence of a novel order, and reveal the one-dimensional (1D) physics hidden in a material which naively could be considered the most 3D of all columnar chalcogenides. The 1D physics is evidenced by a new selection rule – in two polarization we observe two strikingly different dispersions each closely resembling apparently contradicting results of previous studies of this material.

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I. INTRODUCTION

Recent developments – e.g. in the field of cuprates^{1–6} and pnictides^{7,8} – prompt to seriously consider whether, in an ordered phase, the electrons can self-differentiate in such a way that only some of them develop an order and coexist^{9–11} with the remaining non-gapped carriers¹². This scenario is of uttermost importance in materials with reduced dimensionality where interactions can particularly easily lead to new exotic instabilities^{13–15}, but these systems are both fragile with respect to dimensional crossover^{16,17}, and prone to coupling to lattice vibrations. This is unfortunate, because they completely pre-empt all exciting non-Fermi liquid phenomena which could take place at the lowest energies^{18–20}.

Materials where distinct carriers independently governed by each of these perturbations can potentially coexist, give us an opportunity to overcome this longstanding stalemate. Here we report Angle Resolved Photoemission Spectroscopy measurements with sub- μm spatial resolution (NanoARPES) of NbSe₃, a material that has been considered a paradigm of charge order. Our new data question a canonical scenario for charge-density-wave (CDW) formation²¹ and suggests the emergence

of a novel kind of order. The resulting electrons' self-organization reveals the one-dimensional (1D) physics hidden in a material which naively could be considered to be the most 3D of all columnar chalcogenides.

The quasi-1D compound NbSe₃ has a columnar structure, shown in Fig. 1(a)²². It undergoes two successive CDW transitions, which affect electrons on distinct columns^{23–25}, at $T_{CDW1} = 145\text{ K}$ with wave vector $\mathbf{q}_1 = (0, 0.241, 0)$, and at $T_{CDW2} = 59\text{ K}$, with wave vector $\mathbf{q}_2 = (0.5, 0.259, 0.5)$ ^{26,27}. The resulting charge ordering is not strong enough to remove the entire FS^{26,28}, and metallic conduction is observed even below T_{CDW2} . The instabilities are usually interpreted in terms of imperfect nesting of the warped multi-sheet Fermi surface (FS). However, the nature of the gapless states has proven quite elusive, with several proposals for the location of residual pockets in the Brillouin zone^{28–30}.

Previous ARPES experiments have reported dispersive bands and CDW-related gaps^{21,31} and, more recently, possible signatures of 1D physics³². In our measurements an electronic *self-organization*, driven by interactions, is revealed by emergent polarization-dependent selection rules, which reflect the underlying 1D nature of the electronic states. The number of observed bands

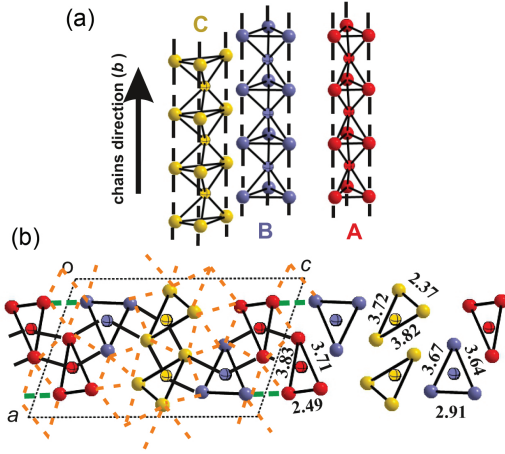


FIG. 1. (a) The crystal structure of NbSe₃ (monoclinic, $a = 10.01 \text{ \AA}$, $b = 3.48 \text{ \AA}$, $c = 15.63 \text{ \AA}$, $\beta = 109.5^\circ$) is built out of prismatic columns of three types, hereafter labeled column A-C, running along the b axis. (b) ac plane cross-section. Green (orange) dashed lines indicate strong (weak) Se...Se intercolumnar contacts.

is also doubled with respect to a single-particle picture. The ability to zoom in on a small selected, disorder-free area of the sample was crucial to observe these features, which escaped previous investigations.

The outline of the paper is as follows. After a description of the experimental methods in Sec. II we present the experimental ARPES results in Sec. III. We illustrate our DFT+U study of the material in Sec. IV and derive in Sec. V the ARPES selection rules that explain the striking polarization dependence of the ARPES data. Finally, in Sec. VI we present a consistent interpretation of our both experimental and theoretical results.

II. EXPERIMENTAL METHODS

NbSe₃ single crystals with typical dimensions of $0.01 \times 10 \times 0.05 \text{ mm}^3$ grown using the chemical vapor transport method³³ were mounted on the sample holder, as shown in Fig. 2. Samples were cleaved “in-situ” in an Ultra High Vacuum (UHV) system at room temperature to expose the bc plane. As detailed below, with the help of the spatial photoemission scanning system it was possible to focus the beam on one of the best cleaved NbSe₃ whiskers.

We performed NanoARPES measurements with the k -microscope of the ANTARES beamline at the SOLEIL synchrotron^{34,35}, with spatial and energy resolution of 100 nm and, respectively, 20 meV. The microscopy capabilities of the experimental end-station are schematically depicted in Fig. 3. A photon beam of variable energy and polarization is focused on a sub- μm spot by means of a Fresnel zone plate (ZP). An order sorting aperture (OSA) removes undesirable higher-order diffraction ef-

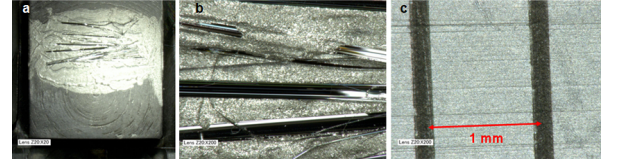


FIG. 2. (a) Sample holder with several NbSe₃ samples; (b) Optical microscope image of NbSe₃ whiskers. The scale of the image is given in (c).

fects. The sample is mounted on a high-precision scanning stage with five degrees of freedom comprising linear and angular motion. Piezoscanners and an interferometric control of the sample and ZP positions guarantee zero backlash and enable sub- μm accuracy and reproducibility as different parts of the sample are scanned through the beam. All these parts ensure spatial resolution of the acquired data without sacrificing any of the qualities of conventional ARPES. Images of the sample chemical composition and angle-resolved valence band states at a sub- μm scale may be acquired by the synchronized scanning of the sample with respect to the focused beam, while the electron analyzer collects photoelectrons of a selected kinetic energy.

Spatially resolved Se 3d intensity scans were obtained at different lateral scales and shown in Fig. 4(a,b). The integrated intensity of the Se 3d core level spectrum is represented as a function of position in a color scale, yielding a “real-space” mapping of NbSe₃ micrometric fibers. Figure 4(c) shows the Se 3d core level spectrum acquired in a high-intensity area in one of the best quality chains (red area). The solid line is the result of a fit of the spectrum with five spin-orbit doublets. The complex line-shape, which reflects inequivalent Se sites, is a direct indication of the quality of the photoemission data acquired with sub- μm lateral resolution.

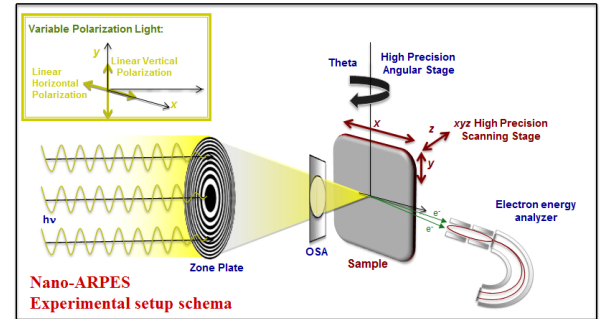


FIG. 3. Sub- μm ARPES experimental setup scheme. The incoming light is focused in a sub- μm region by a zone plate. The sample is mounted on a high-precision 5 degrees of freedom manipulator. Linear horizontal and linear vertical polarized light is available.

