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UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

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WORKSHOP ON SPACE PHYSICS:
"Materials in Micorgravity"
27 February - 17 March 1989

"HgI_2 Crystal Growth"
(up to now)

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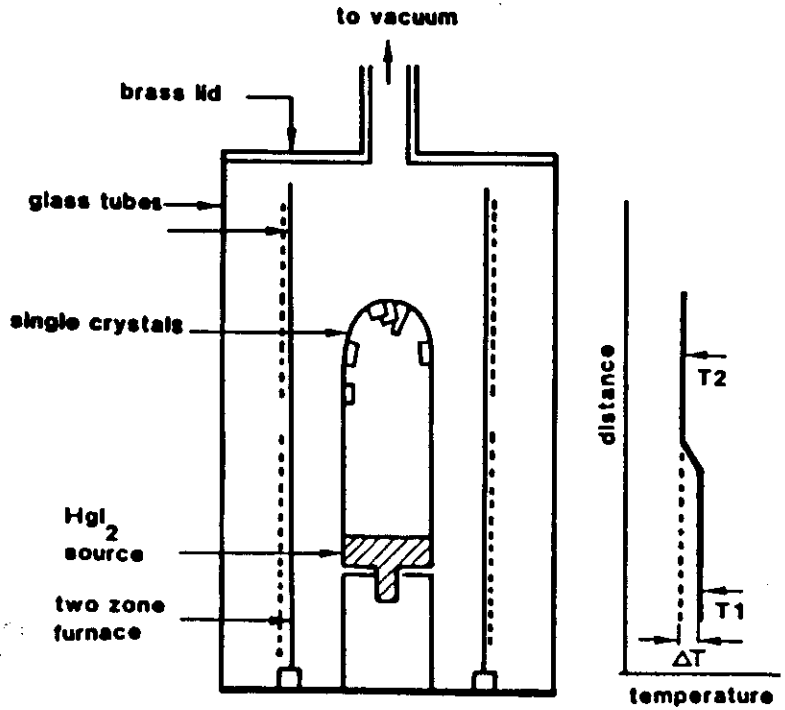


FIG. 5.9 Schematic drawing of the apparatus used for crystal growth of α-HgI_2 by static sublimation. (After KOBAYASHI et al., 1983).

Possible reasons
- competition growth kinetics with mass transport
- increasing thermal resistance with size
- decrease of mass transpot rate due to evolution of impurity gases
- step poisoning

