CDW signatures in the electronic structure of LaSb$_2$ at 13 K and metal-insulator transition

I. Palacio$^{1,*}$, J. Obando-Guevara$^{2,3}$, L. Chen$^{2,*}$, M. N. Nair$^1$, M.A. González Barrio$^3$, E. Papalazarou$^2$, P. Le Fèvre$^1$, R.F. Luccas$^4$, H. Suderow$^4$, P. C. Canfield$^5$, A. Taleb-Ibrahimi$^1$, E.G. Michel$^6$, A. Mascaraque$^3$, A. Tejeda$^{1,2}$

$^1$ Synchrotron SOLEIL, L’Orme des Merisiers, Saint-Aubin, 91192 Gif sur Yvette, France
$^2$ Université Paris-Saclay, CNRS, Laboratoire de Physique des Solides, 91405, Orsay, France.
$^3$ Depto Física de Materiales, Universidad Complutense de Madrid, Spain
$^4$ Laboratorio de Bajas Temperaturas y Altos Campos Magnéticos, Departamento de Física de la Materia Condensada, Instituto Nicolás Cabrera and Condensed Matter Physics Center (IFIMAC), Unidad Asociada UAM-CSIC, Universidad Autónoma de Madrid, E-28049 Madrid, Spain
$^5$ Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames Laboratory, Ames IA 50011, USA
$^6$ Depto Física de la Materia Condensada, and Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, 28049 Madrid, Spain

* Corresponding author

Abstract

Light rare-earth antimonide LaSb$_2$ is a material susceptible to nesting and exhibits a Charge Density Wave (CDW) at 355 K as well as superconductivity below 1.2 K. In the seek for additional CDW transitions, we have studied the temperature-dependent of LaSb$_2$ at 200 and 13 K and infer CDW manifestations by combining angle-resolved photoemission spectroscopy (ARPES) measurements and density functional theory (DFT) calculations. ARPES measurements at 200 K show a metallic system while it appears to be semiconducting at 13 K, at odds with existing resistivity measurements. At 13 K, ARPES shows the band folding of the inner Fermi surface pockets, with considerable spectral weight on the folded band. We find a nesting vector at $q = 0.25\pm0.02 \ \text{Å}^{-1}$. In addition, we observe Umklappes of other bands due to the onset of the new periodicity, together with a semiconducting behavior in the whole reciprocal space. Calculations demonstrate that the folded band is associated with the La-Sb layer and that in-plane distortion is the most probable structural modification in the system, probably affecting the whole unit cell.

* Now at Instituto de Ciencia de Materiales de Madrid, CSIC, C/ Sor Juana Inés de la Cruz 3, 28049 Madrid, Spain
Charge density wave (CDW) states, associated to a periodic distortion of the atomic positions and a corresponding modulation of the electron density, have brought great interest in condensed matter physics due to its competition or even coexistence with superconductivity [1-6]. For many years, two dimensional (2D) layered materials have been suitable model systems to understand these phenomena. Among them, light rare-earth diantimonides stand out because of their complex physical phenomenology [7].

LaSb$_2$ is a material exhibiting superconductivity and CDW. It shows 2D features, with very large superconducting transitions and reports of critical temperature varying between 0.4 K and 2.5 K [8-10]. The magnetoresistance (MR) of LaSb$_2$ exhibits a puzzling behavior. It is very large, linear, and with no sign of saturation up to fields of 45 T [11]. Both its magnitude and its linearity are surprisingly at odds with the standard semi-classical theory of magnetoresistance [11,12]. According to band structure theory, the resistance of metals increases quadratically with the magnetic field, except in materials with open Fermi surface orbits, in which case the MR eventually saturates. Because of the obvious failure of this model, several mechanisms have been suggested to explain the MR. They rely on local fluctuations in carrier density [13], high field quantization effects [14], disorder or inhomogeneities [15], or magnetic breakdown effects in CDW materials [16]. However, the magnetization of LaSb$_2$ displays quantum oscillations, ruling out inhomogeneity and disorder. This leaves a CDW as a likely possibility to explain the observed MR.

In fact, the strongly 2D features of LaSb$_2$ reminds other layered compounds, such as NbSe$_2$ or TaSe$_2$, which also display a large linear MR and a CDW. Calculations predict significant nesting at the Fermi surface of LaSb$_2$ [17] and a CDW is observed in the related compound LaAgSb$_2$ [18,19], where the CDW ordering has been related to linear bands [20,21]. A CDW was finally found in LaSb$_2$ above RT, identified at 355 K by a kink in the resistivity [22]. Interestingly, the CDW evolves towards lower temperatures when substituting La with Ce in (La$_{1-x}$Ce$_x$)Sb$_2$ and coexists with magnetism for x>approx. 0.3 and up to x<approx. 0.9. The periodicity of the CDW has been estimated from a Fourier analysis of STM images on (La$_{0.6}$ Ce$_{0.4}$)Sb$_2$ and it points towards a charge modulation of the order of 4 nm$^{-1}$ [22].

