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A systematic use of Cu $K\alpha$ and Cu $K\beta$ for collecting intensity data. By T. WATANABÉ and I. TAGUCHI,* *Faculty of Science, Osaka University, Osaka, Japan*

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In collecting intensity data by the visual method, it is usual to estimate the photographic density of each reflection, using a standard intensity scale. At small angles $K\alpha_1$ and $K\alpha_2$ emerge into a single spectrum and at very large angles they are completely separated. Between these two extremes, these doublets are partly overlapped so that one has to consider this effect if he wishes to get integrated intensity. The splitting depends not only upon the angle of reflection but also upon the collimator and the size of the crystal, and it is usual to use some conventional means to convert the observed values into integrated intensity. The inaccuracy caused by these conventional means can be removed by the use of the integrating type of Weissenberg camera. However, this technique requires considerable time of exposure and moreover the widely separated doublets appearing near the edge of a film cannot be integrated, if one has to use a very small crystal, which is often the case.

We have been using Cu $K\alpha$ as well as Cu $K\beta$ in collecting intensity data in a systematic way. This systematic use of the two radiations has proved not only to increase the number of reflections but also to give a reliable correlation factor for those partly splitted spectra. There are some more advantages in this technique as described in the following.

If the intensity of spectra is estimated along with those due to Cu $K\alpha$ as well as Cu $K\beta$ in the same photograph, two series of intensity data can be obtained simultaneously. Intensity data from Cu $K\beta$ must, of course, be obtained by using a standard intensity scale made of Cu $K\beta$, which can be obtained simultaneously on the same film when an intensity scale of Cu $K\alpha$ is prepared. Two series of relative $|F_o|^2$ values corresponding to Cu $K\alpha$ and Cu $K\beta$ can be obtained if appropriate geometrical corrections are made. The linear absorption coefficients μ (Cu $K\beta$) for heavier atoms, if necessary, can be obtained using Walter's λ^{-3} rule.

Plotting the ratios of the two series of relative $|F_o|^2$ values versus $(\sin \theta/\lambda)^2$, a correlation factor of Cu $K\alpha_1$ and Cu $K\alpha_2$ can automatically be obtained. The ratios to be obtained are schematically shown in Fig. 1. The crosses in the region *A* are the ratio $|F_o|_{\alpha_1}^2/|F_o|_{\beta}^2$, where the numerator is obtained from partially overlapped spectra due to $K\alpha_1$ and $K\alpha_2$. The values designated as crosses decrease gradually with increase of $(\sin \theta/\lambda)^2$. The curve *a* obtained is nothing but a correlation curve for Cu $K\alpha_1$ and Cu $K\alpha_2$. The small circles in the *C* region in Fig. 1, where the splitting is perfect, show the ratio of $(|F_o|_{\alpha_1}^2 + |F_o|_{\alpha_2}^2)/|F_o|_{\beta}^2$. The curves *c* and *a* must intersect with each other at $(\sin \theta/\lambda)^2 = 0$, since the $|F_o|^2$ values obtained from the two wave lengths should be the same. The values in the intermediate region *B* are those where the intensities are estimated in the two ways, as perfect splitting (\circ) and as partially superimposed (\times).

The final relative $|F_o|^2$ values can be obtained by averaging the two series of values putting an appropriate weight for each. For those spectra whose intensities are too weak to be estimated for Cu $K\beta$, the intensities are estimated by the Cu $K\alpha$ spectra and they are reduced to the $|F_o|^2$ values using the curve *a* or *c*, according to the way by which they are estimated. For those spectra which lie outside or near the surface of the limiting sphere of Cu $K\alpha$, the intensities are estimated from the Cu $K\beta$ spectra. It is well known that the spots due to Cu $K\beta$ for $(10h, 10k, 10l)$ lie so closely to those due to Cu $K\alpha_2$ for $(9h, 9k, 9l)$. For such groups of spectra, the intensities can well be estimated by the Cu $K\alpha_1$ and Cu $K\beta$ spectra for $(9h, 9k, 9l)$, and by Cu $K\alpha_1$ and Cu $K\alpha_2$ for $(10h, 10k, 10l)$, though they are few in number for crystals whose axial lengths are of the order of 10 Å.

The deviations from the mean values of $|F_o|_{\alpha_1}^2$ and $|F_o|_{\beta}^2$ can be taken as errors of $|F_o|^2$ values. The errors of film factors can also be checked in the course of intensity estimation, because the ratio of the film factors for Cu $K\alpha$ to Cu $K\beta$ must be a constant,

$$\exp(-\mu_{\alpha}r)/\exp(-\mu_{\beta}r),$$

where r is the path of X-rays and μ_{α} and μ_{β} are the linear absorption coefficients of Cu $K\alpha$ and Cu $K\beta$ for the film respectively. Moreover, accidental errors, if any, in the course of intensity estimation can easily be found.

For the same time of exposure, more spectra can be obtained with unfiltered Cu K radiation than with filtered Cu $K\alpha$ radiation. The number of spectra with higher angle reflections can be considerably increased by virtue of the shorter wave length of Cu $K\beta$. This fact seems to have been overlooked, or at least, not widely used. With the *b*-axis Weissenberg photographs of monoclinic aniline hydrobromide, the number of reflections observed ($h0l$) was increased from 140 to 160.

In the practical course of structure analysis, particularly in the refinement stage, more intensity data are often desirable. In such a case, the use of Mo $K\alpha$ is usually recommended. However, Mo $K\alpha$ requires high applied voltages, associated with more white radiations

* Deceased, 26 May, 1959.

