Semi-automatic Identification and Quantification of Point Defects on Quantum Materials from Atomic-resolution Electron Microscopy Data

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Introduction & Objective

Quantum materials have the potential to revolutionize the world of electronics, however, much is still unknown about the phenomena that induce their exotic properties. Understanding how a material's structure impacts the properties of interest requires close analysis of its nanoscale structure. Here, we use scanning transmission electron microscopy data to characterize the low symmetry C2/m atomic scale structure of La3Cd2As6, which exhibits a vacancy ordering in the cadmium sites. This system is of special interest because it was found to be a narrow-gap semiconductor with a band gap of 105 meV. Disorder-free narrow-gap semiconductors are of interest because of their potential in fields such as thermoelectricity and dark matter detection. Furthermore, the La3Cd2As6 system showed a thirteen order of magnitude increase in electrical resistivity upon cooling which suggests that the system has a remarkably clean insulating ground state.

Objective

In this work, a semi-automated analysis procedure is presented to quantify the degree of partial occupancy. Identifying these point defects may help understand the origin of the material's remarkable electronic properties.

Understanding Vacancy Ordering

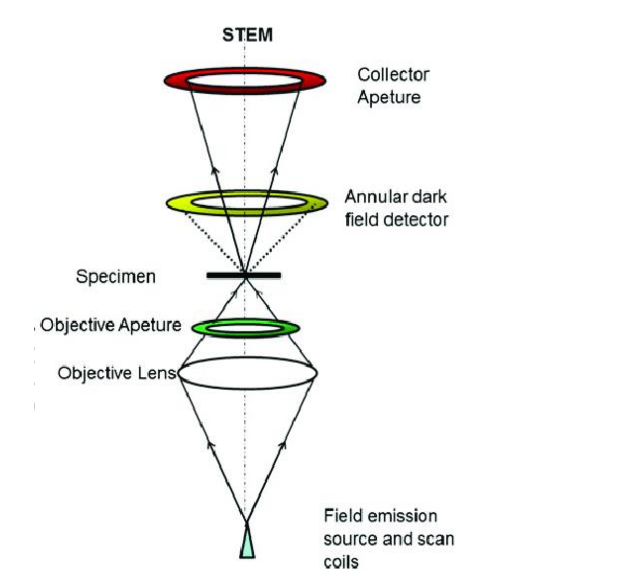


Figure 1: Schematic of the workings of a scanning transmission electron microscope

Scanning transmission electron microscopes (STEM) has lenses which are adjusted to create a focused electron beam which then scans across the sample and signals are collected point-by-point to form an image. This image allows us to determine the relative location of atoms within the crystal lattice. This degree of accuracy in microscopy is really exciting to material scientists because the analysis of a material's structural components can give us insight into why exotic properties arise.

This material's exotic electronic properties are associated with its vacancy ordering. Recognizing a vacancy ordering can be difficult to recognize at first but, if we focus on the the cadmium atoms, we see a pattern emerge. We see that there is a pair of atoms and then a gap and a pair of atoms and then a gap and so on. A point defect or partial occupancy occurs when there is an atom within this gap as detailed by the blueish dots in the diagram.

