# Photoinduced phase transitions in VO$_2$: visualizing the time-dependent crystal potential using ultrafast electron diffraction data

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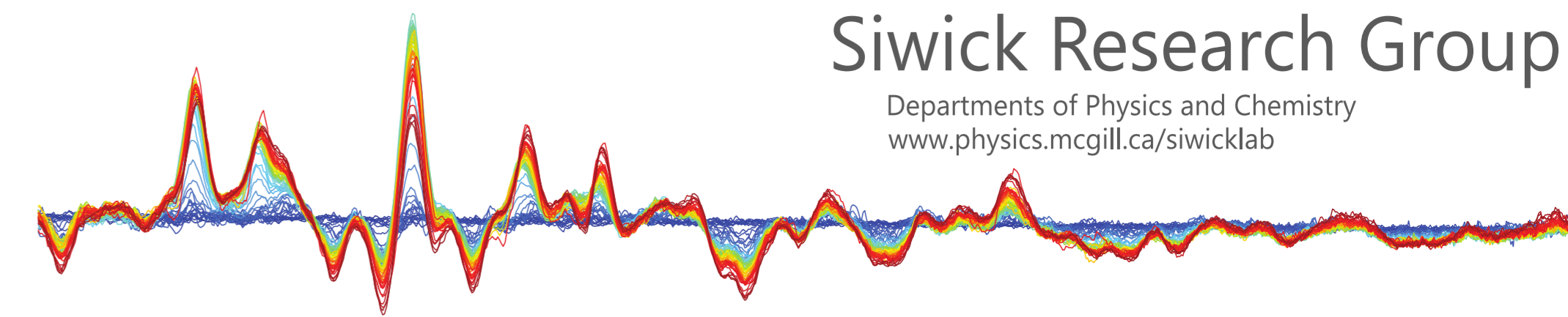
Motivation

Vanadium dioxide is notable for exhibiting several low-T insulating phases and having a very well studied insulator-metal transition (IMT) at ~68°C that is associated with a crystallographic change from monoclinic semiconductor (M1) to rutile metal (R). The nature of the IMT has been the subject of vigorous debate since 1959, with recent work suggesting that the electronic properties of both phases emerge from a complex interaction of lattice, orbital and charge degrees of freedom.
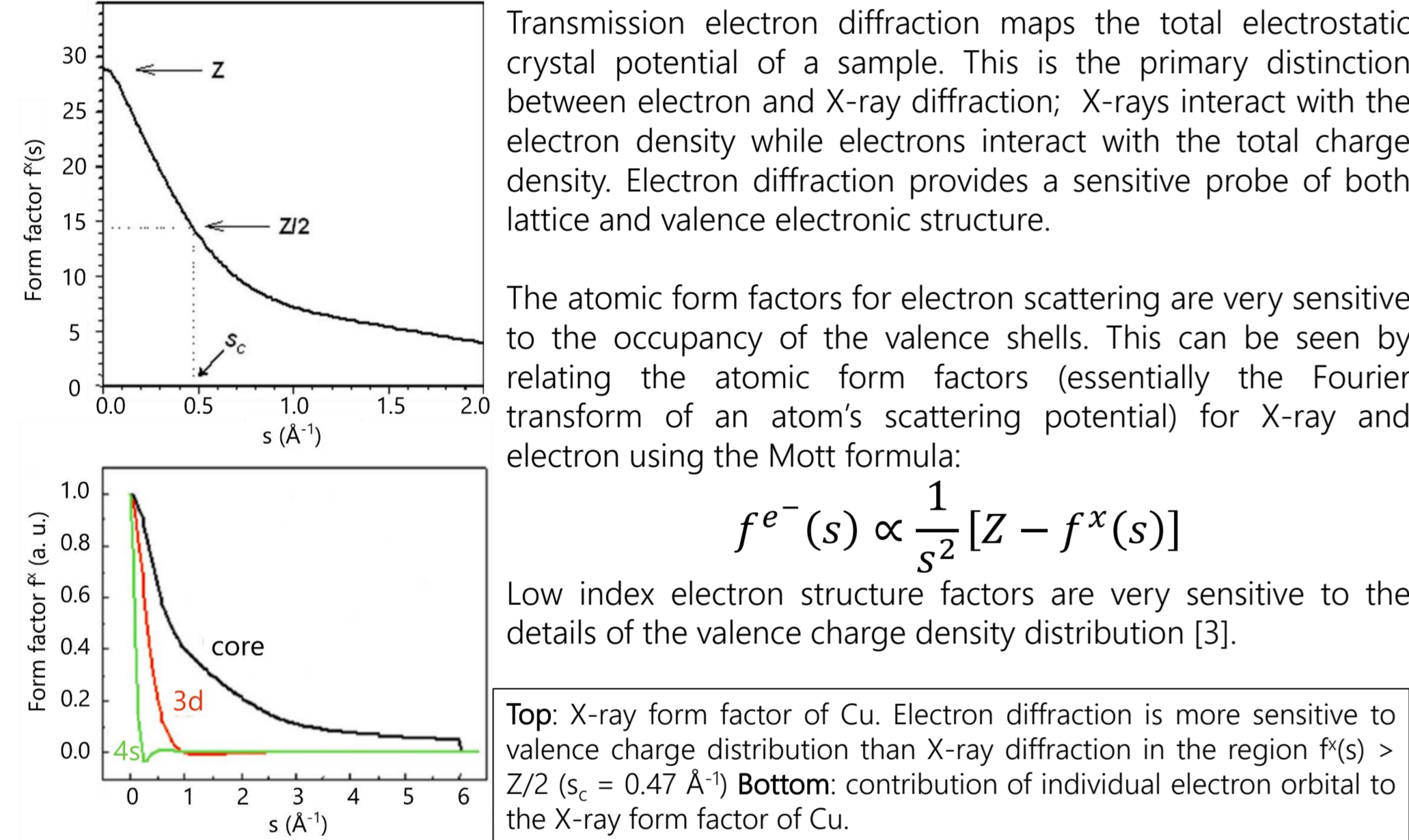
Using a combination of ultrafast electron diffraction (UED) and broadband spectroscopy, we have recently demonstrated that photoexcitation of monoclinic vanadium dioxide crystals below a threshold fluence induces a transition to a metastable state with monoclinic crystallography, but metal-like optical/electronic properties [1]. This long-lived metallic phase appears to have no equilibrium analog. A detailed structural characterization of this phase is the subject of this poster.