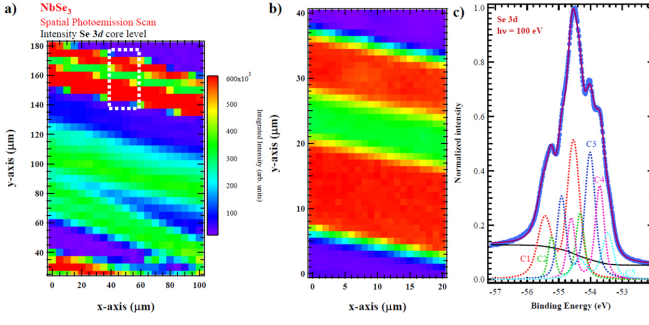


FIG. 4. (a) Spatially resolved Se 3d intensity scan on NbSe₃ whiskers, and (b) Higher resolution scan of dashed area. (c) Se 3d core level and the result of a fit with five spin-orbit doublets.

III. ARPES RESULTS: POLARIZATION DEPENDENT BAND DISPERSION

ARPES measurements of NbSe₃ are challenging. Crystals grow in the form of very thin whiskers, parallel to the b axis, that assemble in bundles. It is thus difficult to ensure that standard ARPES results are not affected by inhomogeneities or by averaging over several domain orientations. In our experiment we took advantage of the sub- μm photon spot size to select a flat homogeneous area of a well-cleaved single crystal whisker. This is especially important for the analysis of the dependence of the spectra on the light polarization, that will be presented below. Data were collected at 100 eV photon energy with light polarized either within (p -polarization) or perpendicular to (s -polarization) the horizontal scattering plane, which contained the b axis of the sample.

Figure 5 shows ARPES intensity maps measured at 55 K, below T_{CDW2} , along the $b^* \parallel b$ axis. We used a soft median filter to remove spikes, and then symmetrized the data around $k = 0$. The average incoherent background, estimated from the noise level at $k > 0.6 \text{ \AA}^{-1}$, is monotonous and can be fitted with a Shirley function, which was then subtracted from the ARPES intensity. Curvature plots³⁶ extracted from (a) and (b) to enhance the visibility of the bands are shown in panels (c) and (e) in a smaller region around Γ . Figure 6 (a,b) shows the corresponding raw, non-symmetrized, data, and Fig. 6 (c,d) the Energy Distribution Curves (EDCs) extracted from those maps. For a quantitative analysis we fitted the line shapes of EDCs and Momentum Distribution Curves (MDCs) extracted from ARPES intensity maps to determine the energy and wave vector of the dispersive features. The resulting peak positions are shown with different symbols in panels (d) and (f) of Fig. 5 and by colored tick marks on the EDCs panels (c) and (d) of Fig. 6.

For s -polarization, in Fig. 5 (c,d), we observe 3 parabolic bands, labeled $A1^+$, C2 and $A3^+$, near the Fermi energy (E_F). Extrapolating their dispersions to E_F yields $k_{F1} = 0.14 \pi/b$; $k_{F2} = 0.22 \pi/b$ and $k_{F3} =$

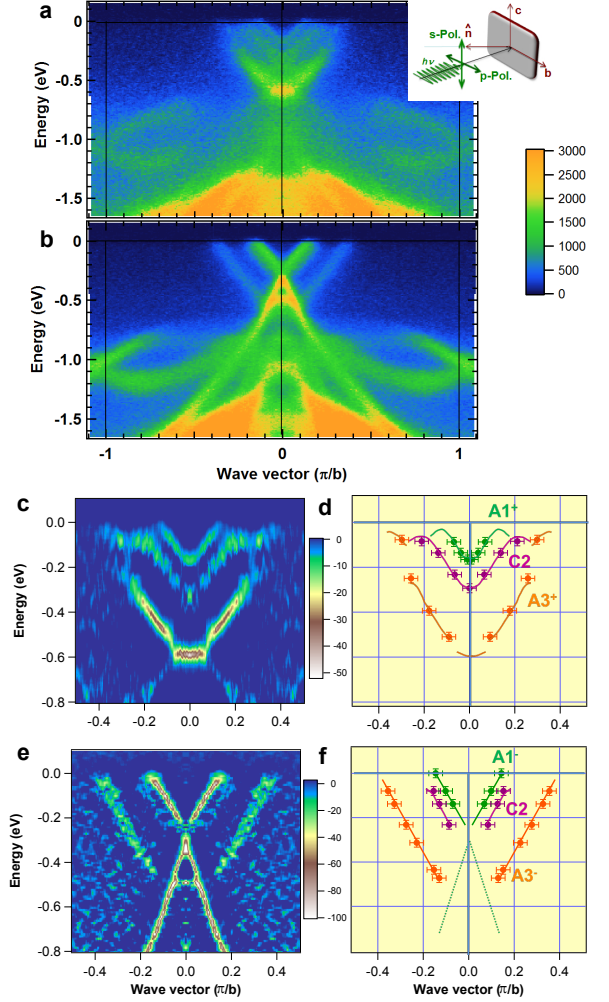


FIG. 5. ARPES intensity maps ($h\nu=100 \text{ eV}$; $T=55 \text{ K}$) measured along the $b^* \parallel b$ axis ($\pi/b=0.89 \text{ \AA}^{-1}$) with (a) s -polarization, and (b) p -polarization. The inset shows the experimental geometry. The s -polarization is perpendicular to the long axis (i.e. to the b axis) of the NbSe₃ crystalline whiskers. The p -polarization has components along the b axis and perpendicular to the bc cleavage plane. (c) and (e) are curvature plots obtained from (a) and, respectively (b). Peak positions determined from EDCs and MDCs are shown in (d) and (f). The lines are guides to the eye.

$0.37 \pi/b$. A gap opens at E_F in band C2 owing to the change of periodicity induced by CDW1. Further analysis of the data at k_{F1} and at k_{F3} reveals a reduction of spectral weight near E_F (see, e.g., Fig. 9 and Fig. 10). This suggests the incipient opening of gaps due to CDW2, which were estimated at $\approx 20 \text{ meV}$ by low-temperature ARPES measurements^{21,31}.

Data taken with p -polarization, in Figs. 5 (b,e,f) and 6 (b,d), present a quite different picture. We now observe two linearly dispersing bands, labeled $A1^-$ and $A3^-$, which *do not* correspond to any of the spectral features observed with s -polarization for the same area

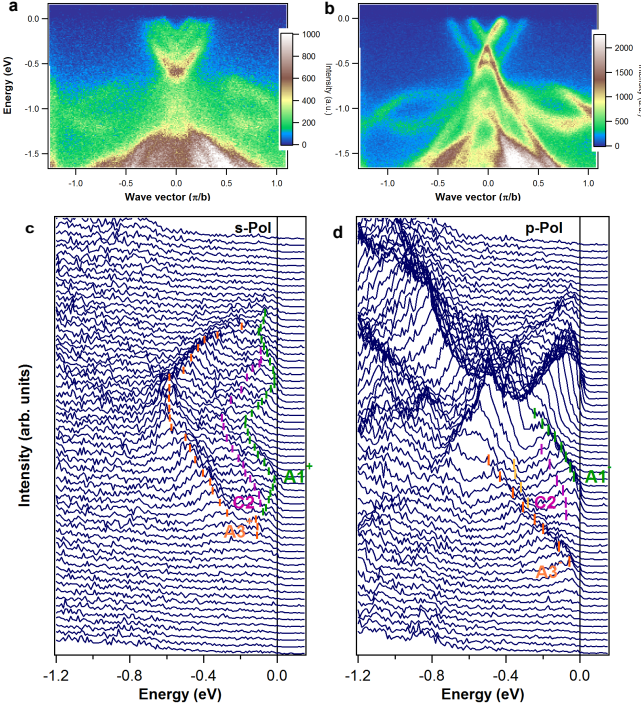


FIG. 6. ARPES intensity maps (raw data; $T=55\text{ K}$; $h\nu = 100\text{ eV}$) for (a) s -polarization and (b) p -polarization. The collection time was 8 hours for each map. (c, d) Energy Distribution Curves (EDCs) extracted from (a) and, respectively, (b). Tick marks indicate peak positions of the various spectral features. The inset in (c) is an intensity map near the Fermi level for s -polarization, obtained by applying the curvature procedure to the raw data.

of the single crystal, and cross E_F with no indications of CDW-related gaps. This dramatic polarization dependence suggests that two different types of carriers, separable by some selection rule, are simultaneously present in a homogenous crystal.

