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Seeing Electrons in Chemical Bonds – John Spence's Vision for Electron Microdiffraction and How to Realize it for Molecular Crystals

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By 1985, when I walked into John's office seeking a Ph. D project, John CH Spence had already published prolifically on HREM/STEM, electron channeling and ALCHEMI, cathodoluminescence, coherent bremsstrahlung, and CBED. But in that bgs (before google scholar) age, all I knew was from talking to the small community of Chinese students and visitors at ASU. I learnt about the excellence in electron microscopy at ASU, and John as one of star professors in this area. The project John initially assigned me was to determine the structure of Si (111) 7x7 surface reconstruction, which did not get far as the promised UHV TEM did not arrive and the structure was soon solved by Prof. Yagi's group at Tokyo Institute of Technology. Later we settled on CBED, also known as electron microdiffraction. My task was to measure the structure factors of GaAs and map the bonding charges. While post-doctoring at Oxford University, John developed a deep understanding of the dynamical theory of electron diffraction. In 1981, John had given a conference talk, entitled "The crystallographic information in localized characteristic loss electron images and diffraction patterns", in which he reported "the intensity distribution of energy-filtered intermediate and large energy loss images and diffraction patterns has been calculated. It is concluded that satisfactory interpretation of experimentally obtained images and diffraction patterns can only be achieved by matching with the calculated ones" [1]. From these insights and with John's constant encouragements, quantitative CBED method was developed based on the refinement of the energy-filtered experimental rocking curves with the calculated dynamical diffraction intensity using the Bloch wave method [2].

John is a true believer of experimental measurement. One of his often-said quotes is that new measurement leads to new science. This belief is vividly displayed in John's book "Lightspeed : The Ghostly Aether and the Race to Measure the Speed of Light", published by Oxford University Press in 2019. The book combines four of John's many passions, scientific history, sailing, writing and experimental measurement that he often talked about at almost daily lunch together, which I was privileged to be part of during 1990s. One time he told me that if he hadn't got the ASU position, he was going be to a science writer.

Our first experiment on GaAs was performed on a Philips 400T analytic TEM equipped with a Gatan Model 607 serial energy-loss spectrometer. The quality of experimental data is critical to the success and accuracy of structure factor refinements. To measure the rocking curves, I resorted to deflect the diffraction pattern over the entrance slit using a PDP-11 computer with a self-written Fortran and Assembly language code with advice from Peter Rez. It was difficult to keep a good CBED pattern throughout the serial recording for all the usual suspects that a TEM experiment could go wrong. The parallel recording of CBED patterns could be done by film, but the dynamical range is very limited. John got hold of a Photometrics (Tucson, AZ) CC210 charge-coupled device (CCD) camera, which was cooled by liquid nitrogen and was previously used in astronomy. By coupling to an electron scintillator designed for electrons of 100 keV, we recorded the first CBED pattern in parallel with a large dynamical range. Earlier, Peggy Mochel at University of Illinois introduced a CCD camera to VG STEM using optical lens coupling. The design at ASU used the scientillator/fiber-optical-coupling/CCD design, which minimizes the photon loss [3] and was widely adopted that led to the digital revolution in TEM .

John had a deep appreciation of what it takes to do a good measurement and a keen sense of latest developments. At ASU, John brought the first W-energy filter TEM (LEO 912, later became part of Zeiss) equipped with a Gatan CCD camera and the first imaging plates system (Fuji FDL 5000) in 1990s, which made quantitative CBED broadly applicable to inorganic crystals as well as energy-filtered diffuse scattering analysis [4]. In the same period, John also started his point projection microscopy and in-line holography reconstruction project, which evolved into coherent diffractive imaging, diffract and destroy and serial crystallography [5].

The crowning achievement of quantitative CBED is the observation of d-holes in cuprite (Cu_2O) [6]. The study of cuprite was suggested by Michael O'keeffe, a close collaborator and long-time friend of John. Michael investigated Cu_2O early in his career for its semiconductor properties and was intrigued by the two inter-penetrating network of linear Cu-O-Cu bonds. He had a beautiful cubic mineral sample of Cu_2O, which he gave to me. I cut it up and measured the structure factors together with Miyoung Kim, a student in John's group at that time. To obtain the electron densities, we developed a multipole model and fitted with the combination of low order electron structure factors and X-ray structure factors for medium and high order reflections. This took a while, but the result came out beautifully (Fig. 1). The d-holes image was published on the front cover of Nature and generated quite a bit of excitement. The New York Times reported the news and quoted John as saying: "It was as difficult as weighing the captain of a ship by weighing a ship with the captain on it and then subtracting the weight of the ship."

One of the challenges of quantitative CBED is how to apply to crystals with large unit cells, where the number of structure factors increases while the first-order Bragg diffraction angle decreases, which makes the rocking curve measurement difficult. With the development of direct electron detectors and beam technology and fast computers, these difficulties now can be overcome. Meantime, low-dose electron diffraction also becomes possible. These latest developments will be reviewed in this talk. Maybe in not-so-distant future, John's vision in seeing electrons in chemical bonds can be realized in molecular crystals for the study of molecular bonding, all thanks to John's impact on all these around him. I was lucky to be one of these.

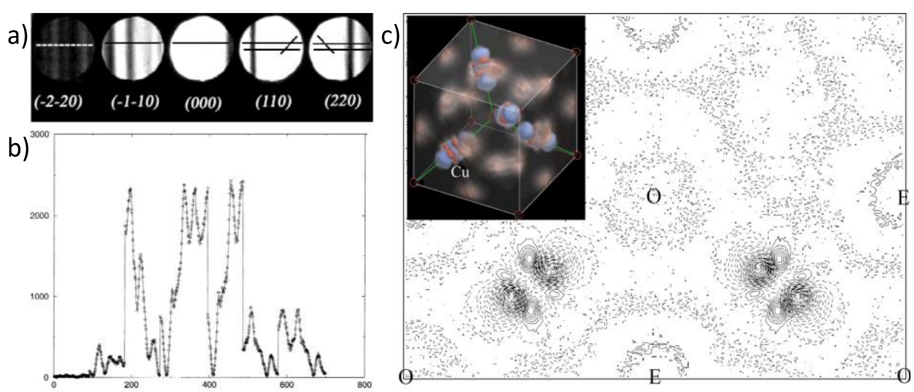

Figure 1. Measurement of electron densities in Cu_2O by quantitative CBED. a) Experimental CBED pattern, b) Intensities (open circles) taken along lines in a) and the fitted theory (line), c) The obtained 3D difference charge density and 2D section on containing the Cu-O-Cu bond [6].

References:

[1] J.C.H. Spence, Ultramicroscopy, 7 (1981) 107-107.
[2] J.M. Zuo, J.C.H. Spence, M. O'keeffe, Bonding in GaAs, Phys. Rev. Lett., 61 (1988) 353-356.
[3] J.C.H. Spence, J.M. Zuo, Review of Scientific Instruments, 59 (1988) 2102-2105.
[4] J.M. Zuo, J. Pacaud, R. Hoier, J.C.H. Spence, Micron, 31 (2000) 527-532.
[5] H.N. Chapman, S.S. Hasnainb, U. Weierstall, *John C.H. Spence (1946–2021)*, IUCrJ **8,** (2021) 705.
[6] J.M. Zuo, M. Kim, M. O'Keeffe, J.C.H. Spence, Nature, 401 (1999) 49-52.

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