## Ultrafast Electron Diffraction
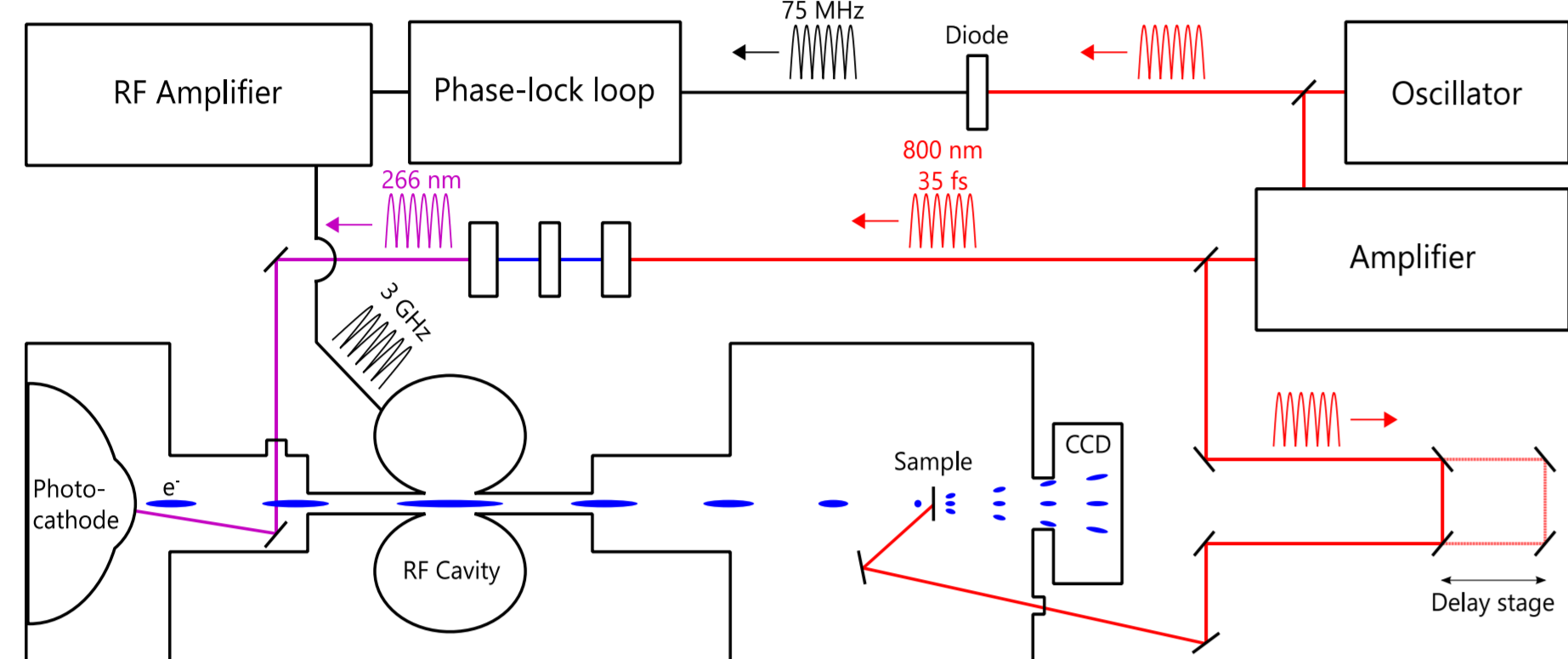
The ultrafast electron diffraction (UED) instrument probes samples with short (~100fs) bunches of ~100 keV electrons. The setup is synchronized with an oscillator that drives both a laser system and a radio-frequency cavity. This cavity is used to counteract the Coulomb repulsion that stretches the electron bunches. Therefore, the RF-UED system is not subject to the historical trade-off between a high signal-to-noise ratio (electron pulse fluence) and time-resolution (short electron bunches) [2].