The accurate determination of the Fermi energy is crucial to address the behavior of the electronic states affected by CDW instabilities in low dimensional materials. The Fermi level position in Fig. 6 (c,d) was determined from the Fermi cutoff of a polycrystalline gold sample. We have verified that it coincides with an internal energy reference extracted from the raw data. To this end we have quantitatively analyzed the energy-momentum dispersion of the linear band $A1^-$, which provides a clear and distinct ARPES signal. We have extracted from the intensity map of Fig. 6 (b) MDCs at various energies for the $k > 0$ branch and integrated the intensity under the corresponding peak. The resulting energy-dependent momentum-integrated intensity (Fig. 7) exhibits a clear cutoff which coincides with the Fermi energy determined from the gold sample. This MDC-based E_F determination, besides being intrinsic, is largely unaffected by possible pitfalls affecting the more standard EDC-based procedure (see e.g. Ref. ³⁷).

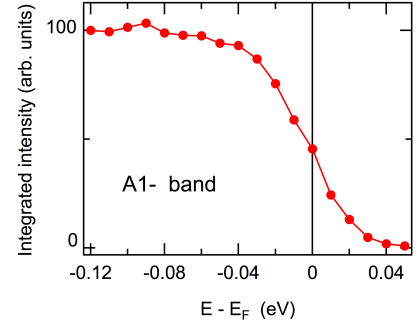


FIG. 7. Energy-dependent ARPES intensity in the $k > 0$ branch of the $A1^-$ band, obtained by integrating the corresponding peak in momentum-distribution curves (MDCs) extracted from Fig. 6 (b). The inflection point determines the Fermi level position.

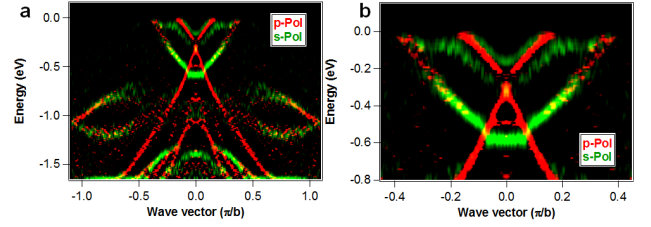


FIG. 8. (a) Comparison of curvature plots obtained from data measured with s -polarization (green) and p -polarization (red). (b) A close-up of panel (a) near the Fermi level.

Figure 8 presents combined images of intensity plots obtained from data recorded with s - and p -polarizations. The images support the idea of distinct dispersions for the bands close to the E_F measured with the two polarizations. This is clear in particular for the $A1^\pm$ bands. We also notice that $A3^+$ exhibits a large gap at $k \sim \pm 0.3\pi/b$ associated with the CDW1 superlattice potential. By contrast, $A3^-$ exhibits a continuous, unaffected dispersion.

Figure 9 shows the second derivative of the spectral intensity with respect to the energy near E_F . This procedure enhances the visibility of the band edges and therefore of the opening of energy gaps, same was used in Ref. ^{31,32}. It is based on the fact that a maximum of a curve always implies a presence in a vicinity of an inflection point of the curve (to be precise, mathematically, there are two inflection points flanking the maximum). From panel c) one sees that it is a good method to follow a dispersion as the dashed lines follows reasonably well the green/yellow area of the raw data. One has to keep in mind that the value of the gap extracted in panel a), although our best attempt, is only an estimate on which one needs to put 20meV error bar (due to all resolution effects). Nevertheless, our estimated value falls close to CDW2 gap extracted from a finite temperature tunneling spectroscopy³⁸ which gives $\approx 15\text{ meV}$ in our

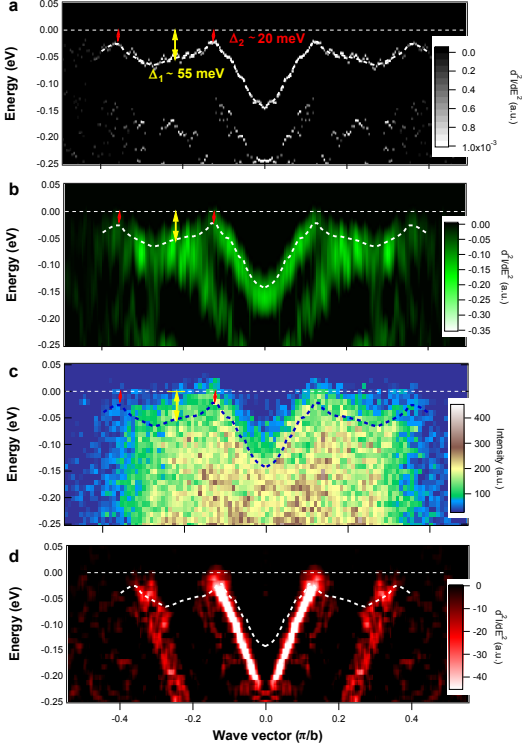


FIG. 9. (a,b) 2nd derivative with respect to energy of the ARPES intensity measured with s -polarization shown in (c). The contrast of image (a) was chosen to plot the line profile following the *inflection* point of the spectral intensity at the vicinity of E_F . The wiggling line is reported in images (b) and (c) in order to evidence the backfolding resulting from the hybridization of bands $A1^+$, $A2^+$ and $C2$. The gap amplitude can be estimated from the distance between the E_F and the edge profile. (d) 2nd derivative with respect to energy of the ARPES intensity measured with p -polarization. The spectral intensity exhibits a gapless behavior and a linear dispersion with no backfolding evidences.

temperature range (with $\pm 10 \text{ meV}$ error bar for uncertainty of temperature and their uncertainty of zero energy gap). Leaving the exact value of the CDW2 gap aside, it is well known that bands' dispersion backfolding is an equally good hallmark of the presence of CDW. With s -polarization the wiggling of the spectral intensity underlines the hybridization of the $A1^+$ - $C2$ and $C2$ - $A3^+$ bands and reveals the backfolding produced by their anti-crossing. By contrast, the $A1^-$ and $A3^-$ bands measured with p -polarization exhibit linear dispersion and metallic behavior. Undoubtedly, the two (on panels b) and d) represent different behaviour.

For a detailed assessment of bands dispersion near E_F it is convenient to adopt a symmetrization procedure that removes the perturbing effect of the Fermi-Dirac distribution function. Specifically, to an EDC measured at k_F is added a mirror image of the spectrum with respect to E_F . This yields the underlying spectral function $A(k_F, E)$ free from the Fermi-Dirac cutoff, with the usual mild assumption $A(k_F, E) = A(k_F, -E)$. The re-

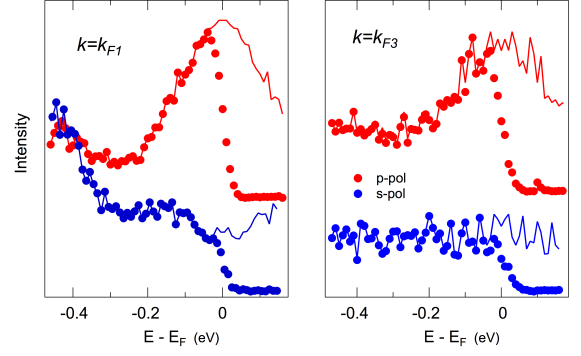


FIG. 10. (left) EDCs measured at k_{F1} with s - (blue symbols) and p -polarization (red symbols), extracted from the intensity maps of Fig. 6. (right) Same for k_{F3} . The solid lines are obtained by symmetrizing the raw spectra around E_F

sults of this procedure applied to band $A1^\pm$ at k_{F1} and to band $A3^\pm$ at k_{F2} are illustrated in Fig. 10. Symmetrization of the spectra measured with p -polarization yields in both cases prominent peaks centered at E_F , consistent with gapless metallic behavior. The situation is qualitatively different for the spectra measured with s -polarization where, even after symmetrization, one observes a nearly constant intensity at k_{F3} , and even a dip at k_{F1} . There is no direct evidence of CDW2 gaps, which have been estimated at $\approx 20 \text{ meV}$ from low-temperature ARPES data (following the same procedure as Ref.³¹). However one must consider that our data have been measured close to T_{CDW2} , where the gap is smaller than its zero-temperature limit³⁸. It would not be possible to observe a direct signature of such a reduced gap opening with our experimental resolution. Nevertheless, the symmetrized spectra of Fig. 10 suggest an underlying incipient gap, consistent with results shown on Fig. 9 and previous tunneling transport³⁸, optical spectroscopy^{28,39} and spectral^{31,32} properties of NbSe_3 . Theoretical prediction for the spectral function (without finite resolution broadening and in-gap states included) have been proposed in Ref. 40 where (in Fig. 2 therein) we observe that even very moderate temperature produces a broad EDCs with rather soft gap.

