

## Anomalous Scattering of X-Rays by Centro-Symmetric Crystals

### II. Tutton's Cobalt Salt, $(\text{NH}_4)_2\text{Co}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$

A. C. HAZELL

*Department of Inorganic Chemistry, University of Aarhus, Aarhus C, Denmark*

As part of an investigation into the use of the anomalous scattering of X-rays in the determination of centro-symmetric crystal structures a study has been made of the  $hk0$  projection of  $(\text{NH}_4)_2\text{Co}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$ . In this case the imaginary part of the anomalous scattering of  $\text{CuK}\alpha$  radiation by cobalt ( $\Delta f'' = 3.95$ ) is too large to be neglected.

The problem is simplified by the fact that the cobalt atom lies on a special position and so the two sets of data (recorded with  $\text{CuK}\alpha$  and  $\text{MoK}\alpha$ ) may be scaled relative to each other *via* the reflections to which the cobalt atom does not contribute.

As part\* of an investigation into the use of the anomalous scattering of X-rays in the determination of centrosymmetric structures a study has been made of the  $hk0$  projection of Tutton's cobalt salt,  $(\text{NH}_4)_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

In the determination of structures containing anomalous scatterers by the comparison of intensities recorded with two radiations the problems are as follows: correct scaling of the data, determination of the positions of the anomalous scatterers, and the determination of the signs of the structure factors relative to those calculated from the positions of the anomalous scatterers alone.

The cobalt atom in Tutton's salt lies on a special position which means that the position of the anomalous scatterer is known, it also means that there is a class of reflections to which the anomalous scatterer does not contribute and so this group of reflections provides a means for obtaining the relative scale factor between the two sets of data. Thus the first two problems are solved and the  $hk0$  projection provides a model for testing a procedure previously described<sup>1</sup> for the determination of signs in cases where the imaginary component of the anomalous dispersion (Table 1) is too large to be neglected.

\* The notation used is that of Part I.<sup>1</sup>

Table 1. Anomalous dispersion corrections<sup>7</sup> for cobalt.

Radiation	$\Delta f'$	$\Delta f''$
CuK $\alpha$	-2.51	3.95
MoK $\alpha$	0.37	1.06

## EXPERIMENTAL AND CRYSTAL DATA

The salt is monoclinic with space group  $P2_1/a$  ( $C_{2h}^5$ , No. 14) and cell dimensions<sup>8</sup>  $a = 9.247 \pm 0.001$ ,  $b = 12.519 \pm 0.001$ ,  $c = 6.239 \pm 0.001$  Å,  $\beta = 107^\circ 2' \pm 1'$ . There are 2 formula units per cell. The linear absorption coefficient is  $\mu = 129.3$  cm<sup>-1</sup> for CuK $\alpha$  radiation and  $\mu = 16.55$  cm<sup>-1</sup> for MoK $\alpha$  radiation. The crystals are elongated in the [001] direction.

Intensities were measured with both CuK $\alpha$  and MoK $\alpha$  radiations. The same crystal, a pillar of cross section  $0.23 \times 0.24$  mm was used for both sets of data.

Intensities for the  $hk0$  projection were recorded with a linear diffractometer of the Arndt-Phillips design.<sup>3</sup> With molybdenum radiation a scintillation counter was used in conjunction with balanced filters (SrO, ZrO<sub>2</sub>), and a pulse height analyser; two out of each four possible symmetry related reflections were measured. For the copper radiation a proportional counter was used together with a Ni filter and a pulse height analyser. As with the molybdenum data pairs of symmetry related intensities were measured, but in this case each intensity was measured twice. The upper limit of the Bragg-angle attainable with the diffractometer for equatorial layers is 30°; whilst this gives sufficient data with MoK $\alpha$  radiation this is not so for CuK $\alpha$  radiation. Additional data with CuK $\alpha$  radiation were obtained from integrated Weissenberg-photographs; the intensities were measured photometrically and scaled against the diffractometer data.

