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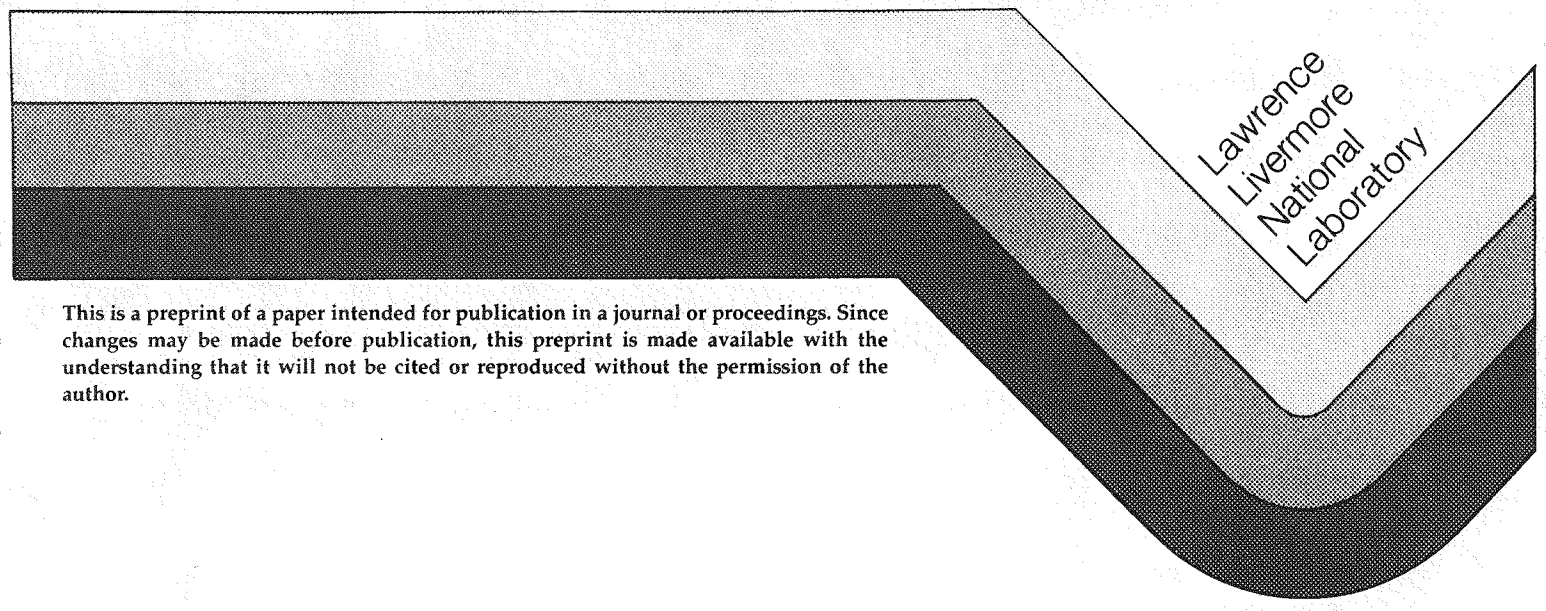

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ABSTRACT

YB_{66}, a complex binary semiconducting compound, cubic in crystal structure with a cell parameter of 23.44 Å, has been singled out as a potentially useful soft x-ray monochromator for dispersing synchrotron radiation. There is no intrinsic absorption by the constituent elements in the region 1-2 keV (the Y L_3-edge is at 2080 eV). Using the known structure factors for the (400) and (222) reflections having 2d values of 11.76 Å and 13.53 Å respectively, their rocking curves have been calculated and are shown to be comparable to or better than that of beryl ($10\bar{1}0$). In terms of vacuum compatibility, resistance to radiation damage, thermal and mechanical stability, YB_{66} satisfies all the material requirements for use as a monochromator for synchrotron radiation in the soft x-ray region. Recent experiments in growing single crystals of this material large enough to intercept 1 mrad of radiation are discussed. Rocking curve measurements, etch pit density, and x-ray white beam topography are used to characterize the quality of these large crystals as a function of some critical growth parameters such as pulling rate and thermal gradient at the crystal-liquid interface. From this study, it is clear that future work should be directed toward the control and retention of convexity of the crystal-liquid interface during growth, a key factor to achieve high perfection crystals.

Introduction

With the advent of brighter and more intense synchrotron radiation sources and novel devices like undulators and wigglers there is revived interest and need for crystals for long wavelength spectroscopy in the soft x-ray region of 6-30 Å [1]. Property requirements for use as soft x-ray dispersing elements in synchrotron sources may be classified according to (A) x-ray diffraction characteristics such as (i) high reflectivity, (ii) high resolution and (iii) large d-spacing, i.e., 2d ~ 12 Å for Na K-edge (1070 eV); and (B) material properties such as (i) high-vacuum stability (ii) thermal stability, (iii) good mechanical strength, (iv) radiation-damage resistance, (v) low thermal expansion and (vi) availability in suitable quantity and size as well as good single crystal quality.

Candidate dispersing elements may be classified according to their chemical nature and physical structure as (a) inorganic crystals, (b) organic crystals, (c) intercalation complexes, (d) soap films of the Langmuir-Blodgett type and (e) multilayers. From the point of view of material property requirements, materials in systems (b), (c), and (d) may be eliminated for use as dispersing elements in x-ray synchrotron radiation. Organic crystals such as potassium acid phthalate (KAP) with 2d=26.6 Å (which is commonly used for dispersing soft x-rays from relatively low-flux x-ray tube sources) suffer severe radiation and heat damage in a matter of minutes in synchrotron radiation. Intercalation complexes such as intercalated graphites and metal disulphides are generally vacuum unstable - the intercalant molecules have high vapor pressure and are easily pumped out in a vacuum, collapsing the complex to the original low d-value matrix. Soap films, though they have large 2d values (>50 Å), are both vacuum and thermally incompatible in a synchrotron radiation environment. We are then left with a few inorganic crystals and synthetic multilayers.