The differences illustrated in Fig. 10 support the claim that the spectral features observed with different polarizations can be attributed to different bands with distinct near- E_F properties. This conclusion is strengthened by differences in the MDCs line shapes for the two polarizations. The MDCs of Fig. 11 were extracted for $k > 0$ 30 meV below E_F , i.e. close to E_F , and yet sufficiently far to prevent artifacts due to the finite temperature and experimental resolution. Both line shapes exhibit peaks corresponding to bands $A1^\pm$ and $A3^\pm$. Band $C2$ is visible as a distinct feature with s -polarized light but, because of matrix elements, only as a shoulder to $A1^-$ for p -polarization. A comparison of the two MDCs demonstrates that the momenta of the $A1$ and $A3$ ARPES fea-

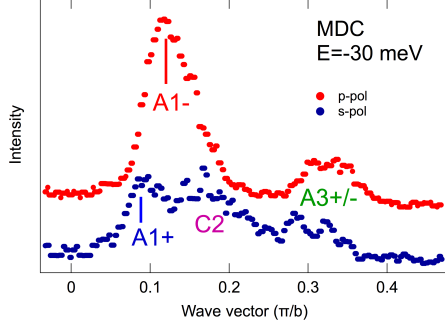


FIG. 11. MDCs extracted 30 meV below E_F for the two polarizations.

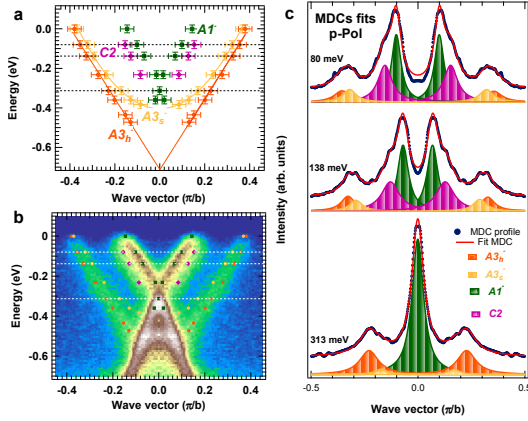


FIG. 12. (a) Band dispersion obtained from MDC fits for p -polarization. (b) Results of the MDC fits superimposed on the ARPES intensity image. The dashed lines indicates the energy profiles for MDC shown in panel (c). Dark and light orange features display the double structure composing band $A3^-$ related to possible spinon and holon contributions.

tures are not the same in the two polarizations, and that therefore they must be attributed to different bands.

A further analysis of the p -polarization ARPES data reveals an even more complex picture. Figure 12 presents fits of MDCs extracted at selected binding energies. Best fits are obtained when two peaks, with k -dependent separation, are used to fit the $A3^-$ band. They are labelled $A3_h^-$ (dark orange) and $A3_s^-$ (light orange). A possible interpretation can be made in terms of 1D signatures of spin-charge separation and will be discussed elsewhere⁴¹. The MDC fits confirm the presence of the C2 band, visible as a satellite of the more intense $A1^-$ band.

IV. DFT STUDY

As a first step to interpret our data we performed (GGA+ U) DFT calculations. Compared to previous DFT calculations on this material²¹ the inclusion of a local interaction term U allows us to better differentiate Nb atoms with formally different oxidation states. The main

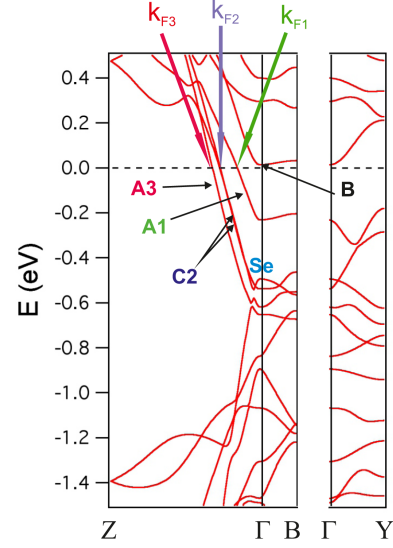


FIG. 13. Theoretical DFT GGA band calculations including finite $U = 4$ eV. The bands can be associated with their experimental counterparts in Fig. 2 by comparing their respective Fermi wave vectors.

results are shown in Fig. 13. The present calculations

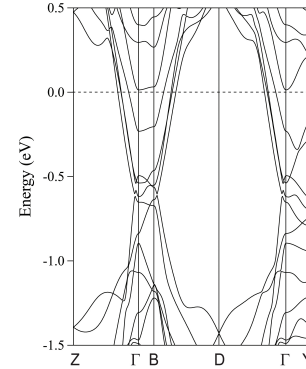


FIG. 14. Calculated band structure for NbSe_3 at 298 K. The energy zero corresponds to the Fermi level. $\Gamma = (0, 0, 0)$, $Y = (1/2, 0, 0)$, $Z = (0, 1/2, 0)$, $B = (0, 0, 1/2)$ and $D = (0, 1/2, 1/2)$ in units of the monoclinic reciprocal lattice vectors.

were carried out using a numerical atomic orbitals density functional theory (DFT) approach,^{42,43} which was developed for efficient calculations in large systems and implemented in the SIESTA code.^{44,45} We have used the generalized gradient approximation (GGA) to DFT and, in particular, the functional of Perdew, Burke and Ernzerhof⁴⁶. Only the valence electrons are considered in the calculation, with the core being replaced by norm-conserving scalar relativistic pseudopotentials⁴⁷ factorized in the Kleinman-Bylander form⁴⁸. We have used a split-valence triple- ζ basis set including polarization orbitals with an energy shift of 50 meV for all atoms⁴⁹. The energy cutoff of the real space integration mesh was

250 Ry. An on-site Coulomb energy (U) of 4 eV has been taken into account within the rotationally invariant DFT+ U approach of Dudarev et al⁵⁰. The Brillouin zone was sampled using grids of $(8 \times 8 \times 8)$ and $(30 \times 30 \times 30)$ k -points⁵¹ for determination of the density matrix and the Fermi surface, respectively. The x-ray crystal structure at 298 K was used in the calculations²².

The calculated band structure at 298 K as well as its fat band analysis are reported in Figs. 13 and 15, respectively. The calculated Fermi surface as well as several particular sections are shown in Figs. 16 and 17, respectively.

They confirm that the $A1^+$, $A3^+$ and $C2$ bands observed with s -polarization are associated with crystal columns A and C. The calculated k_F values are in good agreement with the measured data. The two bands labeled $C2$ are degenerate near E_F as seen in the ARPES experiment where they appear as a single band, $C2$, implying a very small hybridization within a pair of C columns. The bands crossing E_F mainly derive from d orbitals of a given Nb atom, but the d weight is never more than 50%, a rather different situation from e.g. transition metal oxides. This is a manifestation of the covalent character of the Nb-Se bonds and implies that the electron clouds are not locked on the Nb d orbitals, and can be deformed by the CDW potential. The band dispersion has quasi-1D character, but the anisotropy is moderate: the calculated bandwidth is $W_b = 2.5$ eV along the b axis and up to 250 meV along perpendicular directions. Previously proposed band structures^{21,29,30} hold also when local correlations are included, but U shifts band B above E_F . This is consistent with scanning tunneling microscopy measurements²⁵ where a significant spectral weight appears just above E_F , and also with our experiment, where no extra band is detected close to the Γ point. By contrast, the sample of Ref. 32 appears to be slightly electron doped, possibly owing to a small off-stoichiometry.