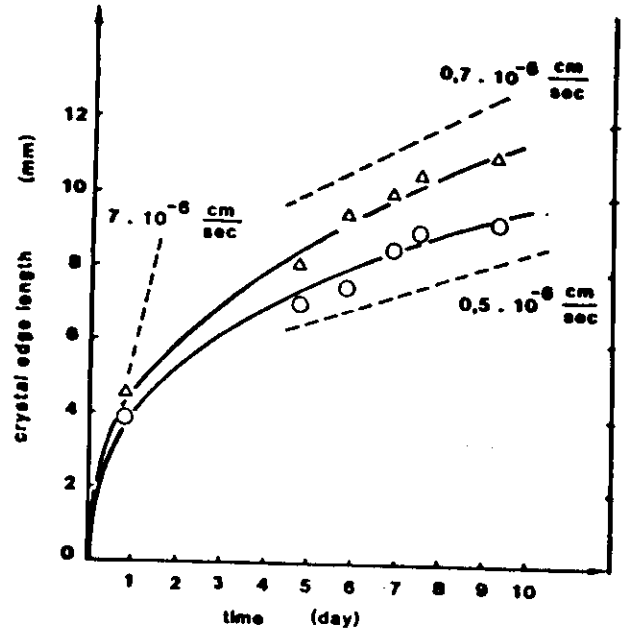
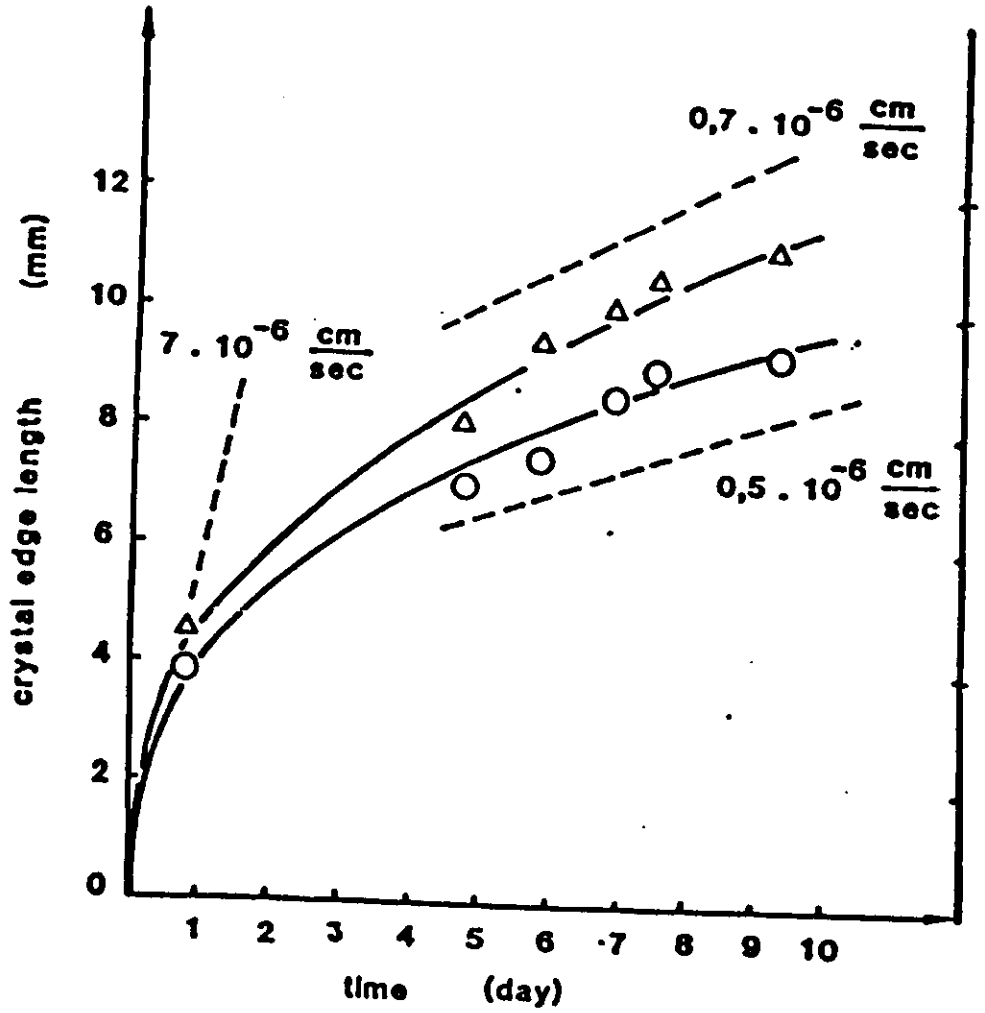


FIG. 5.11 Linear dimensions of α-HgI_2 crystal as a function of growth time. The two solid curves correspond to the largest edge of the c-plane of two different individuals. The dashed lines correspond to the given values of linear growth rate. (After KOBAYASHI et al., 1983).



