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# On the Preparation of Large Single Crystals of Ferrous Sulfide

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**Abstract**

Some experiments for the formation of single ferrous sulfide crystals (about 1.5 cm × 1.0 cm $\phi$) having stoichiometric and congrent compositions (FeS and $Fe_{0.934}S$) were carried out by the Bridgeman method. The crystals obtained were examined by X-ray diffraction, optical and polarized light microscopy, and their orientations were determined by the pole figure method. The best sound crystal can be obtained by the sulfide having a congruent composition with a lowering rate of 0.33 cm/h produced in a vertical electric furnace and maintained at the highest-temperature part ($\geq$1200°C). Its crystal orientation had a (100) plane perpendicular to the crystal growth direction.

## 1. Introduction

According to the experimental stand points obtained from numerous researches on sulfurization of iron and its binary alloys[1),2)] it is significantly important to have the knowledge of diffusion process in sulfide scales, and also the sulfides themselves formed on the metals and alloys to elucidate mass transport mechanism in the scale. Therefore, it is necessary to obtain large crystals (for example, in the order of cm in diameter) to study the diffusion process in sulfides in connection with sulfurization[3)].

There are many researchers who used pyrrhotite single crystals in their studies. Birchenal *et al*[4)], Barraclough *et al*[5)] and others[6),7)] have reported their own methods to obtain single crystals.

The method used in the present experiment consists of melting the starting powdered material at a high temperature and freezing it very slowly. This method has been also called a Bridgeman-Stockbarger method which was originated by Bridgeman[8)] and then developed by Stockbarger[9)]. The present paper gives some suggestions for the preparation of ferrous sulfide single crystals of a large size by this method, and to determine their crystal orientations.

## 2. Experimental

### 2-a Crystal compositions to be prepared

Figure 1 shows a part of an Fe-S binary phase diagram[10)]. According to this

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diagram, there are a eutectic point (980°C) and a highest melting point of pyrrhotite (1188°C). The arrow lines in this figure mean the compositions of the sulfide which was prepared as a single crystal, that is, a stoichiometric composition (FeS), and a congruent composition in which both liquidus and solidus curves are in contact with each other. This composition is found to be $Fe_{0.934}S$ in chemical formula and about 52 atomic % sulfur.

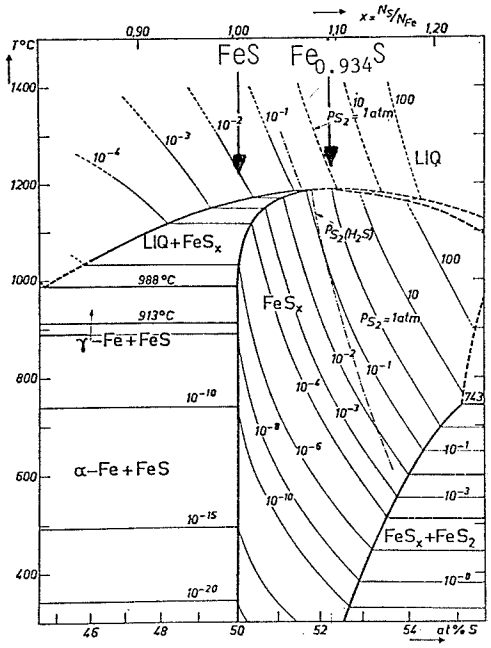



**Fig. 1.** Partial phase diagram of an Fe–S system.

### 2–b Experimental technique

Figure 2 shows the apparatus to prepare the preliminary sulfide. Both electrolytic iron (99.9%) and guaranteed sulfure powder were weighed precisely (10～15 gr) and the mixture was heated by an electric furnace in a double guartz ampoule as shown in the figure for one day at 450°C. After determining that there was no sulfur remaining in the ampoule, it was heated gradually from 450°C to 650°C for about 1 week. After manitaing the temperature at 650°C for 1 day, the ampoule was cooled in air.

The composition of above-treated samples was identified by comparing lattice constants of pyrrhotite with the standard data[11].

