Direct Imaging and Electronic Structure Modulation of Double Moiré Superlattices at the 2D/3D Interface

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The atomic structure at the interface between a two-dimensional (2D) and a three-dimensional (3D) material influences properties such as contact resistance, photo-response, and high-frequency performance1–3. Moiré engineering has yet to be explored for tailoring this 2D/3D interface, despite its success in enabling correlated physics at 2D/2D twisted van der Waals interfaces4–9. Using epitaxially aligned MoS2/Au{111} as a model system, we apply a geometric convolution technique10 and four-dimensional scanning transmission electron microscopy (4D STEM) to show that the 3D nature of the Au structure generates two coexisting moiré periods (18 Å and 32 Å) at the 2D/3D interface that are otherwise hidden in conventional electron microscopy imaging. We show, via ab initio electronic structure calculations, that charge density is modulated with the longer of these moiré periods, illustrating the potential for (opto-)electronic modulation via moiré engineering at the 2D/3D interface.
Following the success of moiré engineering in modulating (opto-)electronic properties of graphene/hexagonal boron nitride (hBN) heterostructures, studies have extended the moiré toolbox to include systems such as double bilayer graphene, trilayer graphene, and van der Waals (vdW) heterostructures composed of transition metal dichalcogenides (TMDCs) and hBN-graphene-hBN stacks. Recently, moiré engineering has been extended beyond vdW heterostructures, to 3D/3D oxides. Here, we report moiré engineering at the quasi-vdW interface between a 2D material and 3D metal. Engineering such 2D/3D interfaces is key to device applications where 2D materials make contact, through a well-controlled junction, to a 3D material such as a metal or semiconductor. We chose MoS$_2$/Au{111} as a model 2D/3D system, relevant to TMDC (opto-)electronics. In contrast to 2D/2D heterostructures, moiré engineering at the 2D/3D interface requires detailed models of the stacking of atomic planes in the out-of-plane direction.

The ability to image moiré superlattices directly is required to map electronic property modulation onto atomically-resolved structure. Various techniques have been used to observe moiré superlattices. These include reciprocal space imaging via low energy electron diffraction (LEED) and convergent beam electron diffraction (CBED); spatially resolved property measurement via scanning transmission microscopy (STM), atomic force microscopy (AFM) modalities, near-field optical microscopy, and infrared nanoimaging; and direct imaging of transmitted intensity via high-resolution and dark field (S)TEM. While many techniques have enabled detailed analysis of 2D/2D vdW systems, unsolved issues in the direct imaging of 2D/3D moirés, such as discrepancies in periodicity measurement between imaging techniques, have made bridging the gap between atomic structure and mesoscale properties for 2D/3D systems challenging. The MoS$_2$/Au{111} system highlights these challenges, since superlattices observed via STM and TEM exhibit different periodicities, 32 Å and 18 Å respectively.

To reconcile such discrepancies and map moiré structure-property relations at the 2D/3D interface, we combine an analytic convolution technique and a versatile imaging method based on 4D STEM to decouple the spectrum of higher order moiré patterns. *Ab initio* electronic structure calculations show that MoS$_2$/Au{111} charge density modulation follows a longer periodicity than seen in conventional TEM, a result that can be understood by considering the ABC stacking of the 3D metal in the out-of-plane direction. 3D stacking in fact introduces an additional tuning parameter in 2D/3D systems for modulating moiré properties that is not available in 2D/2D heterostructures. Together these findings highlight the utility of direct imaging via 4D STEM for elucidating the effects of 3D structure on electronic moiré engineering.

An example of the MoS$_2$/Au{111} interface is shown in Figure 1. In contrast to the mechanical transfer processes employed for fabricating vdW heterostructures, the 2D/3D systems studied here were formed by direct epitaxial growth in ultra-high vacuum conditions (Methods). The resulting samples consist of flat, faceted Au{111} nanoislands (Figure 1a, S1) that are epitaxially aligned on suspended MoS$_2${0001}, with uniform moiré periodicities.
across micrometre-scale areas (Figure 1b, S2). Selected-area electron diffraction (SAED) confirms 0° rotation between Au and MoS₂ with a standard deviation of 0.2° (Figure S3). In Figure 1b and other SAEDs, we observe spots indexed as \( \frac{1}{3}\{422\} \) Au reflections. These are classically forbidden for the FCC structure but their presence is consistent with Au nanoisland literature\(^{27}\) (Section S1).