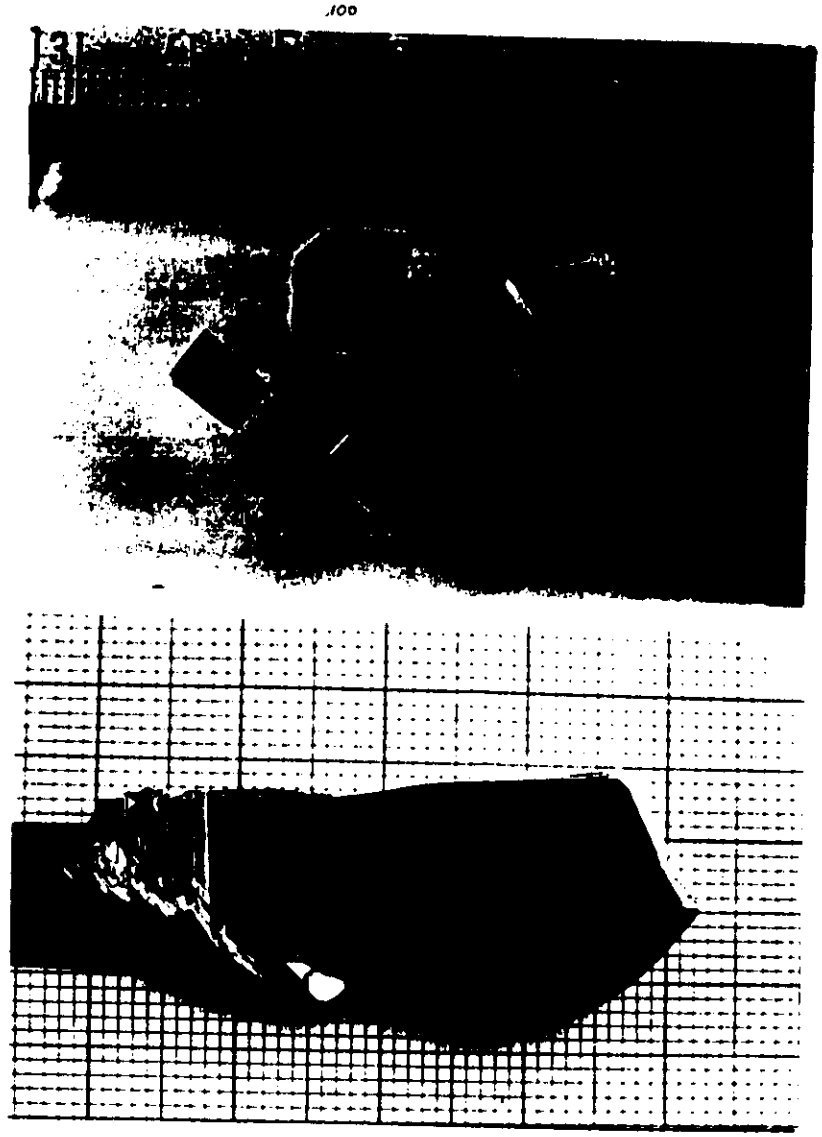
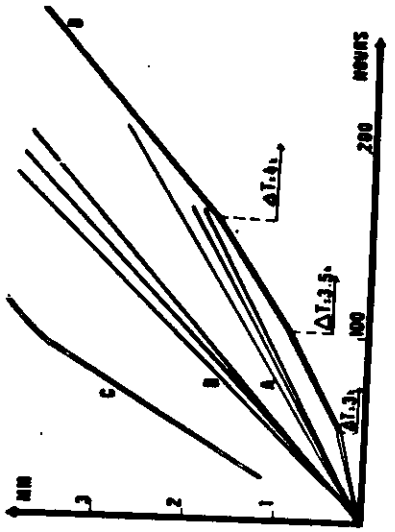
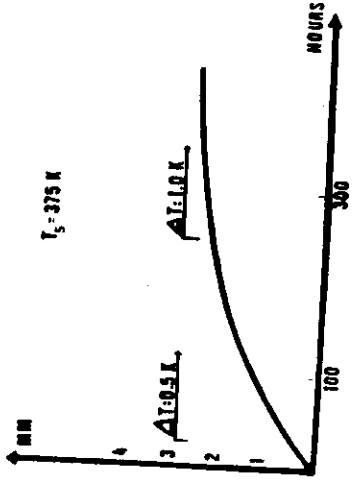


FIG. 5.10 Single crystals of α-HgI_2 grown by static sublimation in an apparatus shown in Fig. 5.9. Smallest subdivisions in 5.10a and 5.10b are millimeters. (After KOBAYASHI et al., 1983).



b



a

FIG. 5.12 a) <001> crystal height as a function of time of a crystal obtained at the end of a tube in "free diffusion" regime. (After OMALY et al., 1981).

b) <001> crystal height as a function of time of crystals obtained with a two-zone furnace. See also Tab. 5.2. (After OMALY et al., 1981).

dimensions of 4 mm, their growth rate diminishes and defects in a high concentration appear leading to a deterioration of the crystals also due to additional nucleation. Curve D in Fig. 5.12 shows that for a crystal grown at 97° C with $\Delta T = 2°$ C (nucleation period 48 hr) a stepwise increase of undercooling increases slightly the lateral dimensions of the (001) face. Therefore, no great difference in the growth rates ∥ and ⊥ to the c-axis is evidenced in these results.

TABLE 5.2

Influence of the time necessary for the appearence of a nucleus on its growth rate. Crystal temperature 105° C, $\Delta T = 3°$ C. Curves refer to Fig. 5.12. Data from OMALY et al., 1981.