Radiation with energy above 2000 eV is adequately dispersed with Ge(111) as is being used in a soft x-ray vacuum jumbo spectrometer at SSRL [2] and elsewhere. The low energy limit of this semiconductor is 1980 eV, which is just below the K-edge of

phosphorus (2149 eV). With increasing interest in lower Z element EXAFS, say down to the K-edge of Na ~ 1 keV, and x-ray microscopy needs at longer wavelengths, crystals with large 2d-spacing are desirable. Mica (002) with 2d-19.84 Å, has been used at LURE in Orsay with moderate success. Beryl and β-alumina are also attractive alternatives [3] because of their high 2d values, but have limited energy windows due to absorption of constituent elements (Al, Si for beryl and Na, Al in β-alumina in the 1-2 KeV region (see Fig. 1)). In fact, a three-crystal system using Ge(111), InSb(111) and beryl ($10\bar{1}0$) has been developed at Stanford to extend the soft x-ray range down to 800 eV [2].

Multilayers are synthetic thin-film structures [4] obtained by sequential vapor deposition (usually by sputtering) of alternate layers of dissimilar metals (like Nb, Cu) or a metal and a non-metal (e.g. W, C). The effective 2d value of the structure is obtained by controlling deposition rates of each composite film. These multilayer metal films are promising as soft x-ray dispersing elements as they satisfy essentially all the materials requirements of vacuum compatibility, thermal stability, fabricability in large area pieces by sputtering (e.g. 3" diameter or larger) and radiation resistivity because of good electrical and thermal conductivity. Furthermore, an additional advantage is that when deposited on a bendable substrate, like Si wafers, they can also be used to focus the x-ray beam. Disadvantages, however, are the small glancing angle and the large width of their rocking curves, i.e. low energy resolution [3].

A promising possibility is YB_{66}. The material is refractory and has a melting point of 2100°C. It is semiconducting [5] and should be stable to synchrotron radiation exposure like Si and Ge. The crystal is cubic and has a cell parameter of 23.44 Å [6]. The (400) reflection, which has a 2d value of 11.76 Å, is very strong and has a calculated Darwin width of <<1 eV (see later) in the range 1-2 keV, in which there are no intrinsic absorption edges of the constitutent atoms in YB_{66}. This is ideal for K-edge structure and EXAFS studies of Na, Mg, Al and Si as well as L- and M-edges of higher Z elements. Thus YB_{66} satisfies the basic property requirements for use as a soft x-ray monochromator

in synchrotron radiation. In this paper recent advances in the crystal growth of YB_{66} and materials characterization are reported. An overall goal is to achieve large and perfect enough single crystals of this material to intercept at least 1 mrad of radiation at most synchrotron beam lines.

Crystal Structure of YB_{66}

YB_{66} was discovered in the late 1950's by Seybolt [7]. Its crystal structure was determined by Richards and Kasper [6], and is perhaps one of the most complex binary compounds known. The unit cell is cubic with edge length 23.44 Å; the space group is Fm3c (O_h^6). There are 1584 boron atoms and 24 yttrium atoms in the unit cell. The majority of the boron atoms (1248) reside in substructures of 156 atoms each, which may be called "super-icosahedra". A super-icosahedron is a cluster of twelve B_{12} icosahedra surrounding a central B_{12} icosahedron; the outer icosahedra are themselves oriented icosahedrally along the bonds radiating outward from the central icosahedron along the fivefold (pentagonal pyramid) axes. The super-icosahedra are oriented with respect to the unit cell so that the three mutually perpendicular mirror planes of the super-icosahedra are perpendicular to the cubic axes. Within this constraint, there are two distinct orientations of the structure relative to any given axis. Centers of the super-icosahedra are located at nearest-neighbor distances of a/2 and the orientations of alternating super-icosahedra are rotated by 90° in any given planar projection. Portions of 27 super-icosahedra (8 complete units in all) form the cubic structure of the unit cell (Figure 2).

Along the axes at (1/4, 1/4), (1/4, 3/4), (3/4, 1/4), and (3/4, 3/4) relative to any cube face, there are voids in the packing of super-icosahedra. It is along these void axes that the yttrium atoms lie, surrounded by a complex (and somewhat statistical) coordination of the non-icosahedral boron atoms. The yttrium equilibrium positions are approximately 0.98 Å above and below the planes parallel to the cube faces intersecting the super-icosahedral centers at spacing a/2, and the occupation of these sites is 0.50. Figure 3

shows the projection of the icosahedral boron atoms and the yttrium atoms onto two of these planes. On computing the structure factors, the contribution of the yttrium scattering amplitudes to the total amplitude is strongly dependent on the plane involved. The overwhelming stoichiometric abundance of low-Z material in this compound suggests relatively long absorption depths, hence potentially high resolving power. Since large, high quality beryl crystals are scarce, a compelling motivation exists for the search for an alternative.

Calculated Rocking Curves for YB_{66}

Using the data of Richards and Kasper [6] we recalculated the YB_{66} structure factors for the (222) and (400) reflections. For (400) [2d=11.76 Å], which intersects many yttrium sites, the total amplitude is largely that of the yttrium alone. For (222) [2d=13.53 Å], the yttrium and boron scattering contributions each amount to about half the total. With these factors, a number of simulations were made using a BRAGG Code [8] to calculate the reflectivity for both YB_{66} and beryl (since relative results may be more trustworthy and perhaps more meaningful than absolute values) at several x-ray energies. The number of atomic layers summed (from ~10000 to over 60000, depending on the crystal and photon energy) corresponds to five absorption lengths. The results for photon energies at 1100 eV and 1500 eV are summarized in
Table 1.

