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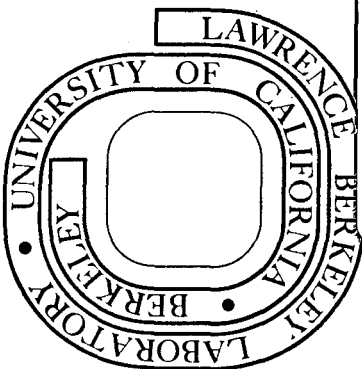
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A VIEW OF THE PRESENT STATUS AND FUTURE  
PROSPECTS OF HIGH PURITY GERMANIUM\*

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SUMMARY

The present state of our knowledge of the properties of high purity germanium is reviewed. The role of excess vacancies, oxygen and high dislocation density in producing trapping in detectors is discussed. By the application of Fourier Transform Spectroscopy, the major impurities have been identified and aluminum has been found to be the dominant one in most crystals. Analysis has shown that the principal source of aluminum is the polycrystalline starting material. The material problems related to detector fabrication are surveyed and a spectrum taken with a 43 cm<sup>3</sup> coaxial detector is presented. It is concluded that the important problems of material development are well delineated but that their solutions will require intensified effort.

I. INTRODUCTION

The development of high purity germanium as a detector material has now progressed enough so that some general statements can be made about our present understanding, and the areas where further research is needed can be rather sharply defined. Given the limited resources which have been applied to developing high purity germanium, the progress to date has been better than could have been anticipated. Simple analytical tools have been adapted to allow a rapid characterization of the quality of crystals.<sup>1,4</sup> The recent application of Fourier Transform IR Spectroscopy has led to the identification of all the important impurities. Several hundred detectors of all sizes have been made and, in the process, crystal properties important to device performance have been illuminated.

In order to make the presentation more compact, we will discuss the principal experimental results without too much attention to the rather devious route by which conclusions were reached. However, the evolution of our present understanding can be divided roughly into three areas; 1) the role of excess vacancies, 2) impurities and impurity distributions and 3) the concern for dislocations and structural defects.

II. THE ROLE OF EXCESS VACANCIES

An important acceptor level in high purity germanium can be produced by an excess of vacancies over the ambient temperature equilibrium value. Crystals grown from a melt incorporate a concentration

of vacancies equivalent to their solubility at the melting temperature. As the crystal cools it becomes strongly super-saturated unless some low energy condensation nuclei are present. In germanium the vacancy solubility at the melting point is  $>10^{15}/\text{cm}^3$  and at room temperature is insignificant.<sup>2</sup>

If no condensation nuclei are present, (e.g., dislocations), the strong super-saturation of vacancies cause their precipitation as vacancy clusters or voids.<sup>3</sup> These vacancy clusters, which can be revealed by chemical etching (Fig. 1) are always accompanied by acceptor centers with an activation energy of about 80 meV and a concentration of 2 to  $4 \times 10^{11}/\text{cm}^3$  (Fig. 2).<sup>4,5</sup> Centers with this activation energy are efficient traps at 77°K<sup>5</sup> and as a result, detectors containing vacancy clusters give completely unacceptable performance.

It is clear that this important effect makes dislocation-free crystals useless for detectors. The dislocation density required to avoid local effects of vacancy super-saturation depends on the effective "capture-radius" of dislocations. This radius was measured by selecting a partially dislocated slice of a crystal which was slightly n-type ( $<10^{10}/\text{cm}^3$ ) in the well dislocated regions and by metal point probing the typeness in the region of isolated dislocations. Because the undislocated parts of the crystal contain more than  $10^{11}/\text{cm}^3$  acceptors, sharp junctions are found at the limit of the radius of action of the dislocation. We find that the thermal history that our crystals experience during cool-down from growth produces a capture-radius in the range 0.5 to 1 mm. To be free of trapping caused by vacancy clusters, it is essential that a crystal contain no dislocation-free areas larger than a few millimeters squared. Selection of high-grade detector material must therefore include a dislocation etch to look for small dislocation free regions. These selection criteria presumably also should be applied to germanium to be used for lithium drifting, since it is believed that the trapping centers associated with vacancies survive the drift process.<sup>6</sup>