V. EMERGENT SYMMETRY RULES

From the DFT results one could infer that, at temperatures smaller than the band dispersion, electrons should move coherently in the crystal in all directions, and in particular perpendicular to the chains. Then the symmetry of the electronic system would be that of the $P2_1/m$ monoclinic space group of NbSe_3 , with only two mirror symmetry planes, both parallel to the ac plane. Since the scattering plane in our experiment is perpendicular to these symmetry planes, no definite polarization selection rule⁵² should apply and one should thus observe *identical* dispersions for both polarizations⁵³, albeit with very different intensity. This is in stark contrast with the results of Fig. 5. In this section we introduce the concept of selection rules in ARPES (Sec. V A), then briefly discuss the result that would have been observed if the system were an usual 3D material (Sec. V B), then develop symmetry rules for the 1D case (Sec. V C) and analyze the outcome

separately for each column (Sec. V D and Sec. V E). We conclude that the experimental data imply that, in contrast to the DFT results, the coherent motion of the electrons within the $a - c$ plane is inhibited, endowing NbSe_3 with a stronger 1D character than anticipated.

A. Definitions

ARPES is a probe where a high frequency electromagnetic wave suddenly removes an electron from a given electronic orbital. We probe the propagation (and subsequent recombination) of an excited photo-hole. The ARPES intensity is approximately given by (see e.g.⁵⁴)

$$I(\vec{A}, \vec{q}, \omega) = |M_{fi}(\vec{A})|^2 \mathbf{A}(\vec{q}, \omega) f(\omega) \quad (1)$$

where ω and q are respectively the energy and the in-plane momentum deposited by the photon, and \vec{A} is the vector potential of the photon field. $\mathbf{A}(\vec{q}, \omega)$ is the one-particle spectral function, f the Fermi factor⁵⁵. $|M_{fi}(\vec{A})|^2$ is the matrix element we will focus on in this section. It depends on the shape of the initial and final states and the photon polarization.

The matrix elements are defined between one-body wave functions in the initial and final state:

$$M_{fi}(\vec{A}) = \langle \psi_f | \vec{A} \cdot \vec{P} | \psi_i \rangle \quad (2)$$

where \vec{P} is the momentum operator. Typically $|\psi_f\rangle$ will have the symmetry of a plane wave whose wave vector \vec{k}_f defines, together with the incident photon wave vector, the scattering plane. In the following we denote it σ_l . The polarization of the incident light can thus be perpendicular to this plane (s -polarization; $\vec{A} \perp \sigma_l$) or within the plane σ_l (p -polarization). Note that if we choose a gauge with zero scalar potential we can rewrite the interaction term as $\vec{E} \cdot \vec{R}$, where \vec{R} is the position operator. This makes the symmetries of (2) more transparent, especially if one re-writes the states as real space wave functions $|\psi_i\rangle \equiv \psi_i(\vec{r})$ and integrates over space to obtain $M_{fi}(\vec{A})$.

In the following we use a shorthand bra-ket notation $|e, o\rangle$ to indicate an even/odd state with respect to the plane σ_l . The final state $|\psi_f\rangle$ is always even, thus $|e\rangle$, because it can be expressed as an even parity plane-wave state on the detector's surface⁵². Therefore, we have two possibilities depending on the polarization. For s -polarization the initial state $|\psi_i\rangle$ must be *odd* with respect to the plane σ_l to make the overall space integral $M_{if} \sim \langle e|o\rangle \neq 0$. On the contrary, for p -polarization the initial state $|\psi_i\rangle$ must be *even*.

In most systems, electron hopping can be considered reasonably isotropic, and the electronic states are well represented by Wannier functions, which are coherent superpositions in the three directions of the local orbitals. $|\psi_i\rangle$ is a quantum coherent sum of these local entities, which we need to sum to get the M_{if} . Actually, this

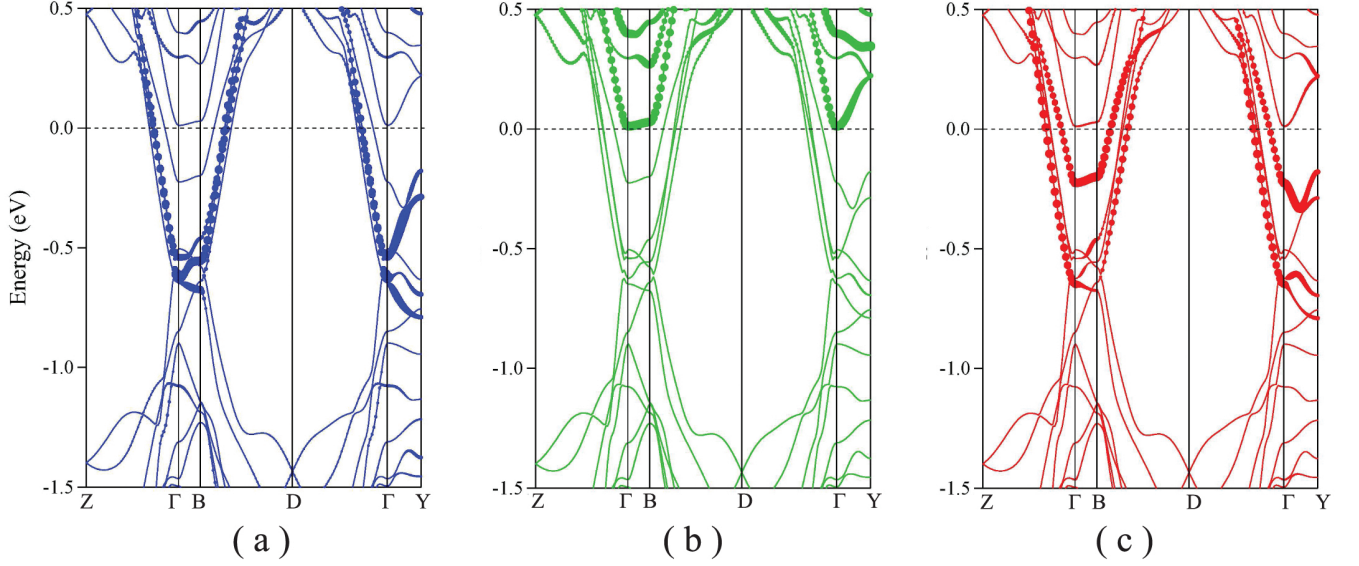


FIG. 15. Band structure for NbSe₃ at 298 K where the size of the blue (a), green (b) and red (c) circles is proportional to the contribution of the niobium atoms in chains C, B and A, respectively.

summation allows us to pick a state with a well defined quasi-momentum inside a crystal. We see that, in order to have a well defined symmetry, the plane σ_l must coincide with a true symmetry plane Σ of the 3D crystal lattice⁵². Then the bands observed in s - and p -polarization can be different. If this is not the case, then there is no symmetry protection and there will be in general a mixing of the two signals. In the NbSe₃ crystal lattice, where the space group is $P2_1/m$, there are two possible Σ planes, both parallel to the ac plane (see Fig. 1(a)), thus perpendicular to the σ_l plane. We conclude that, if the system could be reasonably described as a three dimensional material, the spectra should be essentially independent of light polarization.

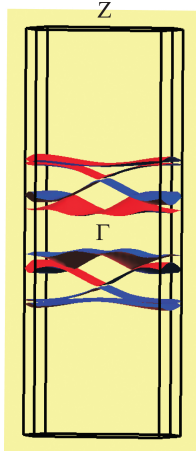


FIG. 16. Calculated Fermi surface for NbSe₃ showing the four pairs of warped sheets.

