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ABSTRACT

$LaSb_2$ has a layered crystal structure along the *c*-axis with ~2% difference between the in-plane orthorombic *a* and *b* axes. Here, we report on the thermal conductivity, electrical resistivity, and Seebeck coefficient from 10 to 300 K as well as the magnetoresistance at 10 K. Using the van der Pauw technique on single crystal samples, the in-plane electrical resistivity tensor has been measured and it is found to be isotropic. An anisotropic crystal structure may have isotropic properties, but in the present case, the isotropic nature stems from crystal imperfection. Single crystal X-ray diffraction provides evidence of a mixing of the in-plane *a*- and *b*-directions leading to observed diffraction intensity where systematic absences are expected. Whether the underlying structural mechanism is twinning or stacking faults is unknown, but it could be the origin of the previously observed charge density wave states, and it may also explain the high unsaturating linear magnetoresistance reported here. At ambient conditions, $LaSb_2$ is found to be stable in air, with no sign of bulk degradation after 5 years of storage; however, some change is observed in the amorphous background scattering.

I. INTRODUCTION

Lanthanum diantimonide adopts the layered orthorhombic $SmSb_2$ structure,[1,2] which can be seen in Fig. 1. The structure consists of pseudo-tetragonal layers stacked along the *c*-direction with each subsequent layer being shifted with respect to the previous by a displacement along the *b* direction. Crystals of $LaSb_2$ generally terminate on these pseudo-tetragonal layers,[3] though termination on pure Sb surfaces found in the middle of these layers has also been observed.[4]

The superconductivity and high linear magnetoresistance of $LaSb_2$ has inspired many studies.[3–11] The superconducting phase was originally reported to have a critical temperature of 0.4 K.[5] Later reports showed that the superconducting transition is broad and with an onset temperature up to 2.5 K in the *a*,*b*-plane and 1.0 K along the *c*-axis and achieving full superconductivity between 0.4 and 0.7 K.[4,9,10] The critical field is observed to be higher in-plane than out-of-plane. Applying a pressure results in a narrowing of the superconducting transition to near step-like with a critical temperature in and out-of-plane of 1.7 K, showing that pressure stabilizes the superconducting state and changes it from 2D to 3D behavior.[9,10]

$LaSb_2$ has been suggested as a high magnetic field sensor due to the high linear magnetoresistance, which shows no signs of saturation even at 45 T.[7] The linear magnetoresistance of materials with similar structures has been attributed to the presence of a charge density wave (CDW). Transition metal dichalcogenides with the 2H structure (TaS_2, $TaSe_2$, $NbSe_2$) exhibit nearly linear magnetoresistance as a result of CDWs in the materials.[12–18] $LaAgSb_2$ is another example that has a CDW state and a large magnetoresistance that shows no signs of saturation at 18 T.[19–22] This has led many to search for the presence of a CDW in $LaSb_2$, and despite not observing direct evidence of a CDW, many still cite it as a likely explanation for the linear magnetoresistance.[3,4,7–9] Evidence of a CDW transition was eventually observed in a solid solution with Ce and correlated to a kink in the resistivity that changes with Ce concentration, where the kink for pure $LaSb_2$ is at 355 K.[11] The authors hypothesized that the observed CDW arose due to stacking faults present in all their samples independent of Ce concentration.