	Growth rate (cm/sec)	Time for nucleation (hr)
Curve A	$4.2 \cdot 10^{-7}$	48
Curve B	$5.8 \cdot 10^{-7}$	20
Curve C	$9.3 \cdot 10^{-7}$ (up to $1.7 \cdot 10^{-6}$**)	1 hr*

* For nucleation at $\Delta T = 5°$ C, after appearance of the seed to $\Delta T = 2°$ C and after reaching 1 mm^3 $\Delta T = 3°$ C

** quick deterioration of the rapidly growing crystallites.

The only explanation which we can give at present to the relationship between growth rate and nucleation has to do with the perfection of the nucleus. A rapidly appearing nucleus is formed on an active site of the substrate near a defect and contains probably also defects which increase the growth rate and lead soon to deterioration.

KOBAYASHI et al., 1983 investigated the morphology of (100) faces with SEM (scanning electron microscope) using a cooling stage to avoid evaporation and could show clearly the existence of growth spirals (Fig. 3.9). In agreement with this result the initial vapor growth rate (at the beginning of the growth history) measured by KOBAYASHI et al., 1983, OMALY et al., 1983 and SCHIEBER

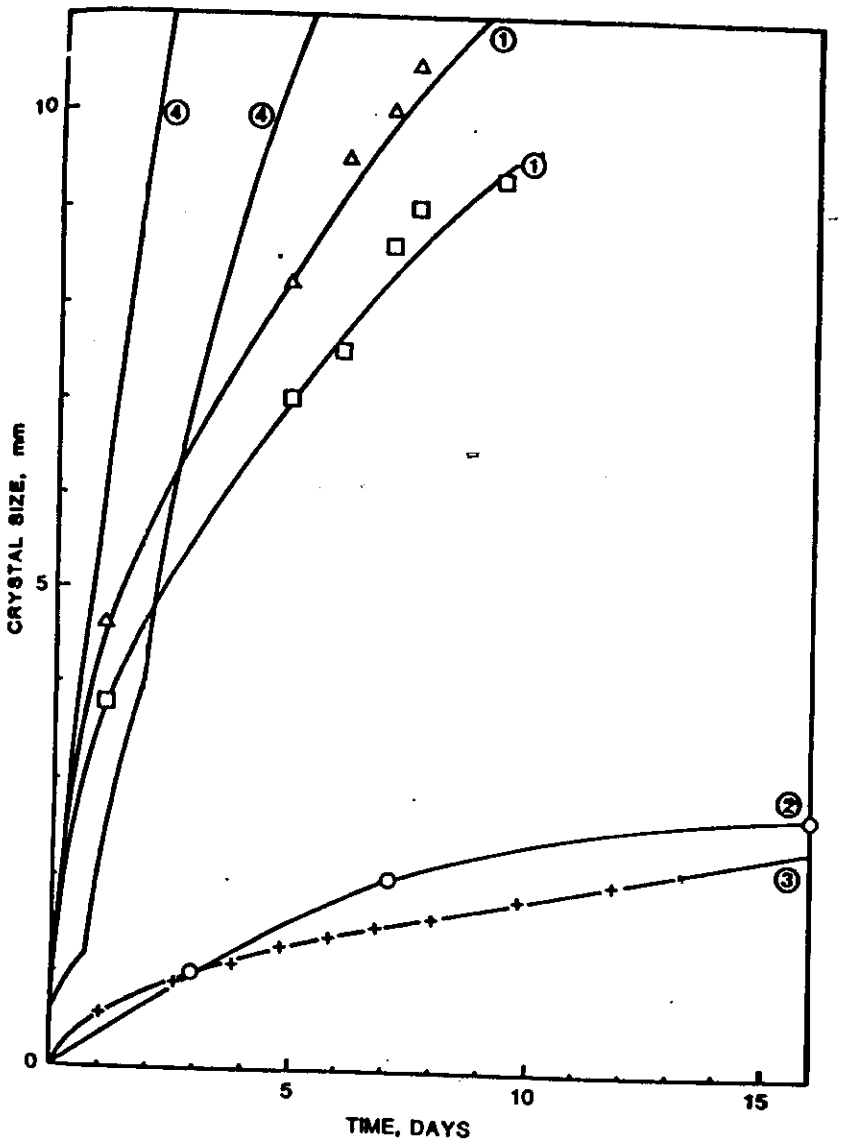


FIG. 5.14 Increase of crystal size with growth time for vapor growth of α-HgI_2 as measured by various authors: 1 - KOBAYASHI et al., 1983; 2 - OMALY et al. 1983; 3 - PIECHOTKA , 1984; 4 - ZALETIN et al., 1985. Note the decreasing slope of the curves, i.e. decrease in linear growth rate with time