## Sensitivity of UED to valence charge distribution

Transmission electron diffraction maps the total electrostatic crystal potential of a sample. This is the primary distinction between electron and X-ray diffraction; X-rays interact with the electron density while electrons interact with the total charge density. Electron diffraction provides a sensitive probe of both lattice and valence electronic structure.

The atomic form factors for electron scattering are very sensitive to the occupancy of the valence shells. This can be seen by relating the atomic form factors (essentially the Fourier transform of an atom's scattering potential) for X-ray and electron using the Mott formula:

$$f^{e^-}(s) \propto \frac{1}{s^2}[Z - f^x(s)]$$

Low index electron structure factors are very sensitive to the details of the valence charge density distribution [3].

Top: X-ray form factor of Cu. Electron diffraction is more sensitive to valence charge distribution than X-ray diffraction in the region $f^e(s) > Z/2$ ($s_c = 0.47$ Å^{-1}). **Bottom:** contribution of individual electron orbital to the X-ray form factor of Cu.

UED of vanadium dioxide

The structure of the VO$_2$ unit cell *during* the photoinduced IMT was observed over a broad range of pump fluence using ultrafast electron powder diffraction. This study revealed qualitatively distinct 'fast' and 'slow' structural reorganizations. The fast change is associated with a transition to the rutile phase, while the slow change is associated with a 1D reorganization that preserves monoclinic crystallography [1]. At pump fluences below ~9 mJ/cm^2 only the slow dynamics are observed.
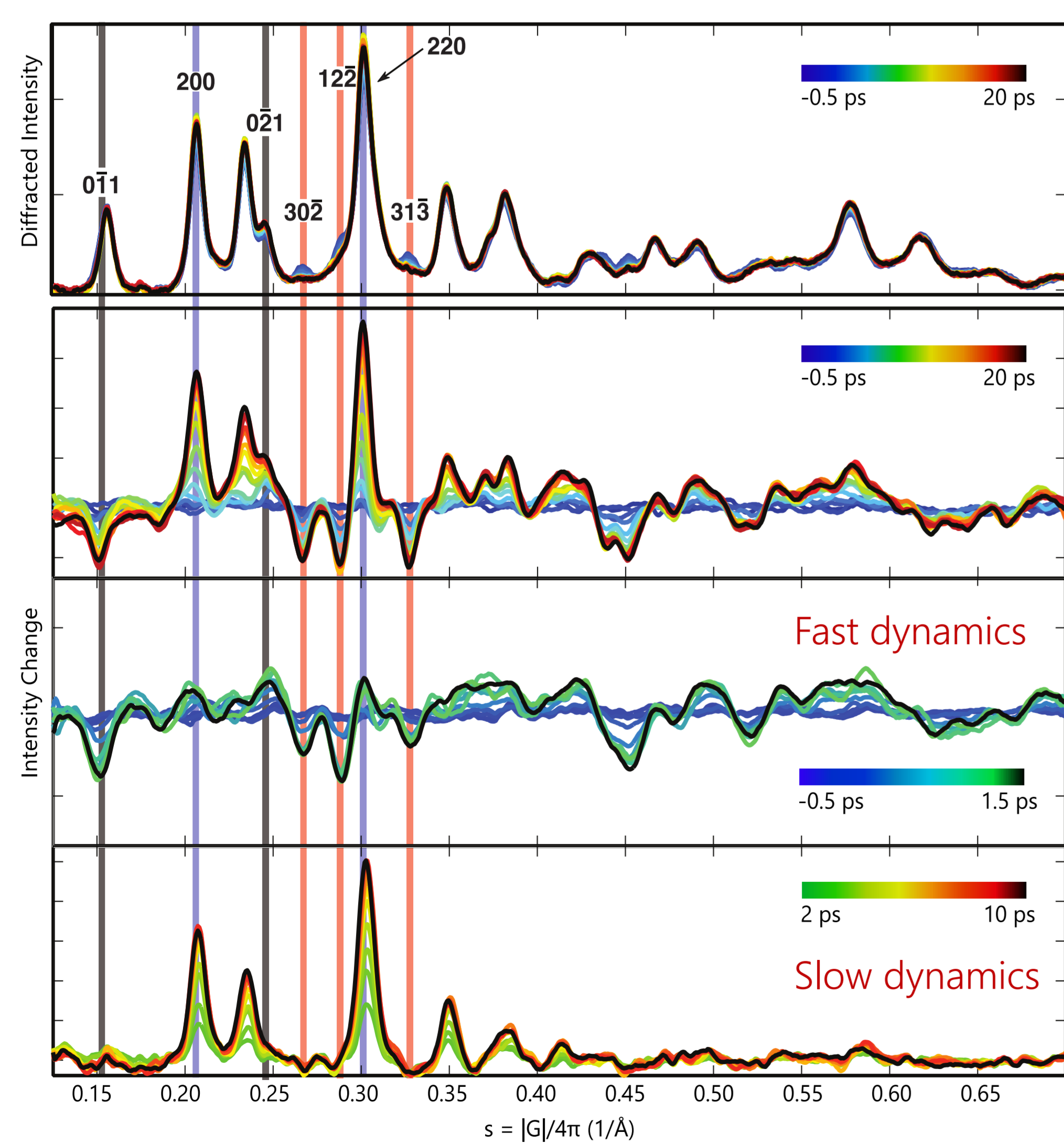
Above: time-resolved radially-averaged polycrystalline diffraction pattern. **Below:** radially-averaged diffraction changes for various time scales. Red overlays corresponds to peaks allowed in a monoclinic but not rutile. Blue overlays indicate peaks that appear in both equilibrium phases. Grey overlays designates structural changes orthogonal to c_R.

