

Table 3. Corrected step heights for growth steps on crystals with structures resembling known polytypes where the step height is known to better than  $\pm 0.5$  basic layers

| Crystal number | Step height*<br>in multiples of<br>$M=6.84 \text{ \AA}$ | Corrected<br>step height<br>( $M$ units) | Structure<br>type | Is there a<br>correlation<br>between step<br>height and<br>unit cell<br>dimension? |
|----------------|---|--|-------------------|--|
| 33             | (i) $33.34 \pm 0.38$                                    | 25.6                                     | Resembles $2H$    | Yes  |
|                | (ii) $22.19 \pm 0.49$                                   | 17.0                                     | Resembles $2H$    |  |
| 39             | $59.21 \pm 0.48$  | 45.4                                     | Resembles $2H$    | Yes  |
| 47             | $17.0 \pm 0.05$   | 13.05                                    | Resembles $2H$    | Yes  |
| 49             | $30.02 \pm 0.11$  | 23.0                                     | Resembles $2H$    | Yes  |
| 60             | $47.34 \pm 0.43$  | 36.3                                     | Resembles $2H$    | Yes  |
| 61             | $48.27 \pm 0.30$  | 37.0                                     | Resembles $2H$    | Yes  |
| 6              | $34.38 \pm 0.23$  | 26.4                                     | Resembles $4H$    | Yes?   |
| 12             | $44.36 \pm 0.34$  | 34.0                                     | Resembles $4H$    | Yes  |
| 17             | $17.20 \pm 0.49$  | 13.2                                     | Resembles $4H$    | No   |
| 18             | $52.33 \pm 0.40$  | 40.1                                     | Resembles $4H$    | Yes  |
| 26             | (ii) $25.86 \pm 0.13$                                   | 19.8                                     | Resembles $4H$    | Yes  |
| 32             | $31.33 \pm 0.35$  | 24.0                                     | Resembles $4H$    | Yes  |
| 34             | $24.02 \pm 0.20$  | 18.4                                     | Resembles $4H$    | Yes?   |
| 36             | $13.51 \pm 0.42$  | 10.4                                     | Resembles $4H$    | Yes  |
| 41             | $59.94 \pm 0.16$  | 46.0                                     | Resembles $4H$    | Yes  |
| 44             | $38.92 \pm 0.14$  | 29.9                                     | Resembles $4H$    | Yes  |
| 68             | (i) $18.00 \pm 0.37$                                    | 13.8                                     | Resembles $4H$    | Yes  |
|                | (ii) $16.30 \pm 0.31$                                   | 12.5                                     | Resembles $4H$    | Perhaps  |
| 65             | $18.94 \pm 0.32$  | 14.5                                     | Resembles $8H$    | No   |
| 62             | $18.19 \pm 0.12$  | 14.0                                     | $2H+14H$          | Yes  |

\* From Triguñayat &amp; Verma (1962)

hills and the  $c$  dimension of the unit cell for most  $\text{CdI}_2$  crystals with structure types  $2H$  to  $20H$ . These results are thus consistent with the dislocation theory of spiral growth (Frank, 1951).

The crystals where correlation is not observed may be those in which slip has occurred in the last stages of growth. The measured step height in such cases would not be representative of the structure of the bulk of the crystal and correlation would not be expected. The available results suggest that slip may occur more readily in crystals having unit cells with large  $c$  dimensions.

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**The unit cell and space group of the antiferroelectric phase of copper formate tetrahydrate.** By M. J. BIRD and T. R. LOMER. *Department of Physics, The University, Birmingham, 15 England*

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X-ray single-crystal photographs of copper formate tetrahydrate, taken at temperatures below the antiferroelectric transition temperature ( $-38^\circ\text{C}$ ) showed that at these temperatures the unit cell was doubled, due to a doubling of the  $c$  axis, compared to the room temperature cell. The low temperature space group was  $P2_1/a$  instead of  $P2_1/a$  at room temperature.

It has been shown by Kiriya (1954) that at room temperature copper formate tetrahydrate is monoclinic with space group  $P2_1/a$ , and that the structure contains layers of water molecules which alternate with layers made up from copper and formate ions, all layers being parallel to (001). Neutron diffraction studies by Okada, Kay, Cromer & Almodovar (1966) indicated that the orientation of the water molecules was disordered. The antiferroelectric phase transition at

$-38^\circ\text{C}$  was first observed by Kiriya (1962) during a study of dielectric properties. X-ray diffraction studies of this low-temperature phase by Kiriya (1962) and by Okada *et al.* (1966) failed to show any changes in the number or intensity of diffracted spectra, but Turberfield (1967) using neutrons detected additional reflexions which indicated a doubling of the  $c$  axis and the loss of the glide plane. More recently, Molineaux (1969) working in this laboratory

observed some additional very weak X-ray reflexions when a crystal of copper formate tetrahydrate was cooled below its transition temperature.