Qualitatively, it is evident that the (400)-reflection in YB_{66} is comparable to or better than beryl at 1100 eV, with a narrowing rocking curve going to higher energies (resulting in lowered integrated reflectivity). The (222)-reflection in YB_{66} suffers a factor of 6-8 lower integrated reflectivity when compared to beryl, but has approximately a 3x narrower width, and a larger 2d spacing than the (400) reflection, allowing for sub-kilovolt spectroscopy. Thus it looks as though there are no intrinsic problems associated with the concept of utilizing YB_{66} as a soft x-ray monochromator in the 1-2 keV region. The

emphasis must now be placed on the material aspects of the problem (i.e. growing large and perfect single crystals).

Crystal Growth

The first effort to grow single crystals of YB_{66} were made by Oliver and Brower [6] using a pedestal technique developed by Dash [9] with a 3 MHz RF generator and BN support for the YB_{66} pedestal and seed. Crystal boules of size ~10 mm long by ~0.5 mm diameter, were grown along the (100) and (110) axes. Pronounced faceting was noted in the (100) direction. Boules with a (111) axis exhibit a variety of planes which facet, but to a lesser degree than (100). Cleavage on (100) planes was observed. Simple back Laue reflection photographs (see Fig. 4a) of these early (100)-crystals revealed twinning and subgrain structure in accordance with the mosaic structure misorientations reported by Oliver and Brower [6]. In addition, both NaOH-based etch [10] and boiling nitric acid etch revealed a high density of defects that appear to be grown-in in nature as shown in Fig. 4(b) and (c). Preliminary rocking curves measurements at CuKα energy using a Si(400) as the first crystal revealed multi-peaks having an overall width of ~0.5 degree.

Recent efforts by Tanaka et al. [11] successfully scaled the growth process to produce large single crystals of YB_{66}, 50 mm x 10 mm diameter using a novel indirectly heating floating zone (IHFZ) method. Growth directions along (100) or (110) were achieved by seeding. An example of such crystals is shown in Figure 5. The size of such crystal is sufficient to intercept 1 mrad of radiation at most synchrotron beamlines. The growth process consists essentially of three steps: (a) pre-forming a polycrystalline sintered rod of YB_{66} by reacting a stoichiometric mixture of YB_6 and amorphous boron, which constitutes the feed rod for single crystal growth; (b) a seed crystal of either (100) or (110) orientation is then brought in contact with a molten end of the feed rod, and a necking process follows; and (c) may be a single pass or multiple pass to enhance crystal quality. Indeed, it was found that crystals grown with a single pass exhibit multi-peaks in the rocking curves with varying structure from seed end to final part of the boule. For double

pass crystals, the rocking curve reduced to essentially a single peak, still with some low intensity side peaks [11]. The density of etch pits in these IHFZ crystals is much lower than those grown earlier with the pedestal technique shown in Figure 4(b) and (c).

In a more recent effort by Tanaka and coworkers [12], YB_{66} was synthetized by a borothermal reduction method: $Y_2O_3 + 135B = 2YB_{66} + 3BO$ in vacuum at 1700C for 20 hours. Smaller grain size of YB_{66} material was obtained with this process compared with the $YB_6 + B$ synthesis. This in turn reduces excess crushing before sintering to form the feed rod for crystal growth. Single crystals were then grown with the IHFZ method, which is now modified to generate a larger heating zone (larger diameter and length of the tungsten heating ring) in order to reduce the temperature gradient at the crystal-liquid interface during growth. The floating zone was doubly passed with the second pass in reverse direction of the first. Rocking curves at CuKα were measured as a function of growth rate in the range 6 mm/hr to 100 mm/hr. It was found that the optimal rate was at 25 mm/hr. With this improvement in crystal growth, single peak rocking curves with FWHM ~12 minutes have been obtained at the seed end of the crystal as shown in Figure 6. This is very encouraging. The single peak, however, degenerates into multiplet structure at the bottom end of the crystal. The degradation in crystal quality from seed to bottom end may also be followed in an etch pattern on the (100) plane vertically cleaved by thermal shock of sudden stop of the zone pass [12]. The observed striations correspond to shape of the crystal-liquid interface during growth and show a change from convex curvature at the seed end (whereupon defects are ejected into the melt) to concave curvature (whereupon defects are incorporated into crystal) at about quarter way from the seed end and remain concave at the bottom of the crystal. Indeed white light synchrotron reflection topographs (Fig. 7) of a sister crystal, cut along growth direction substantiate transition range of curvature change of the growth striations from convex to concave away from the seed. It also exhibits higher crystal quality at the seed end and gradual deterioration

towards the bottom of the crystal with appearance of subgrain structure and lattice deformations.

Discussion and Concluding Remarks

From a consideration of both the x-ray requirements in terms of large d-spacing, reflectivity, and energy resolution, and materials properties in terms of UHV compatibility, radiation damage resistant, thermal and mechanical stability, YB_{66} satisfies the basic requirements from use as a monochromator for synchrotron radiation in the region 1-2 keV. Our rocking curve simulations based on the known structure factors of the (400)- and (222)-reflections show that YB_{66} is intrinsically comparable to beryl if not better.

Single crystals of size 10 mm diameter by 50 mm long can now be grown routinely. This size of crystal can intercept 1 mrad of radiation at most synchrotron beamlines. What is still needed is high crystal perfection to yield narrow rocking curves for high resolution spectroscopic applications in the soft x-ray region. Work is currently directed toward first controlling the thermal gradient at the solid-liquid interface to retain a convex curvature (this is prime goal of our future crystal growth effort); second, post-growth annealing to reduce or eliminate twinning and sub-grain structure; and double-crystal rocking curve measurements in the region of 1-2 keV with a synchrotron radiation source.

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Table 1. Calculated rocking curves for Beryl and YB_{66} using the "BRAGG" code [8].