Change in PDF associated with the slow dynamics as computed directly from the data above. This function shows the changes to the autocorrelation function of the electrostatic crystal potential (radially averaged). The negative (positive) features that are the dominant contribution correspond to V – O (V – CDW) distances in the M1 structure of VO$_2$ not the V-V distances as was determined for the fast dynamics [1].
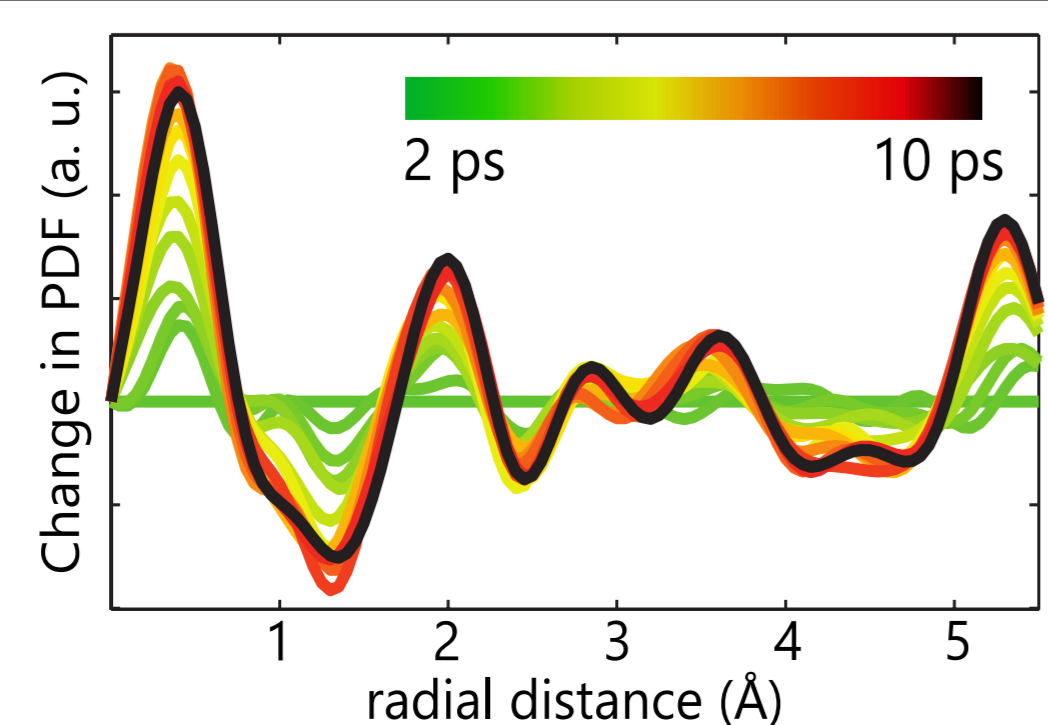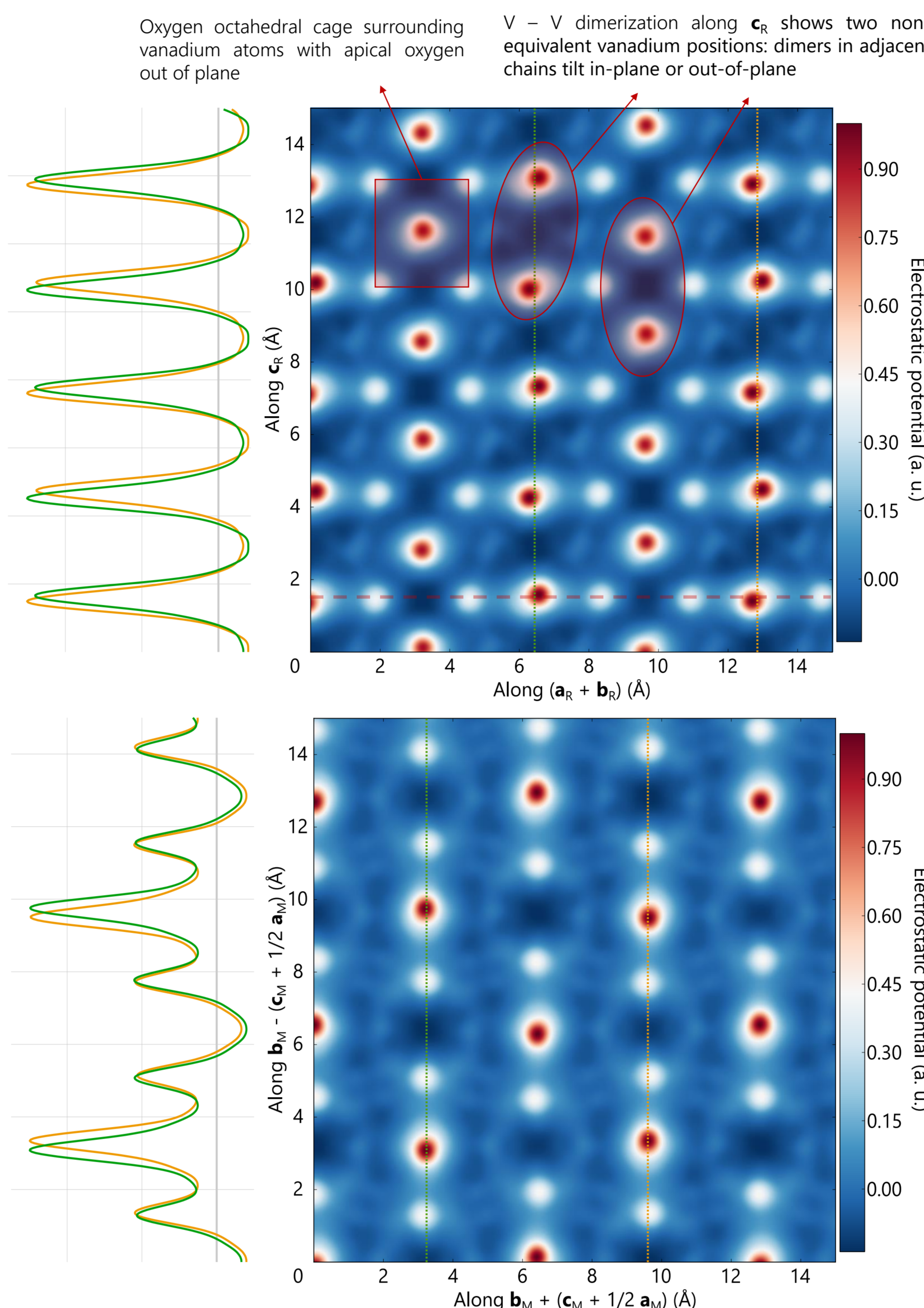
Scattering potential maps

For the case of centrosymmetric crystals, diffraction phases are either 0 or π radians. From structure factor calculations, we can assign phases for each reflection. Then, an inverse Fourier transform can be used on the diffraction data to get the scattering potential map:

$$\phi(r) = \sum_{\{G\}} I_G \, e^{i\chi_G} \cos(G \cdot r)$$

for scattering (electrostatic) potential ϕ, real-space position vector r, reflections $\{G\}$, and diffraction intensity and phase I_G and χ_G. Diffraction intensity was corrected for overlapping reflections and polycrystalline sample texture.