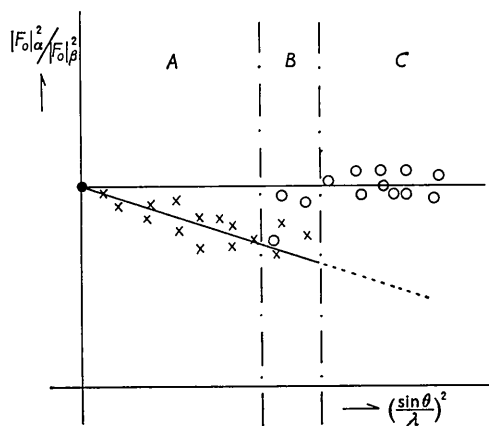


Fig. 1. Schematic representation of $|F_o|_{\alpha_1}^2/|F_o|_{\beta}^2$ versus $(\sin \theta/\lambda)^2$.

and its sensitivity to photographic emulsions is far less than that of Cu K . Moreover, the denser background will result from the Compton scattering and fluorescent radiations. At present, there is not any appropriate anticathode material available between copper and molybdenum. Under these circumstances, we believe that the combined use of both radiations Cu $K\alpha$ and Cu $K\beta$ in the Weissenberg technique is far superior to the use of the filtered radiation when structure analysis is attempted to carry out of crystals, particularly organic ones, whose axial parameters are of the order of 10 Å or longer.

Finally the multiple reflections associated with the strong reflection of lower Bragg angle are so sensitive to wave length that the simultaneous use of the two radiations will be effective in detecting these (Jellinek, 1958).

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Unit-cell data for some anhydrous potassium borates. By J. KROGH-MOE, *Svenska Silikatforskningsinstitutet, Göteborg, Sweden*

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Phase relationships in the system potassium oxide-boron oxide have been reported by Rollet (1935, 1936). Unit-cell data have previously been given for three phases in this system, namely $K_2O \cdot B_2O_3$ (Zachariassen, 1937), $\alpha K_2O \cdot 5 B_2O_3$ (Krogh-Moe, 1959a) and $\beta K_2O \cdot 5 B_2O_3$ (Krogh-Moe, 1959b). In the following, data will be given for three other phases in the system.

1. *Potassium diborate*, $K_2O \cdot 2 B_2O_3$. Crystals of potassium diborate were prepared by fusing together stoichiometric amounts of p.a. potassium carbonate with p.a. boric acid in a platinum crucible at 1000 °C. for a short time and then annealing the resulting glass melt below 800 °C. Single crystals of sufficient quality for X-ray work could be found in the devitrified glass. Since the crystals are rather hygroscopic, they were mounted inside a protecting capillary tube. X-ray Weissenberg and oscillation photographs showed a triclinic cell. The photographs were taken (with Cu $K\alpha$ -radiation) around the b and c axes of the reduced cell. From the information thus obtained, the following unit-cell dimensions of the direct lattice were computed:

$$a = 6.46, b = 9.56, c = 10.38 \text{ \AA}; \\ \alpha = 90.7, \beta = 102.6, \gamma = 101.2^\circ.$$

The calculated density is 2.53 g.cm.⁻³ with 4 formula units of $K_2O \cdot 2 B_2O_3$ in the cell.

2. *Potassium triborate*, $K_2O \cdot 3 B_2O_3$. Potassium-borate glasses of the triborate and the tetraborate composition were prepared in the same manner as the diborate glass described above. It was assumed that the composition was determined by the weights of the original powders, though a slight change in composition due to preferential evaporation of one compound should not be overlooked. Whereas a glass of the triborate composition refused to crystallize within a couple of weeks at a temperature between 700 and 800 °C., a glass of the tetraborate composition was readily crystallized at 780 °C. It was first believed that the resulting crystalline phase was a tetraborate. (See the phase diagram by Rollet (1935)). The observed density of the phase, however, can be reconciled with the density calculated from the X-ray data only if the phase is a triborate. This result does not disprove the existence of a potassium tetraborate, but it does indicate that a reinvestigation of the phase diagram

in the region around 20 mol.% potassium oxide would be desirable.

Weissenberg and rotation single-crystal X-ray photographs were taken around three non-coplanar rational axes (of which two turned out to be the b and c axes of the reduced cell). From these photographs, the phase was established as triclinic with the following cell dimensions:

$$a = 10.63, b = 10.64, c = 13.01 \text{ \AA}; \\ \alpha = 90.7, \beta = 95.2, \gamma = 114.2^\circ.$$

The calculated density is 2.26 g.cm.⁻³ with 6 formula units of $K_2O \cdot 3 B_2O_3$ in the cell. The observed density, 2.23 g.cm.⁻³, was determined by flotation of the crystalline powder in heavy liquid mixtures.

It might be pointed out that the potassium triborate cell approaches hexagonal symmetry, and has a cell content of 6 formula units.

3. *γ potassium pentaborate*, $\gamma K_2O \cdot 5 B_2O_3$. The unit cell and the space groups of the two stable modifications of potassium pentaborate are known. Rollet mentions, however, a third metastable modification, which is obtained from the α -modification below 690 °C. A crystalline phase obtained accidentally in the pentaborate region during the present investigation is conjectured to be identical with the metastable phase reported by Rollet. A single crystal of this new material was oriented along the c -axes, and from a rotation photograph and from Weissenberg zero and first layer photographs, the following monoclinic unit cell was deduced:

$$a = 11.59, b = 17.80, c = 12.99 \text{ \AA}; \beta = 95.8^\circ.$$

The cell contains 8 formula units of $K_2O \cdot 5 B_2O_3$, corresponding to a calculated density of 2.20 g.cm.⁻³. Systematic extinctions in the general hkl reflections for $h+k=2n+1$ were observed.

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