The concentration 2 to  $4 \times 10^{11}/\text{cm}^3$  of vacancy-associated acceptors in dislocation free crystals appears to be the equilibrium solubility of these defects at ~300°C. Dislocation free crystals, when heated above 300°C, show an increase in the 80 meV level, while those annealed below 300°C show a decrease. These effects are illustrated schematically in Fig. 3. If these crystals are annealed for long times at, say, 200°C, the density of the 80 meV level can be reduced to about  $10^{10}/\text{cm}^3$ . After this treatment the carrier trapping in detectors is greatly decreased, but not sufficiently to make high quality devices.

In speculating about the origin of this unusual annealing behavior, fast diffusing impurities (Cu, Ni) might immediately be suspected. Impurities which enter germanium by the dissociative-diffusion mechanism have a solubility which is governed by a mass action law<sup>7</sup> between interstitial and substitutional impurities and vacancies. The high concentration of

\* This work was done under the auspices of the United States Atomic Energy Commission.

vacancies in dislocation-free crystals will greatly increase the solubility of the substitutional form over that in dislocated crystals. Figure 3a shows the high temperature portion of an expanded plot of the crystal in Fig. 3 before and after annealing. The energy level shown (44 meV) is apparently due to the well known single ionization state of substitutional copper in germanium. Since, as seen from Fig. 3a, the copper impurity clearly does not participate in the annealing process, it is likely that other fast diffusing impurities will behave similarly.

Crystals which are reasonably uniformly dislocated nevertheless often show a constant impurity concentration over most of their length with concentrations varying from  $10^{10}$  to  $10^{12}/\text{cm}^3$ .<sup>7</sup> For a long time, the lack of impurity segregation along the length of crystals made us suspect that vacancies were responsible, but recent work has shown that the hypothesis of Hall<sup>8</sup> who suggested the presence of a non-segregating chemical impurity was better founded, as detailed in the next section.

### III. IMPURITIES AND IMPURITY DISTRIBUTIONS

Most of our crystals have a background donor impurity which segregates toward the tail end so that this end is usually n-type. Many crystals exhibit a uniform net acceptor concentration along most of the length with the tail becoming n-type. Analysis of these crystals by Fourier Transform Spectroscopy (FTS) has shown that the n-type impurity is phosphorus and the p-type is aluminum.

A high concentration is sometimes found at the head ends of crystals. FTS shows that this is due to boron which always segregates to this end. Furthermore, these crystals have all been grown from the head ends of zone refined bars.

Occasionally crystals are found where the acceptor concentration increases from the head to the tail. FTS shows that this impurity is gallium or, in a few cases, indium.

On the basis of the distribution of the four impurities, we can explain all of our resistivity profiles. Indeed from an examination of the type of profile, we can usually infer the nature of the impurities in a given crystal.

### IV. THE ROLE OF ALUMINUM

Once having taken into account the effects of excess vacancies, the most common type of impurity distribution that needs explaining is shown by the examples in Fig. 4. As can be seen in this figure, the conductivity of the crystals appears to be dominated by an acceptor with a segregation coefficient very close to 1.0. Low temperature measurements give an activation energy near 10 meV for this acceptor. All of the group III and V impurities have activation energies near 10 meV but have segregation coefficients far from 1.0 under our crystal growing conditions. The segregation coefficients of other common elements are known in germanium, and all are very far from 1.

We have long observed abundant secondary evidence that the non-segregating impurity is aluminum. Attempts made to grow aluminum-doped crystals showed that aluminum was very strongly getterred by the quartz crucible. Melts to which  $10^{16}/\text{cm}^3$  aluminum atoms were added gave crystals with only  $5 \times 10^{12}$  acceptors/ $\text{cm}^3$

and were non-segregating. Also when aluminum contamination might be suspected due to machining of crystal grower parts, crystals were often observed with an apparent non-segregating impurity. Hall<sup>8</sup> had suggested aluminum as the non-segregating impurity on the basis partly of chemical affinities and also on the basis of his suspicions as to possible sources of contamination. He proposed a model for a distribution between quartz and melt which would fit his impurity profiles, but it seemed that the model could hardly be stretched to fit ours. Thus, although the evidence for aluminum was, in retrospect very strong, we refused to accept it until the direct analytical evidence obtained by FTS made it clear that Hall's hypothesis was correct.