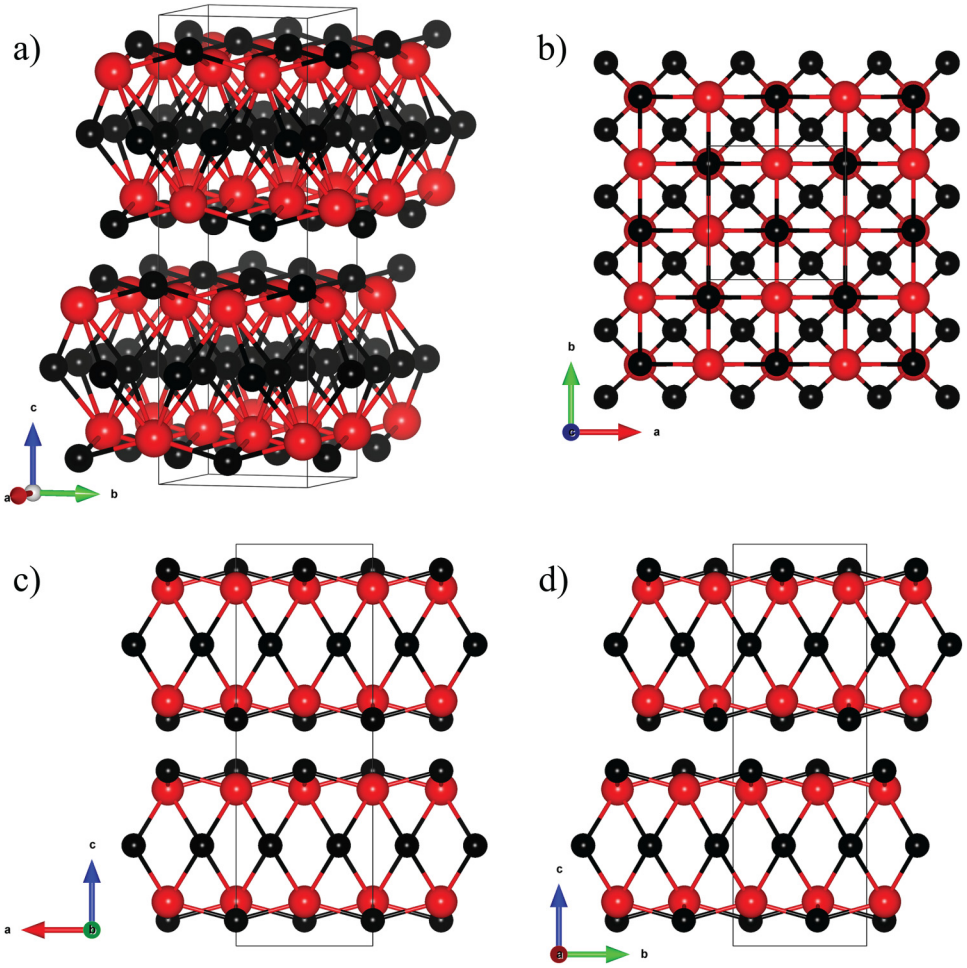

FIG. 1. The layered crystal structure of $LaSb_2$ with Sb in black and La in red. The layers are each approximately tetragonal, as shown in (b), while the stacking of the layers is different in the *a* and *b* directions, as shown in (c) and (d) (illustrated using VESTA[50]).

Thermoelectric materials often have relatively large and complex crystal structures such as skutterudties[23] or clathrates,[24,25] but simple metal pnictogenides or chalcogenides also exhibit excellent thermoelectric properties with prominent examples being $FeSb_2$,[26,27] Zn_4Sb_3,[28] Mg_3Sb_2,[29] GeTe,[30] and PbTe.[31–33] Very strong interest has concerned layered metal-chalcogenides such as Bi_2Te_3,[34] SnSe,[35,36] and Cu_2Se.[37] However, the metallic behavior of $LaSb_2$ means that it is not of immediate interest as a thermoelectric material.

Because $LaSb_2$ adopts an orthorhombic structure, in-plane anisotropy of the transport properties may be present. In general, anisotropic crystal structures potentially can have isotropic properties, but the reverse is not possible. We have recently developed the van der Pauw method to measure anisotropic resistivity tensors,[38–40] and since $LaSb_2$ only has 2% in-plane anisotropy in the crystal structure, it represents a challenging material for testing the method. As detailed below, the in-plane resistivity was found to be isotropic in magnetic fields between 0 and 9 T at 10 K and in the temperature range from 10 to 300 K. The lack of anisotropy in the resistivity in such a large field and temperature range indicates a deviation from a perfect single crystal with possible structural mixing of the *a*- and *b*-directions. This explanation is supported by single crystal X-ray diffraction data, which show that the crystal structure is closely related to a tetragonal structure[1,41,42] with missing intensity extinctions arising from a 90° rotation of the layers.