	Beryl ($10\bar{1}0$) [2d=15.95Å]	YB_{66} (400) [2d=11.76Å]	YB_{66} (222) [2d=13.53Å]
1100 eV			
peak refl.	.0962	.142	.0358
FWHM	3.23×10^{-4} rad	2.53×10^{-4} rad	1.22×10^{-4} rad
integ. refl.	4.27×10^{-5} rad	5.06×10^{-5} rad	6.71×10^{-6} rad
1500 eV			
peak refl.	.226	.159	.0810
FWHM	1.40×10^{-4} rad	5.24×10^{-5} rad	3.49×10^{-5} rad
integ. refl.	4.54×10^{-5} rad	1.39×10^{-5} rad	5.35×10^{-6} rad

Figure Captions

Fig. 1 Soft x-ray monochromators for synchrotron radiation. Positions of constituent absorption edges are marked by vertical bars for each material.

Fig. 2 The general structure of the YB_{66} unit cell. Each sphere represents a super-icosahedron of 13 B_{12}-icosahedra. Channels along the (1/4, 1/4) equivalent axes contain the Y atoms and non-icosahedral borons.

Fig. 3 Projection of the icosahedral structure of YB_{66} onto the (x,y,0) plane, showing central B_{12} icosahedra lie: (1) at intersections of axes, (2) halfway between interactions along edges and (3) at center of projection. B_{12} icosahedra whose centers lie out of the plane are not shown in this projection for clarity.

Fig. 4 Crystal defects and micro structure of YB_{66} crystals grown by Oliver and Brower [6]. (A) Back reflection Laue photo exhibiting double spots, (B) NaOH-etch and (C) nitric acid etch surfaces revealing morphology and density of etch pits.

Fig. 5 Boule of YB_{66} (100) single crystal grown with the improved IHFZ method by Tanaka et al. [12].

Fig. 6 Examples of hard x-ray rocking curves of a crystal shown in Fig. 5. Upper four curves show the rocking curves at the seed end of the crystal and the lower four are those from the bottom part of the crystal. The curves were measured using a laboratory ($CuK\alpha$) x-ray diffractometer by fixing the counter at 15.13^{o} (2θ) and rotating the crystal only [12]. This set up is not the conventional (normal) double-crystal set up for rocking curve measurements.

Fig. 7 X-ray white beam reflection topograph of the seed end side of a YB_{66} (100) crystal grown by IHFZ method at 25mm/hr and cut along growth direction. The topograph, taken at beam line X19C at Brookhaven NSLS, reveals growth striations perpendicular to the growth axis and demonstrates a higher crystal perfection at the seed end compared to the center part that exhibits some subgrain structure and lattice deformations.