High resolution (HR)-TEM shows that the islands are single crystalline, with no evidence of misfit dislocations and low angle grain boundaries (Figure 1c). The discontinuity in the moiré pattern visible at some boundaries arises from island coalescence, and suggests a rigid body displacement between coalesced islands (Figure 1d). The uniform moiré periodicity and sinusoidal intensity modulation show that the Au and MoS₂ lattices are undistorted even near the island edge, with an absence of lattice distortion in the plane of the interface. This is different from the case of twisted vdW structures, which frequently display reconstructions\(^{24,25}\). The absence of distortion can likely be attributed to weak quasi-vdW bonding at the MoS₂/Au\{111\} interface\(^1\). This is supported by motion of islands at room temperature, illustrating loose binding of the Au nanoislands to the underlying substrate (Movie S1). During their motion, the islands exhibit rotation up to 0.3°, visually amplified in the angle of the moiré pattern (Figure 1d, Figure S3). These MoS₂/Au\{111\} interface structures are consistent for a range of Au thicknesses, and are uniform across samples (Figure S4).
Fig. 1 HR-TEM and (S)TEM provide an atomic model for the epitaxial MoS$_2$/Au{111} moiré. 

a, Schematic of epitaxially aligned Au deposited on suspended MoS$_2$ on a TEM grid. 
b, Reciprocal space model and experimental selected area electron diffraction pattern of the Au {111} zone aligned on MoS$_2$ {0001}, with $1/3\{422\}$Au spots (see text) aligned with {1010}MoS$_2$. 
c, HR-TEM image of Au nanoisland on MoS$_2$, showing 18 Å-period moiré pattern. Scale bar, 20 Å. 
d, Larger area STEM image recorded using integrated differential phase contrast (iDPC) mode. Scale bar, 100 Å. A coalescence boundary is marked by a red arrow, as evidenced by a translation in the moiré pattern without a change in periodicity. Blue arrows show two islands where the moiré patterns are rotated 5° with respect to each other, corresponding to a 0.3° rotation of the Au lattice with respect to the MoS$_2$ lattice. This is the maximum angle observed (average 0°, standard deviation 0.2°). 
e, Side view of MoS$_2$/Au{111} showing ABC Au stacking. 
f, Plan view projection showing 18 Å moiré unit cell.
The period of the MoS$_2$/Au{111} moiré superlattice imaged by HR-TEM in Figure 1c,d is 18 Å. This can be explained using an atomic model in which the out-of-plane coordinate of the 3D structure is ignored. The resulting Au “projected lattice” is hexagonal with an atomic spacing of 1.66 Å (Figure 1e,f). However, a more accurate view of electron scattering through the Au crystal requires us to include the full face centred cubic (FCC) structure. Using a reciprocal space convolution theorem, we consider the full set of spatial frequencies of the Au{111} FCC crystal, and predict the entire spectrum of possible moiré periodicities in MoS$_2$/Au{111} (Methods). The geometric interpretation of the convolution theorem indicates that periodicities arise from the pairwise vectors connecting all spatial frequencies of the MoS$_2$ and Au lattices$^{10}$ (Figure 2a). In Figure S5 and Table S1, we calculate these periodicities and intensities as a function of rotation angle between the two crystals. The four largest periodicities are shown in Figure 2b. Additional higher order moirés are also predicted which often exhibit smaller periodicities and weaker intensities (Figure S5). However, at zero rotation, alongside the previously observed 18 Å moiré, a coexisting moiré is predicted with a larger 32 Å period (Figure 2b). We confirm this assignment of moiré periods by showing the experimental fast fourier transform (FFT) of Figure 1c (Methods, Figure 2c). The two coexisting moiré superlattice periods emerge as two sets of satellite peaks around the central spot. The simulated FFT pattern in Figure 2d is in quantitative agreement with the FFT of the acquired image, predicting coexisting 18 Å and 32 Å moiré periodicities at the 2D/3D interface.