II. EXPERIMENTAL

Single crystals of $LaSb_2$ were grown using the self-flux method.[43,44] Prior to synthesis, the lanthanum (Koch-Light

Laboratories Ltd., ≥99.7%) was handled in a glovebox where it was polished and further purified using an arc melter (Edmund Bühler GmbH, MAM-1 Glovebox Version). Antimony (ChemPUR, 99.9999% metal basis) and purified lanthanum were mixed in a 9:1 molar ratio in an alumina crucible, which was sealed in a fused silica ampoule with a static vacuum of less than 10^{-4} mbar. Synthesis was carried out in a tube furnace with the ampoule encased in alumina sand to stabilize potential temperature fluctuations. The ampoule was heated to 1173 K at 150 K/h with a 6 h dwell and then cooled to 913 K at 1 K/h where the furnace was switched off. During cooling but after the flux has solidified, the alumina crucible broke. Flux and crystals were separated using centrifugation. The resulting crystals are layered with an easy cleavage plane and metallic luster after cleaving, and they were confirmed to be $LaSb_2$ by Powder X-ray Diffraction (PXRD) on powder obtained from a ground piece.

Powder of $LaSb_2$ was also prepared to evaluate the air sensitivity of the compound and a stoichiometric mixture of lanthanum and antimony sealed in a fused silica tube with a static vacuum of less than 10^{-4} mbar. This ampoule was then heated up to 1273 K at 100 K/h and held at that temperature for 125 h after which the furnace was turned off. The resulting matte gray polycrystalline lump was ground into a black powder with mortar and pestle and confirmed to be $LaSb_2$ with PXRD.

The PXRD data were collected on a Rigaku SmartLab diffractometer using Bragg-Brentano optics geometry and monochromatic $CuK_{\alpha 1}$ radiation. Evaluation of single crystallinity was done using a Bruker X8 Apex II with a monochromatic micro source $I\mu S_{Ag}$ $AgK_{\alpha 1}$ and a 2D APEXII detector. Additionally, single crystal X-ray diffraction experiments were performed at the ChemMatCARS beamline at the Advanced Photon Source (APS), USA, on several crystal specimens in an attempt to ascertain whether the mixing of the *a*- and *b*-directions is due to twinning or stacking faults.

Physical properties in the *a*, *b*-plane were measured using a Physical Property Measurement System (PPMS) quantum design. The Seebeck coefficient, thermal conductivity, and electrical resistivity were measured using the Thermal Transport Option (TTO), while the magnetoresistance and electrical resistivity were measured using the Alternating Current Transport (ACT) in van der Pauw (vdP)[38,39] configuration (described in application note 1076-304). In order to measure the resistivity in vdP geometry, the gold wires had to be connected as a line contact along the full thickness of the sample due to the comparatively high through plane resistivity.[6,45] Samples for ACT-vdP measurements were parallelepipeds around 3 × 3 × 0.15 mm. The sample for TTO was a bar measuring 12.6 × 1.8 × 0.5 mm with a lead separation of 4.9 mm. All geometries were averaged from a minimum of ten measurements and the standard deviation was used as the uncertainty. This uncertainty in geometry translates to an error of around 5% on the transport properties measured with the four-point bar method, which is also the expected error using this method.[46–49]