Monoclinic M1 VO$_2$

Oxygen octahedral cage surrounding vanadium atoms with apical oxygen out of plane

V – V dimerization along c_R shows two non-equivalent vanadium positions: dimers in adjacent chains tilt in-plane or out-of-plane

Right: electrostatic potential map of monoclinic M1 VO$_2$, for two complementary projections, using unpumped diffraction intensity data. The red line across the top map corresponds to the intersection between the top map and the bottom one. **Left:** Line cuts through atom chains colored on the map highlighting both V – V dimerization and charge-density modulation.

Monoclinic (M1) VO$_2$ structure described using rutile lattice vectors. Shows are the V – V distances (blue) and fractional V – V dimers (blue to black)

2.65 Å   3.16 Å
1.31 Å   4.41 Å
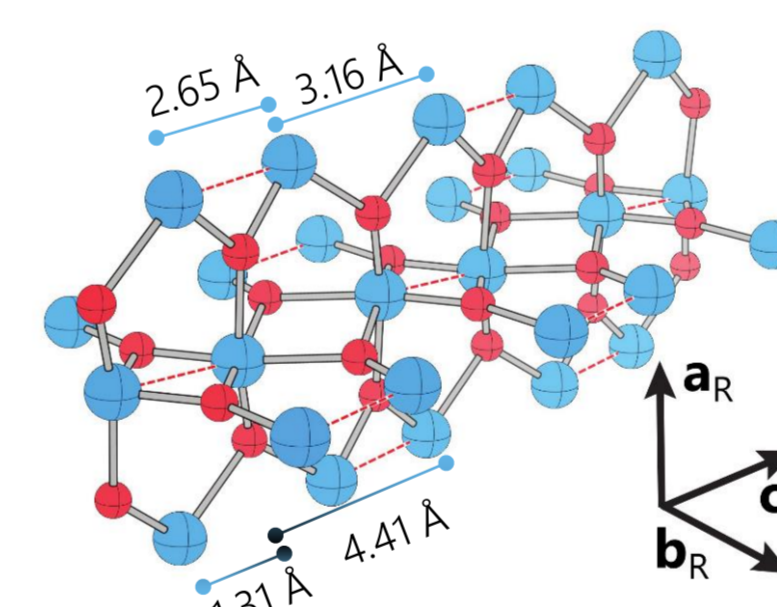
Comparison of pair-distribution functions

We test the validity of this approach by comparing the radial pair-distribution function (PDF). The PDF can be obtained from the radial-average of the (reduced) Patterson function $P(r)$ [4]:

$$P(r) = \sum_{\{G\}} \mathcal{I}_G \exp(iG \cdot r)$$

where $\mathcal{I}_G$ is the reduced experimental intensity

$$\mathcal{I}_G = I_G / \sum f(G)^2$$

involving a sum of form factors f evaluated at scattering vector G over all atoms in the unit cell.