B. Rough selection rules

Note that in addition to the symmetry selection rules above, the strength of interaction with light does depend on the shape of the orbitals which are at the root of the Wannier functions. From (2), we see that the amplitude is expected to be larger, the electric dipole moment e_j bigger, when the transition involves a j -orbital that is extended in the direction given by \vec{E} . The orbitals spread along the c -axis are likely to lead to larger visibility with the s -polarized light, while those which have a large cross-section within the σ_l plane will be more visible in the p -polarized light. From this we deduce that the p_x component of Se occupancy (and a minor d_{xy} com-

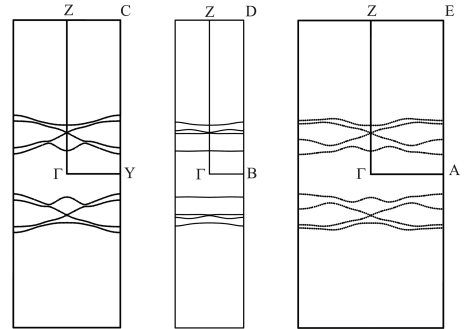


FIG. 17. Particular sections of the Fermi surface of NbSe₃. $\Gamma = (0, 0, 0)$, $Y = (1/2, 0, 0)$, $Z = (0, 1/2, 0)$, $C = (1/2, 1/2, 0)$, $B = (0, 0, 1/2)$, $D = (0, 1/2, 1/2)$, $A = (1/2, 0, 1/2)$ and $E = (1/2, 1/2, 1/2)$ in units of the monoclinic reciprocal lattice vectors.

ponent of Nb occupancy as well) will favour interaction with s -polarized light while all other components with p -polarized light.

Such “rough selection rules” are based on a single electron 3D description. Both tight binding and DFT result yield the atomic content for each electronic band near the Fermi level. It is therefore possible to predict their visibility according to this rough selection rule. There are two tests that we can run against our experimental data: one qualitative and one quantitative. Quantitatively, we notice that the p_x component is about half of the total Se (for atoms on short bond) occupancy while the probability of finding one electron from the A1/3 band on Se atom is approximately 1/3 (note that apical Se atoms have less p_x content). Hence the ratio of intensities of s -vs p -polarization should be (at most) $[(0.5 * 0.3(3) + 0.1 * 0.6(6))^2 / (1 - (0.5 * 0.3(3) + 0.1 * 0.6(6))^2)] = 0.058$ (and here we added an extra 10% d_{xy} component of Nb occupancy). We conclude that, if we were observing *the same 3D state* in both polarizations, then such state would be visible above the noise level only in one polarization, in clear contrast with the result of our experiment. This prediction clearly contrasts with the experimentally observed ratio ≈ 0.5 . Actually, since the beamline throughput is larger for p -polarization, the intrinsic ratio is even closer to 1.0 (i.e. equal intensities for both polarizations).

Qualitatively, one observes a substantial drop in the intensity of the A3 band at binding energy 0.25 eV, but only in s -polarization. The orbital components do not exhibit any anomaly for the corresponding momenta. For $k_c, k_a \approx 0$ we see only a very weak dependence of orbital content on momentum and nearly identical orbital content for the A1 and A3 bands (in accordance with an intuitive two-leg ladder model proposed below). Actually, no sensible model for lattice hybridization could explain a sudden variation of A3 content without any visible change of A1 content.

Finally, one could point out that the different sensitivities of different atoms to light at a given energy should be taken into account. Indeed in our case there is a larger photo-ionization cross-section for the Se atomic sites, but at the same time the hybridization along the b -axis is much stronger than along the c -axis (note, that for the moment, for the sake of argument we are considering 3D system, but it is an anisotropic 3D system) hence the elongation is larger along the former direction. It is safe to assume that these two secondary effects compensate each other.

C. New (1D) selection rules

The summation that defines $|\psi_i\rangle$ is done over a quantum coherent part of the electron liquid. Thus new possibilities for Σ arise in a quasi-one dimensional material. If the hopping between one-dimensional entities, which will be discussed below, is small compared to the inverse time-scale of the ARPES process $t_\perp \ll t < \hbar\omega$, hopping

in the direction perpendicular to the chains is essentially incoherent^{16,17,56}. In this high-energy limit the electron liquid is then in a 1D regime. At low energy the gaps $\Delta_{1,2}$ that appear in the spectrum (see⁵⁷) also prevent single particle hopping between chains. Thus, in both limits the electronic waves perpendicular to the b -axis are incoherent. In that case, the matrix element in (2) must be computed for a single entity only, and thus the symmetry is based on a wave function for a single entity. One could think naively that the entities to be considered are the chains themselves, in which case any plane that would contain the columns (see Fig.1a)) could be a good symmetry plane. However one should not neglect the col.A(1)-col.A(2) hybridization, which manifests itself as a splitting of the b1/b3 bands. The symmetry plane Σ must accommodate these strong links, and a plane perpendicular to the bc plane must be chosen. This plane coincides with the scattering plane, σ_l . We thus find that in the 1D regime $\Sigma = \sigma_l$ and that the selection rules are *strictly* obeyed. Let us now examine the consequences for each column or group of columns.

D. Column C

The prisms out of which col.C is built are strongly distorted. This means that the high symmetry of an ideal D_{3h} chain, out of which the double prismatic columns are made, is lowered to C_{2h} . The d_{z^2} orbital, which is decoupled in a D_{3h} environment, for C_{2h} crystal field contains an admixture of $d_{x^2-y^2}$, because now d_{z^2} and $d_{x^2-y^2}$ belong to the same, rank-1 symmetry class a_1 . The two orbitals $Nb(C) - d_{z^2}$ and $Nb(C) - d_{x^2-y^2}$ remain split by the crystal field potential, but its effect can be effectively reduced owing to a relatively large value of the Hund coupling (one peculiarity of Nb ⁵⁸), which in a mean field treatment favours the symmetry-allowed orbital mixing.

So far, we have used the primed system of coordinates, related to a local Nb atom, because the local crystal field is associated with a given Nb site, see Fig. 18. However, while the admixed orbital is the $d_{x^2-y^2}$ in the local system of coordinates, in the system of coordinates linked with the scattering plane σ_l the spatial shape of the admixed Nb d orbital is very close to a d_{xy} orbital. This is due to the tilting of the col. C prisms with respect to the bc plane (the tilt angle is $\alpha = 43^\circ$). This explains why C2 is visible in s -polarization. Actually, the amplitude of this s -polarization signal can be stronger than one could expect solely from a rather weak Nb- d_{xy} component. The Nb-Se bond has mostly a covalent character, with nearly 50% Se p spectral weight. The admixed d_{xy} has a larger overlap (than d_{z^2}) with the p -Se orbitals (including the p -Se(B)) and thus it plays a bigger role in p - d overlap integrals. These in turn determine the symmetry properties of the outer part of the “C2-molecular orbital”, the ψ_i^{C2} in our ARPES description. This expectation can be put on more solid ground. From our DFT calculation, we

obtain that the p -Se part of the “C2-molecular orbital” is located on a *short* side of col.C prisms (as expected), the Se($C^<$) atoms, and the Se-Se bond has mostly a π character, turned away from Nb-site, thus with larger Se p_y component (in a system of coordinates of Fig. 18). Then indeed the p -Se part has stronger odd character vs. σ_l . The local part of the initial wave function corresponding to band C2, this must be convoluted with Bloch wave along b-axis and anti-symmetrized to get the full $\psi_i^{C2}(\vec{r})$, is a composite orbital:

$$\psi_i^{C2}(\vec{r}) = \sum a_{d_{z2}} \chi_{d_{z2}}(\vec{r} - R_{Nb(C)}) + a_{d_{xy}} \chi_{d_{xy}}(\vec{r} - R_{Nb(C)}) + a_{p_y} \chi_{p_y}(\vec{r} - R_{Se(C^<)}) + \dots \quad (3)$$

where $\chi_j(\vec{r} - \vec{R}_0)$ is an atomic orbital j localized around a given site \vec{R}_0 and a_j are coefficients of the expansion, the Se($C^<$) indicates atoms on the *shorter* edge of the prism. Ellipsis accounts for further p -Se contributions present on all surrounding atoms. Assuming that there is no interaction between the outgoing photoelectron and other carriers (this is at the core of the sudden approximation), then the symmetry character of the composite orbital $\psi_i^{C2}(\vec{r})$ is a weighted sum of the symmetry characters of its atomic constituents. The M_{fi} becomes a weighted sum of a_j coefficients: $M_{fi} = \sum_j w_j a_j$, where only a_j with an appropriate symmetry contribute. Since we have linked our system of coordinates to σ_l it is straightforward to establish whether a given χ_j contributes or not for a given polarization. In the case of $\psi_i^{C2}(\vec{r})$ we have $\chi_{d_{z2}} \equiv |e\rangle$, $\chi_{d_{xy}} \equiv |o\rangle$ and $\chi_{p_y} \equiv |o\rangle$ thus one expects: $M_{fi}^p = \sum_j w_{d_{z2}} a_{d_{z2}} + \dots$ and $M_{fi}^s = \sum_j w_{d_{xy}} a_{d_{xy}} + w_{p_y} a_{p_y} + \dots$