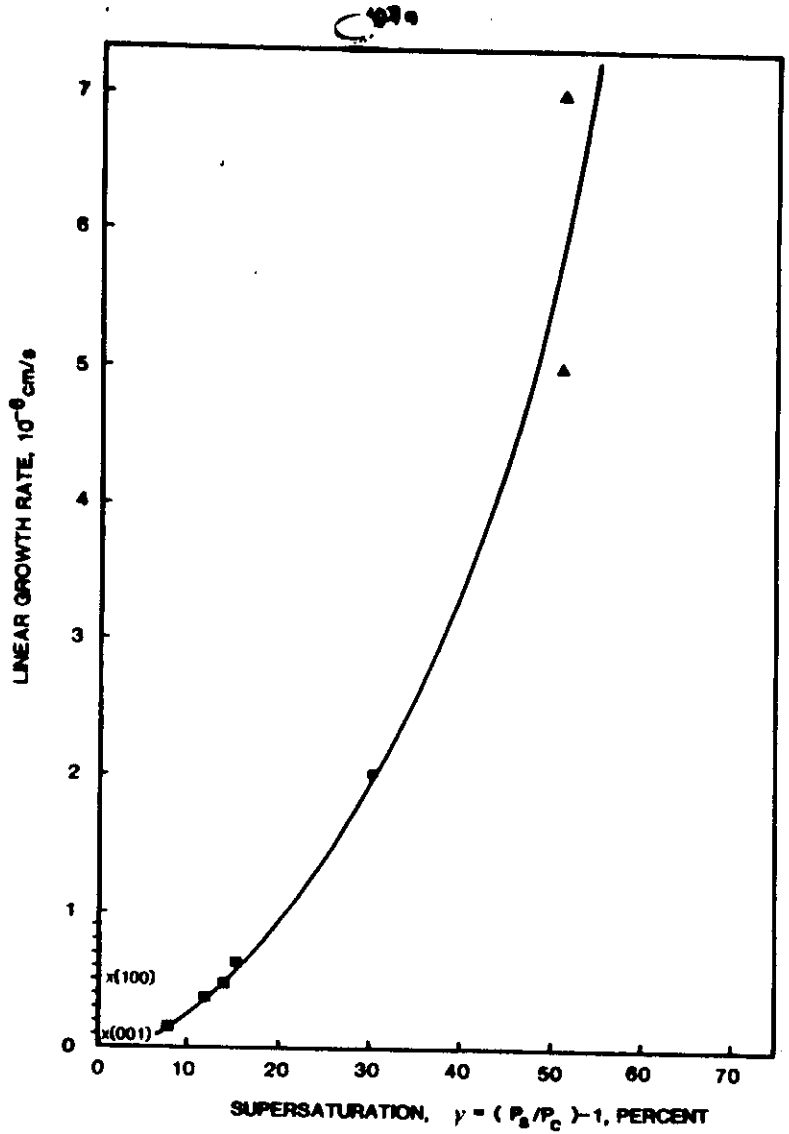


FIG. 5.13 Linear growth rate of α-HgI_2 crystals grown from the vapor as a function of supersaturation.

- ■ T_c = 378 K, ΔT = 2-4 K, <001> direction (OMALY et al., 1983).
- ● T_c = 393 K, ΔT = 10 K, < ? > direction (SCHIEBER et al., 1974).
- ▲ T_c = 377 K, ΔT = 6 K, <110> direction (KOBAYASHI et al., 1983).
- × T_c = 298-313 K, ΔT = 2-3 K