Fig. 2  Geometric convolution technique to predict moiré spectrum. a, Schematic representation of satellite spot generation. Spatial frequencies due to a single lattice shown in the top left panel (orange) are overlaid on those arising from a second lattice on the top right (cyan). The convolution of these two sets of spatial frequencies (i,ii) can be understood as the pairwise vectors connecting spatial frequencies of the two lattices (iii,iv,v - bottom, left). These convolutions generate moiré frequencies (iii, iv, v) shown as black dots in the bottom right panel. b, Calculated moiré period vs rotation angle for the four largest moiré supercells in the MoS₂/Au{111} system, illustrated for small (± 1 %) Au lattice strain. Black dotted lines represent the experimentally observed moiré periods from the FFT, two of which (18 Å and 32 Å) are predicted at 0° relative rotation angle. The moirés are colour coded according to the reflections they arise from, with blue arising from the \{2\bar{1}10\}₉MoS₂ : \{220\} Au, green \{10\bar{1}0\}₉MoS₂ : 1/3 \{422\} Au, orange \{6\bar{3}30\}₉MoS₂ : \{642\} Au, and grey \{20\bar{2}0\}₉MoS₂ : \{220\} Au reflections respectively. The inset shows the variation of moiré angle with relative rotation angle near 0°. c, FFT of atomic resolution HR-TEM image of the MoS₂/Au{111} image in Figure 1c showing 1/3 \{422\} reflection and two visible moiré periodicities around central spot. Scale bar, 0.5 Å⁻¹. d, Simulated FFT for Au/MoS₂ generated via the geometric convolution technique with each spot coloured to show its origin. Area of spots is proportional to absolute intensity, but with inner moiré spots magnified 2x for clarity. Scale bar, 0.5 Å⁻¹.
This apparent double moiré at the 2D/3D interface can be explained via simple atomic models. The 18 Å moiré is observed when differences between the A, B, and C layers in the out-of-plane direction are ignored (Figure 3a,c). In contrast, the 32 Å moiré is generated by treating the relative shifts of the A, B, and C layers of Au in the out-of-plane direction as distinct sites (Figure 3b,d). Consider a location where an Au atom from the A layer (orange) is directly above a pair of S atoms, as in the centre of Figure 3g-top. This site repeats every 32 Å, shown by the orange squares in Figure 3d. Sites that appear similar (red and blue squares in Figure 3d) instead have Au atoms from the B or C layers above the S atoms (Figure 3g-middle, g-bottom). The inequivalence of the three sites can be further illustrated via radial distribution functions, which show the quantitative difference in atomic location (Figure 3h). TEM multislice calculations for one Au unit cell on MoS$_2$ do not show differences between these sites, and hence the 18 Å cell is observed (Figure 3a,c,e, Methods). However, by varying the numbers of A, B, and C layers in the sample, the sites show inequivalent intensities and the 32 Å periodicity becomes visible (Figure 3b,d,f). The geometry is consistent with a 11$_{Au}$ x 10$_{MoS_2}$ unstrained superstructure. This 32 Å moiré periodicity is obscured in conventional HR-TEM images by the 230% higher intensity reflections of the 18 Å moiré (Table S1).

![Fig. 3 Atomic model and radial distribution functions (RDFs) of 18 Å and 32 Å moirés.](image)

- **a**: Atomic model [100] zone axis for the 18 Å and **b**, 32 Å moiré. Note the Au atoms have been coloured differently to highlight relative stacking of A, B, and C sites.  
- **c**: Plan view atomic model for the 18 Å and **d**, 32 Å moiré. Boxed areas represent three different sites in the 32 Å moiré, which are equivalent in the 18 Å pattern.  
- **e,f**: Simulated multislice TEM image with 3 and 4 monolayers of Au respectively, showing 18 Å and 32 Å moiré patterns. Scale bars 20 Å.  
- **g**: Close up plan-view image of each of the sites highlighted in **d**, with clear distinction between the three inequivalent sites in the 32 Å moiré.  
- **h**: Corresponding radial
distribution functions (RDFs) of the three inequivalent sites in the 32 Å moiré, where colours represent the different atomic Au planes.