The diffractometer data were processed using an algol program written by Rita Grønbaek Hazell, the data were corrected for absorption assuming the crystal to be cylindrical and using the values tabulated in *International Tables*.<sup>4</sup>

## SCALING OF DATA

The two sets of data were scaled and corrected for an overall temperature factor by Wilson's method.<sup>5</sup>

As there are only 2 molecules in the cell the cobalt atom must lie at the origin and so the contribution of the cobalt atom is:

$\cos 2\pi(hx + ky) = +1$  for  $hk0$  reflections with  $h + k = 2n$ , and  
 $\cos 2\pi(hx + ky) = 0$  for those with  $h + k = 2n + 1$ . For those reflections

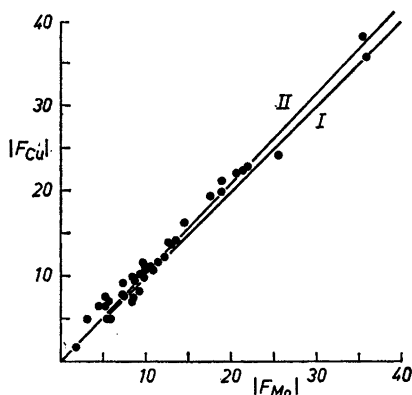


Fig. 1.  $|F_{Cu}|$  vs.  $|F_{Mo}|$  for  $hk0$  reflections with  $h + k = 2n + 1$ . Line I has gradient 1.00, line II is the least-squares best line of the form  $|F_{Cu}| = M|F_{Mo}|$  through the points and has gradient 1.045.

with  $h + k = 2n + 1$   $F_{\text{Cu}} = F_{\text{Mo}}$  and so a plot of  $|F_{\text{Cu}}|$  vs.  $|F_{\text{Mo}}|$  should give a straight line through the origin, the gradient giving the relative scale factor between the two sets of data. This is shown in Fig. 1. Ideally the gradient should have been unity, but in fact a value of 1.045 was obtained. The data were placed on the correct relative scale and then scaled to the mean value from the Wilson plots.

#### SIGN DETERMINATION

A plot of  $|F_a(H)| / |\sum_a \cos 2\pi H \cdot \theta_a|$  against  $|F(H)| / |\sum_a \cos 2\pi H \cdot \theta_a|$  should consist of three curves<sup>1</sup> corresponding to  $S_F = S_A$ ,  $S_F = -S_A$  and  $\sum_a \cos 2\pi H \cdot \theta_a = 0$ . In this case  $\sum_a \cos 2\pi H \cdot \theta_a = +1$  for reflections  $hk0$  with  $h + k = 2n$ . The observed values of  $|F_{\text{Cu}}|$  are shown plotted against  $|F_{\text{Mo}}|$  in Fig. 2 together with the curves calculated for  $\Delta f' = -2.88$  and  $\Delta f'' = 3.95$ . In Fig. 2 reflections for which  $S_F = S_A$  are represented by open circles, and those for which  $S_F = -S_A$  by full circles.

As may be seen the majority of points lies close to the appropriate curve and that with the notable exception of 040 the phases of all but some of the weakest reflections can be determined by inspection.

The correct signs are taken to be those obtained after a least-squares refinement carried out with Mo-data. The structure of  $(\text{NH}_4)_2\text{Co}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$  has not been previously determined; however, the salt is one of an isomorphous series, of which the structures of several have been determined, *e.g.* the nickel salt.<sup>6</sup> The starting parameters were the fractional coordinates of the nickel

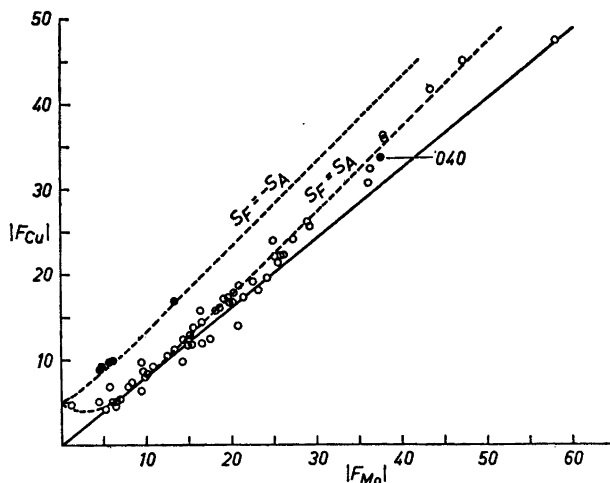


Fig. 2.  $|F_{\text{Cu}}|$  vs.  $|F_{\text{Mo}}|$  for  $hk0$  reflections with  $h + k = 2n$ . Reflections for which  $S_F = S_A$  are represented by open circles, those for which  $S_F = -S_A$  by full circles. The calculated curves for  $\Delta f' = -2.88$ ,  $\Delta f'' = 3.95$  are shown by broken lines. The line