Nonetheless, no CDW has been identified on LaSb$_2$ below RT so far, closer to the superconductivity regime. Photoemission at 140 K [23], X-ray diffraction at 80 K [22] or STM at 0.15 K [10] do not observe evidences of a CDW. In this work, we report a temperature-driven phase transition that modifies the Fermi surface and the band structure, leading to the appearance of a band folding at 13 K associated to a reciprocal lattice vector $q$ related to $k_F$. Umklapps to other bands with this periodicity also appear at the Fermi surface. Density functional theory (DFT) calculations on distorted and undistorted structures allow to delve into the origin of the phase transition and to identify it as the stabilization of a CDW.
Experimental and calculation details

LaSb$_2$ single crystals, plate-like, have been grown from high purity La and Sb by the metallic flux method [7,24-26]. ARPES measurements were carried out at the CASSIOPEE beamline of SOLEIL synchrotron, equipped with a 5-axis liquid He cryogenic manipulator and a with a Scienta R4000 electron analyzer having a ±15° acceptance angle with a base energy resolution lower than 1 meV and 0.1° angular resolution. The photon energy in the experiments was $h\nu = 118$ eV, out of the minimum of the inelastic mean free path [27]. In order to obtain information on the bulk electronic states, we cleaved the surface (parallel to the Sb planes) under ultrahigh-vacuum conditions immediately before the photoemission experiments [28]. At 200 K the Fermi level of the sample was determined through the inflection point of the experimental spectrum of a metallic band, which follows a clear Fermi-Dirac distribution. The same band was considered at 13 K for determining the energy reference from the inflection point of the Fermi-Dirac distribution function, although at 13 K the intensity is highly reduced, as expected for a bad metal. The intensity at the Fermi level in Fermi surfaces was obtained by integrating the spectral weight in a window of ±20 meV around the Fermi energy.

The electronic band calculations were performed with density functional theory [29] by combining the Vienna \textit{ab initio} Simulation package (VASP) [30,31] with post-processing VASPKit package [32]. The exchange-correlation potential was adopted by the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) function [33]. The cutoff energy was set to 500 eV. A Monkhorst-Pack [34,35] k-mesh with a size of $8 \times 8 \times 2$ for LaSb$_2$ primitive cell and a size of $8 \times 2 \times 2$ for LaSb$_2$ supercell were used for the geometry optimization and the self-consistent field convergence for the total energy and the force variation were set as $10^{-6}$ eV and 0.001 eV/Å, respectively.

Results and discussion

Fig.1(a) shows the crystal structure of LaSb$_2$, which has SmSb$_2$-type structure, with a centrosymmetric Cmce space group (No. 64). There are two Sb sites. In one of these, Sb atoms form two-dimensional sheets (Sb1 site), while in the other Sb atoms (Sb2 site), together with the La atoms, are part of La/Sb bilayers. The 2D Sb sheets are sandwiched between corrugated La/Sb bilayers along the c axis. Fig. 1(a) shows the primitive cell, together with a conventional cell more convenient for visualizing the structure and the symmetries. The $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{a}'$, $\mathbf{b}'$ are the lattice vectors of the primitive and conventional cells in 2D plane, respectively. Fig.1(b) shows the Brillouin zone of the LaSb$_2$ primitive cell and the K$_x$, K$_y$, K$_z$ axis corresponding to the a, b, c axis in real space in Fig.1(a),
respectively.

Fig. 1 (color on line) (a) Layered LaSb$_2$ crystal structure exhibiting Sb sheets and La/Sb bilayers. The primitive and conventional cells are marked with blue and red lines, respectively. $a$, $b$ and $a'$, $b'$ are the lattice vectors of the primitive and conventional cells in the 2D plane, respectively. (b) The corresponding bulk Brillouin zone and (001) surface Brillouin zone of the LaSb$_2$ primitive cell. (c)-(g) Theoretical electronic band structure of LaSb$_2$. (c) The calculated Fermi surface of LaSb$_2$ for the primitive cell projected on (001) surface. The high symmetry points are marked by adding overhead bars, correspondingly, as shown in (b). (d)-(g) Electronic band structures of LaSb$_2$ along $\Gamma$-Y-S-X-$\Gamma$ K paths. The band structure is projected on the Sb atoms of Sb-sheet (e), La atoms of La/Sb bilayer (f) and Sb atoms of La/Sb bilayer(g). The color scale indicates the projection of each state at each atom (red is higher). The crossing points $a,b,c,d,e,f$ of the bands with the Fermi level are marked roughly in (c) and (d). The different colored Fermi surface parts (c) origin from different bands crossing the Fermi level. Those bands are marked by corresponding colors in (d).

