

Using the Dispersion Corrections on either side of an absorption edge of an atom in a crystal to solve its crystal structure.

### Synopsis.

Near the absorption edge of an item, the atomic form factor changes, and this change is expressible by the formula  $f = f_0 + \Delta f' + i\Delta f''$  (Honl 1933).  $\Delta f'$  exists on either side of the edge while  $\Delta f''$  exists only on the shorter wavelength side. The effect of  $\Delta f'$  is mostly to decrease the scattering factor by a rather small amount. In spite of this small changes it has most elegantly been used to distinguish atoms whose atomic numbers are close to each other (Mark and Szillard 1925, Bradley and Rodgers 1934, Jones and Sykes 1937).

Changing the wavelength of the incident radiation near about the absorption edge of an atom in a crystal is, therefore, equivalent to replacing the atom isomorphously by another having a slightly different scattering factor. To see if this can be used to solve crystal structures intensity data was collected of  $\text{KMnO}_4$  using  $\text{CuK}\alpha$  [ $\Delta f'(\text{Mn}) \approx -1$ ] and  $\text{FeK}\alpha$  [ $\Delta f'(\text{Mn}) \approx -4$ ]. The radiations were obtained by changing the targets in a Shearer and later in a Coolidge tube. hko and hol data were collected from a cylindrical crystal using 15 to 20° oscillation photographs. The multiple film technique was used - the first film was used as an effective filter to cut off <sup>the</sup> excessive fluorescent radiation present when the incident radiation was  $\text{CuK}\alpha$ . Visual estimates of intensity were made using a calibrated film strip. In reducing the data the film to film "ratio" was determined for each of the two radiations. We faced many experimental problems - the scaling between different sets of oscillation photographs, absorption correction and

absolute scaling but these were not insurmountable. This was demonstrated by the considerable differences that were observed for the two radiations - these differences being greater at larger angles of scattering.  $F_{CuK\alpha}^2$  or  $F_{FeK\alpha}^2$  Pattersons gave the position. But the purpose of the exercise was to determine the heavy atom position of the Anomalous Atom by comparing the data obtained at different wavelengths.  $(F_{\lambda_1}^2 - F_{\lambda_2}^2)$  synthesis similar to the isomorphous difference Patterson of Buerger (1942) was much clearer Patterson as the Normal Atom interactions had been eliminated. A rather novel form of the Patterson  $(F_{\lambda_1} - F_{\lambda_2})^2$  gave only the interactions of the Anomalous Atoms i.e. only Mn atom interactions were present in the map. The map clearly indicated that this method works. With Mn positions known it was easy to phase the reflections, get the Fourier Projections and solve the structure. Data on  $KClO_4$  is also being collected to compare the isomorphous and Anomalous methods. It seems to us that we have established the feasibility of this method. With sealed tubes, Weissenberg cameras the experimental problems will be much less.

Can we then use this new technique for solving non-centro symmetric structures? In theory, yes. For we can use the method similar to the isomorphous method used by Bokhoven, Schoone and Bijvoet (1951) for solving the structure of Strychnine Sulphate (Selenate). In our two radiation methods also we will have a similar ambiguity in phases - the two possible phase angles for any particular reflection being symmetrical about the real axis in the Argand diagram. Can we resolve this ambiguity? We believe we can.

The inspired suggestion made by Bijvoet (1949) that the

violation of Friedel's Law when the incident radiation is close to but shorter than the absorption edge (Coster, Knoll and Prins (1930)) can itself be used to determine the phases of X-ray reflections. (It seems most strange to me that this remarkable method which has so much implication to X-ray crystallography has not yet been exploited sufficiently)

If, therefore, the intensity of a reflection and its inverse are measured and the actual magnitude of  $\Delta f''$  is known the phase could be determined. However, there would again be an ambiguity but this time the two possible alternatives will be symmetric about the imaginary axis! This is because  $\Delta f''$  (unlike  $\Delta f'$ ) is scattered a quarter cycle in advance of the real part. We, therefore, feel that by combining our method of using  $\Delta f'$  and that of Bijvoet of using  $\Delta f''$  the inherent ambiguity can be removed.

Strychnine Sulphate (with  $\text{CuK}_\alpha$  or  $\text{FeK}_\alpha$  radiation) may not be the best substance to test out this idea. Strychnine Selenate may be a better substance.

Eight figures illustrate this lecture. In this work which posed many experimental problems, I was most ably assisted by Mr. Venkatesan, my young and diligent doctoral student.

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