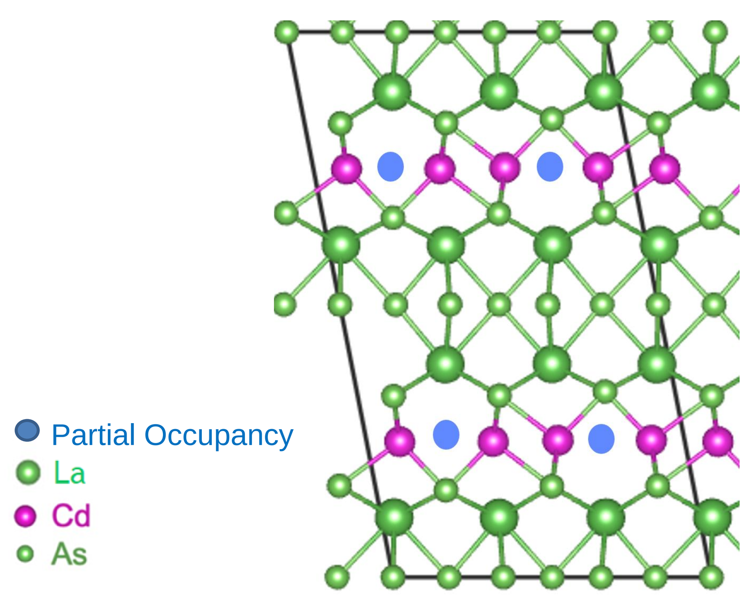


Figure 2: Structure of the La3Cd2As6 system

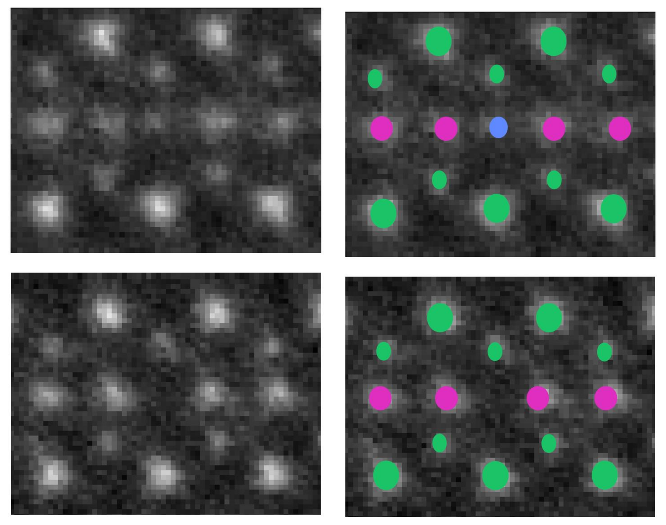


Figure 3: Side-by-side comparison of STEM of the La3Cd2As6 system with atoms overlayed to highlight an instance of partial occupancy

From Model to STEM Data

Looking at the model it's easy to spot these but now we look at the STEM data it is a bit harder to see. While it might take a trained eye a second to spot an instance of partial occupancy, we can see how this can be a tedious process when you have multiple data sets to look through with hundreds if not thousands possible instances of partial occupancies.

Methods

Finding the Cadmium Atomic Rows

The first step in the analysis process is to locate the atomic row of interest, in this case of the $La_3Cd_2As_6$ the cadmium atomic row. To facilitate processing, I began by rotating the HAADF STEM image so that the atomic rows ran vertically. Next utilizing a python package "photoutils" I implemented atom tracking and row finding functions to identify the rows of the largest atoms in the system. Once these were recognized I used relative pixel positions to identify the start and end point locations of the atomic rows of cadmium, the element of interest.

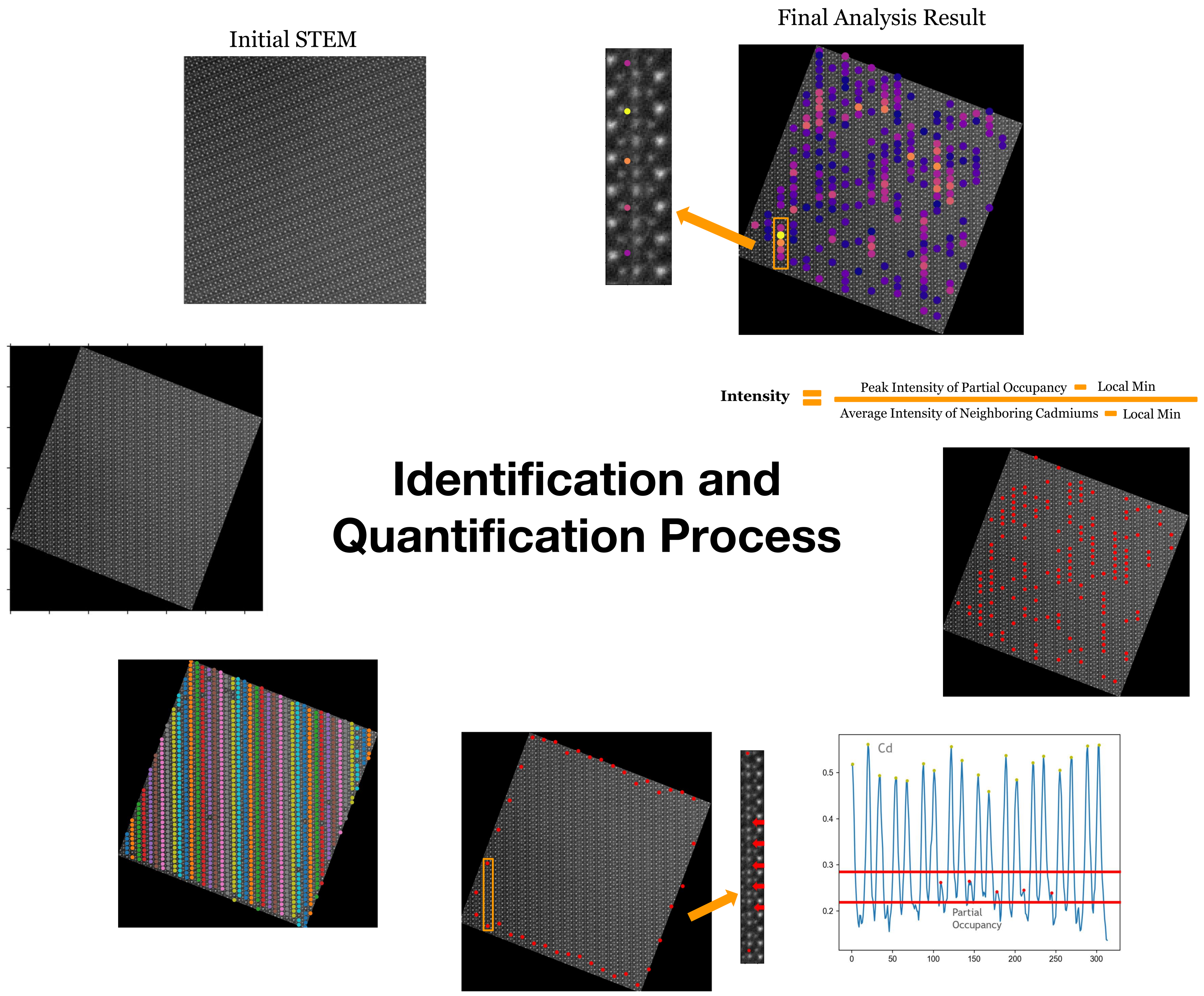
Analyzing Line Profiles and its Challenges

