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On the fidelity and importance of first structural determinations

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The dawn of the X-ray diffractometric methods for determining crystal structures at the beginning of the 20th century is well known in the crystallographic community worldwide. It has been extensively described in many crystallographic textbooks as a milestone in the development of all natural sciences. The crystal structures determined by Max von Laue, William Henry Bragg, William Laurence Bragg, Victor Moritz Goldschmidt, Linus Pauling, Gregori Aminoff, Robert James Havighurst, Lars Vegard, John Desmond Bernal, William Houlder Zachariasen, Kathleen Lonsdale and other structural-crystallography pioneers between 1912 and 1929, *i.e.* about a century ago, to today are the most elementary examples in solid-state physics and chemistry courses. The first experimental setups established the basis of the most fundamental classification of diffractometric methods into polychromatic and monochromatic ones. The photographic cameras designed by Laue and Weissenberg (1924) were standard diffractometric equipment in X-ray laboratories until the advent of automatic diffractometers in the 1970s. Apart from the simplest highest-symmetry crystal structures of such minerals as halite, fluorite, diamond, graphite and metals, the structures of organic compounds, such as hexamethylenetetramine (Dickinson & Raymond, 1923; Gonell & Mark, 1923) and hexamethanebenzene (Lonsdale, 1928; Lonsdale, 1929), were also revealed and published. They remain seminal and milestone structures, which commenced the ongoing pursuit of understanding the microscopic basis of chemistry, physics and biology (Pauling, 1939). Considering the immense progress in technologies between the first decades of the 20th century and now, the question arises as to whether the quality of those first determinations is compatible with today's standards. In particular, these structures are deposited in crystallographic databases and serve not only as historical records but also as structures used—alongside more recent results—in ongoing analyses and research.

The validation of the crystal structures of organic compounds appears straightforward, as it can be performed by inspecting the bond lengths, bond angles, standard deviations, presence and location of hydrogen atoms, refined isotropic or anisotropic atomic-displacement parameters, rigid-bond test (Hirshfeld, 1976), R and other reliability factors. The Cambridge Structural Database (CSD) provides some routine tools for the validation, such as the R or estimated-standard deviations cut-offs, not to mention the *PLATON* program (Spek, 2020). Nonetheless, mistakes are inevitable (*e.g.* Marsh, 2009; Marsh *et al.*, 2002; Podsiadło *et al.*, 2007). For ionic crystals, the validation may be even trickier. In this issue of *Acta Crystallographica B*, Peter Gross & Nik Reeves-McLaren (2026) undertook the survey and the validation of all the 464 structures reported until 1929 and deposited in the Inorganic Crystal Structure Database (ICSD). They applied the methodology of bond-valence sums (Brown & Altermatt, 1985), the global-instability index (Salinas-Sanchez *et al.*, 1992) and the Madelung contribution to lattice-cohesion energy (Madelung, 1918; Hoppe, 1995). In this way, in a small portion of these historical determinations, they identified mistakes, analysed their origins and proposed a method to indicate the inconsistencies in the ICSD deposits. Gross & Reeves-McLaren (2026), by undertaking the evaluation of 'historic' deposits, have demonstrated that the majority of them are consistent with the later structural determinations.

When taking into account the immense technological gap between the sophisticated diffractometers, refined methods and computer software available in the 21st century, and the first X-ray equipment from the second and third decades of the 20th century, when the diffraction cameras and spectrometers were designed and built by researchers, including the blowing of X-ray tubes, one can wonder if some inconsistencies are bound

to occur. Not to mention the arduous work of performing the computations 'manually', with slide rulers and logarithmic tables, before the Beevers–Lipson strips (Beevers & Lipson, 1934; Lipson & Beevers, 1936) or electronic computers were invented.

There are obvious differences in the complexity of the tackled structures on one hand but on the other hand, in very many cases, the time dedicated to the determinations is significantly different, too. Dame Kathleen Lonsdale devoted three years between 1927 and 1929, when she held an Amy Lady Tate Scholarship at Leeds University, to determining the crystal structures of hexamethylbenzene and hexachlorobenzene (Glazer, 2026, private communication). Her seminal papers clarified the structure of the benzene ring (Lonsdale, 1928; Lonsdale, 1929). The accuracy of her structure is remarkable, although the precision of the experimental method and the level of theory for processing the data fell significantly short of current standards. But does it justify the exclusion of these structures from the CSD?

Naturally, each structural determination should be carefully analysed. Undoubtedly, it is important to review the deposited structures, not only the first ones but also those presently determined with modern sophisticated tools designed for this purpose, so that the databases of crystal structures provide a reliable source of information for their users.

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