Counting the Microscopic States of Molecular Specimens Using Electron Diffraction

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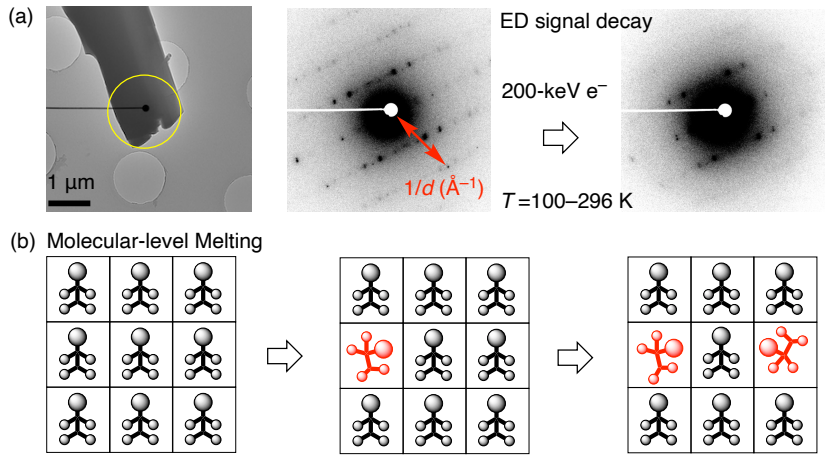
The ensemble properties of crystals are governed by distinct microscopic states (W_d). If the value of W_d of crystals can be quantified, it becomes comparable between crystals regarding properties, stabilities, and the molecular-level understanding of phase transition. However, there is currently no direct method to count the value of W_d experimentally.

Taking advantage of the unique local interactions between fast electrons (200 keV or above) and atoms, here, we propose a straightforward method to count the W_d of molecular crystals of sub-micrometer by electron diffraction (ED). Although ED is an established method for structural analysis,[1] we exploit its potential by kinetic analysis of diffracted intensity decaying and find the disordering of crystallinity under electron beam illumination is strongly related to the melting process of the bulk crystals. Using electrons to disorder molecular crystals (more than 15 examples) at variable temperatures (4−296 K), the sample-dependent decaying rates and temperature-dependent disordering behaviors allow us to derive the frequency factors A using the Arrhenius equation. Therefore, by applying Boltzmann's entropy formula, we could measure the W_d based on an experimentally determined cross-section-related constant. The values of W_d are degenerated into the countable range of tens to thousands, which greatly facilitates the understanding of various molecular crystals.



1) C. G. Jones, *ACS Cent. Sci.* **2018**, *4,* 1587.