The recognition of a partial occupancy is illustrated by the instance of a peak where we expect a trough. To find instances of partial occupancies I used existing peak finding functions to recognize the peaks within a certain desired range. Using a set threshold to find instances of partial occupancies was problematic because the average intensity of the peaks changed as we advanced through the image. To overcome this challenge, I designed a method to adjust the range threshold for each line profile that considers the difference in sample thickness across the sample.

Quantification

In the analysis, the motivation for the quantification of the partial occupancy is to see if were able to recognize patterns across multiple images of a sample that might give us insight into the rise of this material's exotic electronic properties. To do so a normalization was necessary to counteract the impact of the increasing thickness across an image. To overcome this challenge, I implemented this intensity normalization formula:

$$\text{Intensity} = \frac{\text{Peak Intensity of Partial Occupancy} - \text{Local Min}}{\text{Average Intensity of Neighboring Cadmiums} - \text{Local Min}}$$



Results

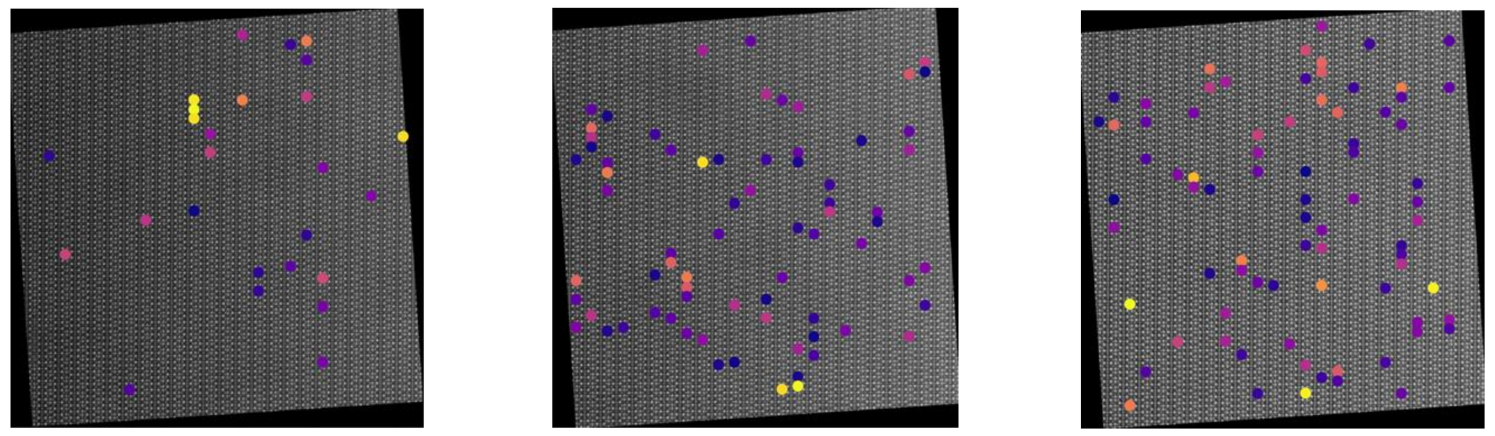


Figure 4: STEM data of the La3Cd2As6 system after its partial occupancy sites have been identified and quantified, ordered in increasing thickness sample.

After a close examination of the quantification trends, we saw that the instances of partial occupancies increase as the thickness of the sample increased. This trend correlates to initial intuitions about interstitial point defects because we are able to see the impact of more atomic layers of the sample. However, to really understand how this can possibly correlate to physical properties more research and analysis is needed.

Conclusions & Future Work

After designing a semi-automatic system with replicable results across a multitude of HAADF STEM data sets, I have the following findings:

- There is a quantifiable increase in clustering of partial occupancies as the thickness of a sample increases.
- A significant presence of point defects was observed despite this material being a clean insulating ground state. This goes against the general intuition that a good insulating ground state is free of point defects and is a subject of further research.

Future Work:

Continue to study the relationship between partial occupancies and the rise of exotic electronic properties by conducting similar analysis.

References

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