stallplatten auszuschliessen. Sicher liesse sich der R-Wert der Struktur durch Einführung anisotroper Temperaturfaktoren um einige Prozente senken, doch wurde der geringen kristallchemischen Wahrscheinlichkeit wegen darauf verzichtet. Die wahrscheinlichste Lösung ist noch eine Symmetrieerniedrigung zur Raumgruppe *Cm* — in der noch in Frage kommenden Raumgruppe *C*2 lässt sich die Aufspaltung von Mangan (1) oder H_2O(2) nicht deuten — in der die Punktlagen nur um weniges, schätzungsweise im Durchschnitt um 0,1 Å aus ihrer zentrischen Lage entfernt sind. Mit 2-dimensionalen Methoden dürfte die Entscheidung darüber wie die Auslängungen der Punktlagen zur erklären sind, schwierig sein. Auch eine 3-dimensionale Verfeinerung innerhalb des Kupferstrahlungsbereiches der Weissenberg-Kamera würde wahrscheinlich zu keinem Ergebnis führen, da sich der Effekt der Aufspaltung erst nach Hinzunahme aller äusseren Reflexe stark hervorhob. Von einer 3-dimensionalen Verfeinerung im Molybdän-Bereich wurde vorerst abgesehen, da die zu erwartende leichte azentrische Verzerrung des Gitters an den Bauprinzipien der Struktur nichts ändern kann.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

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On the structure and polymorphism of potassium iodate, KIO_3.

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Potassium iodate is stated to be cubic ($a=4\cdot46$ kX.) with the perovskite-type structure (Goldschmidt, 1926). It has been shown by Náray-Szabó (1947) that the strongly birefringent and piezoelectric KIO_3 is only pseudocubic and is really monoclinic with $a\sim b\sim c=8\cdot92$ kX., $\beta\sim90°$. On the other hand, Smith & Welch (1960) give it a rhombohedral cell with $a=4\cdot410$ Å, $\alpha=89\cdot41°$. Their crystals were extensively twinned and they tried to minimize this effect by slow evaporation just above 0 °C.

The lattice of this salt must contain IO_3 radicals which have been found without doubt in $NaIO_3$ (van Eck & McGillavry, 1943), in $Ce(IO_3)_4$ (Cromer & Larson, 1956), in $Ce(IO_3)_4.H_2O$ (Ibers, 1956) and in HIO_3 (Rogers & Helmholz, 1941). The small cubic cell of Goldschmidt could not accommodate an IO_3 group with $I–O=1\cdot81$ Å as found by the above authors; the iodine would be octahedrally coordinated in it with a distance $I–O=2\cdot23$ Å. In $RbIO_3$, NH_4IO_3 and $CsIO_3$ the distance I–O would be still larger if the structure would be of the perovskite type with the small cubic cell.

Potassium bromate, $KBrO_3$, on the other hand is rhombohedral (Zachariasen, 1928) (type GO_7) with $a=4\cdot403$ kX. and $\alpha=86°$; this is very near to the above cell of Smith & Welch (1960). Their crystals could have this type of lattice. The type GO_7 does, however, not belong to the perovskite family (Náray-Szabó, 1943, 1947), since its structure does not contain a three-dimensional continuous network of octahedra with shared corners. Therefore the type GO_7 could be called a pseudo-perovskite type.

We prepared by slow evaporation at room temperature small cubes of KIO_3 with an edge of a few tenths of millimetres. They are anisotropic, evidently made up of subparallel twin lamellae; their Laue diagram shows only elongated streaks. We succeeded in getting good oscillation diagrams from them with copper radiation; these show the layer lines of the pseudo-cell and between them

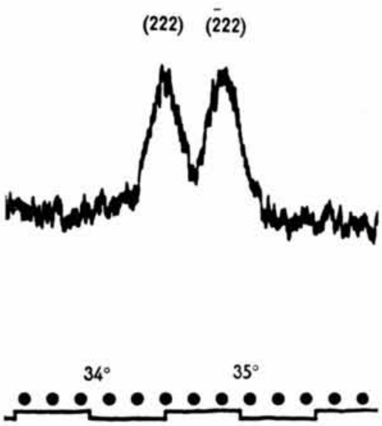

Fig. 1. Part of a diffractogram of powdered common KIO_3 with Cu $K\alpha$ radiation; reflections (222) and ($\bar{2}22$).