The physical interpretation of the Patterson function is that it represents the autocorrelation of the scattering potential $\phi(r)$. It is thus possible to calculate the PDF in two equivalent but separate ways: directly from the diffraction intensity data and via autocorrelation of the generated electrostatic potential maps. There is very good agreement between these two PDFs, which provides further evidence that the potential maps are accurate.
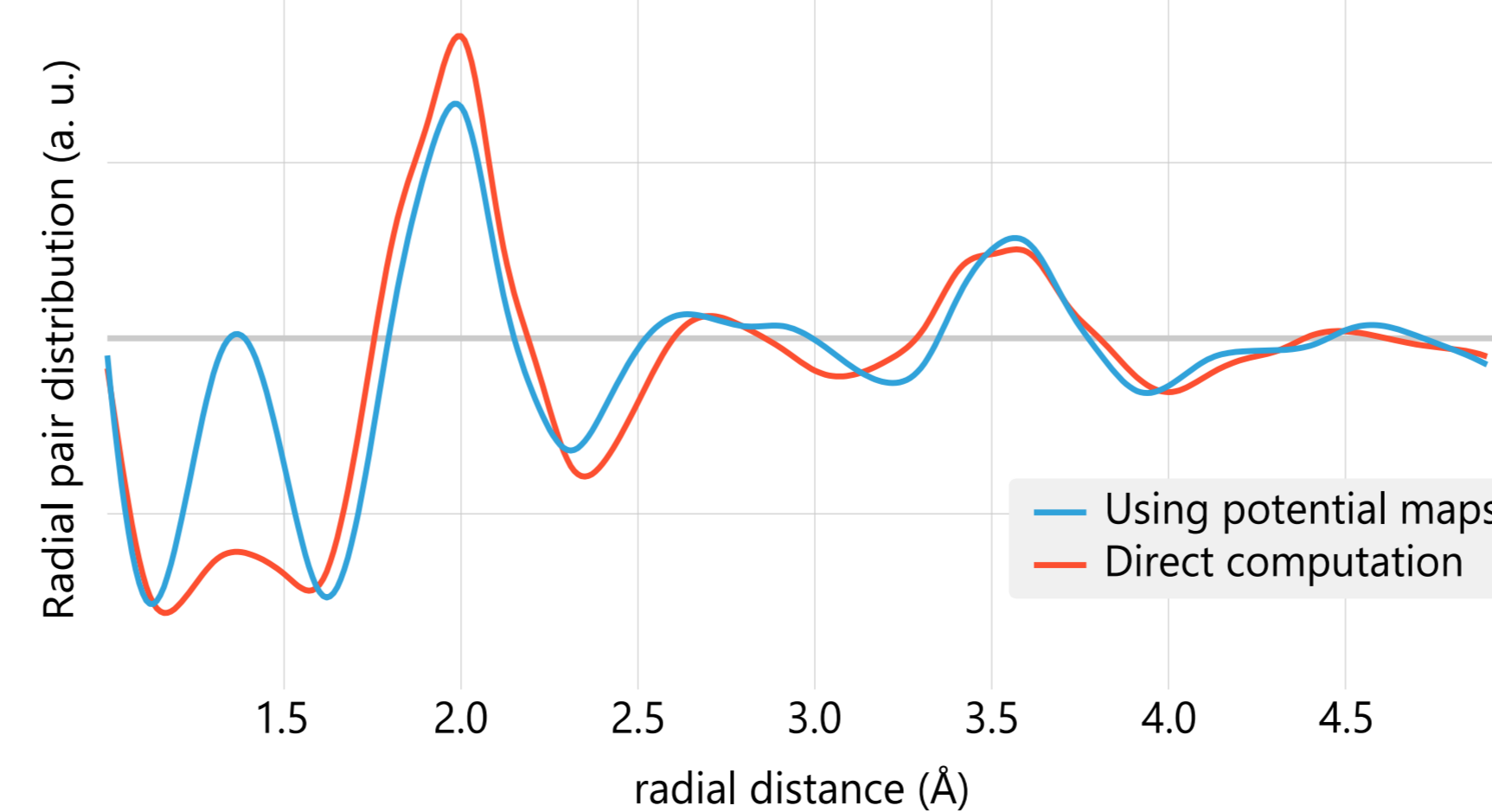
Radial pair-distribution function comparison between a direct calculation from the unpumped intensity data and an autocorrelation of atomic potential calculation.

Photoinduced changes

Electrostatic potential maps provide a much richer way to visualize the structure of the material than the radial pair-distribution functions. We generate difference electrostatic potential maps from the UED data in the range (1.5ps – 10ps) to determine a detailed view of the structural changes associated with the slow dynamics.

Looking at the plane spanned by c_R and ($a_R + b_R$) allows probing both non-equivalent vanadium positions in the same map. The difference map shows that the electrostatic potential increases at vanadium and oxygen positions and decreases in the 1D charge density waves along c_R while the tilting and dimerization of the vanadium atoms associated with the monoclinic M1 structure remains.