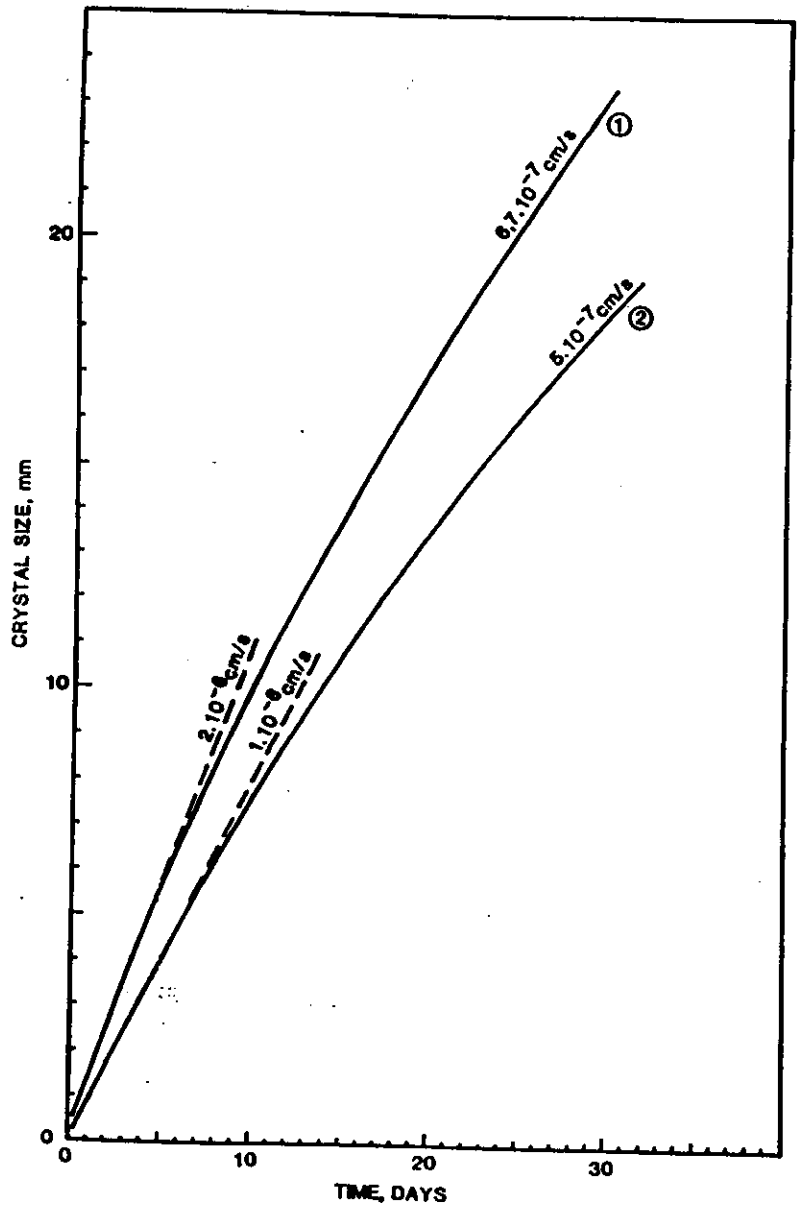


FIG. 5.16 Calculated change in crystal size with growth time for an α-HgI_2 crystal which starts to grow with ALGR of $1 \cdot 10^{-6}$ cm/s (curve 1) or $2 \cdot 10^{-6}$ cm (curve 2). The actual supersaturtion decreases with increasing dimensions of the crystal due to increasing heat resistance, thus the growth rate also decreases (decrease in the slope of the curves).

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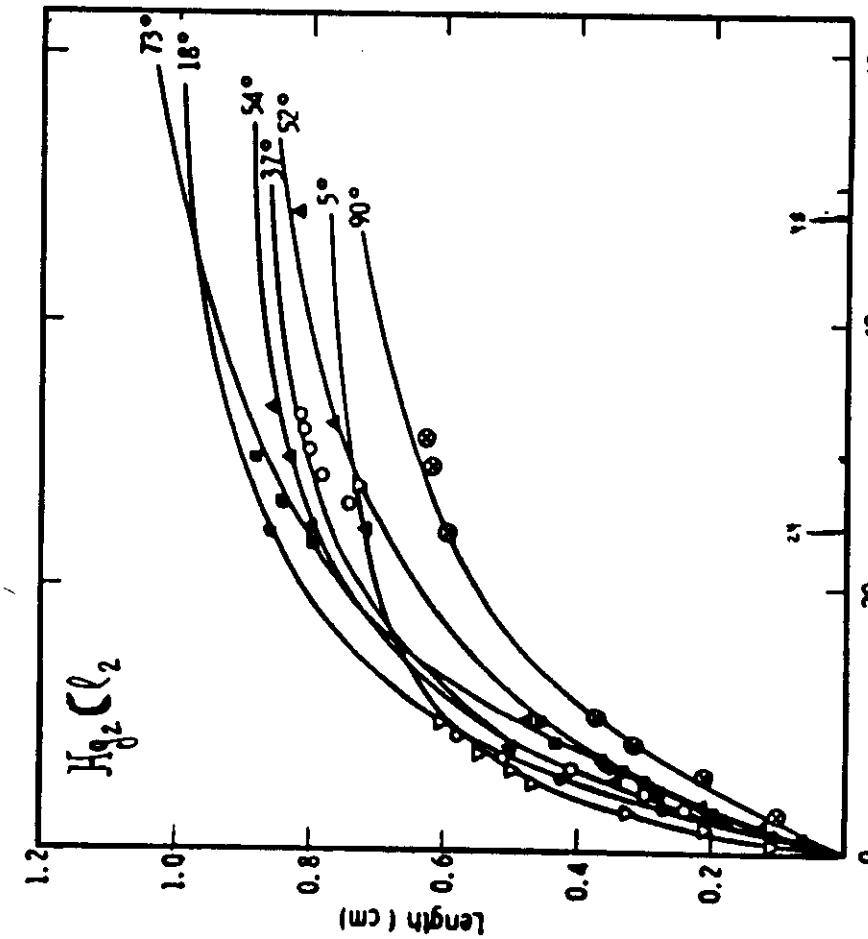