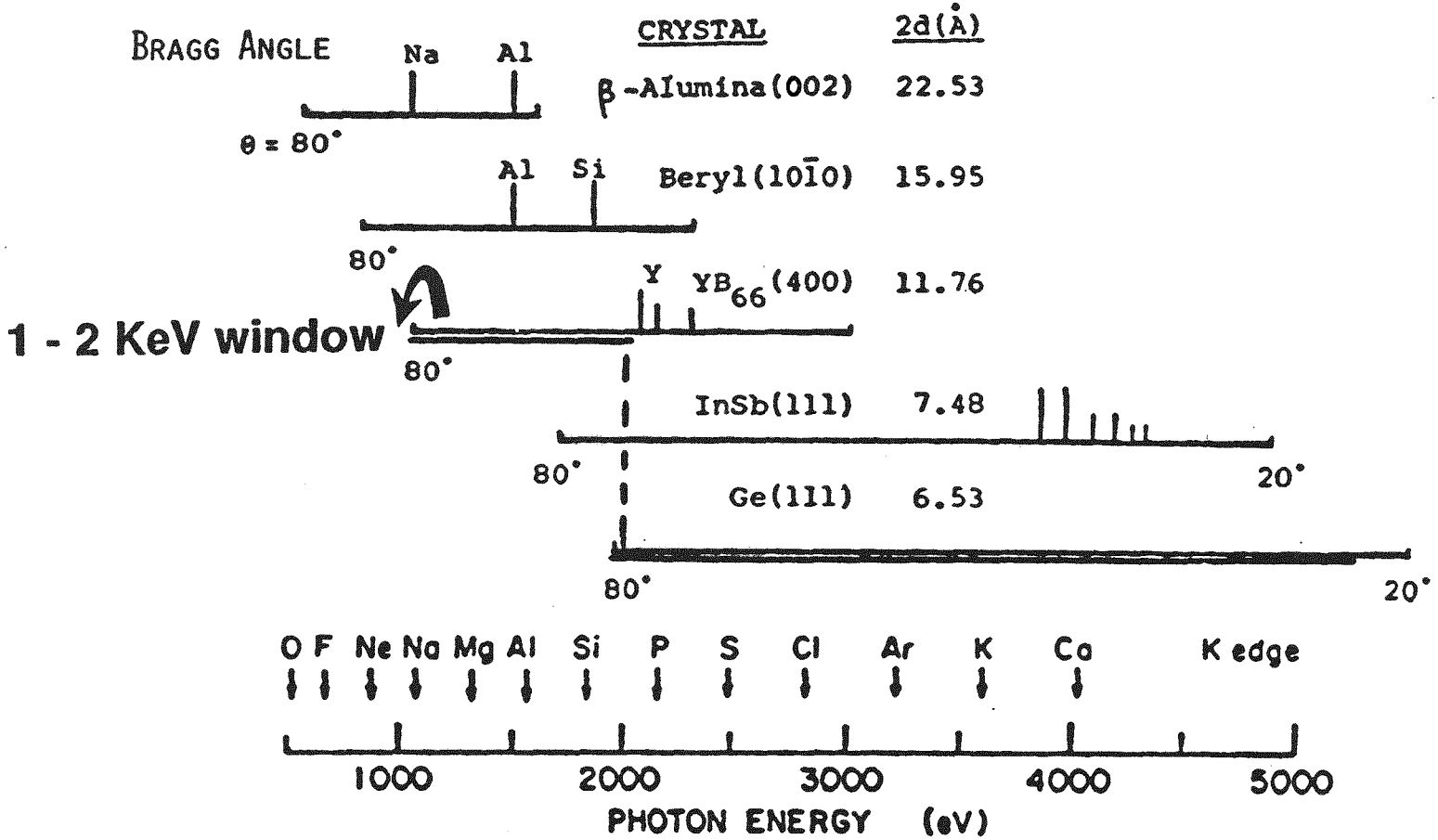

BRAGG ANGLE
Na
Al
CRYSTAL
2d(Å)
β-Alumina(002) 22.53
θ = 80°
Al
Si
Beryl(10$\bar{1}$0) 15.95
80°
Y
YB_{66}(400) 11.76
1 - 2 KeV window
80°
InSb(111) 7.48
80°
20°
Ge(111) 6.53
80°
20°
O F Ne Na Mg Al Si P S Cl Ar K Ca K edge
1000
2000
3000
4000
5000
PHOTON ENERGY (eV)

Fig. 1

Fig. 2

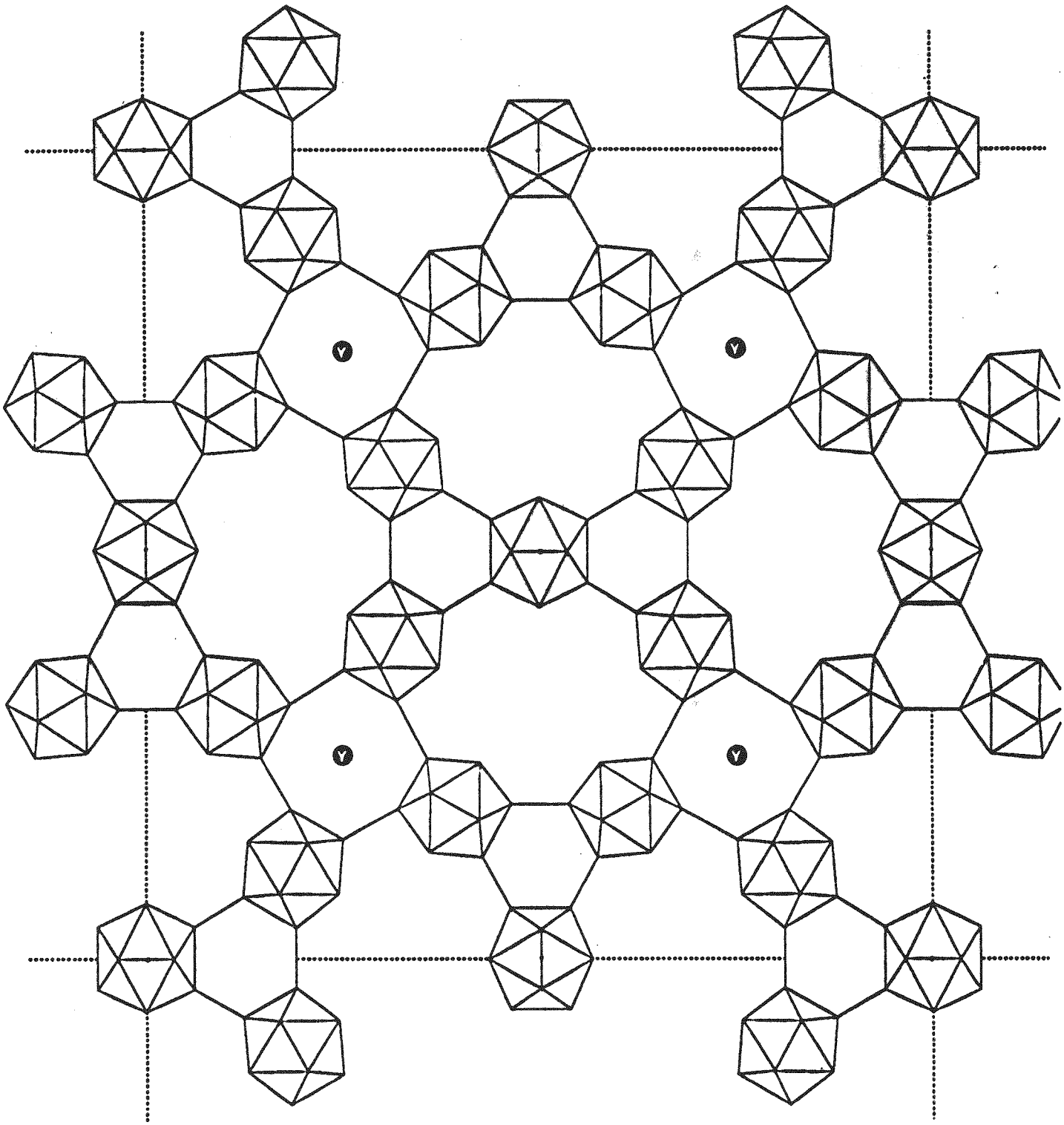
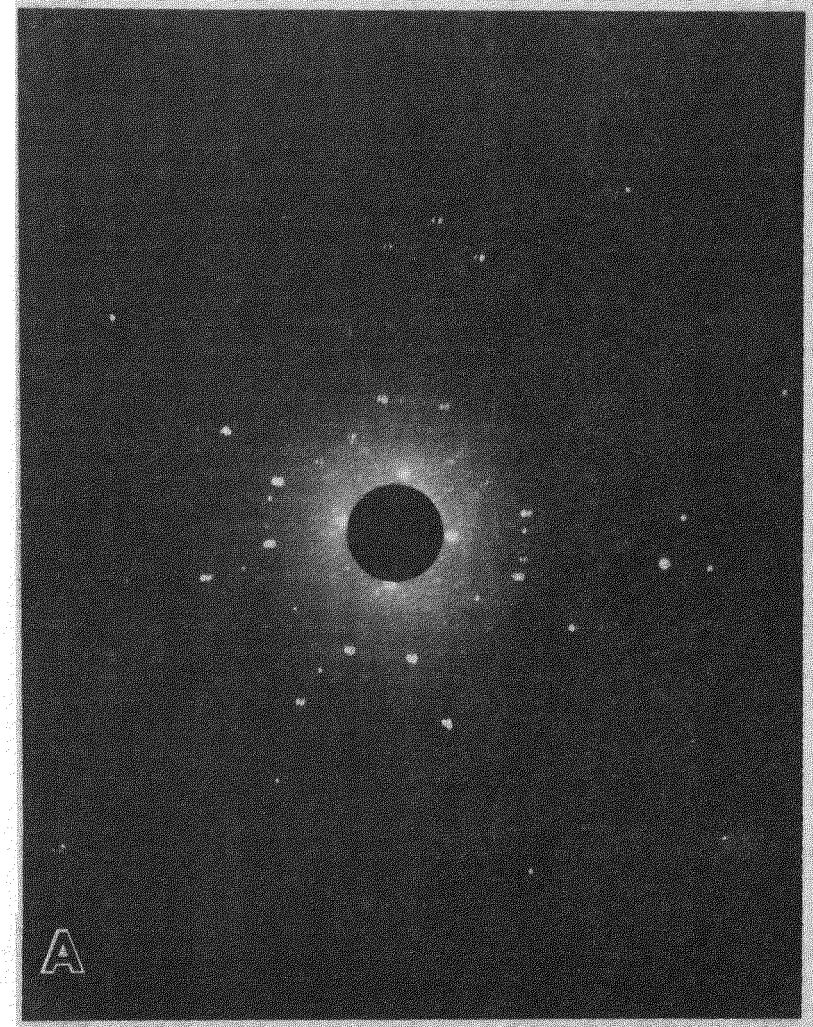
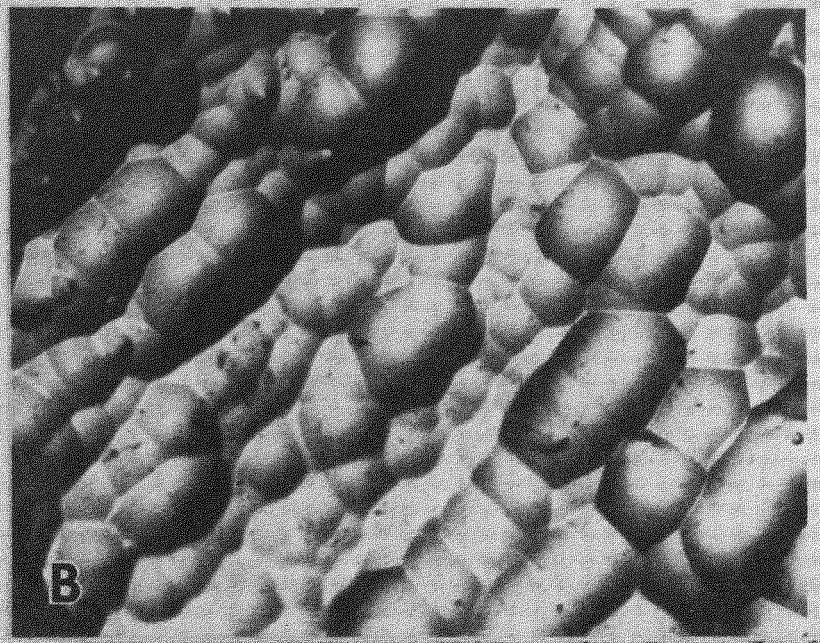


