Short Communications

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Incorrect unit-cell dimensions revealed by anomalous scattering.

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The unit-cell dimensions of hollandite, $BaFeMn_7O_{16}$, were given by Mukherjee (1960) as

$$a = 10\cdot03,\ b = 5\cdot76,\ c = 9\cdot90\ \text{Å};\ \beta = 90°\ 42',$$

space group $P2_1/n$, whereas Byström & Byström (1950) gave $b = 2\cdot87 \pm 0\cdot01$ Å. The latter took powder, rotation and Weissenberg photographs with Cr $K\alpha$ radiation; from structural considerations they concluded that a double b axis would be preferable, but they stated that *in none of the rotation photographs of different hollandites is there any indication of an extra layer line.*

Mukherjee used Fe $K\alpha$ radiation and his rotation photograph (Fig. 1(*a*)) does clearly show a weak first layer line corresponding to $b = 5\cdot76$ Å, although a corresponding Cu $K\alpha$ rotation (Fig. 1(*b*)) does not. Thus with Cu $K\alpha$ (as with Cr $K\alpha$) the apparent identity distance along b would be only one-half the true value as revealed by Fe $K\alpha$ radiation. The third layer line, even if present, would not be observable under the experimental conditions used.

The weakness of the odd layer line in Fig. 1(*a*) indicates that along the **b** direction two closely similar arrangements alternate at a $b/2$ interval (Lipson & Cochran, 1953). If the main difference between these two parts lies essentially in an alternation of Mn and Fe, separated by $b/2$, then the disappearance of the first layer lines on Cu $K\alpha$ and Cr $K\alpha$ b-rotation photographs is accounted for by the approximately equal scattering powers of Mn and Fe for either of these radiations. Tables 3·3·2B and 3·3·2A of *International Tables for X-ray Crystallography* (1962) show that although there is a dispersion correction to be applied, for each radiation the corrections for Mn and Fe are closely similar. The *International Tables* do not give values of the dispersion corrections for Fe $K\alpha$, but it is clear that they will be very different for Mn and Fe (see Table 1, where interpolated values are suggested).

Table 1. *Dispersion corrections for* Mn, Fe *and* Ba *corresponding to various radiations*

		Cr $K\alpha$	Fe $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
Z		2·290 Å	1·936 Å	1·541 Å	0·709 Å
25	$\Delta f'$ Mn	−1·8	(−4·0)	−0·5	0·4
	$\Delta f''$ Mn	0·8	0·6	3·0	0·9
26	$\Delta f'$ Fe	−1·6	(−2·0)	−1·1	0·4
	$\Delta f''$ Fe	0·9	0·7	3·4	1·0
56	$\Delta f'$ Ba	(−11)	(−6)	−2·1	−0·4
	$\Delta f''$ Ba	8	13	8·9	3·0

The difference in scattering power thus produced accounts for the appearance of the weak odd layer line on the Fe $K\alpha$ b-rotation photograph. It follows that when it is necessary to distinguish between two atoms having nearly the same scattering power for X-rays, it may be possible to do so by using a radiation for which their dispersion corrections are different, in either magnitude or phase.

The case of Mo $K\alpha$ radiation (Fig. 1(*c*)) is interesting. Here there is no differential dispersion correction, but a weak, diffuse third layer line *streak* occurs, indicating some disorder in the structure. There is a sharp cut-off in the spectra of all the reflexions at $\lambda = 0\cdot36$ Å, which is presumably $\lambda_{\min}$ for the tube voltage used. If there had been a first layer line it would have occurred just within this position and should have been observable, since Fig. 1(*a*) shows that the first layer-line spots do not lie on the white-radiation streaks corresponding to the second layer-line spots. No such first layer line occurs. This absence would be expected, since the dispersion corrections for Mo $K\alpha$ radiation do not differentiate between Mn and Fe.

Any structure determination must of course allow for the large dispersion corrections of the Ba scattering factor, if Cr, Fe or Cu $K\alpha$ radiations are used.

Cu $K\alpha$ radiation, however, is contraindicated because of its high absorption by both Fe and Mn (see Table 2).