Based on the LaSb$_2$ primitive cell, we calculated the electronic structure of the system. Fig.1(c) shows the whole Fermi surface along the $K_x$, $K_y$ reciprocal plane. The Fermi surface consists of two main parts: a diamond (warped square) and two pockets which have a glasses-like shape, showing good consistency with the results in ref. [17]. Unlike CeAgSb$_2$ or LaAgSb$_2$ [36], in LaSb$_2$ there are no FS sheets centered around the $\Gamma$ point. The two glasses-like pockets are inside the warped squared contour and run along the $\Gamma\rightarrow Y$ direction. The warped square extends to the edges of the Brillouin zone and the corners of the square are positioned halfway between the X and Y points (i.e., the S point).
The electronic band structure along Γ-Y-S-X-Γ K paths is shown in Fig.1(d)-(g). A wider energy range can be seen in the Supplementary Material. Fig.1(d) provides a first indication of the bands crossing the Fermi level (crossing points marked by c,d,e,f). In order to better relate the band structure and the Fermi surface, the crossing points are also indicated in the Fermi surface of Fig.1(c). Further information on the Fermi surface sheets can be extracted from the atomic origin of the bands. Fig. 1(e)-(g) show the atom-projected band structures. Fig. 1(e) corresponds to the projection on the Sb atoms of the Sb-sheets, Fig. 1(f) on the La atoms of the La/Sb bilayers and Fig. 1(g) on the Sb atoms of La/Sb bilayers. It can be observed that the warped square part of the Fermi surface is mainly originated from the conical bands associated with the Sb atoms in the Sb sheets (Fig. 1(e)). The La and Sb atoms in the La/Sb bilayers give the leading contribution to the other bands (Fig.1(f) and (g)), which reveals that the two glasses-like pockets in the Fermi surface arise mainly from the orbitals of La and Sb atoms in the La/Sb bilayers. Besides, the orbital character of the band structure has also been extracted shown in the Supplementary Material. The Fermi surface results mainly from the d orbitals of the La atoms and the px, py orbitals of the Sb atoms which suggests that there is a strong 2D nature, in agreement with the 2D character of the Fermi surface outer square.

An overall inspection of the previously presented Fermi surface shows parallel sheets that are susceptible to nesting and therefore to CDW instabilities, as it was previously suggested [17]. Nesting implies that significant parts of the Fermi surface (FS) can be connected by a wave vector q [37]. When that is the case, replicas of FS sheets appear at low temperature [38,39]. In the seek for a CDW in LaSb2 at low temperature, that has been elusive up to now, we have performed ARPES measurements as a function of the two directions of the k parallel vector (kx and ky). Figure 2(a) shows the experimental FS of LaSb2 at T=200 K, that exhibits a good agreement with our calculations. A larger region of the reciprocal space is shown in the Supplementary Material. At T=13 K, the shape of the FS dramatically changes. As seen in Fig. 2(b), the FS is replicated along the ΓY direction, the same direction along which the "glasses"-like pockets are oriented. In order to analyze these changes in detail, we have made several cuts in the FS along this direction, which are marked in Fig. 2 with red lines. The cuts have been made both perpendicular to the diamond-shaped outer edge and along the "glasses". Those corresponding to the diamond shape (labelled with numbers) are represented in panels (c) and (d) of Fig. 2. In these panels we have marked the maxima of the intensity with colored dots. While at T=200 K only one maximum appears, at T=13 K a replica is perfectly observed. The measured constant separation of both maxima gives a value of q= 0.25 ± 0.02 Å⁻¹, which is of the order of magnitude of the q vector determined from STM for the doped compound (La0.6 Ce0.4)Sb2 [22], the difference being attributed to the modification of q in the Ce doped compound. Supplementary Material shows additional analysis of FS regions interconnected by this q vector.
Fig. 2. (color on line) Experimental k-space mapping at 0 binding energy obtained from the plot of the ARPES intensity as a function of the $k_x$ and $k_y$ vectors near the Fermi level ($h\nu= 118$ eV). The intensity is integrated in an energy window of 20 meV. The measurements were done at two different temperatures, (a) above the CDW transition ($T=200$ K) and (b) below ($T=13$ K). In the panels the first and second Brillouin zones of the primitive unit cell are covered. The yellow arrows indicate the places where cuts of the FS are performed. The cuts corresponding to the second Brillouin zone, labeled by numbers, are represented in panels (c) and (d) respectively. The dots in these panels indicate the intensity maxima. While at high temperature there is only one maximum, i.e., one band crossing the Fermi level (blue dots), at low temperature there are two bands. Both maxima are separated by a distance $q= 0.25\pm0.02$ Å$^{-1}$. This same vector (length and direction) is depicted in panel (b).

We present the electronic structure measured by ARPES along the high symmetry directions of the Brillouin Zone ($\Gamma Y SX \Gamma$) in Fig. 3, measured at 200 K and at 13 K. The strongest difference as a function of temperature, close to the Fermi level, where electronic instabilities play a role, is in the neighborhood of $\Gamma$ along the $\Gamma Y$ direction. This modification of the band structure corresponds to the “glasses”-like pockets associated with the La-Sb bands (red rectangle in panels (a) and (b)). Inside the rectangle, it can be appreciated how these bands are folded at low temperature. The spectral weight in the folded band is very strong, indicating a strong potential inducing the folding. This folding is associated to the nesting vector $q$, excluding that the band structure modifications arise from different domains in the sample. Replicas are an intrinsic feature of the low
temperature phase. Concomitantly with the band folding at low temperature giving rise to a semiconducting band, the energy difference between the two low-dispersing bands (binding energies around -0.5 eV and -1.0 eV at high temperature) increases. Also, it is observed that bands shift to lower binding energies at low temperature, indicating that the system is more sensitive to charging during the photoemission process, further confirming the poorer conductivity of the system at low temperature. The semiconducting nature of the system at low temperature, together with the modifications of the band structure, do not allow an accurate determination of the Fermi level of the low temperature phase and therefore to quantify the band gap associated to the CDW.