Monoclinic metal: difference in electrostatic potential compared to M1

The following maps are projections equivalent to the maps to their left.
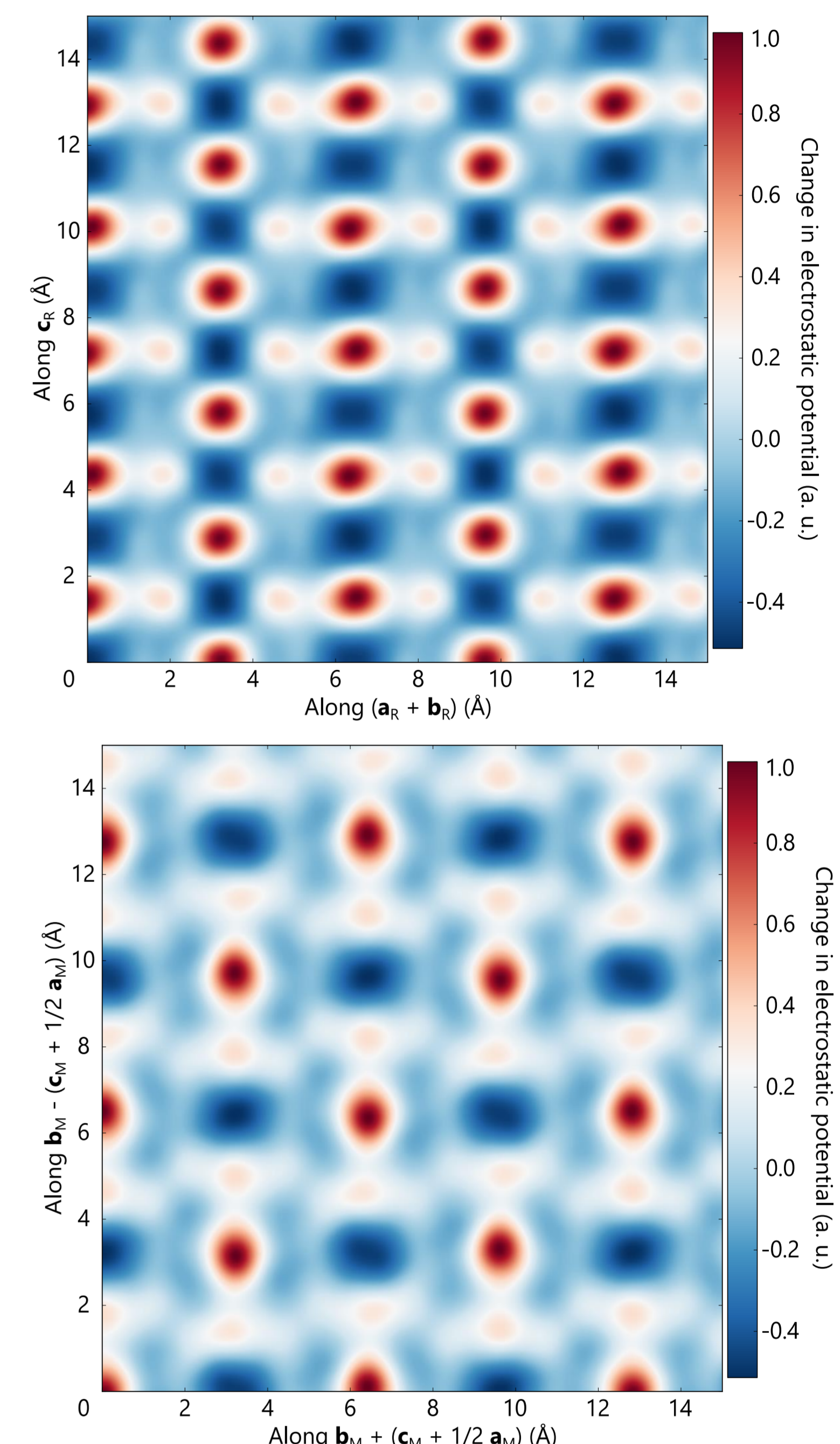
Electrostatic potential map computed from difference intensity data of 10ps (referenced at 1.5 ps). Both V and O atoms get more positive as the electrons move to reinforce the charge-density wave.

As can be seen from the above figure, the photoinduced metastable metal-like state of monoclinic vanadium dioxide is not associated with a change in the crystallographic phase. The changes in electrostatic potential are dominated by dynamics in electronic (not lattice) structure. The valence charge reorganization results in an effective modification of the atom's atomic form factors that is easily seen in UED.

Outlook

The computation techniques of atomic potential maps generated from powder UED data was demonstrated for VO$_2$. This tool reveals more information about the real-space charge distribution than the radial pair-distribution function analysis alone. Combined with electron diffraction's high sensitivity to changes in valence charge distribution, this technique can be used to investigate dynamics in orbital occupancy and orbital/charge order in strongly correlated materials. UED should be seen as a powerful probe of electronic structure, not only lattice structure in condensed matter.

The computation of potential maps can easily be generalized to non-centrosymmetric crystals, (provided that the interrogated structure is known) and other scattering probes.

Acknowledgements

References

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