III. RESULTS

A. Stability

Early reports on $LaSb_2$ noted it to be very stable under ambient conditions in air;[1] however, a later report noted it to be highly air-sensitive stressing the importance of cleaving crystals in vacuum.[3] Therefore, a study of the air-sensitivity of $LaSb_2$ was performed, and PXRD data are shown in Fig. 2. No major sample degradation or reactions in air were observed in a 5 year (rounded up from 4 years and 10 months) period; however, a minor change in the amorphous background scattering has occurred. The micaceous nature of $LaSb_2$ results in a high degree of preferential orientation, which can be seen by comparing the expected and observed relative PXRD reflection intensities. The change in the amorphous background was only observed after long-term storage, showing that the change is slow despite all handling, storage, and grinding to a fine powder was done in air. Whether it is caused by adsorption, surface reconstruction or reactions is unknown. The observed stability and slow change in amorphous contribution is in agreement with later reports, where no surface contamination was observed despite cleaving the crystals in air to allow for the removal of leftover loose flakes from the cleaving process.[4,11] These loose flakes could also be the reason for an earlier study not observing any diffraction spots in their Low Energy Electron Diffraction experiments.[3] The fact that $LaSb_2$ is stable enough to be handled and cleaved in air could be useful for obtaining very thin samples; however, the strong interaction between the layers, which is evident from termination having been observed at the pure

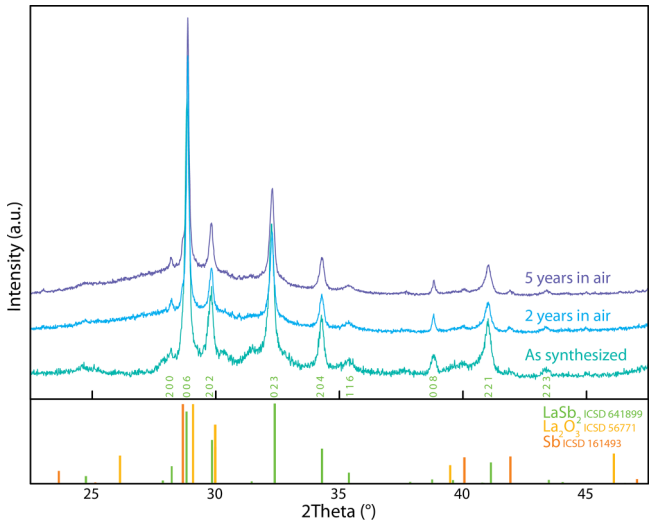

FIG. 2. Powder X-ray diffractogram of $LaSb_2$ after synthesis in turquoise, after 2 years in blue, and after 5 years in purple. Below are the expected peak positions and intensities for relevant phases obtained from ICSD, $LaSb_2$ in green, La_2O_3 in yellow, and Sb in orange. Additionally, Miller indices of selected reflections of $LaSb_2$ are written in green.

antimony layer,[3] does make exfoliation difficult. Additionally, the strong interaction also suggests that bonds are being broken in the process, which may make the material unstable when it becomes too thin.

B. Transport properties

The single crystal pieces resulting from the flux varied in size with the largest being around 10 × 10 × 1 mm, all with high metallic luster and well-defined terraces and edges. The crystals used for measurements are of high quality in the *a*, *b*-plane with large Residual Resistivity Ratios (RRRs) of 50-53 $\left(\frac{\rho(300\,\mathrm{K})}{\rho(10\,\mathrm{K})}\right)$, which are comparable to earlier reports of between 45 and 68 when corrected for different minimum temperatures. The actual reported RRR values were between 60 and 90 with minimum temperatures of 2 or 4 K.[4,6,7,10] These RRRs are calculated from the ACT-vdP measurements and the TTO measurement, with the TTO data shown in Fig. 3. Further evidence of high crystal quality in the *a*, *b*-plane is also seen in the thermal conductivity in Fig. 3(c), where the crystalline peak is at a comparatively high temperature, indicating that the phonons, just like the electrons, have a long mean-free path.[9,10] A long phonon mean-free path indicates a low concentration of scattering sites (defects, impurities, etc.) within the $LaSb_2$ layers. The thermal conductivity above 180 K has been grayed out, as the radiative heat loss becomes significant, and this leads to a measured thermal conductivity that is too high.[46] However, extrapolating with a T^{-1} dependence yields a room temperature thermal conductivity of 13-14 W/m K, which is comparable to other metals with heavy elements.