Fig. 3 also shows that the system at low temperature is semiconducting along all the high symmetry directions, meaning that the system exhibits a band gap independently of a particular \( \mathbf{q} \) vector. Electronic correlation is a possible explanation for an isotropic band gap opening [40]. In 1T-TaSe\(_2\) it has been proposed that the CDW there induces flattened backfolded bands that reduce the bandwidth \( W \), reducing the \( W/U \) ratio (\( U \) being the Coulomb energy) and triggering a Mott transition [41]. An analogous mechanism can explain the experimental band gap across the whole Brillouin zone, especially because electronic correlations are enhanced in two-dimensional systems as LaSb\(_2\), where the Fermi surface is mainly originated by \( d \) orbitals from La.

We conclude that at low temperature, the experimental results show a clear folding of the glass-like features, i.e. the La-Sb band associated to the nesting vector \( \mathbf{q} \). In addition to this electronic change, there are replicas of all the bands (Umklappss) with the same \( \mathbf{q} \) vector, as seen at the FS. Replicas are connected to the original spectral feature by the size of the La-Sb pocket. This corresponds to one-third of the \( \Gamma-Y \) distance, so in real space, the periodicity of the atomic structure should be enlarged 3 times along the \( \mathbf{a}+\mathbf{b} \) direction (i.e. \( 3\mathbf{b}' \)). A supercell which contains 3 conventional cells along the \( \mathbf{b}' \) direction must therefore be constructed, since this size will allow us to describe the observed \( \mathbf{q} \) vector. Fig. 4(a) shows a supercell with no structural modification (called hereafter perfect supercell) with respect to the high temperature phase. In order to obtain an effective primitive cell band structure, unfolded band structures [42] are calculated for the supercells studied in this work. Fig.4(b) shows the unfolded band structure of the perfect supercell, in reasonable agreement with the bands of the primitive cell (Fig.1).
Fig. 3 (color on line) Experimental band structure along high symmetry directions (ΓYSXΓ) above and below the CDW phase transition, corresponding to FS in figure 2. Panels (a) and (b) show the curvature plot of the ARPES intensity obtained with a photon energy of $h\nu=118$ eV on a wide range of binding energy for 200 K and 13 K respectively. The low temperature energy reference is determined with respect to the inflection point of a Fermi-Dirac fitting at the maximum of the folded band. (c) and (d) are zooms of the areas indicated with a red square in panels (a) and (b) respectively. Panel (d) shows $q$ along Γ-Ȳ, corresponding to the maxima of the bands originating the “glasses”-like features at the Fermi level in the high temperature phase. An analogous analysis for another Brillouin zone is shown in the Supplementary Material.

Once the supercell satisfactorily describes the high temperature phase (200 K), we focus on describing the low temperature phase with a 3$b^*$ periodicity in the crystal structure and replicas in the band structure. However, such calculations are hard to obtain straightforwardly through DFT calculations, as DFT calculations are static simulations and temperature-dependent situations are difficult to mimic. Therefore, to simulate the low temperature crystal structure, we have induced different structural modifications on the perfect supercell with displacements related to the experimental $q$ vector of the CDW (Fig.4(a)) to artificially introduce a CDW on the system. We have analyzed several structural modifications with a 3$b^*$ periodicity. In particular, we have introduced displacements on the Sb sheets, on part or all of the atoms of one conventional
cell. Fig. 4(c) shows a longitudinal-wave-like modification in the Sb sheets (method 1), where Sb atoms are displaced along $b'$ direction. The two middle Sb atoms in the Sb sheets were moved towards each other along the $b'$ direction, reducing their distance by 0.03 Å. Then we fixed those atoms, and the positions of the rest of the atoms were relaxed. Fig. 4(e) shows the displacement of half of the atoms in the conventional unit cell. Atoms on the right side of the unit cell were shifted by 0.02 Å along -$b'$ direction and then the right-part of the conventional cell was fixed and again all the other atoms were relaxed (method 2). Fig. 4(g) shows the displacement of the whole middle conventional cell along the $b'$ direction by 0.02 Å (method 3). Besides, we have also tried two transverse-wave-like modifications of Sb atoms in Sb sheets along $a'$ and $c$ directions, which are shown in the Supplementary Material. The unfolded band structures of these different modified structures are shown in Fig. 4.

In addition, from our calculations, we are able to estimate the value of the atomic distortion that originates the CDW. The atomic displacements introduced in most of the methods have values of 0.02-0.03 Å. For smaller displacements, band replicas are hard to observe, and for higher displacements, the band structure deviates seriously from the original one (see for instance Fig.S4(f)). Since the experimental low temperature bands and Fermi surface keep the original shape except for the replicas, the structural modifications cannot deviate much from the above-mentioned values.