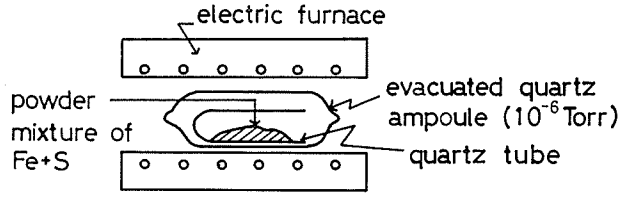



**Fig. 2.** Apparatus for preliminary sulfide materials.

### 2–c Preparation of large crystals

The preparation of large crystals from the samples was carried out by using the crystal growth apparatus shown in Fig. 3, where a quartz ampoule in which 4～6 gr of starting sample was filled in the graphite crucible was suspended from the top above the electric furnace consisting of an inner and a main furnace, and was lowered very slowly through the highest-temperature part towards the lower temperature part, as shown in this figure, by means of a synchronous motor (conf. Table 1). Here, the temperature gradient was 19°C/cm near 1150°C and 47°C/cm mear950°C.

The molten sample in the graphite crucible begins gradually to freeze and grow into a large crystal. When the cooling rate is too high, the crystal usually becomes

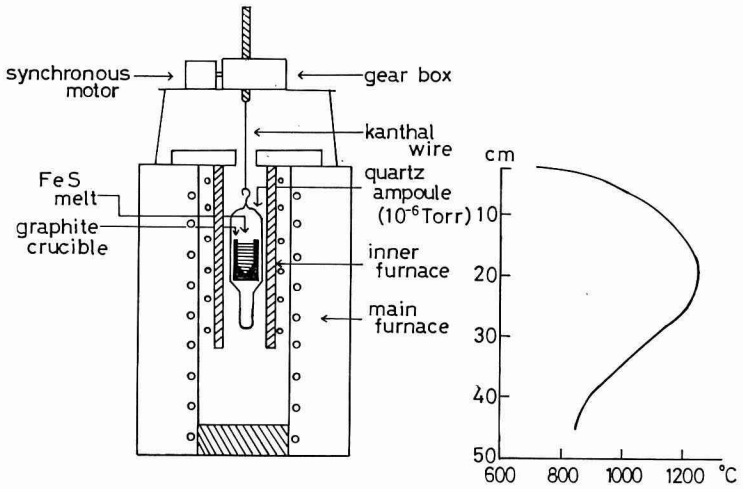



**Fig. 3.** Apparatus for crystal growth of ferrous sulfides.

a polycrystalline solid. Thus it is very important to obtain optimal conditions under which the solid sulfide becomes a single crystal of a given size. In this case, the lowest rate is confined, as shown in the table, owing to the apparatus used at present.

Another cooling method was used in this case, that is, the ampoule was fixed, but the temperature of the furnace was gradually decreased by using a siliconit furnace, in which the cooling rate was 16.8°C/h.

All sulfides were annealed at about 900°C for 40 to 100 h and cooled in the furnace.

The summary of the processes were listed in Table 2. Here the crystals prepared were numbered.

Figure 4 shows an overall view of massive crystals. The conical part is down-

**Table 1.** Lowering rate of quartz ampoule

| High | Medium | Low |
|---|---|---|
| 10.0 cm/h | 1.7 cm/h | 0.33 cm/h |

**Table 2.** Summary of crystal-formation process

| Process / Composition | High | Medium | Low | SiC $F^{ce}$ |
|---|---|---|---|---|
| FeS | Crystal 1 | Crystal 2 | Crystal 3 | Crystal 7 |
| $Fe_{0.934}S$ | Crystal 6 | — | Crystal 4, 5 | Crystal 8 |