Fig 3

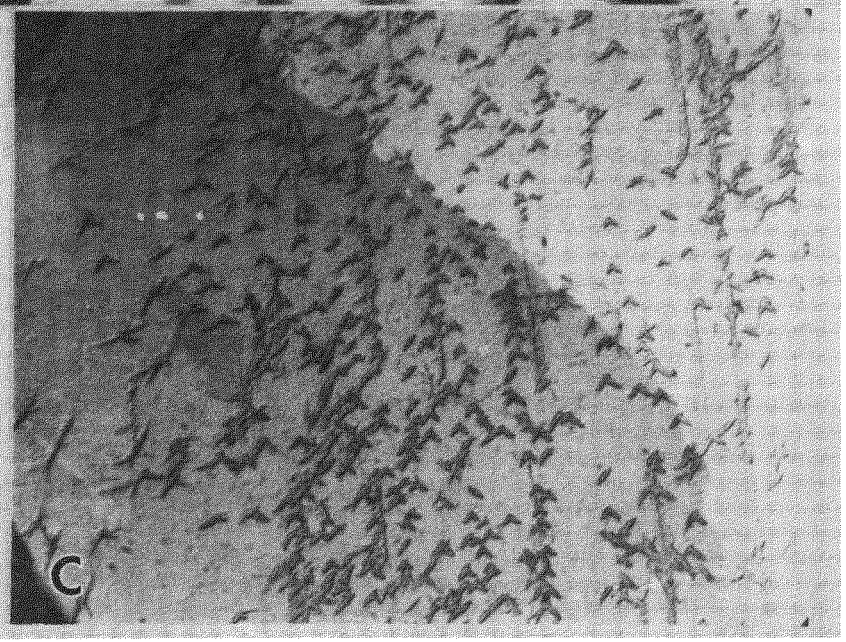
Crystal Defects and Microstructure of YB_{66}