From the unfolded band structures, we observe that distorted structures introduce more bands compared to the perfect supercell. Band replicas can be clearly observed in some structural deformations in Fig. 4 and in the Supplementary Material. However, it is worth noticing that not every structural modification with the experimental periodicity reproduces the experimental band structure. In particular, the displacement of all the atoms within the conventional middle cell along $b'$ direction shows more clearly band replicas and also the band shapes are almost preserved (Fig.4(h)). Details of the experimental and calculated band structures with this structural distortion are shown together for comparison in Fig.4(i). Although a perfect description of the bands is not expected due to the coarse trial models, there is a relatively good agreement, with the presence of wavy-shaped bands just below the Fermi level. This rough model captures the essential physics of the system. From it we suggest that the temperature-driven phase transition of LaSb$_2$ results from the displacement of most of the atoms in one conventional cell along the $b'$ direction, although due to the finite number of explored configurations, experimental structural techniques would be helpful to shed further light on this issue.
Fig. 4. (color on line) Structural modifications and the corresponding band structure. (a) Supercell of LaSb$_2$ containing 3 conventional cells along $b'$ direction. (b) Unfolded band structure of the supercell in (a). (c), (e), (g). LaSb$_2$ supercells with modified atomic positions to simulate the periodicity of the CDW: (c) displacement of the Sb atoms in Sb sheets along $b'$ direction to introduce a longitudinal-wave-like modification in the Sb sheet (e) Displacement of half of the atoms in the conventional unit cell (those in the right side). (g) Displacement of the whole middle conventional cell by 0.02 Å along the $b'$ direction. (d), (f), (h). The unfolded band structures correspond to the modified supercells in (c), (e), and (g), respectively. (i) Detail close to the Fermi level from the experimental band structure from Fig. 3b and theoretical band structure of an atomic distortion affecting all the atoms within the unit cell (h). Green dotted lines are a guide for the eye to indicate the theoretical states that could give rise to the experimentally observed states.
Summarizing, the combination of ARPES measurements and theoretical calculations has allowed us to observe changes in the band structure associated to a CDW transition in LaSb$_2$ between 200 K and 13 K. ARPES shows that the periodicity of the distortion corresponds to a nesting vector $\mathbf{q} = 0.25 \pm 0.02 \text{ Å}^{-1}$ that connects regions inside the “glasses”-like pockets of the Fermi surface. The nested bands exhibit the band folding associated to the low temperature phase of a CDW transition. Moreover, the new structural periodicity at low temperature promotes replicas. All the changes in the electronic structure at low temperature are related to the $\mathbf{q}$ vector, indicating that they correspond to an intrinsic property of the CDW phase. All these manifestations of a CDW are clear at 13 K in the photoemission data, close to the superconducting state of the system. The superconducting state at 0.15 K was studied by STM [10] and no superperiodicity associated to a $\mathbf{q}$ vector of 0.25 Å$^{-1}$ was observed at the surface, possibly because the competition between the superconducting and the CDW phases. Calculations show that the glasses-like pockets involved in the CDW transition exhibit La-Sb character. Calculations also indicate that the transition corresponds to a distortion affecting all the atoms in the unit cell.

The critical temperature of the transition depends on the number of intrinsic defects of the compound and lose layers might also decrease the critical temperature. Concerning the critical temperature associated to the CDW manifestations experimentally observed in photoemission, two scenarios are possible and evaluated below. The first one corresponds to a critical transition between 200 K and 13 K and most probably below 80 K since X-ray diffraction measurements between 300 K and 80 K do not observe a structural periodicity analogous to the electronic periodicity observed in photoemission [22]. In this situation, LaSb$_2$ will thus exhibit a series of CDW transitions as a function of the temperature, as many others that have been reported [41,43,44], including in the related compound LaAgSb$_2$ [18]. In this scenario, there will be a first CDW at 355 K [22] and the one at low temperature identified in this work. Since the nested regions correspond to a small fraction of the Fermi surface, there will be no evident resistivity anomaly. Even though there is a faint and smeared resistivity anomaly around 260 K [7], this anomaly is mainly associated to the out-of-plane resistivity, so there is no evidence in extensive transport data of an in-plane CDW transition in the 200 K or lower temperature region, although in occasions CDW take place without a particular change in resistivity [41,45]. Resistivity and magnetic susceptibility manifestations of the CDW can also happen at much higher temperatures than the critical temperature [46] or exhibit behaviors not expected from the experimental band structure measurements [41,45].

The second scenario corresponds to considering that a second CDW is not needed to explain photoemission, resistivity and magnetic susceptibility
measurements as a function of temperature. Within this scenario, the CDW manifestations in photoemission at 13 K would be related to the single CDW of the system, with a transition temperature of 355 K as determined by macroscopic measurements [22]. In this picture, since distortions grow with temperature (i.e. as an order parameter) it is plausible that they are not large enough to make the new periodicity detectable by ARPES at 200 K and are resolvable at 13 K. This scenario is moreover supported by the absence of resistivity or magnetic susceptibility anomalies below 200 K.