The detailed results of the application of far infrared spectroscopy will be presented in a separate paper in this meeting. Here we will present some general results and try to convey our enthusiasm for this technique. Aside from the unexpected simplicity of applying FTS, we were immediately surprised by the high sensitivity. In the range of concentrations of interest here, ( $10^9$  to  $10^{12}/\text{cm}^3$ ) the signal-to-noise ratio increases with impurity concentration while the natural line widths of the optical transitions decrease with decreasing impurity concentration, so the detectability hardly changes with impurity concentration. Crystals which contain  $10^9/\text{cm}^3$  acceptors give spectral lines with very good signal-to-noise ratios. At the same time, the natural line widths of these high purity crystals are so small ( $<0.1 \text{ cm}^{-1}$ ) that all impurities are unambiguously separated.

Application of FTS to crystals exhibiting the non-segregating impurity proved that this impurity was always aluminum--even in the purest crystals. Since low temperature conductivity measurements indicated that the total impurity concentration was due to levels near 10 meV, and FTS showed only the single dominant spectrum of aluminum, virtually all the electrical activity is accounted for without the need to invoke other sources such as vacancies, dislocations, strain, etc.

The knowledge that the non-segregating impurity is always aluminum allows us, for the most part, to dispense with such ideas as fortuitous compensation, equilibrium solubility of some structural defect, etc., but still gives no hint why the aluminum does not segregate. However, some recent observations lead to a simple explanation for this lack of segregation.

Experiments showed that a crystal grown in a quartz crucible that was etched for a long time, say 10 minutes in HF, exhibited an aluminum concentration much lower than from a lightly etched crucible. This suggests that if the aluminum is strongly getterred by quartz it must remain bound in the surface. It would clearly be useful to prove this high surface concentration by analysis. However, due to the strong matrix effect produced by the large quantity of neutral quartz which must be analyzed along with the aluminum doped quartz, most analysis techniques are very insensitive. In order to get some secondary evidence about the depth of surface diffusion during crystal growth, the crucible surfaces were examined for germanium--a much easier problem. Using X-ray fluorescence analysis after successive etching in HF, it was found that 5 minutes etching was needed to reduce the germanium content below about 100 ppm. It is not unlikely that the aluminum could diffuse an equal distance during crystal growth and thus require a 10 minute etch for its removal.

Assuming that aluminum diffuses into quartz to a similar depth as does germanium it would be expected that a light etching of the crucible would remove only a fraction of the aluminum-doped surface. This

is in accord with Hall's observation that successive generations of crystals have only a moderate reduction of the non-segregating impurity.

Our conclusion is that the surface of the quartz crucible often contains a very high concentration of aluminum which gives the necessary aluminum source during crystal growth. There are strong indications that an initially clean crucible acquires aluminum from the melt so we conclude that the primary aluminum source is not the quartz but the germanium; and the only way to reduce the aluminum is to improve the starting material and/or to getter it by heavily etching the crucible prior to crystal growth. This conclusion emphasizes the need for analysis of the starting material for impurities, including aluminum.

## V. OBSERVATIONS ON IMPURITIES

All of the starting germanium used by us for crystal growth is polycrystalline. We have been surprised to find that FTS is capable of analyzing this highly disordered material while other analytical methods, such as Hall-effect measurements, give no useful results on polycrystalline germanium. We observe that polycrystalline germanium contains about  $6 \times 10^{11}/\text{cm}^3$  acceptor centers at 77°K due to structural defects. Since the type-ness can never change on cooling, i.e., the Fermi level can never cross midband, we are restricted to examining only p-type impurities if the n-type concentration is less than  $6 \times 10^{11}/\text{cm}^3$ . For example, if a sample contained  $5 \times 10^{11}$  phosphorus and  $10^8$  aluminum atoms, only the aluminum would be detected by FTS. Since the n-type concentration in the starting material never approaches  $6 \times 10^{11}$ , and therefore cannot be seen by FTS, we are forced to guess its probable concentration based on observations on the tail-ends of single crystals pulled from the starting material.