To evaluate M_{fi} we need to know the weights $w_j = \rho_j \bar{w}_j$, where ρ_j is the already discussed geometric factor, which is certainly largest for a well delocalized orbital p_z -Se(C). \bar{w}_j is the bare photoionization cross-section tabulated in Ref. 59. For $\hbar\omega=100$ eV the Nb $4d$ cross-section is close to the Cooper minimum^{59,60}, while the Se $4p$ orbitals have a relatively large cross-section (around eight times larger). Then, surprisingly, the Se p part enters with larger weight. As a result the band C2 has a significant odd component with respect to σ_l and thus it can be well visible in s -polarization.

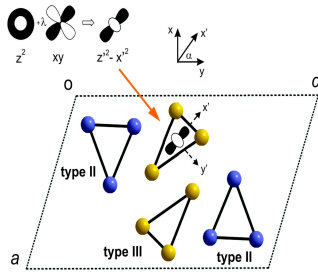


FIG. 18. Mixing of Nb d orbitals on column C yields composite orbitals visible in both polarizations.

An issue is why the even component of C2 is not well visible in p -polarization, since the new 1D-selection rules and the DFT results imply that for p -polarization M_{fi} is close to that of the odd part⁶¹. It should be noted that previous experiments, performed with different photon energies, revealed the doubly degenerated band C2 as the strongest, in accordance with the expectation from the DFT and the sudden electron approximation. Thus spectral weight is missing at the particular condition we probe. We need to search for a cause that depends on energy and on the fact that electrons are ordered. A possible explanation lies beyond the sudden electron approximation. For the chosen photon energy the wavelength of the excited photoelectrons matches well the distance between the nearest Nb(C) sites. This enhances photoelectrons back-scattering, which reduces the ARPES signal. Mathematically, these processes would produce strong vertex corrections to $\bar{w}_{d_{z2}}$, a coefficient that enters in M_{ij}^p . Only the p -polarization part of C2 is strongly affected, because this is the one that originates mostly from an on-site Nb(C)- d_{z2} .

E. Column A

Contrary to the wave function ψ_i^{C2} , which is localized around a given col.C, the “molecular orbitals” corresponding to well split bonding/anti-bonding bands A1 and A3, the ψ_i^{A1} and ψ_i^{A3} , must be delocalized over an entire quartet col.A+col.B. The single column starting point cannot be taken. On the other hand, here the arrangement of most Se p bonds is perpendicular to the σ_l plane. Then, also in accordance with $\bar{w}_{Nb} < \bar{w}_{Se}$, it is more convenient to start with the Se p part of the ψ_i^{A1} and ψ_i^{A3} . In particular we focus on Se p -($A^<$), the orbitals around a short link between col.A-col.B, shown as a green link in Fig. 1.

Focusing on Se p -($A^<$) one can construct two states:

$$\psi_i^{\gamma+}(\vec{r}) = \sum_{R_i} a_{p_y}^{\gamma+} \chi_{p_y}(\vec{r} - R_{Se(A^<)}) + a_{p_y}^{\gamma+} \chi_{p_y}(\vec{r} - R_{Se(A,B)}) + a_{d_{z2}}^{\gamma+} \chi_{d_{z2}}(\vec{r} - R_{Nb(A)}) + \dots \quad (4)$$

where the second term is implied by the σ character of the Se-Se bonds, as determined by the p_y orientation, and:

$$\psi_i^{\gamma-}(\vec{r}) = \sum_{R_i} a_{d_{z2}}^{\gamma-} \chi_{d_{z2}}(\vec{r} - R_{Nb(A)}) + a_{p_{x,z}}^{\gamma-} \chi_{p_{x,z}}(\vec{r} - R_{Se(A^<)}) + a_{p_{x,z}}^{\gamma-} \chi_{p_{x,z}}(\vec{r} - R_{Se(A,B)}) + \dots \quad (5)$$

where we take a sum over all atomic orbitals within a double unit cell that constitute a given eigenstate in real space. By reasoning along the same lines like as for ψ_i^{C2} , taking $\chi_{d_{z2}} \equiv |e\rangle$, $\chi_{p_y} \equiv |o\rangle$ and $\chi_{p_{x,z}} \equiv |e\rangle$, we deduce for the $\gamma+$ state: $M_{fi}^{s\gamma+} = \sum_j w_{p_y} (a_{p_y}^{\gamma+} + a_{p_y}^{\gamma+}) + \dots$,

$M_{fi}^{p\gamma+} = \sum_j w_{d_{z2}} a_{d_{z2}}^{\gamma+}$. Since $(a_{p_y}^{\gamma+} + a_{p_y}^{\prime\gamma+}) > a_{d_{z2}}^{\gamma+}$ and $w_{p_y} > w_{d_{z2}}$ we obtain $M_{fi}^{p\gamma+} \gg M_{fi}^{p\gamma+}$. For the $\gamma-$ state the selection rule is strictly obeyed: $M_{fi}^{p\gamma-} = \sum_j w_{d_{z2}} a_{d_{z2}}^{\gamma-} + w_{p_{x,z}} (a_{p_{x,z}}^{\gamma-} + a_{p_{x,z}}^{\prime\gamma-}) + \dots$, $M_{fi}^{s\gamma-} = 0$. One can also invert the reasoning to realize that we have one initial state that interacts strongly with s -polarized light, while the other only with p -polarized light. It is then quite reasonable to expect that a photohole created by s -polarized light $|\psi_h^s\rangle$ will have a large overlap with only one eigenstate, the $\gamma+$ shown in Fig. 4, that is $\langle\psi_h^s|\psi_i^{\gamma+}\rangle \approx 1$ and by analogy $\langle\psi_h^p|\psi_i^{\gamma-}\rangle \approx 1$. Then one observes a double dispersion of bands A1, A3 because the two different initial states are probed with the two different polarizations.

VI. THEORETICAL INTERPRETATION

In the previous section we showed that ARPES selection rules can emerge due to the one dimensional character of the material. We now need to check if the peculiar physics of NbSe₃ can be captured in this situation. *Obviously, the standard nesting scenario for the lower CDW transition, based on a warped 2D Fermi surface, must be abandoned.* Note that such nesting scenario was already hardly compatible with results from X-ray diffuse scattering⁶². It has been proposed already long ago²⁷ that phase transitions in NbSe₃ must be considered from the perspective of strong interactions, but so far experiments managed to avoid, albeit sometimes narrowly²¹, to tackle this admittedly very complex theoretical issue. However, any nesting-based weak coupling analysis could hardly explain the observed *doubling* of the bands. Therefore, an interpretation of our results cannot avoid correlations (due to interactions) that are only partly taken into account in DFT calculations.

In order to see how interactions and low dimensionality could affect the DFT results, we first consider bands C2, which are degenerate and nearly commensurate, and hence act as a doublet of 1D chains, prone to a Peierls distortion. Indeed the C2 dispersion is clearly back-folded, an effect of the CDW1 with wave vector \mathbf{q}_1 , for which a charge distortion is known to be located mostly on C columns^{23,25,27}. The 1D character of this transition manifests itself in an anomalously large ratio $(\Delta_1/k_B T_{CDW1}) = 6.7$ ⁵⁷. The CDW1 transition thus partitions the rest of the electronic liquid into 1D subsystems⁶³ located on quartets of A+B columns, where the charge is predominantly on column A. Each pair of A columns acts as a two-leg ladder system, as shown in Fig. 19.