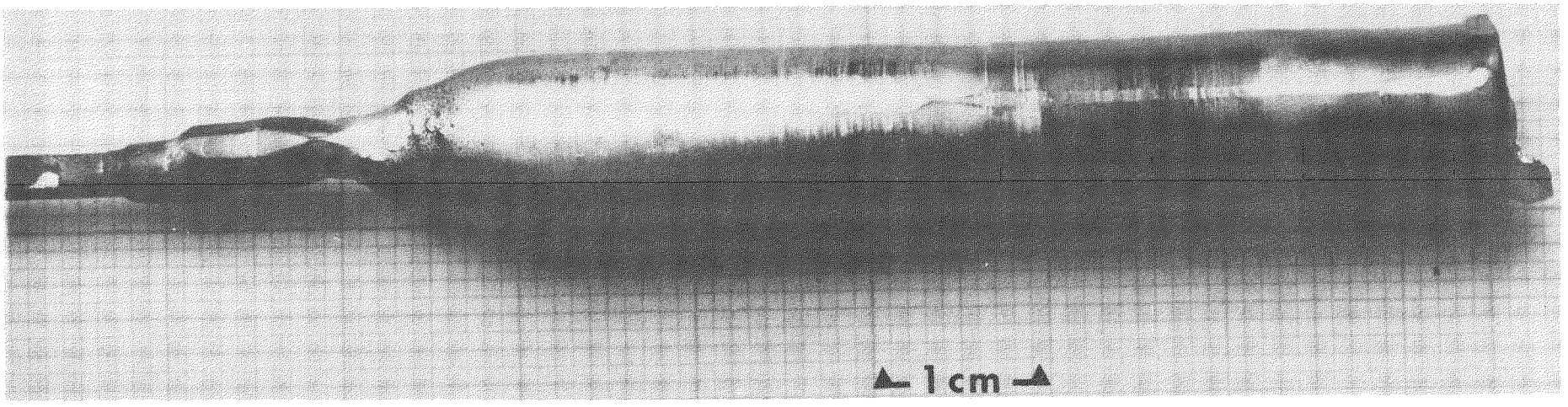


NaoH etch



Boiling acid etch

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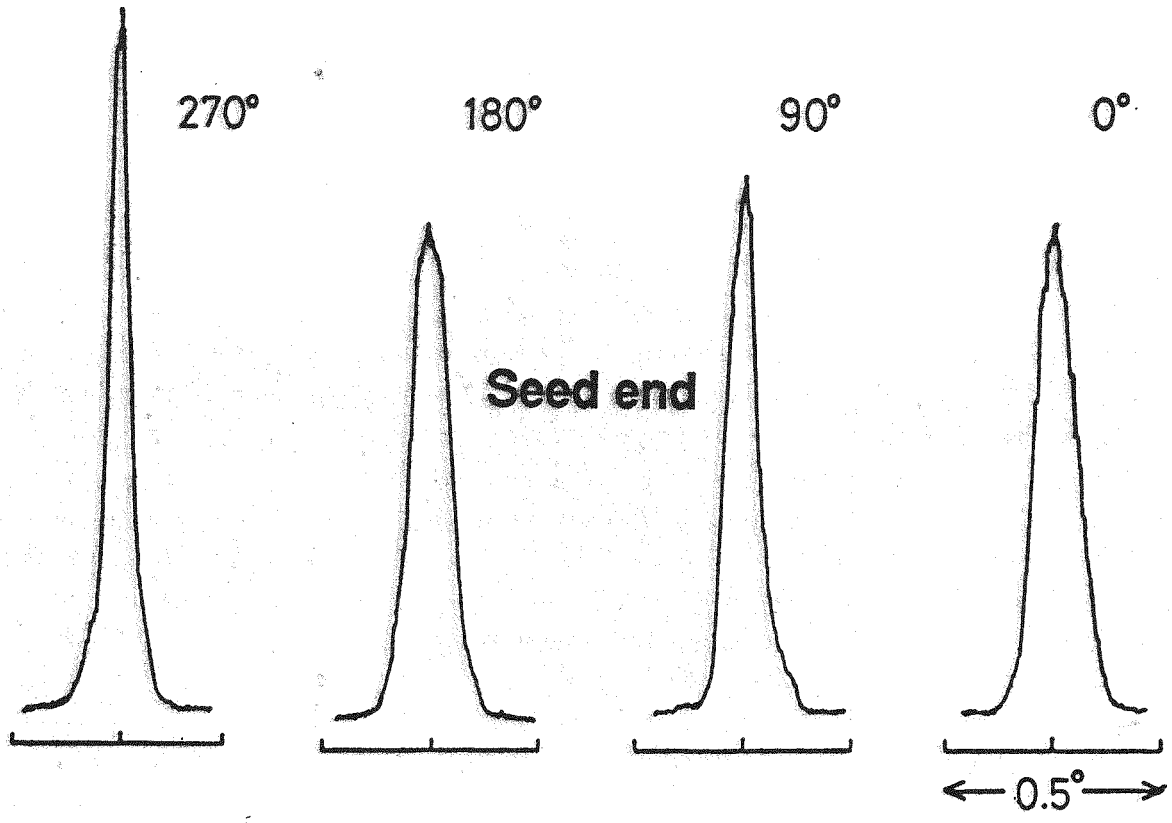