Almost all of our crystals contain a background n-type impurity which segregates with a coefficient of about 0.2 and, based on the tail-end concentrations, it must be present in the initial melt with a concentration in the range of about 0.1 to  $5 \times 10^{10}/\text{cm}^3$ . Returning to Fig. 4, it seems likely that the addition of a normally segregating donor could result in a rather constant p-type concentration along the length of a crystal. By using an analysis similar to Hall's the concentration profiles can be calculated. Figure 5 shows a plot of

$$N = N_A - N_D = k_A N_{AO} - k_D N_{DO} (1-g)^{(k_D-1)}$$

where  $N_{AO}$  and  $N_{DO}$  are starting concentrations of  $N_A$  and  $N_D$  in the melt with  $N_{AO}$  as the variable parameter and  $N_{DO}$  set at a fixed value of  $2.5 \times 10^{10}/\text{cm}^3$ ,  $k_A$  and  $k_D$  the segregation coefficients, are set equal to 0.2 (the normal value for aluminum and phosphorus at 10 cm growth/hr.) and  $g$  is the fraction of the original melt that has solidified in the crystal. If aluminum is chosen as non-segregating, its concentration being determined by an equilibrium between the quartz and germanium, a simple "normal freezing" equation adequately describes the impurity profiles.

There is some art in the coincidence of Figs. 4 and 5 in that crystals were selected which appeared to have roughly the same n-type concentration. However, other profiles could be matched also by only changing the n-type concentration used. The conclusion is that the concentration of aluminum in the

crucible surface is so high that it is able to maintain its equilibrium with respect to molten germanium without being detectably depleted during growth (i.e. a constant source).

The lower dashed curve in Fig. 4 shows the profile of a recent n-type crystal which apparently contains very little aluminum. Thus, while the n-type impurity forms a common background in most of our crystals, its level has little effect on the suitability for detectors. Therefore, although we cannot analyze for n-type impurities in the polycrystalline starting material, they do not seem to appear in important concentrations. FTS analysis of the n-type portions of these crystals prove that this impurity is phosphorus. By selecting the n-type portions of crystals and growing successive generations to concentrate the n-type impurity, Hall<sup>1</sup> has also found his n-type impurity to be phosphorus.

Aluminum appears as the dominant impurity in most of the germanium we have examined. Successive samples taken along a zone refined bar indicate that while aluminum segregates in our zone refiner, it does so at much lower rate than would be predicted by its segregation coefficient. Since our zone refining is done in quartz, the same distribution between quartz and germanium probably exists as in crystal pulling. Intrinsic-grade starting material from Hoboken and Sylvania had aluminum as the dominant impurity. Some recent intrinsic-grade germanium from Eagle-Pitcher contained phosphorus as the dominant impurity--we have not yet evaluated this material through our refining and pulling processes.

Figure 6 is an attempt to illustrate schematically the way the impurities distribute during zone refining together with the impurity profiles to be expected for crystals grown from sections of ingots. All impurities appear to segregate normally except aluminum. Boron is not effectively removed by zone refining but is not often found in significant concentrations. During crystal growth boron is removed rapidly at the head end of the crystal and does not effect the main body. A good correlation has been found between the zoned bar profiles and the profiles expected in the pulled crystals.

The main problem with aluminum is that there is just too much of it in the starting material. Because aluminum is getterd by the quartz crucible, its concentration is decreased while crystal pulling--but this also makes its removal while zone refining less effective. However, now that we have a method of analyzing the zone-refined bars, the problem of reducing the aluminum concentration can be attacked directly.

Aside from the group III and V impurities, occasional lines are seen in FTS which do not correspond to known impurities. These lines have not been of a concentration as to materially effect the crystal purity, and their presence is not associated with trapping. The only other impurity known to effect detector performance is oxygen.