The length of growing crystals in different orientations

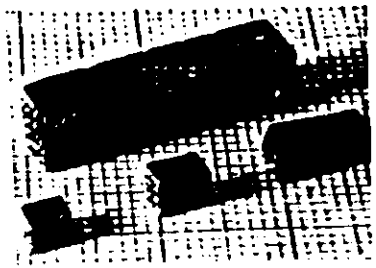

FIG. 5.18 Long prism of an α-HgI_2 single crystal grown from the vapor by GOSPODINOV, 1980.

FIG. 5.19 Rounded single crystal of α-HgI_2 grown by temperature gradient reversal method from the vapor by SCHOLZ, 1974.

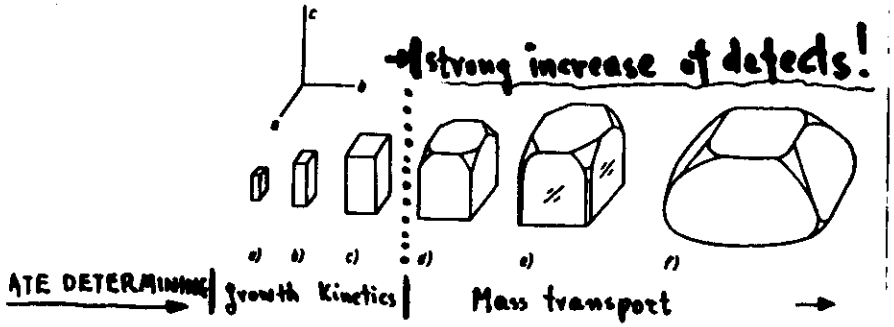

FIG. 5.20 Evolution of habit of the α-HgI_2 crystals grown from the vapor by TOM method. (After ZALETIN et al., 1985).

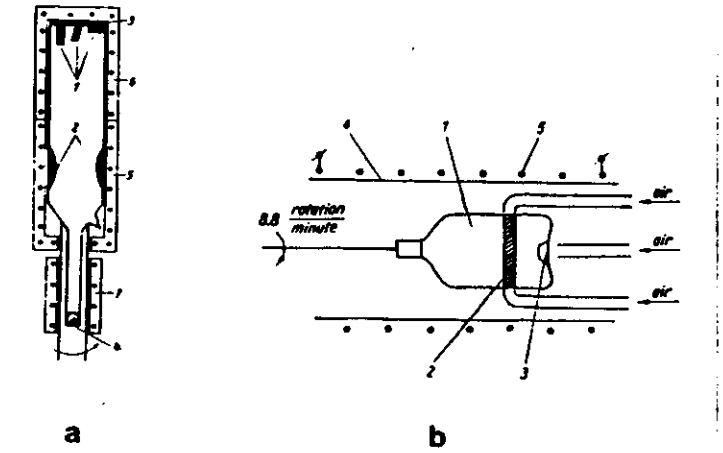

FIG. 5.21 Apparatuses used for growing α-HgI_2 crystal from the vapor by TOM method. a) GOSPODINOV, 1980; b) ZALETIN et al., 1985.