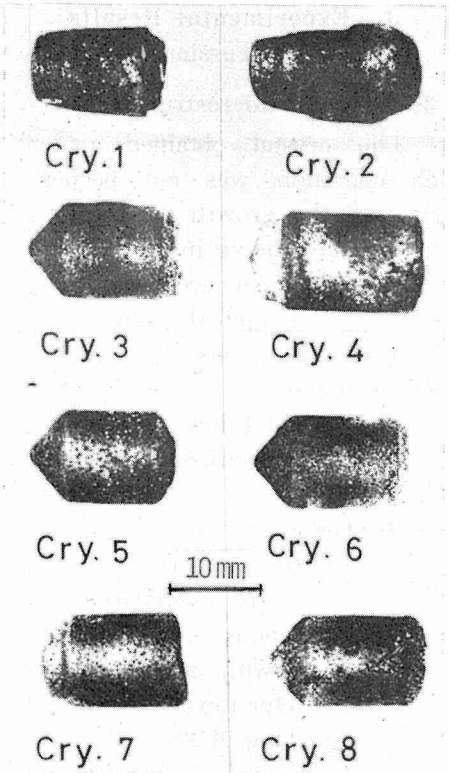



**Fig. 4.** Overall view of massive sulfide crystals obtained under various conditions.

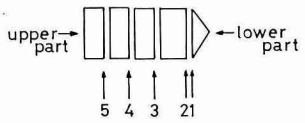



**Fig. 5.** Position numbers of surfaces for observations of a cylindrical crystal.

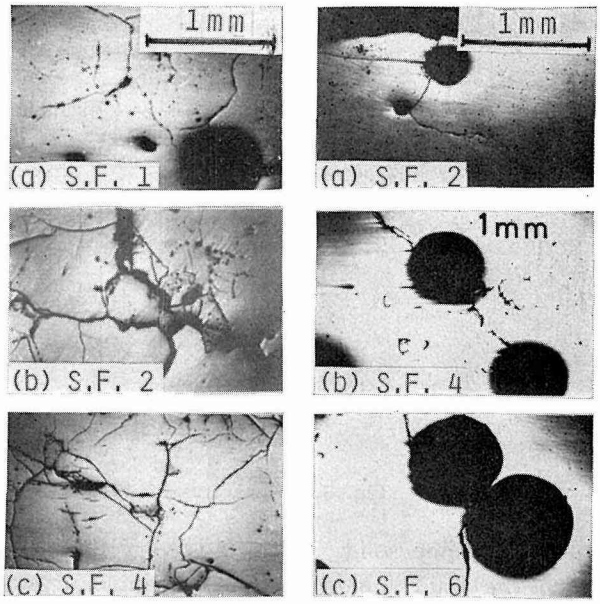



**Fig. 6.** Polished surfaces at different positions of Crystal 1 and 2.

**Fig. 6-1.** Crystal 1.

**Fig. 6-2.** Crystal 2.

ward and the size is 1.7～2 cm in length and about 1 cm in diameter.

## 3. Experimental Results and Discussion

### 3-a Optical microstructures

The crystal obtained under each condition was cut perpendicular to the growth direction as schematically shown in Fig. 5, and each numbered surface was examined with an optical microscope. The observed results are summarized as follows:

1) Crystal 1 has wide cracks and cylindrical holes (conf. Fig. 6-1).
2) Crystal 2 has cracks narrower than Crystal 1 and holes are cylindrical and continuous through the body with an increasing diameter towards an upper part (Fig. 6-2).
3) In Crystal 3 there is no hole, but many cracks remain (Fig. 7-1).
4) Crystal 4 has only small

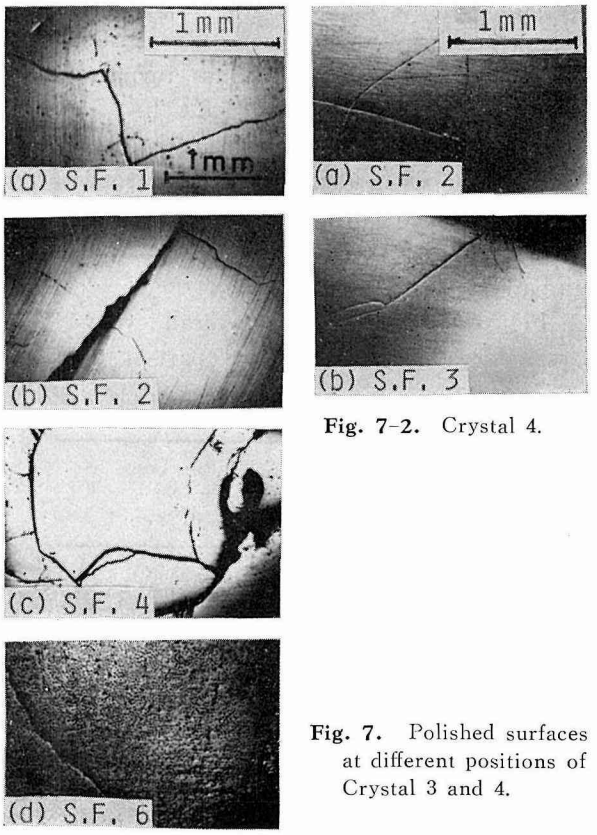



**Fig. 7-1.** Crystal 3.

**Fig. 7-2.** Crystal 4.

**Fig. 7.** Polished surfaces at different positions of Crystal 3 and 4.

cracks and no hole (Fig. 7-2).