As expected for a metallic compound, the Seebeck coefficient is low, negative, and increasing linearly with temperature, with the exception of a small local peak and minimum at 70 K and 110 K, respectively. The measured Seebeck coefficients below 25 K are not shown as the high thermal conductivity and low Seebeck coefficient resulted in a diminishing signal to noise ratio with a random scatter between 0 and −1 μV/K. The only reported Seebeck coefficient for $LaSb_2$ is for a polycrystalline pressed pellet where it was found to be +2 μV/K and virtually constant between 115 and 300 K.[42] However, this difference may be attributed to the influence of the *c*-axis and grain boundary effects.

The in-plane resistivity reported here is slightly lower than what is reported in the literature, where the room temperature value was found to be ~140 $\mu\Omega$ cm.[6] This could be random variation in samples or a difference in the measurement technique. However, based on the illustration of the setup in Ref. 6, contact was only made on the top of the crystal, whereas our samples were specifically mounted such that electrical contact was achieved along the full thickness of the sample to account for the high through plane resistivity.

The magnetoresistance shown in Fig. 4 was measured at 10 K using the ACT-vdP setup, where the magnetoresistivity measured with positive and negative field is overlaid one another. The magnetoresistivity increases slowly with the field up to around 2 T where it starts increasing linearly. The zero field resistivity value is 1.5(3) $\mu\Omega$ cm and reaches 16(1) $\mu\Omega$ cm at 9 T. This is slightly higher than the reported values at 10 K,[9] but when calculating the relative magnetoresistance ratio $\frac{[\rho(H)-\rho(0)]}{\rho(0)}$, the values are nearly identical, suggesting that the discrepancy in absolute values is likely caused by errors in sample geometry.[31] Others report a relative magnetoresistance ratio around 12 to 14 at 9 T and 2 K;[6,7] the higher values are to be expected due to the lower temperature.