Hall<sup>9</sup> has shown that high concentrations of oxygen in germanium give rise to smooth etch pits and that detectors made from these crystals show carrier trapping. By lithium-precipitation studies he has shown that crystals grown in quartz contain about  $5 \times 10^{13}$  oxygen/cm<sup>3</sup> and it is known that these crystals do not give trapping. It is likely that in order for the oxygen to form trapping centers it must have a concentration high enough for the formation of oxygen complexes similar to the O<sub>4</sub>-centers in silicon. Excessive oxygen concentration can be suppressed by growing in a high-purity hydrogen ambient. However, even the smallest leak in the gas system leads to crystals with smooth pits and carrier trapping.

It is concluded then, that with the exception of aluminum, all the impurities are presently at a low enough concentration for any normal detector application. Now that we have an analytical technique in Fourier Transform Spectroscopy, we can hope that this impurity, too, will soon be controlled. We find, though, that even when the impurity concentration is sufficiently low, trapping effects are sometimes seen in detectors which can be attributed to structural imperfections. A more detailed report discussing the reaction of dislocations and charge collection in detectors is in preparation.<sup>13</sup>

## VI. CRYSTAL PERFECTION AND GROWING CONDITIONS

A strong correlation has been observed between poor charge collection in detectors and dislocation density. That this trapping is not due to chemical impurities with deep levels is shown by the fact that crystals which are otherwise equal except for dislocation density do not show trapping. Also the known impurities with deep levels (Cu, Ag, Ni, etc.) all have very small segregation coefficients ( $<10^{-5}$ ) and are readily removed in crystal growing. These impurities also have very small solubilities at room temperature and would not give significant trapping if present in equilibrium concentrations. Therefore to show trapping, the deep level impurities must be present in super-saturated concentrations--this is in conflict with the observation that trapping increases with increasing dislocation density, i.e., concentration of precipitation nuclei.

It will be recalled from the discussion of vacancies that any region greater than a few  $\text{mm}^2$  without dislocations will contain traps due to excess vacancies. This means that the crystal must contain at least several hundred dislocations/ $\text{cm}^2$  which are uniformly distributed. When the crystal contains  $10^4/\text{cm}^2$  dislocations, detectable trapping appears which increases with dislocation density. The limits on dislocation density for crystals to make high quality detectors appear to be about 500 to 5000/ $\text{cm}^2$  and these must be reasonably uniformly distributed.

The high or uneven distribution of dislocations is due to poor thermal conditions in the crystal grower. Enough is known historically about how to grow high-quality germanium crystals except for the fact that we are constrained to grow in hydrogen gas as the only ambient which will produce crystals free of trapping. Hydrogen has a very high thermal conductivity and a low viscosity so it is a source of strong thermal convection and surface cooling of the growing crystal. The problem is illustrated in Fig. 7a. The circulating gas produces surface cooling at the melt-solid interface which results in a turned-down lip at the periphery of the crystal. This lip is one source for dislocation multiplication.

We first tried suppressing the convection cooling by using afterheaters (reflectors) but this added many new problems. The growth rate is greatly slowed and the lack of thermal gradient causes a very unstable melt-solid interface. Also the lack of thermal gradient causes the dislocations at some point down the length of the crystal to wander to the sides and disappear and thereby leave dislocation-free regions in the middle. Clearly what is needed is some type of baffling of the gas circulation that maintains a large thermal gradient but at the same time prevents the excessive cooling of the surface at the melt-solid interface. Several baffles have been tried which have had an effect in the proper direction but

no completely satisfactory results has yet been achieved. The dynamics of the gas circulation are such that the convection which causes the interface cooling does not appear until after several cm of crystal have been grown so that the head ends of crystals almost always have good perfection regardless of the thermal distribution.