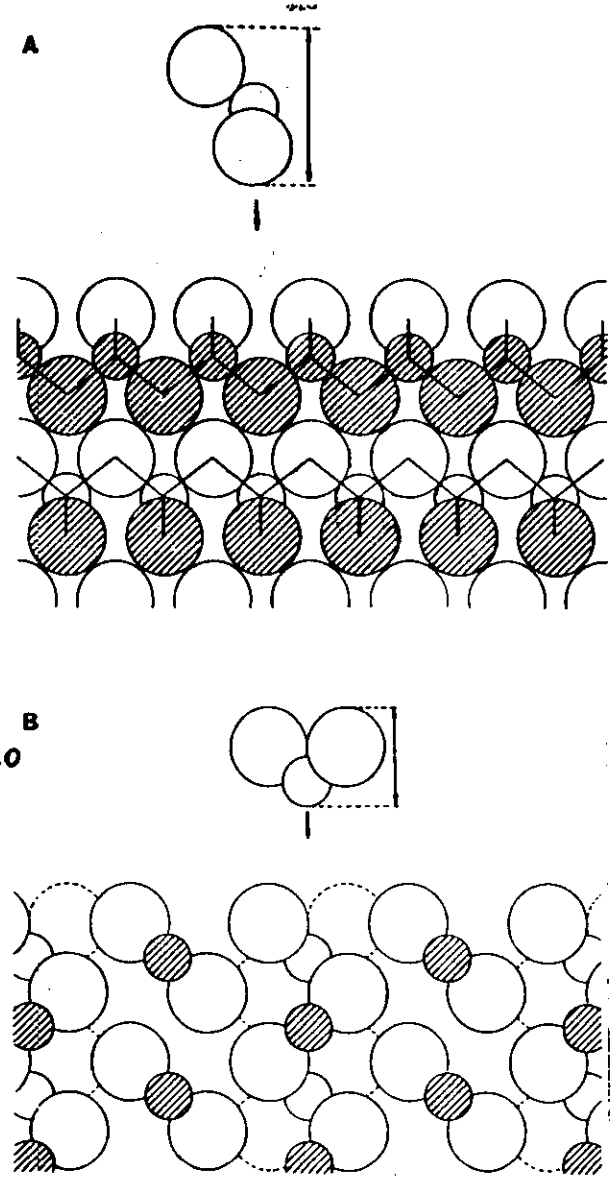

FIG. 5.22 Orientation of the HgI_2 molecule with respect to the growing face: (a) (001) face, (b) (110) face. Note that the single layer thickness on the (001) face is almost twice as large as that on the (110) face.

The results of van den BERG, 1985 and coworkers shown in Table 5.4 support up to a point the hypothesis of ZALETIN et al. (op. cit.). The former observed also a change of the growth rate ratio in the {001} and {110} directions associated with the habit transition (Fig. 5.21). As it can be seen a three times higher growth rate is observed $\perp$ c-axis than $\perp$ a,b axis for small crystals (at the initial growth stage). The question arises what is the reason for it. The answer is given by the Bravais-Friedel law. First, however, it must be noted that the orientation of the crystallographic axes in the figure of ZALETIN et al., 1985 (Fig. 5.20) is probably wrong. The faces ∥ to the c-axis in the α-HgI_2 habit are probably not (100) and (010), as shown in the figure, but the prismatic (110) ones. The reason is, that the former are kink rich (K-faces) and not stable in the habit. Their appearance has never been mentioned up to now by other authors. Therefore, they could only apper in the habit as the result of severe contamination. Nevertheless, the Bravais-Friedel law can be applied with the same results in both prismatic and (100) faces: due to the different orientations of the $^{I}Hg^{I}$ molecule with respect to the growing surface, the thickness of the growth layer is appreciably higher in the case of the pinacoid {001} than in the case of the prismatic {110} faces. The same is true for the unstable {100} faces. Fig. 5.22 shows schematically the two different orientations of the HgI_2 molecules and the width of the growth layers of the {001} and {110} faces. The exact atomic structure is shown in the profiles and projections of these faces (Fig. 4.9 and 4.11). According to the above, the growth rate ratio for the two faces should be

$$= \frac{R\{001\}}{R\{110\}} = 2$$

under otherwise equal conditions. This is in fairly good agreement with the results of ZALETIN et al., 1985 and OMALY et al., 1981 who found 3 and 1.6 respectively.

The up to now existing results of the SL-3 experiments (van den BERG, 1985) seem to be in agreement with the above investigations of the habits. The space crystal (Fig. 5.23) has a habit confined by large flat faces (prismatic and pyramidal) without any rounded corners or curved nonsingular faces. Although not many data are yet existing, the growth rate can be roughly estimated from