5) Crystal 5 has almost no crack and no hole (Fig. 8-1).
6) Crystal 6 has cracks and holes less than Crystal 1 (Fig. 8-2).
7) Crystal 7 and 8 have many cracks yet, but the former has less than the latter (Figs. 9-1 and 9-2).

From above observations it is considered that Crystal 5 will be the best in the present experiment.

### 3-b Observation through a polarized light

Observation of crystals through a polarized light is highly useful when the crystal has optical irregular parts in it, that is, bcc and fcc crystals have no optical irregularity but hexagonal crystals show the color difference depending on their misorientation against an incident light.

Pyrrhotite crystals are hexagonal, and if the crystal consists of other crystalites having different orientations, the polarized light shows different colors depending on their orientation. For example, Fig. 10 shows the result obtained from Crystal 3, where the number of each picture indicates each surface of the crystal as stated previously. According to a series of these pictures, a small part of a different orienta-

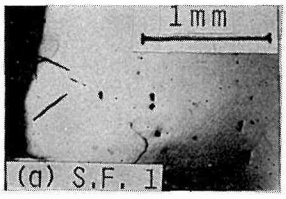



**Fig. 8-1.** Crystal 5.

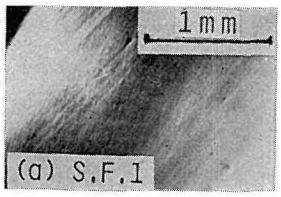



**Fig. 8-2.** Crystal 6

**Fig. 8.** Polished surfaces at idfferent positions of Crystal 5 and 6.

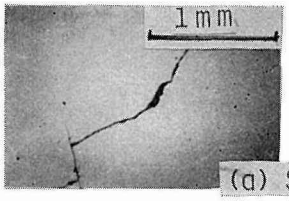



**Fig. 9-1.** Crystal 7.

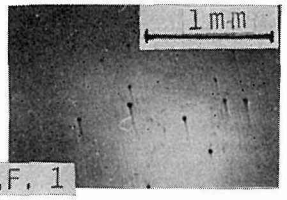
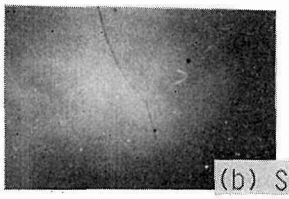
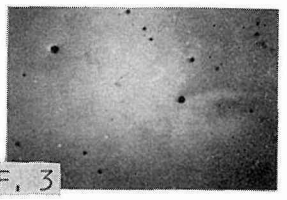


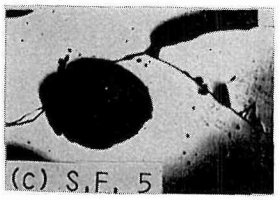

**Fig. 9-2.** Crystal 8

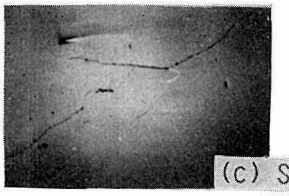
**Fig. 9.** Polished surfaces at different positions of Crystal 7 and 8.

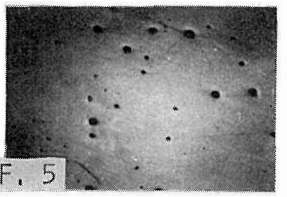


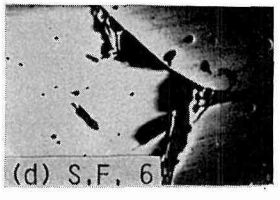


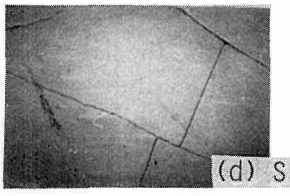



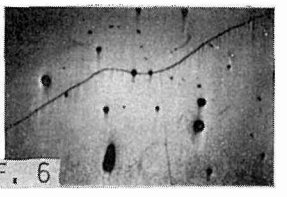
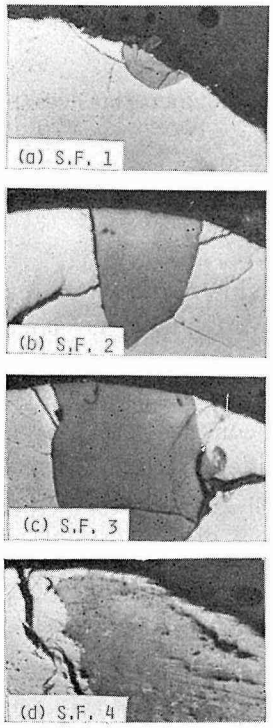



**Fig. 9-1.** Crystal 7. **Fig. 9-2.** Crystal 8




Dark part: different orientation.