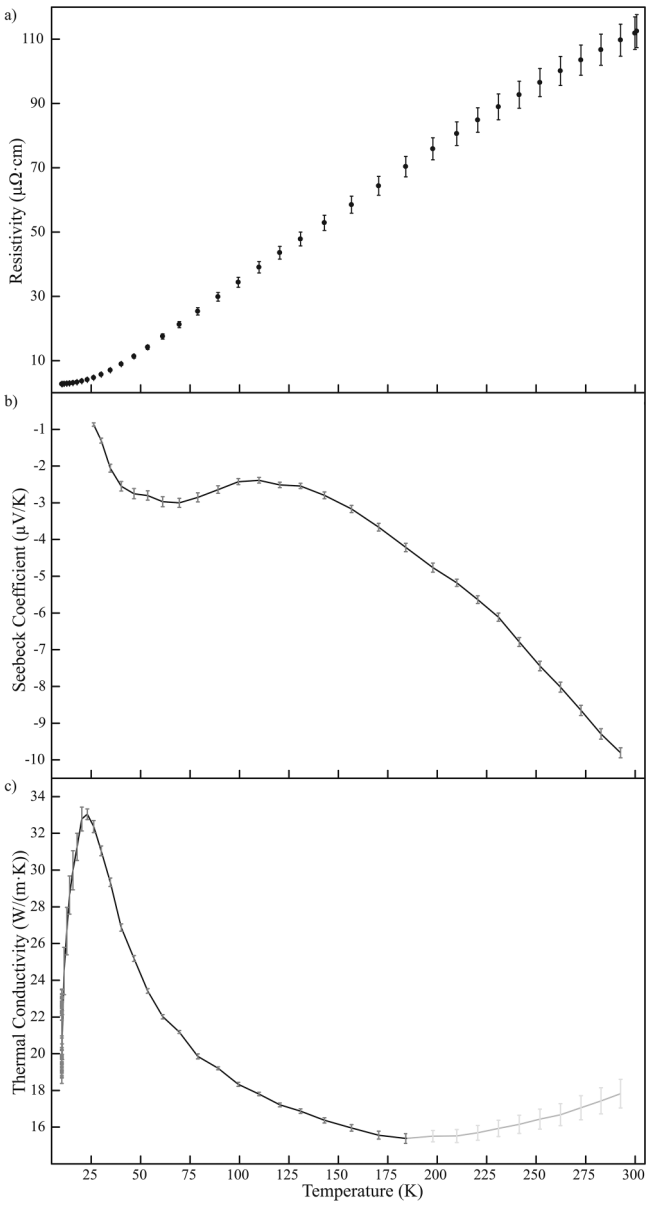

FIG. 3. (a) Electrical resistivity, (b) Seebeck coefficient, and (c) thermal conductivity against temperature.

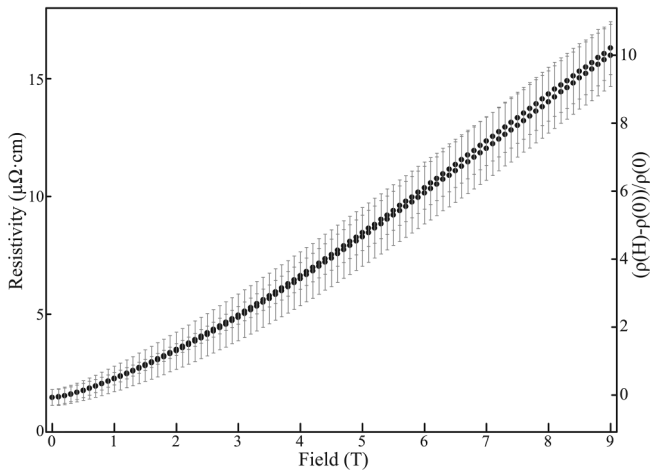

FIG. 4. Magnetoresistance measured at 10 K with positive and negative field overlaid on top of each other, where the measured resistivity is on the left y-axis and the relative on the right y-axis.

Because $LaSb_2$ adopts an orthorhombic crystal structure, one would expect there to be some anisotropy in the electrical transport within the layers as well as out of the layer; however, to our knowledge, no studies have considered the in-plane anisotropy. Using the vdP method on single crystals allows for determination of the in-plane resistivity tensor,[40] but all measurements showed that the in-plane resistivity is isotropic from 0 to 9 T at 10 K and from 10 K to 300 K at 0 T. While one would expect very comparable values along the *a*- and *b*-directions based on the structure, an undetectable anisotropy in such a large temperature and field range is unlikely. As the layers of the crystal are almost tetragonal themselves, it may be expected that stacking faults or twinning could occur where some layers or parts of the crystal are rotated 90° relative to each other, i.e., formation of either stacking faults or crystal twinning.[1,42,43] This could result in an isotropic behavior if there is a mixing of the *a*- and *b*-directions by a 90° rotation between some layers. The observed isotropy strongly suggests such mechanism to be at play. Furthermore, previous reports have also reported low crystal quality in the *c*-direction[6] and weak interlayer interaction,[3,4,9–11] suggesting that this is a common feature of $LaSb_2$ crystals, especially when considering the good agreement between reported properties and RRRs. Another manifestation of the weak interaction between layers is that the irregularities between layers, be it twinning or stacking faults, has little to no influence on the in-plane crystallinity, which is evident from the high RRRs and long mean free path of the phonons and electrons.