the weak but well identifiable spots of the odd layer lines of the true cell with $a = 8{\cdot}94$ Å. This cell is pseudocubic, but the symmetry can hardly be determined from oscillation photographs. The diffractometer curve of the powder of the recrystallized common KIO_3 (not of the single crystals!) does not show the lines of the superstructure, which are too weak. The line 222 appears as a symmetrical doublet on the best diffractogram (Fig. 1), indicating monoclinic symmetry. The two peaks correspond to the indices 222 and $\bar{2}22$ of the true cell; a rhombohedral cell would give an asymmetrical doublet for this reflexion and a symmetrical doublet for the reflexion 210 which is not the case. Our pseudocubic crystals confirm therefore the cell of Náray-Szabó (1947).—If one is content with a moderate accuracy, the lines of the diffractogram can be indexed on the basis of a monoclinic cell with $a \sim b \sim c = 8{\cdot}942 \pm 0{\cdot}001$ Å, $\beta = 89{\cdot}12°$. But diffractograms of different samples are not wholly identical.

When the solution of KIO_3 evaporates at room temperature, the bulk of the salt appears in the form of irregular, cauliflower-like crusts. Between these there are a few small but very well developed, evidently monoclinic crystals (Fig. 2), which are needle-shaped or bulky, perfectly water-clear. No sign of twinning was observed under the polarizing microscope. Oscillation diagrams of these needles gave for the needle axis $c = 6{\cdot}28 \pm 0{\cdot}01$ Å (i.e. $\sqrt{(2)} . 4{\cdot}44$ Å). The other axes are $b = 14{\cdot}52 \pm 0{\cdot}07$ and $a = 22{\cdot}80 \pm 0{\cdot}15$ Å. The monoclinic angle β is near to 90°; the numerous reflections can be indexed with this cell. If the density is of the same order as the measured one of the common salt ($d = 3{\cdot}999$ g.cm.$^{-3}$) then this cell contains 24 formula weights of KIO_3 and its calculated density is $4{\cdot}16$ g.cm.$^{-3}$.

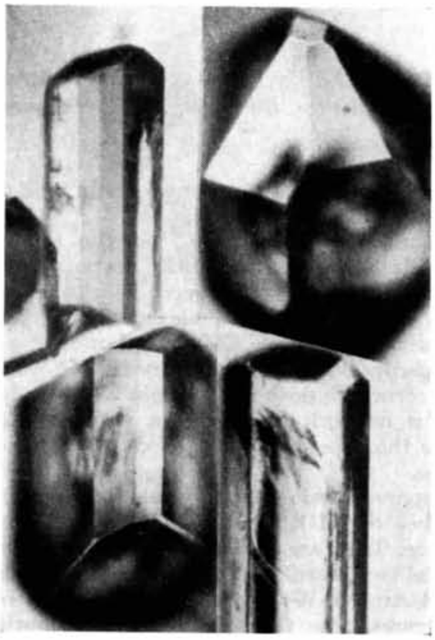

Fig. 2. Crystals of the monoclinic unstable modification of KIO_3, magnification 200 ×.

These needle-shaped monoclinic crystals have been separated and put in saturated solution; however, they never grew further but turned into irregular lumps.

Herlach, Gränicher & Itschner (1959) investigated the nuclear quadrupole resonance of KIO_3 between 20 and 280 °C. Two transitions can be observed at 75° and 220 °C. The same was found with ultrasonic resonance. The symmetry was rhombohedral above 220 °C. ($a = 9{\cdot}012$ Å, $\alpha = 89°\ 14'$ at 220 °C.). Below this temperature some trigonal lines show further splitting which is caused by the deviation from the trigonal symmetry of the high-temperature form to triclinic. Herlach *et al.* (1960) state that the lower transition (at 75 °C.) shows almost no changes in the X-ray diagrams, but the number of iodine sites increases from 1 to 4.

We have made differential thermoanalytic diagrams of KIO_3 and these show a small but well defined endothermic peak which commences at 75 °C.; no effect has been detected at 220 °C. or near to it.

From these observations one can see that at least two monoclinic, two rhombohedral and one triclinic modification of KIO_3 have been found. It is very probable that several modifications of this salt can exist together at room temperature and that they go readily over one in another. The lattice of KIO_3 therefore contains many faults and the diffractograms of different preparations are slightly different. The change of modifications involve small energies, so that the coexistence of them is hardly affected. Similar cases may occur in other crystals.

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