In the present work a crystal, lightly smeared with Vaseline to prevent dehydration, was mounted in a Weissenberg camera and cold gas from boiling liquid nitrogen was passed round it. Filtered Cu  $K\alpha$  radiation was used with the generator running at 40 kV and 20mA to take equi-inclination photographs about the  $a$  and  $c$  axes. With exposure times of four hours and use of Ilford Industrial G film many weak spots were observed in addition to the spots appearing on photographs taken at room temperature.

The unit cell was determined to be  $a=8.17\pm 0.03$   $b=8.12\pm 0.03$ ,  $c=12.64\pm 0.06$  Å,  $\beta=101\pm 1^\circ$  and is thus the same as that of the room-temperature structure except for a doubling of the  $c$  axis. As far as could be judged by eye the intensities of all  $hkl$  reflexions were equal to those of  $h\bar{k}l$  reflexions so that the cell is almost certainly monoclinic. The only systematic absences observed were for  $0k0$  with  $k$  odd: many weak reflexions were observed which preclude the space groups  $P2_1/a$  and  $P2_1/n$ . The space group  $P2_1/m$  must also be precluded for the following reason. No noticeable change in the intensities of the spots common to the high and the low temperature phases resulted when the

crystal was cooled below the transition temperature. This means that only minor shifts in the positions of the heavy atoms can occur during the transition, whereas very large shifts would be required to construct a structure with the symmetry of  $P2_1/m$ . The only possible space group is thus  $P2_1$ .

Some of the additional reflexions observed occur at high angles,  $(\sin \theta)/\lambda > 0.6$  Å<sup>-1</sup>, at which hydrogen atoms contribute negligibly to the diffracted intensities. Thus, although there is convincing evidence that rearrangement of hydrogen atoms in the water layers is chiefly responsible for the antiferroelectric properties below the critical temperature, the present work shows that small displacements of heavy atoms also occur during the transition.

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**Monosemicarbazide hydrobromide** By P. BOLDRINI, *Département des Sciences, Université du Québec à Trois-Rivières, Trois-Rivières, P.Q., Canada.*

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The new salt of semicarbazide with HBr:  $\text{CH}_6\text{N}_3\text{OBr}$  has cell constants  $a=7.800$  (3),  $b=13.509$  (3),  $c=4.725$  (5) Å. Solubility and pleochroism of the compound are explained in terms of a ribbon like structure.

### Crystal data

While studying the combinations of halogenidric acids with semicarbazide:  $\text{H}_2\text{NNHCONH}_2$  (SEM from now on), a second salt of HBr with the base has been characterized. The components here being equimolar, the new salt will have to be called monosemicarbazide hydrobromide, to distinguish it from the disemicarbazide which presents an acid-base ratio of one to two (Boldrini, 1971).

Pseudo-hexagonal, white, shining, elongated prisms of SEMHBr separate by evaporating 50 ml of a 50% ethanol-water solution containing 7.5 g of freshly prepared SEM and 67.6 g of an aqueous solution of hydrobromic acid at 48%. The preparative stoichiometry is one mole of SEM and four of HBr. Crystals of SEMHBr appear always regularly shaped, sometimes one inch long, with prominent forms:  $\{010\}$ ,  $\{121\}$ ,  $\{120\}$ , and  $\{100\}$ . They are pleochroic, optically biaxial, birefringent and present extinction parallel to the elongation axis. In a dry atmosphere the compound is stable, but it is slightly hygroscopic in open air, and when it is exposed to X-ray radiation it decomposes, rapidly becoming yellowish.

A preliminary X-ray investigation has shown that SEMHBr is orthorhombic. Crystallographic data for it and for SEMHCl (Michael, 1919), measured by precession methods with Mo  $K\alpha$  radiation ( $\lambda=0.71069$  Å) and  $\text{PbCl}_2$

as calibrating substance ( $a=7.61892$ ,  $b=9.04443$ ,  $c=4.53345$  Å), are reported in Table 1. The specific gravity has been obtained by flotation in  $\text{CHBr}_3\text{-CCl}_4$  mixtures. Referring to the estimated standard deviations (e.s.d.'s) of Table 1, the difference in accuracy between columns 2 and 3 is due to the more rapid decomposition of SEMHBr. Also comparison of columns 3 and 4 shows that accuracy has been markedly improved for SEMHCl, while the more recent values on the same substance, column 5, appear inaccurate (Nardelli, Fava & Giraldi, 1965). For determining the space group of SEMHBr, extinctions were found only along the three crystallographic axes for reflexions with odd indices. This establishes for SEMHBr the same space group  $P2_12_12_1$  as for SEMHCl (Johnson, 1960).

The structural analogy between the two substances, suspected from the similarity of the two anions and of the cell parameters, is confirmed by a detailed study of their diffraction patterns. They are in fact superimposable and show equal trends of intensities. The four strongest reflexions of SEMHCl, for instance, are also the strongest for SEMHBr, and of comparable orders of magnitude; their indices are reported above as the main crystalline forms found for SEMHBr. It can be concluded then that both salts have the same crystal structure and are made up of halogen anions and  $\text{SEM}^+$  cations, the latter being hydrogen bonded in the direction of the elongation axis