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Anomalous Scattering of X-Rays by Centro-Symmetric Crystals

III. $BaNi(CN)_4,4\ H_2O$*

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The anomalous scattering of Cu$K\alpha$ radiation by the nickel atom in $BaNi(CN)_4$, 4 H_2O has been used to determine the signs of the structure factors for the $hk0$ zone. This is an example of a structure where the anomalous scatterer is not the heaviest atom, and further there is interference from a second type of anomalous scatterer *viz.* barium.

The recent redetermination [1] of the structure of barium tetracyanonickelate(II) tetrahydrate by Krebs Larsen, Grønbæk Hazell, and Rasmussen has provided two accurately measured sets of data. One set recorded with Cu$K\alpha$ radiation using an integrating Weissenberg camera, the intensities being measured photometrically; the other set with Mo$K\alpha$ radiation was recorded with a linear-diffractometer of the Arndt-Phillips design [2] using a scintillation counter in conjunction with balanced filters (SrO, ZrO_2) and a pulse height analyser. The two sets of data were collected from different crystals.

For this work the data were corrected for absorption and for thermal vibrations and were placed on an absolute scale. The scale and overall temperature factors were obtained by Wilson's [3] method.

In the simplest treatment [4,5] there is assumed to be only one type of anomalous scatterer, which is excited by one of the two radiations. Furthermore the imaginary part of the anomalous scattering is neglected. In this case the anomalous scattering by the barium atom is considerable (Table 1); however, it was decided to try the simple approach to see how well it would succeed.

Assuming for the purpose of the example that only the position of the nickel atom is known (*i.e.* at the origin, which means that $\cos 2\pi\, H\cdot\theta_a = +1$) it is sufficient to plot $|F_{Cu}|$ *vs.* $|F_{Mo}|$. The signs of the structure factors may then be determined by inspection. Table 2 contains the number of reflections

* The notation used in this paper is the same as that in Part I.[5]

Table 1. Anomalous dispersion corrections [7] for nickel and barium.

Radiation	Atom	$\Delta f'$	$\Delta f''$
Cu$K\alpha$	Ni	−3.20	0.67
Cu$K\alpha$	Ba	−1.66	8.30
Mo$K\alpha$	Ni	0.37	1.20
Mo$K\alpha$	Ba	−0.48	2.66

for which the signs are correct, incorrect, or indeterminate, and the quantity N which is defined [6] as the percentage of correct signs minus the percentage of incorrect signs. The results so obtained are compared with those calculated from the nickel position alone. The correct signs are taken to be those from the full ($R = 0.047$ for 1269 reflections) structure determination.[1]

Table 2. The correctness of the signs determined from the nickel atom alone and from the anomalous scattering of the nickel atom.

	Correct	Indeterminate	Incorrect	N
Ni alone	65	0	31	35 %
Anomalous scattering	89	3	4	91 %

The rather surprising success of the method in this case is due to the fact that the nickel atom is in a special position so that although $|\Delta f_{Ba}'|$ is large compared with $|\Delta f_{Ni}'|$ the case where $\Delta f_{Ba}' \cos 2\pi\, H\cdot\theta_{Ba}$ is of greater magnitude but of opposite sign to $\Delta f_{Ni}' \cos 2\pi\, H\cdot\theta_{Ni}$ cannot occur. Since the sign of a structure factor will usually be the same as the sign of the barium atom's contribution the large imaginary component $\Delta f_{Ba}''$ will tend to reduce the effect of $\Delta f_{Ba}'$.

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REFERENCES

1. Larsen, F. K., Hazell, R. G. and Rasmussen, S. E. *Acta Chem. Scand. In press.*
2. Arndt, U. W. and Phillips, D. C. *Acta Cryst.* **14** (1961) 807.
3. Wilson, A. J. C. *Acta Cryst.* **2** (1949) 318.
4. Ramaseshan, S., Venkatesan, K. and Mani, N. V. *Proc. Indian Acad. Sci* **A 46** (1957) 95.
5. Hazell, A. C. *Acta Chem. Scand.* **20** (1966) 170.
6. Hazell, A. C. *Acta Cryst.* **17** (1964) 1155.
7. Cromer, D. T. *Acta Cryst.* **18** (1965) 17.

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