C. Crystal structure

Refinement of the powder X-ray diffraction data on $LaSb_2$ gives room temperature unit cell dimensions of $a = 6.3165(5)$ Å, $b = 6.1965(5)$ Å, and $c = 18.495(3)$ Å. Crystal

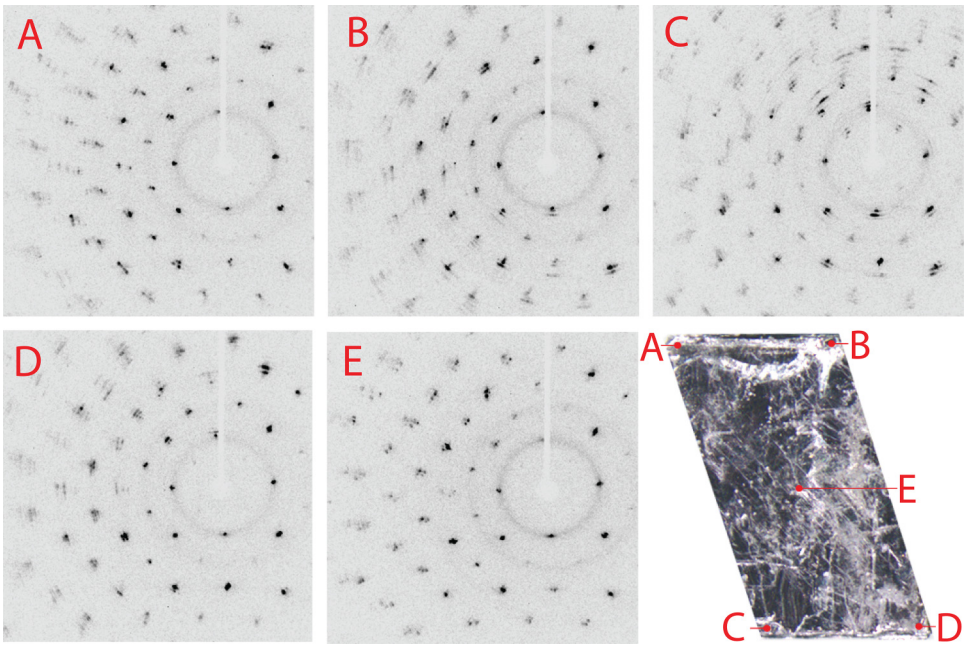

FIG. 5. Single crystal diffraction frames from five locations on the crystal, as indicated with corresponding letters on the picture of the crystal in the bottom right.

quality and homogeneity were evaluated by single crystal X-ray diffraction on a crystal used for ACT-vdP measurements, where frames were collected at different locations on the crystal and compared as seen in Fig. 5. The frames from tested areas look very similar and the crystal is concluded to be homogeneous. The C-frame looks slightly different than the rest and was recorded on the very edge of the crystal in a corner that had a visual indication of potential damage from cutting; however, the difference is slight and should not affect any property measurements of the bulk crystal.

As expected from the earlier literature, the diffraction spots are slightly elongated and split.[1] Evidence of the mixing of the *a*- and *b*-directions can be seen by looking for the systematic absences expected for the Cmca space group. The C centering results in the selection rule that $h+k$ has to be even for all *hkl* reflections, while the *c*-glide plane along the *b* axis gives the selection rule that *l* has to be even for all *h*0*l* reflections.[51] Looking at Fig. 6, one can clearly see that the selection rule from the C centering is obeyed in both the *hk*0 and the *hk*1 planes, where the reflections for which *h* and *k* are both odd are weak. However, the selection rule from the *c*-glide plane is not observed when looking at the *hk*1 plane, where there should be a row of absences along *h*01. Additionally, there is no clear difference between the *h*01 and 0*k*1 reflections, which show the presence of an occasional 90° rotation between layers of the crystals.

