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# Reversible Structure Manipulation by Tuning Electron Dose Rate on Metastable $Cu_2S$

Jing Tao[1], Jingyi Chen[2], Jun Li[1], Leanne Mathurin[2], Jin-Cheng Zheng[3, 4], Yan Li[5], Deyu Lu[6], Yue Cao[1], Lijun Wu[1], Robert J. Cava[7] and Yimei Zhu[1]

[1.] Condensed Matter Physics & Materials Science Division, Brookhaven National Laboratory, Upton, NY.
[2.] Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR.
[3.] Department of Physics, and Collaborative Innovation Center for Optoelectronic Semiconductors and Efficient Devices, Xiamen University, Xiamen, China.
[4.] High Performance Computing Center,Xiamen University Malaysia, Selangor, Malaysia.
[5.] American Physical Society, Ridge, NY.
[6.] Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY.
[7.] Department of Chemistry, Princeton University, Princeton, NJ.

The optimal functionalities of materials are often associated with phase transitions involving simultaneous changes in the electronic structure and the symmetry of the underlying lattice. It is of great importance to disentangle which of the two effects – electronic or structural - is the driving force for the phase transition and to utilize the mechanism to control material properties. However, it is experimental challenging to explore such the "chicken-and-egg" question, which is critical to the understanding of a wide range of functional and quantum materials. Particularly, tuning the electronic structures in a compound by doping alien atoms will often introduce unwanted lattice distortion.

$Cu_2S$ provides an intriguing example to address the above problem. This material consists of highly mobile Cu ions with many applications associated with its emergent properties including superionic conductivity and high thermoelectricity. A phase transition in the bulk material occurs near 100 °C from a semiconducting monoclinic symmetry low-chalcocite phase (denoted as the "L-phase"; space group $P2_1/c$) to an electrically insulating hexagonal symmetry high-chalcocite phase (denoted as the "H-i-phase"; space group $P6_3/mmc$). Here we report the concurrent pumping and probing of $Cu_2S$ nanoplates using an electron beam at various electron dose rate to directly manipulate the transition between the L- and H- phases with distinctly different crystal symmetries and charge carrier concentrations. Our results show that the observed L-H phase transition arises from two mechanisms: charge generation for one phase and charge depletion for the other. We demonstrate that this manipulation is fully reversible and non-thermal in nature. Our observations reveal a novel phase transition pathway in materials, where electron-induced changes in the electronic structure can lead to a macroscopic reconstruction of the crystal structure.

References:

[1]. J. Tao *et al,* Proceedings of the National Academy of Sciences of the USA **114** (2017), p. 9832.

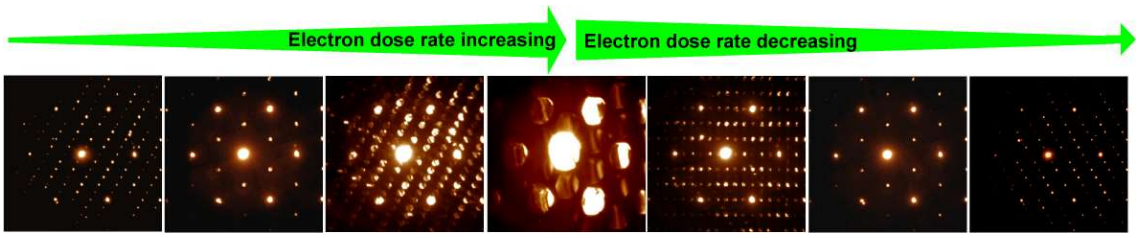


**Figure 1.** Snapshots of the electron diffraction patterns at the [001] zone-axis from an individual single-crystalline $Cu_2S$ nanoplate on increasing and decreasing the electron dose rate. Electron diffraction patterns obtained from the H-phase show hexagonally arranged reflections, whereas electron diffraction patterns from L-phase have additional sets of superlattice reflections due to symmetry breaking to monoclinic structure. In the diffraction series, an L-H-L-H structural transition can be identified when the electron dose rate is monotonically increased, and a reversible H-L-H-L structural transition is recorded as the electron dose rate is monotonically decreased. Because the electron dose rate increases by focusing the electron beam, higher electron dose rate corresponds to larger convergent beam angle and consequently larger reflection spots in the electron diffraction patterns.

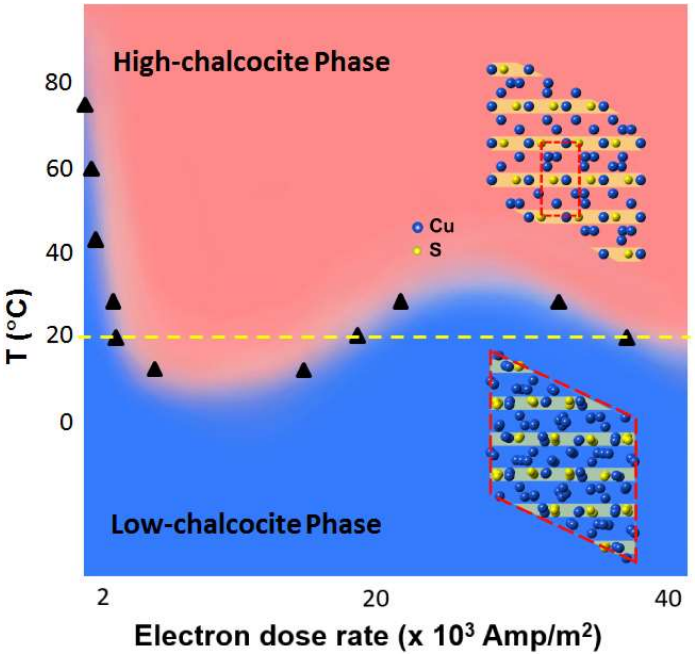


**Figure 2.** The structural phase diagram (temperature of the L-H phase transition as a function of electron dose rate) constructed from TEM experiments from individual $Cu_2S$ nanoplates. Electron-dose-rate values from individual nanoplate at the transitions are shown as black triangles. The structures of different phases are also shown, with their unit cells highlighted. Following the yellow dashed line indicates the sequence of transitions as a function of dose rate at room temperature.

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