$$|F_a(H)| = |F(H)| \sqrt{\frac{k^2}{1 + k^2}}$$

salt<sup>6</sup> and an overall temperature factor ( $B = 1.5 \text{ \AA}^2$ ) from the Wilson plot. Anisotropic refinement using Grønbaek's block-diagonal least-squares program reduced the  $R$ -value to 0.062 with the Mo-data (155 reflections and 49 parameters) and to  $R = 0.065$  for the Cu-data (108 reflections and 49 parameters).

#### DETERMINATION OF $|\Delta F'|$

In general the positions of the anomalous scatterers are not known, but a Patterson function calculated with  $|\Delta F'|^2$  as coefficients will contain only vectors between the anomalous scatterers. It should be possible<sup>1</sup> to extract  $|\Delta F'|$  from the observed data using the equation:

$$|\Delta F'(H)| = \{|F(H)| - \sqrt{(F(H)^2 - (1 + k^2)(F(H)^2 - F_a(H)^2))}\} / (1 + k^2) \quad (1)$$

In this example  $|\Delta F'(hk0)|$  should be  $|\Delta f'_a|$  for those reflections with  $h + k = 2n$  and zero otherwise.

The calculation of  $|\Delta F'|$  from the observed data revealed a computational hazard, *i.e.* for reflections for which  $S_F = S_A$  errors in the data can lead to  $(1 + k^2)(F(H)^2 - F_a(H)^2)$  being greater than  $F(H)^2$  which gives rise to a complex solution for  $|\Delta F'(H)|$ . The limiting values at which this occurs are given by

$$|F_a(H)| = |F(H)| \sqrt{(k^2 / (1 + k^2))} \quad (2)$$

as is shown on Fig. 2. This line is tangent to the curve for  $S_F = S_A$ , touching it at

$$|F(H)| / |\sum_a \cos 2\pi H \cdot \theta_a| = -( \Delta f_a'^2 + \Delta f_a''^2 ) / ( \Delta f_a' ). \quad (3)$$

Thus there is a region where small errors in the data can cause trouble. In such cases  $|\Delta F'(H)|$  can be approximated by  $||F_a(H)| - |F(H)||$  unless this should be greater than  $|\sum_a \Delta f_a'|$  where an arbitrary value, *e.g.*  $|\sum_a \Delta f_a'|$  or zero, could be used.

For  $hk0$  with  $h + k = 2n$  there were 12 out of 67 reflections which gave complex solutions for  $|\Delta F'(H)|$ , for 7 of these  $||F_a(H)| - |F(H)||$  was bigger than  $|\sum_a \Delta f_a'|$ .

#### CONCLUSIONS

The signs of structure factors relative to the sign of an anomalous scatterer may be determined even if the imaginary component,  $\Delta f''$ , is too large to be neglected.

The use of eqn. 1 to obtain  $|\Delta F'|$  from the observed data is not always possible in practice since for some reflections small errors in the data lead to complex solutions of the equation for  $|\Delta F'|$ . In such cases simpler approximations must be used. When eqn. 1 can be used, in this example for about 80 % of the reflections, it gives a better estimate of  $|\Delta F'|$  than is obtained by simpler approximations.

*Acknowledgements.* The author is indebted to the *Carlsberg Foundation* for providing the linear diffractometer, to Rita Grøn­bæk Hazell for her help in collecting the data, and for advice on computing problems, and to Professor S. E. Rasmussen for his interest and encouragement.

## REFERENCES

1. Hazell, A. C. *Acta Chem. Scand.* **20** (1966) 170.
2. Hartman, P. and Woensdregt, C. F. *Acta Cryst.* **17** (1964) 779.
3. Arndt, U. W. and Phillips, D. C. *Acta Cryst.* **14** (1961) 807.
4. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1959, Vol. II, p. 295.
5. Wilson, A. J. C. *Acta Cryst.* **2** (1949) 318.
6. Grimes, N. W., Kay, H. F. and Webb, M. W. *Acta Cryst.* **16** (1963) 823.
7. Cromer, D. T. *Acta Cryst.* **18** (1965) 17.

Received March 7, 1967.