Visualizing and quantifying structural distortions of an unstable phonon-mode

Ishani Cheshire[1], Harikrishnan Kunhikrishnan Premakumari[2], and David Muller[2]

[1] *Department of Physics, University of California, Berkeley, Berkeley, CA*
[2] *School of Applied and Engineering Physics, Cornell University, Ithaca, New York*

August 18, 2023

Abstract

The crystal structure of strontium hexagallate hosts an unstable phonon mode that exhibits signs of spontaneous symmetry breaking, leading to the formation of nanometre-scale polar regions in the material. By analyzing the polarization of individual unit cells and its spatial variation from multislice-ptychography images, we quantify the size of such polar nano-regions. We used the Moran's I coefficient to quantify spatial correlations in the measured polarization, and observed a statistically significant correlation between the spatial position and polarization with a p-value ranging from 0.0020 - 0.018 for different sample regions.

1 Introduction

Polarization can be used to encode information in electronics on an extremely compact nanometre-scale. The structure of strontium hexagallate may facilitate extremely small polar regions, potentially enabling more efficient information storage techniques. Strontium hexagallate's polarization arises from the unstable phonon modes associated with trigonal-bipyramid coordinated gallium atoms that lie on the (0001) planes of strontium atoms. In the absence of any structural distortion, the gallium atoms would remain on this plane, and maintain overall centrosymmetry of the crystal. However, we observe that many of these gallium atoms shift up or down with respect to the mirror plane of strontium atoms due to a spontaneous symmetry breaking process. This movement of the gallium atom polarizes that respective unit cell of strontium hexagallate either up or down.

We sought to understand whether strontium hexagallate possesses polar nano-regions—areas where adjacent unit cells are similarly polarized—and what the typical size of these regions might be. By analyzing the correlation of the polarizations and positions of individual unit cells, we can begin to better understand the theoretical limit of strontium hexagallate's information storage capacity.

2 Methods

We use ptychographically reconstructed images of strontium hexagallate (Guguschev et al., 2022; Chen et al., 2021). This reconstruction creates a 3D rendering of the original sample by producing a series of 2D images or slices spaced at 1 nanometre intervals descending into the sample. It is notable that the resolution in the depth direction of the sample is 2.5 nm, larger than the spacing between individual slices.

For each of these 2D images, we extract the line profile across the polarized gallium atoms within each unit cell of strontium hexagallate, fitting a double gaussian to each profile as in Figure 1. The overall fit is the sum of the two Gaussians. We use the resulting fit to quantify the polarization by taking the position of each Gaussian, weighting it by the height of the Gaussian, then taking the mean of the two values. This yields a value which is positive for unit cells polarized upwards, negative for unit cells polarized downwards, and zero for unpolarized unit cells. We label this value the 'mean weighted position' of the gallium atom's line profile. We then create a 3D visualization of the sample with the polarization of each unit cell over-plotted (Figure 2).

To quantify whether there is a correlation between position and polarization, we utilize the Moran's I statistic. For each gallium atom, we take the mean polarization of every gallium atom within a radius of 2 nanometres. We then plot this value against the polarization of each gallium atom. An example of this calculation performed on one ptychographic frame is shown in Figure 3. Due to the fact that the resolution in the depth direction is less than the separation between each frame, we perform this calculation separately on each frame of the multi-slice ptychographic reconstruction to avoid conflating a lack of resolution in the depth direction with a correlation between position and polarization. Note that we normalize the spread of each axis before plotting. If polarization were strongly correlated with position in strontium hexagallate, we would expect a slope closer to 1, if it were not, we would expect a slope closer to zero. These two values are correlated across all frames, the example first frame having a slope of 0.601.

In order to estimate the statistical significance of this slope, we calculate what the typical slope would be for our sample images if the polarizations are randomly distributed throughout the sample. To do this, we randomly reassign each polarization value to a new gallium atom, then calculate the slope of that fictitious sample. We iterate this calculation 500 times until we produce a distribution of possible slope values given no correlation between polarization and position throughout the sample. This plot is shown in Figure 4, where there is only a 1.8% overlap between the zero-correlation distribution of slopes and the actual observed distribution of slopes across all frames. This means that there is only a 1.8% chance of observing these slopes given a completely random distribution of polarization.

3 Results

In conclusion, we notice a significant correlation between position and polarization, with the p-value ($p = \frac{N_{overlap}+1}{N_{tot}+1}$) ranging from 0.0020 - 0.018 across all ptychographic frames. Therefore, our samples of strontium hexagallate contain similarly polarized nano-regions. In future work, we seek to characterize the typical size of these polar nano-regions for the purpose of determining strontium hexagallate's utility in electronic memory storage.

References

Z. Chen, Y. Jiang, Y.-T. Shao, M. E. Holtz, M. Odstrčil, M. Guizar-Sicairos, I. Hanke, S. Ganschow, D. G. Schlom, and D. A. Muller. Electron ptychography achieves atomic-resolution limits set by lattice vibrations. *Science*, 372(6544):826–831, 2021. doi: 10.1126/science.abg2533. URL https://www.science.org/doi/abs/10.1126/science.abg2533.

C. Guguschev, C. Richter, M. Brützam, K. Dadzis, C. Hirschle, T. M. Gesing, M. Schulze, A. Kwasniewski, J. Schreuer, and D. G. Schlom. Revisiting the growth of large (mg,zr):srga12o19 single crystals: Core formation and its impact on structural homogeneity revealed by correlative x-ray imaging. *Crystal Growth & Design*, 22(4):2557–2568, 2022. doi: 10.1021/acs.cgd.2c00030. URL https://doi.org/10.1021/acs.cgd.2c00030.