In conclusion, and independently of the critical temperature of the phase transition, we have observed unambiguous manifestations of a CDW behavior (nesting, band folding, Umklapps) at 13 K in LaSb$_2$. In addition, ARPES reveals a semiconducting state possibly associated to a Mott insulator phase triggered by the bandwidth decrease due to the CDW band folding (U/W increases). These manifestations appear above the superconducting phase of LaSb$_2$.

ACKNOWLEDGEMENTS

This work was supported by the French Agence Nationale de la Recherche (ANR) contracts ref. NT-09-618999. MAG and AM thank Ministerio de Ciencia e Innovación (project PID2020-117024GB-C43) and Comunidad de Madrid (project S2108–NMT4321) for financial support. HS acknowledges support by the Spanish State Research Agency (PID2020-114071RB-I00, CEX2018-000805-M), by the Comunidad de Madrid through program NANOMAGCOST-CM (Program No.S2018/NMT-4321), and by EU (COST NANOCOHYBRI CA16218). EGM thanks Ministerio de Ciencia e Innovación (project FIS2017-82415-R) and the “María de Maeztu” Programme for Units of Excellence in R&D (CEX2018-000805-M). Ames Laboratory (PCC) was supported by the U.S. Department of Energy, Office of Basic Energy Science, Division of Materials Sciences and Engineering. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358. We also thank all CASSIOPEE staff from synchrotron SOLEIL for support during ARPES beam times and Daniel Malterre, Vincent Jacques and David le Bolloc’h for helpful discussions.
References

[1] Hill H M, Chowdhury S, Simpson J R, Rigosi A F, Newell D B, Berger H, Tavazza F and Walker A R H 2019 Phonon origin and lattice evolution in charge density wave states Phys. Rev. B 99 174110

[2] Yu F H, Ma D H, Zhuo W Z, Liu S Q, Wen X K, Lei B, Ying J J and Chen X H 2021 Unusual competition of superconductivity and charge-density-wave state in a compressed topological kagome metal Nat. Commun. 12 3645

[3] Song Y, Ying T, Chen X, Han X, Wu X, Schnyder A P, Huang Y, Guo J and Chen X 2021 Competition of Superconductivity and Charge Density Wave in Selective Oxidized CsV$_3$Sb$_5$ Thin Flakes Phys. Rev. Lett. 127 237001

[4] Chang J, Blackburn E, Holmes A T, Christensen N B, Larsen J, Mesot J, Liang R, Bonn D A, Hardy W N, Watenphul A, Zimmermann M v, Forgan E M and Hayden S M 2012 Direct observation of competition between superconductivity and charge density wave order in YBa$_2$Cu$_3$O$_6.67$ Nat. Phys. 8 871–6

[5] Castro Neto A H 2001 Charge Density Wave, Superconductivity, and Anomalous Metallic Behavior in 2D Transition Metal Dichalcogenides Phys. Rev. Lett. 86 4382–5

[6] Croft T P, Lester C, Senn M S, Bombardi A and Hayden S M 2014 Charge Density Wave Fluctuations in La$_{2-x}$Sr$_x$CuO$_4$ and Their Competition with Superconductivity Phys. Rev. B 89 224513

[7] Bud’ko S L, Canfield P C, Mielke C H and Lacerda A H 1998 Anisotropic magnetic properties of light rare-earth diantimonides Phys. Rev. B 57 13624–38

[8] Hulliger F and Ott H R 1977 Superconductivity of lanthanum pnictides J. Common Met. 55 103–13

[9] Guo S, Young D P, Adams P W, Wu X S, Chan J Y, McCandless G T and DiTusa J F 2011 Dimensional crossover in the electrical and magnetic properties of the layered LaSb$_2$ superconductor under pressure: The role of phase fluctuations Phys. Rev. B 83 174520

[10] Galvis J A, Suderow H, Vieira S, Bud’ko S L and Canfield P C 2013 Scanning tunneling microscopy in the superconductor LaSb$_2$ Phys. Rev. B 87 214504

[11] Young D P, Goodrich R G, DiTusa J F, Guo S, Adams P W, Chan J Y and Hall D 2003 High magnetic field sensor using LaSb$_2$ Appl. Phys. Lett. 82 3713–5

[12] Ashcroft N W and Mermin N D 1976 Solid state physics

[13] Simon S H and Halperin B 1994 Explanation for the Resistivity Law in Quantum Hall Systems Phys. Rev. Lett. 73 3278–81

[14] Abrikosov A A 2000 Quantum linear magnetoresistance EPL Europhys. Lett. 49 789

[15] Parish M M and Littlewood P B 2003 Non-saturating magnetoresistance in heavily disordered semiconductors Nature 426 162–5

[16] Wilson J A, Di Salvo F J and Mahajan S 1975 Charge-density waves and superlattices in the metallic layered transition metal dichalcogenides Adv. Phys. 24 117–201

[17] Goodrich R G, Browne D, Kurtz R, Young D P, DiTusa J F, Adams P W and Hall D 2004 de Haas–van Alphen measurements of the electronic structure of LaSb$_2$ Phys. Rev. B 69 125114

[18] Song C, Park J, Koo J, Lee K-B, Rhee J Y, Bud’ko S L, Canfield P C, Harmon B N and Goldman A 2003 Charge-density-wave orderings in LaAgSb$_2$: An x-ray scattering study Phys. Rev. B 68 035113