**Fig. 10.** Observation of crystal through a polarized light.

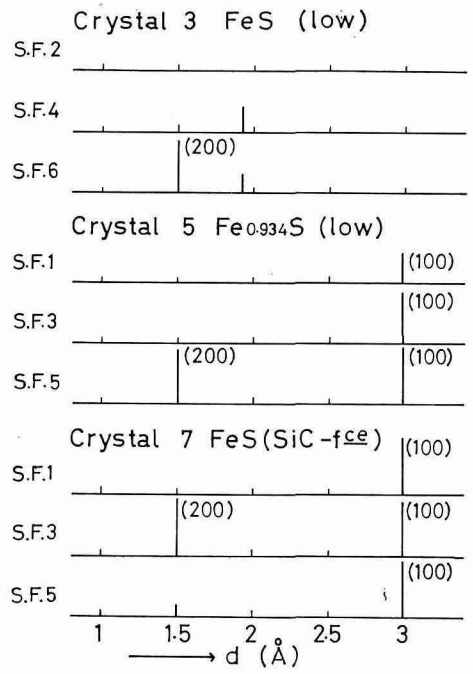



**Fig. 11.** Lattice spacing of some crystals obtained by CoK$\alpha$-ray.

tion from the main part becomes gradually larger towards the upper part of the crystal. Further, cracks were observed in the boundary between two crystals, but at other sites cracks were not observed. Therefore, cracks do not seem to be always a source of misorientation of the crystallite, but misorientation in the crystal will be the source of the crack.

From the above polarizing observation, Crystal 4 and 5 were found to have no such crystallite in the entire crystal.

### 3-c Examination by X-ray diffraction

Crystal 3, Crystal 7 prepared in a siliconit furnace for an FeS composition, and Crystal 5 which seemed to be the best sample for a $Fe_{0.934}S$ composition were examined by X-ray diffraction on its cut surface.

The results obtained were schematically shown in Fig. 11. It can be seen from the figure that some surfaces of the samples have no reflection or only a small number of reflections because of the large or a single crystal grain on the surface. In this case, the reflection from the (h00) plane was very strong. From the result it is assumed that this (h00) plane is perpendicular to the crystal growth direction. Further, Crystal 5 can be considered to be nearly a single crystal in combination with the microscopic observation.