To extract a real space image of this hidden 32 Å moiré, we employ 4D STEM, which generates a 2D CBED pattern at each pixel position (Figure 4a)\(^28\). Subsequently we can select, with a “virtual annular dark field (ADF) detector”, an annular area of each diffraction pattern to reconstruct an image using certain diffraction spots only. Using an annulus that includes the Au\{220\} spots and the MoS\(_2\)\{2\overline{1}10\} spots (Figure 4b, Methods), we observe the hexagonal 18 Å moiré pattern (Figure 4d). The moiré shows uniform periodicity and sinusoidal intensity modulation across the islands. The symmetry is reduced to periodic line patterns in some areas due to sample tilt, but 18 Å periodicity appears across all islands. If instead we generate a second virtual ADF image using the weaker \(1/3\{422\}\) Au and \{10\overline{1}0\} MoS\(_2\) reflections (Figure 4c), we observe a hexagonal pattern of spots with 32 Å moiré periodicity, consistent with our prediction from geometric convolution (Figure 4e).

**Fig. 4 4D STEM imaging of 18 Å and 32 Å moiré periodicities.** a, Convergent beam electron diffraction (CBED) pattern formed by averaging patterns collected over the entire scan area, b, 4D STEM annulus used to isolate 18 Å moiré periodicity (angular range 31-43 mrad) and c, 4D STEM annulus used to isolate 32 Å periodicity (angular range 11-24 mrad). d,e Virtual ADF STEM images revealing 18 and 32 Å period moirés, respectively. Scale bar, 200 Å. Insets show unit cells.

To explore the impact of these coexisting moiré periodicities on ground state charge density of our 2D/3D structure, we next turn to *ab initio* electronic structure calculations (Methods). Figure 5a shows a calculated isosurface of ground-state charge density difference for MoS\(_2\)/Au\{111\} in side-view. The charge density difference is concentrated at the interface, specifically on the upper S layer of atoms, with some penetration to the underlying Mo layer. On the Au side, the charge density difference is concentrated on the first atomic plane, with negligible charge density found in the second Au\{111\} layer. A plan-view of the charge density difference illustrates that, of the coexisting 18 Å and 32 Å moirés, it follows the periodicity of the 32 Å moiré (Figure 5b). To quantify the effect of moiré modulation on band structure and density of states, the supercell electronic states can be unfolded onto a
single MoS$_2$ unit cell (Figure 5c). Accounting for the 32 Å moiré, band structure calculations are in agreement with prior angle resolved photoemission spectroscopy and scanning tunnelling spectroscopy measurements of the MoS$_2$/Au{111} system$^{29}$.

The 18 Å moiré is the most visible in HR-TEM, hence a study using HR-TEM alone would predict that electronic properties should be modulated with a period of 18 Å. However, our findings reveal that electronic modulation instead follows the “hidden” 32 Å periodicity. We conclude that 4D STEM imaging, showing both coexisting superlattices, was necessary for a direct observational link between atomic structure and moiré-induced electronic modulation at this 2D/3D interface$^{23-25}$. The analysis above also explains why the 32 Å moiré is visible in STM measurements while the 18 Å moiré is visible in conventional TEM$^{21,26}$: TEM observes a beating phenomenon that shows 3D atoms in projection, while STM probes the local density of states.

Fig. 5 Electronic structure calculations at the 2D/3D interface a, Charge density difference viewed down a [100] cross section of the 32 Å commensurate moiré (11$_{Au}$ x 10$_{MoS2}$ superstructure). b, Calculated charge density difference at the MoS$_2$/Au{111} interface, as viewed down the [001] axis, showing electronic modulation following the 32 Å moiré periodicity. c, Unfolded band structure for MoS$_2$/Au{111} system (left) and corresponding density of states (right). Colour corresponds to the band’s spectral weight.

To explore the generality of the geometric convolution technique, we also apply it to the hBN/Au{111} structure (Figure S6). Here, the Au lattice is rotated by 10° with respect to the hBN, leading to a more complex situation than the symmetric 0° epitaxy of MoS$_2$/Au{111}. This 10° rotation leads to a strong moiré periodicity of 11 Å. Prediction via geometric convolution technique is necessary in these rotated systems to uncover higher order moirés. For this interface, the convolution technique predicts and explains an additional 19 Å
periodicity visible experimentally, and re-creates the experimental diffraction pattern (Figure S6).