[19] Torikachvili M S, Bud’ko S L, Law S A, Tillman M E, Mun E D and Canfield P C 2007 Hydrostatic pressure study of pure and doped La$_{1-x}$R$_x$AgSb$_2$(R=Ce,Nd) charge-density-wave compounds Phys. Rev. B 76 235110

[20] Shi X, Richard P, Wang K, Liu M, Matt C E, Xu N, Dhaka R S, Ristic Z, Qian T, Yang Y-F, Petrovic C, Shi M and Ding H 2016 Observation of Dirac-like band dispersion in LaAgSb$_2$ Phys. Rev. B 93 081105
[21] Ruszala P, Winiarski M J and Samsel-Czekalowicz M 2020 Dirac-Like Electronic-Band Dispersion of LaSb2 Superconductor and Its Counterpart LaAgSb2 Acta Phys. Pol. A 138

[22] Luccas R F, Fente A, Hanko J, Correa-Orellana A, Herrera E, Climent-Pascual E, Azpeitia J, Pérez-Castañeda T, Osorio M R, Salas-Colera E, Nemes N M, Mompean F J, García-Hernández M, Rodrigo J G, Ramos M A, Guillamón I, Vieira S and Suderow H 2015 Charge density wave in layered La1-xCe_xSb2 Phys. Rev. B 92 235153

[23] Acatrinei A I, Browne D, Losovyj Y B, Young D P, Moldovan M, Chan J Y, Sprunger P T and Kurtz R L 2003 Angle-resolved photoemission study and first-principles calculation of the electronic structure of LaSb2 J. Phys. Condens. Matter 15 L511

[24] Canfield P C, Thompson J D and Fisk Z 1991 Novel Ce magnetism in CeDipnictide and Di-Ce pnictide structures J. Appl. Phys. 70 5992–4

[25] Canfield P C and Fisk Z 1992 Growth of single crystals from metallic fluxes Philos. Mag. B 65 1117–23

[26] Canfield P C 2019 New materials physics Rep. Prog. Phys. 83 016501

[27] Seah M P and Dench W A 1979 Quantitative electron spectroscopy of surfaces: A standard data base for electron inelastic mean free paths in solids Surf. Interface Anal. 1 2–11

[28] Damascelli A, Hussain Z and Shen Z-X 2003 Angle-resolved photoemission studies of the cuprate superconductors Rev. Mod. Phys. 75 473–541

[29] Kohn W and Sham L J 1965 Self-consistent equations including exchange and correlation effects Phys. Rev. 140 A1133

[30] Kresse G and Furthmüller J 1996 Efficiency of ab-initio total energy calculations using a plane-wave basis set Comput. Mater. Sci. 6 15–50

[31] Kresse G and Furthmüller J 1996 Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set Phys. Rev. B 54 11169–86

[32] Wang V, Xu N, Liu J-C, Tang G and Geng W-T 2021 VASPKIT: A user-friendly interface facilitating high-throughput computing and analysis using VASP code Comput. Phys. Commun. 267 108033

[33] Perdew J P, Burke K and Ernzerhof M 1996 Generalized Gradient Approximation Made Simple Phys. Rev. Lett. 77 3865–8

[34] Pack J D and Monkhorst H J 1976 Special points for Brillouin-zone integrations Phys. Rev. B 13 5188–92

[35] Pack J D and Monkhorst H J 1977 “Special points for Brillouin-zone integrations”--a reply Phys. Rev. B 16 1748–9

[36] Arakane T, Sato T, Souma S, Takahashi T, Watanabe Y and Inada Y 2007 Electronic structure of LaAgSb2 and CeAgSb2 studied by high-resolution angle-resolved photoemission spectroscopy J. Magn. Magn. Mater. 310 396–8

[37] Peierls R E and Peierls R S 1955 Quantum theory of solids (Oxford University Press)

[38] Lee E, Kim D H, Denlinger J D, Kim J, Kim K, Min B I, Min B H, Kwon Y S and Kang J-S 2015 Angle-resolved and resonant photoemission spectroscopy study of the Fermi surface reconstruction in the charge density wave systems CeTe2 and PrTe2 Phys. Rev. B 91 125137

[39] Wu D, Liu Q M, Chen S L, Zhong G Y, Su J, Shi L Y, Tong L, Xu G, Gao P and Wang N L 2019 Layered semiconductor EuTe 4 with charge density wave order in square tellurium sheets Phys. Rev. Mater. 3 024002

[40] Cortés R, Tejeda A, Lobo J, Didiot C, Kierren B, Malterre D, Michel E G and Mascaraque A 2006 Observation of a Mott Insulating Ground State for Sn=Ge(111) at Low Temperature Phys. Rev. Lett. 96 126103

[41] Bovet M, Popović D, Clerc F, Koitzsch C, Probst U, Bucher E, Berger H, Naumović D and Aebi P 2004 Pseudogapped Fermi surfaces of 1T-TaS2 and 1T-TaSe2: A charge density wave effect Phys. Rev. B 69 125117
[42] Medeiros P V, Stafström S and Björk J 2014 Effects of extrinsic and intrinsic perturbations on the electronic structure of graphene: Retaining an effective primitive cell band structure by band unfolding Phys. Rev. B 89 041407