### 3-d Direct observations by pole figure method

As Crystal 5 seemed to be a single crystal, it was examined further by a pole

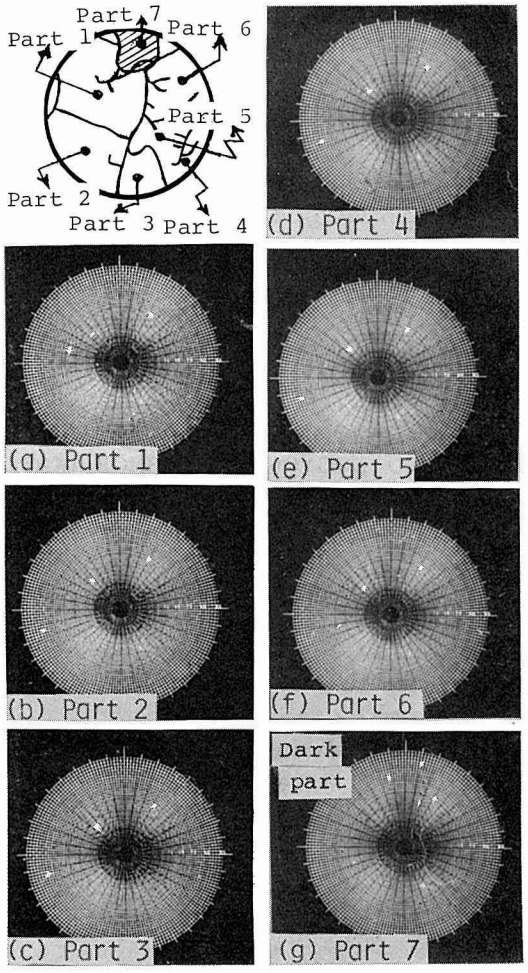



**Fig. 12.** (100) Pole figures at various positions on S.F. 3 of Crystal 3.

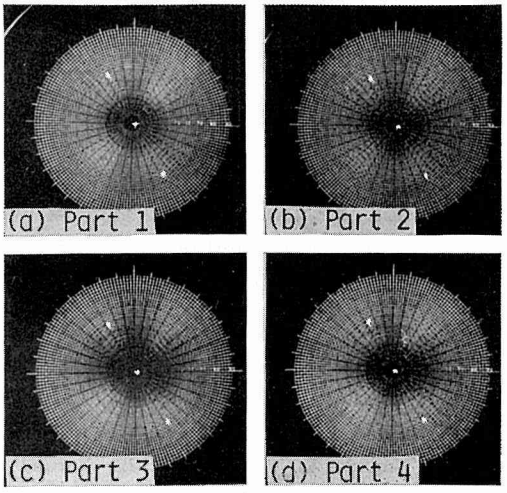



**Fig. 13.** (100) Pole figures at various positions on S.F. 3 of Crystal 5.

figure measurement. This apparatus (Toshiba TAD SU-090) can record directly the X-ray reflection from a specified lattice plane of the crystal surface on a Wulf's net. Experimental condition of this apparatus is as follows; Tube votage: 35 kV, Tube current: 12 mA, Target: CoK$\alpha$ ($2\theta=34.81°$), Collimeter: 0.8 mm$\phi$.

These figures were shown in Figs. 12 (a)~(g) and 13 (a)~(d). These are all taken by using a collimeter with 0.8 mm$\phi$ and an iron filter. For parts examined on the surface of Crystal 5 were far from each other, nevertheless the bright spots are all located in a similar position of the net and a bright spot is found in the central position* of the net. From these figures it can be considered that Crystal 5 has an (100) plane perpendicular to the growth direction of crystal and a large single pyrrhotite crystal.

## Summary

Some experiments were carried out by the Bridgeman method in order to obtain large single ferrous sulfides for the study on diffusion and others. The results obtained are as follows:

1. Preliminary materials for large crystals were prepared by keeping the specified compositions of pure Fe and S powdered raw materials at 450°C for 1 day, heating up to 650°C for 1 week, and marintaining the same temperature for 1 day.

* The bright spot in the central position in each figure seems to deviate only a little from its true position owing to a slight declination of the collimeter.

2. The large sulfide crystals were produced by slow cooling above materials from the temperature over their melting points in a vertical electric furnace with various cooling rates and keeping at 900°C for 40 to 100 h. The crystals obtained were examined microscopically with optical and poralized lights and by the pole figure method.

3. The best sound crystal was obtained from the sulfide having a congruent composition ($Fe_{0.934}S$) with the slowest lowering rate (0.33 cm/h) in the vertical furnace.

4. Pole figure method revealed that for the orientation of the crystal it had an (100) plane perpendicular to the growth direction of sulfide.

## References

1) K. Nishida: Tetsu to Hagane, **61** (1675), 411 (Technical Review)
2) K. Nishida, T. Narita and T. Tani: In press in *Oxidation of Metals*
3) K. Nishida, T. Narita and A. Notoh: ASAHI-GARASU KOGYOGIJUTSU SHOREIKAI KENKYU HOKOKU No. 29 (1976), 123.
4) C. E. Birchenall: Private communication (1960) and R. H. Condit, R. R. Hobbins and C. E Birchenall: Oxidation of Metals, **8** (1974), 409.
5) K. G. Barraclough, H. Geobel and A. Meyer: J. Crystal Growth **26** (1974), 101.
6) J. M. Rolls and H. J. DeBruin: J. Cryst. Growth, **16** (1972), 235.
7) T. Takahashi, O. Yamada and K. Ametani: Ditto, **20** (1973), 89.
8) P. W. Bridgeman: Proc. Am. Acad. Arts Sciences, **60** (1925), 303.
9) D. C. Stockbarger: Rev. Sci. Instr., **7** (1976), 133.
10) W. Burgmann, G. Urbain and M. G. Frohberg: Mem. Sci. Rev. Met., **65** (1968), 567
11) E. T. Turkdogan: Trans. AIME, **242** (1968), 1665.