In summary, a MoS$_2$/Au{111} heterostructure exhibiting perfect rotational epitaxy was used as a model system to extend the moiré engineering toolbox to 2D/3D systems. Two coexisting moirés (18 Å and 32 Å) were predicted in this materials system via analytical geometric convolution, and a method for decoupling and direct imaging of these moiré periodicities was developed using 4D STEM. Electronic structure calculations showed that MoS$_2$/Au{111} charge density modulation follows the 32 Å moiré periodicity. This periodicity is hidden in conventional TEM, therefore direct imaging via 4D STEM was necessary to connect the details of the structure to the modulation of electronic properties. The combination of analysis techniques also solved a discrepancy in the moiré patterns observed by TEM and STM at this 2D/3D interface. These results highlight electronic modulation at the 2D/3D interface, as well as showcasing the growing opportunities for advanced (S)TEM techniques for direct imaging.

Practical development of moiré engineering requires complete control of the structure and orientation of 2D and 3D materials. Emerging fabrication methods suggest this possibility using direct transfer of a 3D metal, such as Au, onto 2D materials$^{30}$, or nanomechanical rotation of a 3D nanocrystal using AFM or STM tips$^{31}$. More complex structures can also be created by stacking and multiple moiré superlattices have been found to coexist in stacked vdW heterostructures$^{15,16}$. Although the effects of these coexisting moirés have been reported, they have not yet been directly imaged. The coupled application of 4D STEM and geometric convolution theorem presented here for analysis of the 2D/3D interface could be extended to directly image higher order moirés more broadly in systems with multiple interfaces and expand opportunities across the field of moiré engineering.

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Author Contributions
K.R., G.V. and F.M.R. conceived the project. K.R. and J.D.T developed the epitaxial deposition and fabricated samples. G.V. extended the geometric convolution model in 2D/3D
systems. K.R. and G.V. performed geometric convolution analysis and analysed the data. K.R. and J.D.T. performed SAED and bright field TEM imaging. A.M.B. performed 60 keV HR-TEM imaging. A.K. and J.M.L performed 4D STEM imaging. K.R. performed 4D STEM data analysis and multislice calculations with input from A.K. and T.P. G.V. performed the density functional theory calculations and made atomic models, with input from P.N. and P.A. The manuscript was written with contributions from all authors.

Competing Interests Statement
The authors declare no competing interests.

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Methods
Suspended MoS2 sample fabrication. Custom TEM chips were fabricated, consisting of a SiNx membrane supported on Si, with 9 holes each 4 µm in diameter. We employed a wedging transfer process to suspend MoS2 on these TEM grids32. Thermally grown 90 nm SiO2/Si wafers were pre-treated with oxygen plasma and MoS2 was mechanically exfoliated onto them using conventional Scotch tape method. Flakes of suitable thickness were identified by their contrast in optical microscopy. A solution of 25 g cellulose acetate butyrate (CAB) in 100 ml ethyl acetate was spin coated onto the sample and baked at 80 °C for 6 minutes. MoS2 flakes were transferred to perforated silicon nitride (SiNx) TEM grids using a wedging transfer technique with deionised water and CAB polymer handle. The transferred flakes were baked at 140 °C for 5-10 minutes to improve adhesion. After dissolving the CAB in acetone for 15 mins, the flakes were dipped in isopropanol and dried using a critical point dryer.

Ultra-high vacuum (UHV) epitaxial deposition. To create epitaxial nanoislands, UHV deposition is used. This reduces impurities trapped at the metal-2D interface33. The main
source of interfacial impurities is polymer residues, which create heterogeneous nucleation sites. Therefore, polymer residue remaining on the 2D material nucleates non-epitaxially aligned nanoislands (Figure S1). This combination of CAB polymer and heat treatment is effective in removing carbon and polymeric contamination\textsuperscript{34}; material transferred using other polymers such as PMMA cannot be cleaned as effectively. MoS\textsubscript{2}/SiN\textsubscript{x} substrates were loaded into UHV sample preparation chambers and cleaned of residual polymer by heating resistively in UHV to \textasciitilde550°C for several hours. Au deposition was carried out in the same multichamber UHV system (base pressure 2 \times 10^{-9} Torr), and was deposited from a homebuilt K-cells using sheet metal placed in a BN crucible at a rate of 0.5 Å/min. The deposited thickness was calibrated by measuring the evaporation rate with a quartz crystal microbalance immediately before and after deposition. There is no intentional heating during deposition but thermocouple measurements show that the sample temperature rises to 50-60 °C.