Such 1D substructure would be at the root of the observed polarization dependence. A complete calculation, taking into account the full ladder structure and its possible instabilities^{15,64–66}, would be beyond the scope of the present paper and will be done elsewhere⁶⁷. We offer here a plausible scenario, compatible with the experi-

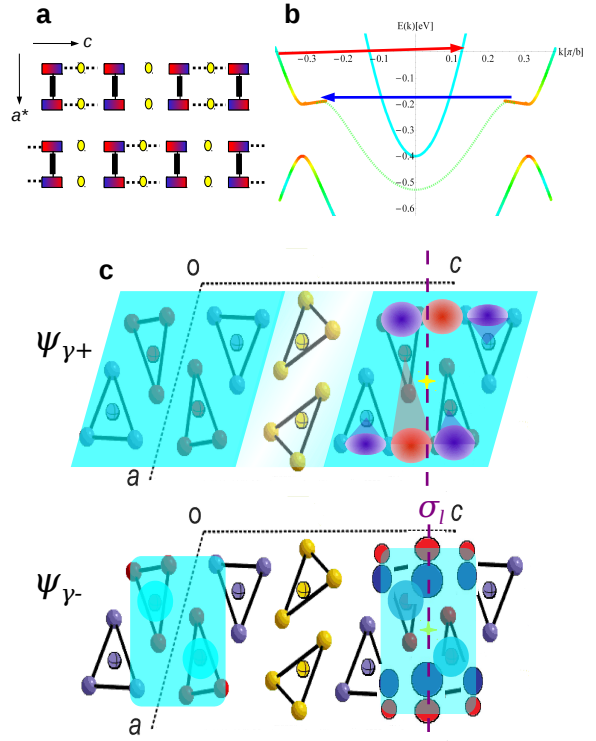


FIG. 19. (a) ac plane cross section showing schematically the perpendicular dimerization and emergent self-organization. Yellow dots represent col. C where CDW1 takes place. Pairs of red-blue rectangles linked by a thick black line are doublets of A+B columns. The perpendicular dimerization is indicated by the dashed lines. (b) Model band structure of re-hybridized γ_+ states showing the proximity of an inter-band $A3^+ \rightarrow A1^+$ back-scattering (red-arrows) to the CDW1 wave vector \mathbf{q}_1 (blue arrow). The colour scale identifies the “hot spot” (c) (Schematic) bonding γ_+ and anti-bonding γ_- orbitals have a different spatial extension. Their amplitude is indicated by the strength of turquoise shading. Red and blue color indicates the phase of the involved p -orbitals. The orientation of a p -orbital determines the direction in which the resulting ψ_γ orbital will be extended. γ_+ (γ_-) exhibits *odd* (*even*) character *vs.* the σ_l plane indicated by the dashed line).

mental data. Let us denote by $\psi_{Ai^+}(r)$ the wave function corresponding to a DFT band Ai^+ . Let us assume a spontaneous dimerization in the ac plane, such transition is permitted since a system of mutually exclusive weak-strong bonds is in essence a 2D Ising model, so a discrete symmetry is broken upon transition. The transition is bringing closer two A-B blocks as in Fig. 4(a), then the $\psi_{Ai}(r)$ orbital will deform, leading to bonding and anti-bonding combinations, denoted γ^\pm in Fig. 4(c). These two combinations have very different interactions with the inner C column, which carries the periodic charge modulation associated with CDW1. For the bonding states $\psi_{\gamma+1,3}(r)$ the *local* coupling, due to the emergent overlap between $\psi_{\gamma+1,3}(r)$ and the electronic orbitals

on C columns, should thus enhance inter-band scattering with large momentum exchange (Fig. 4(b)). The perpendicular deformation is energetically favorable because it allows to harvest electron-electron interaction energy available thanks to the closeness (in momentum space) of a col.A inter-band instability and col.C induced hot-spot in the $A3^+$ dispersion, indicated by red and blue arrows in Fig. 4(b). In the experiment, this manifests itself as a significant re-hybridization with the gapped band C2, an effect clearly visible in Fig. 2(c) and already noticed but not directly addressed²¹.

One consequence of this scenario is that the 1D CDW2 formation is accompanied by a dimerization along the c axis. An organization in the ac plane with a chessboard pattern as in Fig. 4(a) is a natural choice to minimize Coulomb repulsion. It naturally yields the CDW2 periodicity $q_2^\perp = (\frac{1}{2}a^*, \frac{1}{2}c^*)$, which is hard to justify in a standard nesting scenario. Moreover this *ansatz* directly solves several experimental riddles: the band doubling into $A1(3)^+$ and $A1(3)^-$ and their tiny splitting, the number of electrons that remain ungapped, and the presence of gapless carriers close to the Γ point. The hopping between 1D subunits remains incoherent down to very low temperatures. In this case the effective symmetry plane for the 1D system consisting of a quartet of A+B columns must: i) be perpendicular to the c axis, ii) contain the b axis, and iii) cross the center of the quartet. The scattering plane σ_l fulfils these conditions and thus the dipole selection rules emerge. The bonding states γ^+ are by construction delocalized towards column C and involve p -Se σ -hybridization on the short link (green line in Fig. 1(b)). These states are anti-symmetric with respect to the σ_l plane (see Fig. 4(c)) and hence are expected to appear in s -polarization, in agreement with the experiment. A π -bond component on the short bond, required to keep the total density close to the DFT solution, can be absorbed within the anti-bonding state γ^- . These states are symmetric (*vs.* σ_l) and hence visible in p -polarization. Moreover, since they are mostly localized in the core of the quartet and interact weakly with CDW1, they are expected to be gapless. This is what we observe in our ARPES data.

VII. DISCUSSION AND CONCLUSION

We wish to emphasize that results of all four preceding sections has to be taken *altogether* as a proof of the novel physics present in NbSe₃. In experimental part we pointed out the band back-folding in s -pol spectra (as it facilitates data interpretation), but actually a minimal, sufficient claim of our scenario is an (obvious) difference between the spectral functions measured in two polarizations. The DFT+U study shows a substantial agreement with experiment and in this allows us to narrow down the differences caused by further correlation effects. Furthermore, it allows for a precise estimate of ARPES inten-

sities in two polarizations (although we use a three-step ARPES model, our confidence is strengthened by a recent study [cite] which shows that within a one-step model, final state's effects cannot cause a substantial difference at a chosen photon energy) which questions the standard Fermi-liquid scenario and favors the 1D scenario. The emerging 1D scenario indeed captures all details of our experimental data and is in fact in agreement with previous experimental findings. In particular, the new theory allows to connect the re-hybridization of bands C2 and $A3^+$, clearly visible in s -pol (but not in p -pol) and detected already before²¹ (therein called 'mysterious'), with the CDW gap formation, which makes the entire picture consistent.

In summary, we exploited ARPES with sub- μm lateral resolution and polarization control to study the electronic states of NbSe₃. We observed a strong dependence of the dispersion on the light polarization, incompatible with a simple anisotropic quasi-1D "Fermi-liquid" like description of this material. Our results can be explained by a self-organization into orbitally distinct electronic systems. One set of electronic states is gapped as evidenced by back-folding of its electronic dispersion. The other exhibits one-dimensional character and remains metallic. The canonically accepted mechanism for the low-temperature CDW2 formation must be replaced by a new scenario where part of the carries couples more strongly with the preceding CDW1. Experimentally, our results demonstrate that pushing the lateral resolution of ARPES to sub-micron scale can lead to qualitative breakthroughs. This will be especially fruitful for studies of novel and strongly correlated materials, that were so far hindered by small crystal sizes and inhomogeneities. Theoretically, the new scenario for the CDW formation, based on self-differentiation leading to enhanced interaction with the preceding CDW, suggests a re-investigation of other materials where similar sequences of phase transitions are present. These results open the way to new experiments searching for the emergence of hidden 1D dimensional states in strongly correlated materials.

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