[43] Schäfer J, Rotenberg E, Kevan S D, Blaha P, Claessen R and Thorne R E 2001 High-Temperature Symmetry Breaking in the Electronic Band Structure of the Quasi-One-Dimensional Solid NbSe3 Phys. Rev. Lett. 87 196403

[44] Dardel B, Grioni M, Malterre D, Weibel P, Baer Y and Lévy F 1992 Temperature-dependent pseudogap and electron localization in 1T-TaS2 Phys. Rev. B 45 1462–5

[45] Zhu X, Ning W, Li L, Ling L, Zhang R, Zhang J, Wang K, Liu Y, Pi L, Ma Y, Du H, Tian M, Sun Y, Petrovic C and Zhang Y 2016 Superconductivity and Charge Density Wave in ZrTe3–xSex Sci. Rep. 6 26974

[46] Mou D, Konik R M, Tsvelik A M, Zaliznyak I and Zhou X 2014 Charge-density wave and one-dimensional electronic spectra in blue bronze: Incoherent solitons and spin-charge separation Phys. Rev. B 89 201116
Supplementary Material

Fermi surface of LaSb$_2$ and direct observation of a CDW transition

I. Palacio$^{1,*}$, J. Obando-Guevara$^{2,3}$, L. Chen$^{2,¥}$, M. N. Nair$^{1}$, M.A. González Barrio$^{3}$, E. Papalazarou$^{2}$, P. Le Fèvre$^{1}$, R.F. Luccas$^{4}$, H. Suderow$^{4}$, P. C. Canfield$^{5}$, A. Taleb-Ibrahimi$^{1}$, E.G. Michel$^{6}$, A. Mascaraque$^{3}$, A. Tejeda$^{1,2}$

$^1$ Synchrotron SOLEIL, L’Orme des Merisiers, Saint-Aubin, 91192 Gif sur Yvette, France

$^2$ Université Paris-Saclay, CNRS, Laboratoire de Physique des Solides, 91405, Orsay, France.

$^3$ Depto Física de Materiales, Universidad Complutense de Madrid, Spain

$^4$ Laboratorio de Bajas Temperaturas y Altos Campos Magnéticos, Departamento de Física de la Materia Condensada, Instituto Nicolás Cabrera and Condensed Matter Physics Center (IFIMAC), Unidad Asociada UAM-CSIC, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

$^5$ Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames Laboratory, Ames IA 50011, USA

$^6$ Depto Física de la Materia Condensada, and Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, 28049 Madrid, Spain

$\¥$ Corresponding author

* Now at Instituto de Ciencia de Materiales de Madrid, CSIC, C/ Sor Juana Inés de la Cruz 3, 28049 Madrid, Spain
Fig. S1. (a) Electronic band structure of LaSb$_2$ along $\Gamma$-Y-S-X-$\Gamma$ K directions of the primitive cell. Projected band structure on the Sb atoms of Sb-sheet (b), La atoms of La/Sb bilayer (c) and Sb atoms of La/Sb bilayer(d).
Fig. S2. The orbital-projected band structures on the s (a), px (b), py (c), pz (d) and total d (e) orbitals of the Sb atoms in Sb sheet.
Fig. S3. The orbital-projected band structures on the s (a), px (b), py (c), pz (d) and total d (e) orbitals of the Sb atoms in La/Sb bilayers.
Fig. S4. The orbital-projected band structures on the s (a), total p (b), total d (c) and total f (d) orbitals of the La atoms in La/Sb bilayers.
Fig. S5. Experimental measurement of the Fermi surface across several Brillouin zones at (a) 200 K and (c) 13 K. Yellow arrows indicate where the Momentum Distribution Curves in (b) and (d) are taken. As an eye guide, the set of green dots in (b) indicates the intensity maxima at 200 K. These are shown in panel (d) alongside the replicated set that appears at 13 K (magenta dots). Both are separated by a distance $q = 0.25 \pm 0.02$ Å⁻¹.
Fig. S6. Experimental band structure along the GY direction above and below the CDW phase transition temperature. Panels (a) and (b) depict the bands crossing the Fermi level that give rise to the “glasses-like” pockets. To facilitate the identification of the replica, the calculated bands are shown in the insets.
Figure S7. Structural modifications and the corresponding band structures. (a) displacement of the Sb atoms in Sb sheets by 0.03 Å along a’ direction to introduce transverse-wave-like modification in the Sb sheet; (c)(e) displacement of the Sb atoms inside the right-side conventional cell along -b’ direction 0.02Å(c) and 0.04Å (e); (g)(i) displacement of the whole middle conventional cell by 0.02Å along the a’ direction (g) and c’ direction(i). The unfolded band structures correspond to the modified supercells in (b), (d), (f), (h) and (j), respectively.
Fig. S8. Zooms of the curvature plot of the ARPES intensity along $\bar{\Gamma}$-$\bar{Y}$ taken from the second Brillouin zone of Fig. 2.