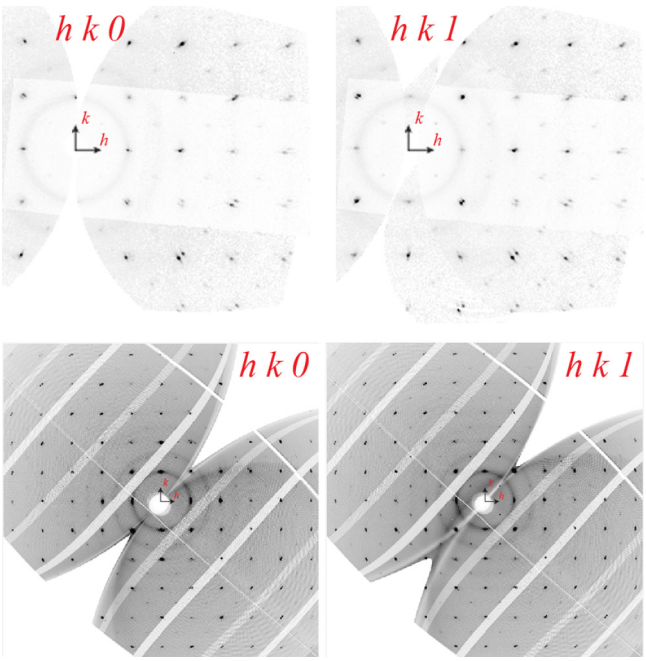

FIG. 6. Unwarped diffraction images of the *hk*0 (left) and the *hk*1 (right) planes recorded on inhouse APEX-II (top) and APS (bottom). *h* and *k* are the horizontal and vertical axes, respectively.

Unfortunately, the micaceous nature of the crystals makes it prohibitively hard to find a crystal of suitable quality and thickness to get sufficient diffraction data quality along *l* to elucidate whether it is stacking faults or twinning. This mixing of the *a*- and *b*-directions on a structural level is in good agreement with what was expected from the observed in-plane isotropy in the resistivity. The good agreement between the measured properties in this and other studies suggests that the crystals in all the studies are very similar; therefore, all the crystals likely exhibit this mixing of the in-plane directions with the same underlying mechanism.

It has previously been noted that the structure of $LaSb_2$ is related to a tetragonal structure,[1,41,42] with the difference, besides unit cell lengths, being a longer shift along the *b*-axis such that the layers line up in the *a*, *c*-plane just like they line up in the *b*, *c*-plane (see Fig. 1). Due to the small difference between the *a*- and *b*-directions and the relation to the tetragonal structure, one could, ignoring the difference in unit cell lengths, equivalently have described this 90° rotation, as a random shift along either of the unit cell axes.

IV. CONCLUDING REMARKS

Ever since the unsaturating linear magnetoresistance of $LaSb_2$ was observed,[6] many attempts have been made at explaining its origin. The presence of CDW states is commonly cited as a likely explanation, but direct evidence for the presence of CDW states has been elusive.[3,4,8,9] Recently, evidence of a CDW transition was observed and hypothesized to arise from stacking faults.[11] In the present study, we have observed an isotropic resistivity in the layers of an orthorhombic crystal. While this is physically possible, then it is unlikely considering the range of temperature and magnetic fields used here. Based on single crystal X-ray diffraction measurements, we demonstrate that the isotropic behavior arises from a structural mixing of the *a*- and *b*-directions. Whether the underlying mechanism is the presence of twinning or stacking faults in $LaSb_2$ could not be resolved due to the micaceous nature of the crystals making crystals of sufficient size elusive. All measured properties are in agreement with the literature demonstrating that this structural mixing of the *a*- and *b*-directions is likely to be omnipresent in $LaSb_2$ crystals grown by the flux method. Applying pressure to the crystal structure may deform the layers and increase the interlayer interactions, possibly causing a shift toward a more tetragonal structure with increased long-range order. This would explain the observed sharpening of the transition to the superconducting phase. The specific nature of the interlayer interactions in $LaSb_2$ is at the heart of the exciting properties, and it would be of interest to pursue further pressure studies of this material. If the irregularities along the *c*-direction are the origin of the CDW, then the linear magnetoresistance should have a dependence on pressure, and in combination with a pressure study of the crystal structure, this could provide important further insight into the transport properties.

Contrary to what one might expect from a lanthanide-containing compound, no indications of bulk air-sensitivity are observed, even over a period of several years. Some change in the amorphous background scattering was observed after prolonged storage, but probably, air contamination should only be a concern for surface studies that are highly sensitive to contaminants.

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