**TEM imaging and data analysis.** A field-emission TEM (JEOL 2010F) was used for selected area electron diffraction and bright-field imaging, operated at 200 kV. HR-TEM imaging was performed with a Hitachi HF-3300V with CEOS BCOR imaging aberration corrector, operated at 60 kV. Figure 1c was obtained from a drift corrected mean of 25 images, where each image was an 8 second exposure, so the total exposure on to the camera was 200 seconds. The electron flux was 500e/Å\textsuperscript{2}/sec so the final image exhibited a total \textasciitilde100,000 e/Å\textsuperscript{2}. Drift tracking over the images gave an average drift of < 7 pm/sec, although most images exhibited less drift. FFTs and line-scans were obtained using Fiji ImageJ software. FFTs of the real-space image are used for observing moiré peaks instead of SAED patterns since moiré peaks cannot be observed using at the energies (80–300 keV) used in TEM\textsuperscript{35}. The FFT in Figure 2c was multiplied by a Hanning window to minimise streaking generated by the ‘hard edge’ of the discrete bound of the image.

**Multislice Image Simulations.** Multislice image simulations were carried out using Java-based Electron Microscopy Image Simulation (JEMS) software. We used an Au/MoS\textsubscript{2} 11x10 supercell, which was converted to orthogonal basis and sliced along the [001] direction. The TEM simulations in Figure 3e,f were carried out using 300 kV accelerating voltage, 1.0 mm chromatic aberration coefficient C\textsubscript{c}, and zero spherical aberration coefficient C\textsubscript{s}. An optimal (Scherzer) defocus of \textasciitilde94 Å was used. These values were chosen to give the maximum possible contrast between the three distinct sites in the 32 Å moiré.

**4D STEM imaging and data analysis.** 4D STEM imaging was performed with a probe-corrected Thermo Fisher Scientific Themis Z G3 60-300 kV S/TEM operated at 60 kV with a beam current of 50-60 pA in the microprobe mode and a semi-convergence angle of 5.42 mrad using an Electron Microscopy Pixel Array Detector. Virtual ADF STEM images were generated from 4D STEM dataset using virtual detectors using the ‘4D STEM Explorer’ program\textsuperscript{36}.

**Geometric convolution technique.** The geometric convolution code was implemented in the computational package Wolfram Mathematica 12.0 and builds on a model previously
described for hexagonal lattices. Frequencies arising from the superposition of the two lattice functions were obtained by the convolution theorem, $F\{t \times b\} = F\{t\} \otimes F\{b\}$, where $t$ and $b$ are the top and bottom lattice functions respectively, $F\{\}$ denotes the Fourier transform, and $\otimes$ denotes the convolution operation. All possible spatial frequencies arising from observed spots in the SAED/FFT were initially obtained and we make no assumptions in the simulation other than the bulk structure of Au and $\{111\}$ orientation. The full set of spatial frequencies of the FCC crystal along the $[111]$ zone axis were used to calculate the moiré periods for all possibilities within the experimentally observed FFT as a function of the relative rotation while allowing for small ($\pm 1\%$) Au lattice strain. The angles can also be calculated (Figure S3). We then evaluate the most likely candidates to explain the experimentally measured moiré periods and angles (Figure S5).

**Electronic structure calculations.** The ground-state charge density difference ($\Delta \rho$) between the Au/MoS$_2$ heterostructure ($\rho_{\text{Au/MoS}_2}$), and pristine Au ($\rho_{\text{Au}}$) and MoS$_2$ ($\rho_{\text{MoS}_2}$) is given by

$$
\Delta \rho = \rho_{\text{Au/MoS}_2} - \rho_{\text{Au}} - \rho_{\text{MoS}_2}
$$

Density functional theory calculations were carried out using the projector augmented wave method implemented in the Vienna ab initio simulation package, VASP. We account for the vdW dispersion interactions using the generalized gradient optB86b-vdW functional. We use a cut-off energy of 400eV on an equivalent Monkhorst-Pack k-points grid of 40x40x1 MoS$_2$ unit cell (and similar density supercell). Bandstructure unfolding was performed using the BandUP code.

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