CC/NUMBEK 39
SEPTEMBER 29, 1980

This Week's Citation Classic

Ibers J A & Hamilton W C. Dispersion corrections and crystal structure refinements.
Acta Crystallogr. **17**:781-2, 1964.
[Chem. Dept., Brookhaven Nat. Laboratory, Upton, NY]

The effects of anomalous dispersion are formulated for incorporation into the least-squares method of crystal struc-ture refinement. A formulation for the Fourier coefficients that renders the re-sultant electron density map indepen-dent of radiation is also given. [The *SCI®* indicates that this paper has been cited over 345 times since 1964.]

James A. Ibers
Department of Chemistry
Northwestern University
Evanston, IL 60201

August 21, 1980

"In 1962 the late Walter C. Hamilton and I were among those few structural chemists who had access to state-of-the-art computers. We were assembling a library of crystallographic programs. Both of us were convinced that the proper way to refine crystal structures was through the full-matrix, least-squares method, in which one minimizes the differences between observations and calculations from a structural model by modifying (and hence refining) the model. The required calculations became feasible in the early 1960s with the introduction of the IBM-704 computer.

"In late 1962 S. Raman, a postdoctoral fellow at Brookhaven, called my attention to the problem of dispersion corrections in crystal structure analysis and asked if I might somehow include such corrections in my current least-squares computer program. The mathematical formulation I derived was extremely simple, as were the necessary modifications to my already heavily modified version of the least-squares program from Oak Ridge.

"Undo Patterson, one of the founders of modern crystallography, about this time distributed to a number of colleagues some comments on the problem of dispersion effects. His paper was subsequently submitted to *Acta Crystallographies* in March and published in December of 1963.[1] It is my recollection that I did not see Patterson's paper in pre-submitted form, but I did see the final paper before publication. Patterson's main thesis was that the observations should be corrected for dispersion effects. I was convinced that my method of handling the problem, already implemented at Brook-haven, was preferable: in the spirit of the least-squares procedure one should leave the observations alone and incorporate dispersion effects into the model. Correspondence with Lindo ensued. While he did not agree that my formulation was necessarily better, he did encourage me to publish it. He also asked how in my formulation I might make electron density maps wave-length independent. I discussed this problem with Walter who evolved the method of handling the Fourier coefficients described in our paper.

"There are several reasons why our paper has been frequently cited. The availability of high-speed computers has led to full-matrix least-squares being the standard method of refinement of small-molecule structures and our formulation was incorporated into widely distributed computer programs for least-squares calculations, including our own and the ORFLS program from Oak Ridge. The formulation in our paper lends itself naturally to the computations necessary for the direct determination of absolute configurations. Finally, it is now realized that dispersion effects can be much more serious than was appreciated in 1963 and that under certain circumstances[2] very large errors can result if these effects are neglected."

1. **Patterson A L.** Treatment of anomalous dispersion in X-ray diffraction data. *Acta Crystallogr.* **16**:1255-6, 1963.
2. **Ueki T, Zalkin A & Templeton D H.** Crystal structure of thorium nitrate pentahydrate by X-ray diffraction. *Acta Crystallogr.* **20**:836-41, 1966