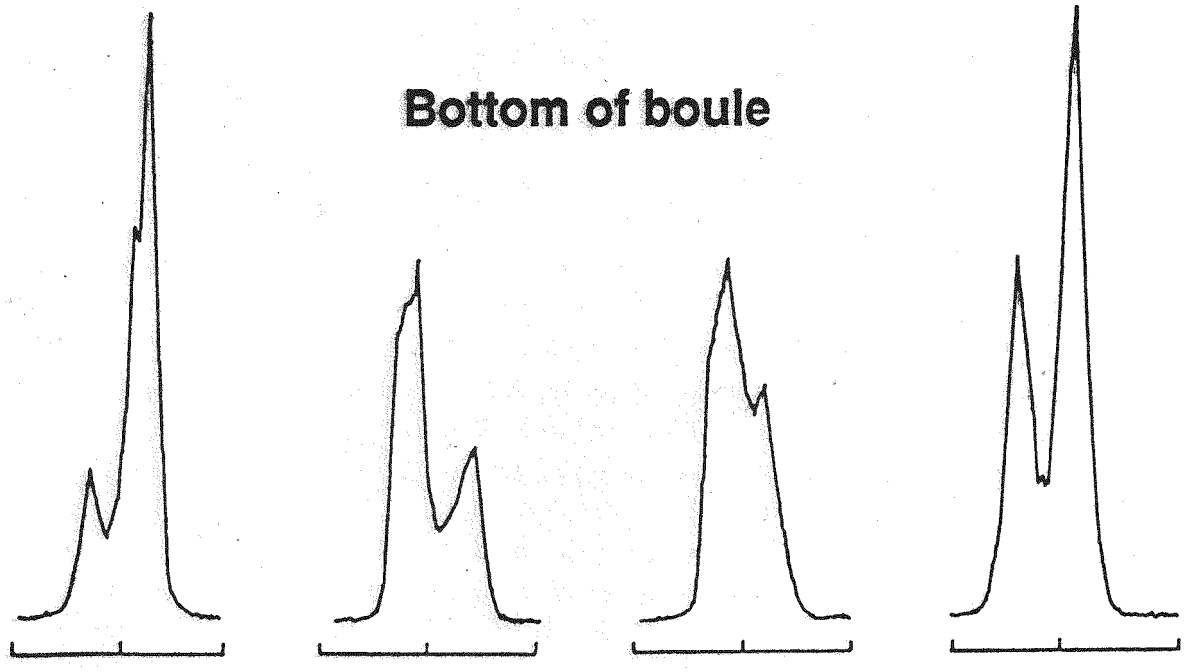
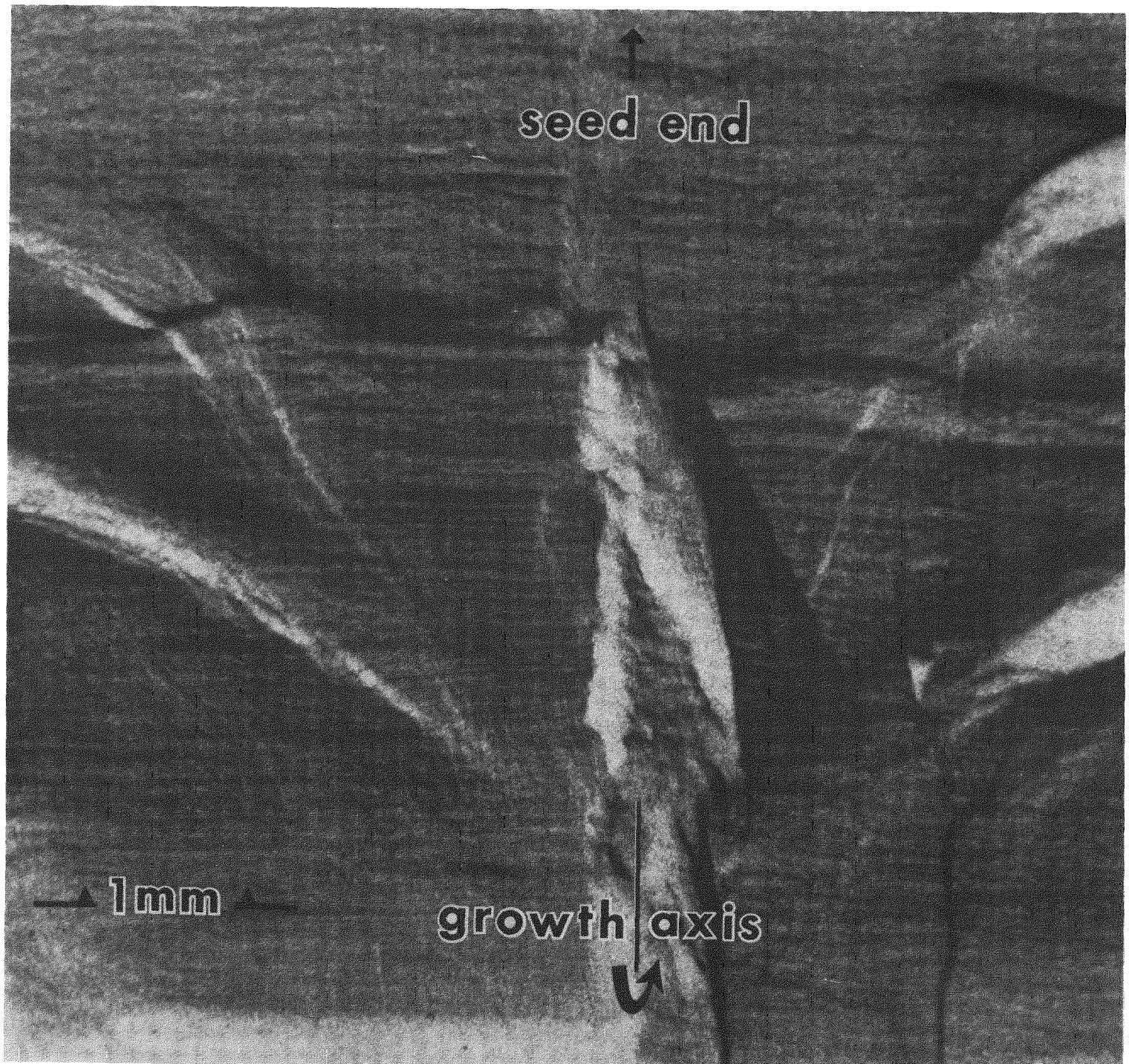


Fig. 6


seed end
1mm
growth axis