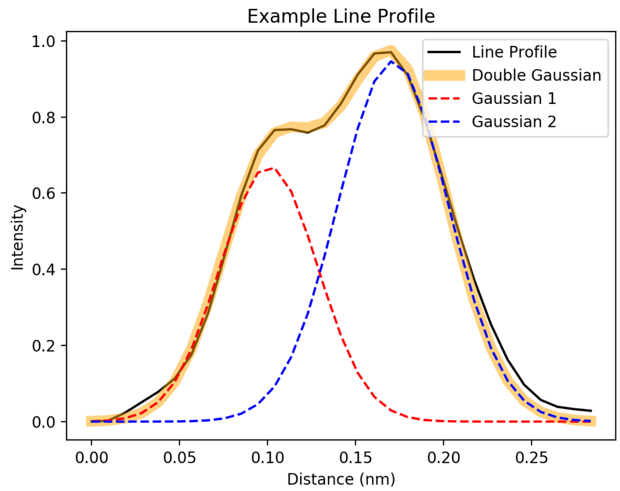

Figure 1: An example of the line profile of a gallium atom which is polarized in the up (left) direction more than in the down (right) direction.

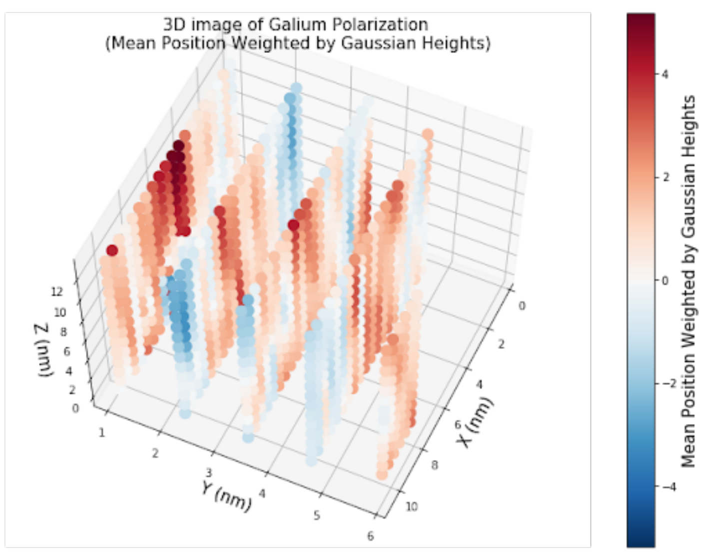

Figure 2: A 3D plot of all ptychographic slices of our first sample image. The polarization of each gallium atom has been quantified using our weighted mean position value, and is represented on this plot by color.

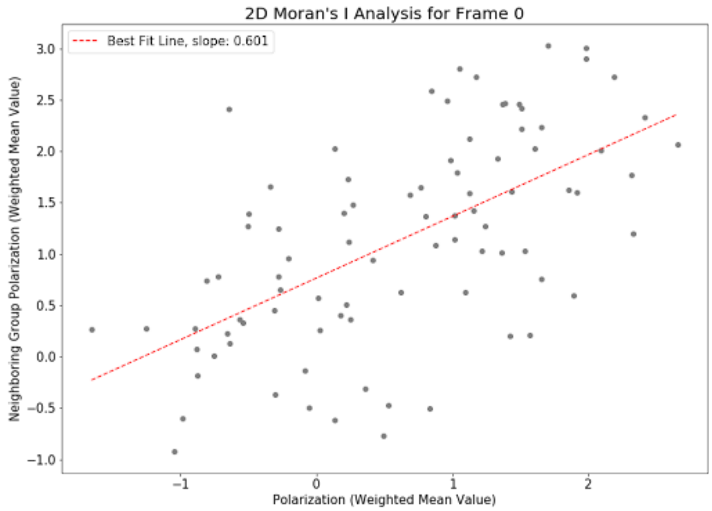

Figure 3: A plot of the average polarization value of every gallium atom within two nanometers versus the polarization value of the gallium atom for one ptychographic frame. The spread of both axes has been normalized before plotting. We observe a slope of 0.601, indicating a correlation between position and polarization.

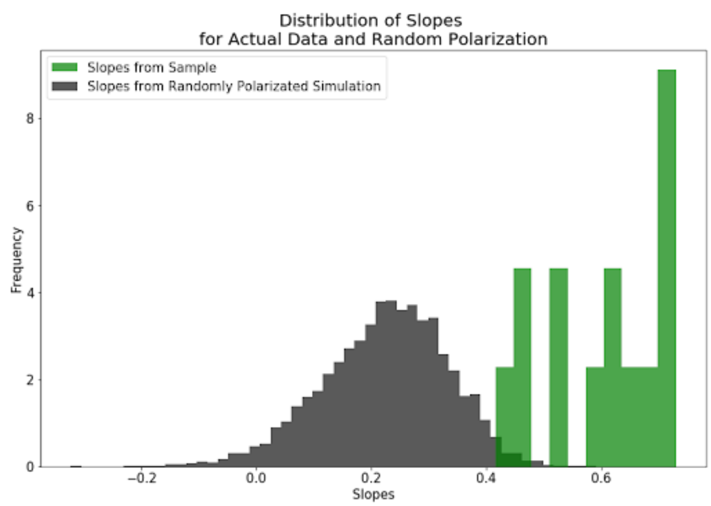

Figure 4: This plot details the distribution of slopes given a completely random distribution of polarizations throughout the gallium atoms in our sample strontium hexagallate. In green, the distribution of slopes calculated from each ptychographic frame of our actual sample image is shown. The overlap of the two groups is around 1.8% ($\frac{N_{overlap}+1}{N_{tot}+1}$) indicating that the correlation between position and polarization we observe is significant.