Table 2. *Absorption by* Mn, Fe *and* Ba *of various radiations*

	Cr $K\alpha$ 2·290 Å	Fe $K\alpha$ 1·936 Å	Cu $K\alpha$ 1·541 Å	Mo $K\alpha$ 0·709 Å
(μ/ϱ)Mn	94	60	285	34·7
(μ/ϱ)Fe	109	70	308	38·5
(μ/ϱ)Ba	460	540	330	43·5

This accounts for the weakness of Fig. 1(*b*) and its high fluorescent background.

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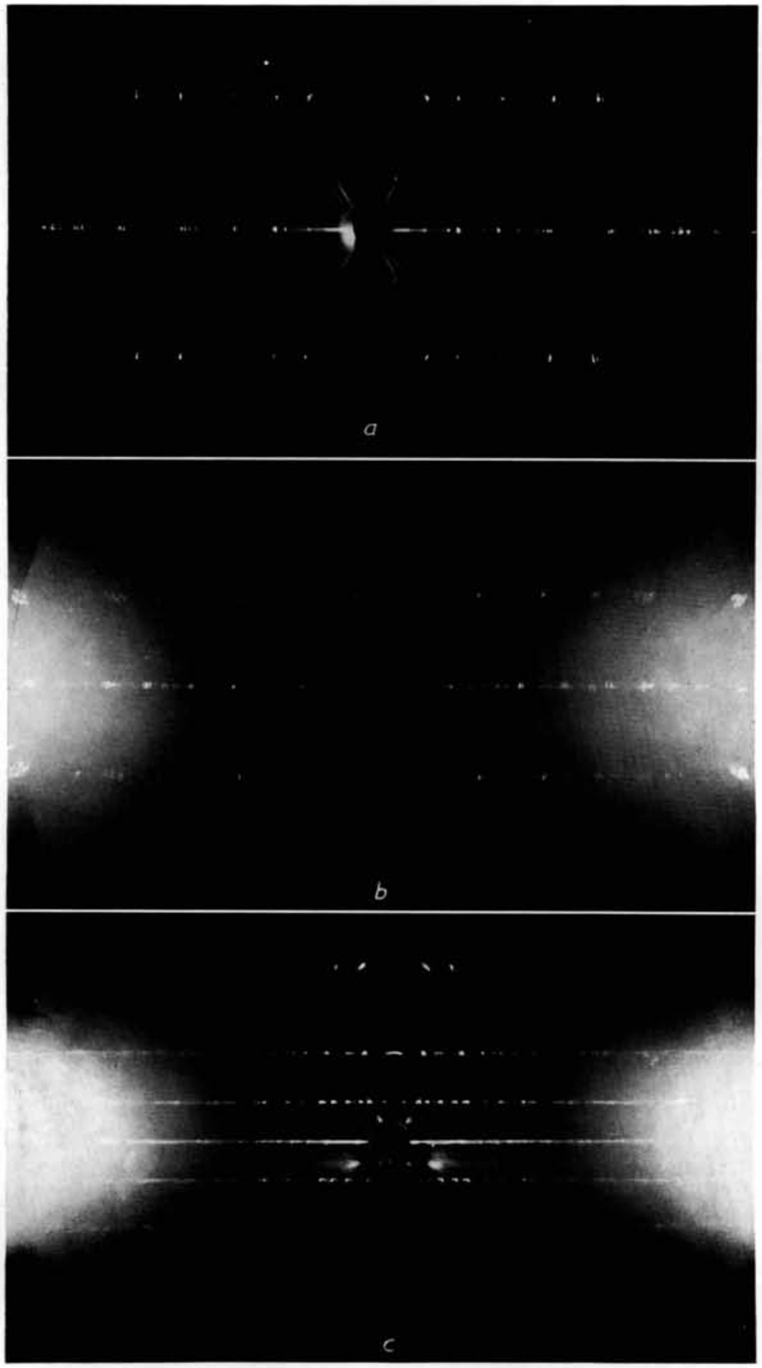

Fig. 1. Rotation photograph of hollandite about the *b* axis.
(*a*) With Fe $K\alpha$ radiation, (*b*) With Cu $K\alpha$ radiation, (*c*) With Mo $K\alpha$ radiation.