The thermal convection while crystal growing can readily be seen by admitting water vapor with the hydrogen and observing the  $\text{GeO}$  smoke. Minor changes in the growing conditions often produce unexpected and gross changes in the heat transport by hydrogen. Consider the following example: our crystal-growing chamber which is 60 cm long and 15 cm bore has the hydrogen admitted coaxial with the seed rod at the top and the exit at the bottom. When the gas flow is increased from 1 l./min to 5 l./min the expectation is that the overall thermal gradient would be increased and the interface surface cooling made worse. The actual effect was to decrease both the thermal gradient and the interface cooling. Visualization with  $\text{GeO}$  smoke showed a gas flow pattern as illustrated in Fig. 7b. The gas circulation broke into two separate eddies with a stagnation layer about 5 cm above the melt which seemed perfectly flat and only about 1 mm thick. This stagnation appears to transport very little heat compared with the high gas velocities observed in the eddies. The net effect of increasing the gas flow was to produce a short eddy above the melt which is not nearly as effective in cooling the crystal as the long circulation with low gas flow.

We have observed that the problem of "coring" is correlated with the thermal gradient while pulling crystals. It is found that crystals which are measured on the surface and found to be p-type often have an n-type or low concentration p-type core which can extend for most of the crystal length. We find that crystals pulled at 10 to 13 cm/hr (high thermal gradient) rarely have any detectable radial resistivity variation even at impurity concentrations as low as  $10^9/\text{cm}^3$  while crystals pulled at 5 to 8 cm/hr (low thermal gradient) usually exhibit "coring". This effect is probably not due to different melt-crystal interface curvatures as an attempt is always made to keep the interface as flat as possible.

Theoretical calculations by Arizumi and Kobuyuki<sup>10</sup> have shown that with free gas circulation and a gas with the thermal conductivity of air, melt-crystal interfaces concave toward the melt are always produced, with the least concave surface with the least afterheating. This is in accord with our observations. However, we expect that a little more experience will lead to constructing a gas baffle that will allow free gas circulation above the melt to maintain a large thermal gradient while at the same time reducing the circulation at the melt-crystal interface.

Until the advent of Fourier Transform Spectroscopy, so much effort was wasted trying to relate the constant impurity concentration to crystal defects that the actual quality declined. Now that the separate nature of these problems is realized, it is to be expected that their solution can be attacked more rationally. However, a great deal of good germanium has been produced and it would be worthwhile to discuss our experience in making detectors from this material.

## VII. DETECTORS

The process of making detectors from high purity germanium is remarkably free of art and complications when compared with making lithium drift devices.<sup>14</sup> Stated simply, good germanium makes good detectors--any fussing with the fabrication is usually an attempt to compensate for some defect in the crystal. As an example, consider the detailed process steps to make a 10 cc planar detector.

- 1) Saw a 1 cm thick slice from 36 mm diameter crystal.
- 2) Slightly lap slice, evaporate lithium on one face and heat in argon at 220 to 280°C for five minutes.
- 3) Etch for one minute, mask lithium side with vinyl tape and etch for three minutes.
- 4) Evaporate 500 to 1500 Å of palladium on side opposite lithium.
- 5) Mask palladium with vinyl tape, etch one minute and quench in methanol.

The detector is ready for use.

The only critical step in the process is the preparation of the surface barrier contact. This requires that the etch be stopped abruptly with methanol and quickly blown dry so as to avoid staining and condensation. If any handling error is made, the surface barrier can be lapped off and reapplied.

Other p-type contact methods (ion implantation, glow discharge, alloying, etc.) and detector geometries (grooves, guard-ring, etc.) have been developed by other groups to "simplify" detector fabrication. We find, however, that the above recipe, applied correctly, leads to full area devices with the theoretically predicted efficiencies. Therefore none of the expensive starting material is wasted.

If a crystal has sufficient purity to be depleted at a reasonable voltage, we find the device performance to be quite indifferent to typeness or even if of mixed typeness (e.g., an n-type core in a p-type crystal). Since the field at the metal surface-barrier is lower with p-type crystals these often make devices capable of sustaining higher reverse bias than n-type. This may allow using poorer quality p-type than n-type crystals, but good quality crystals do not require high voltage. On the other hand, effectively thinner entry windows in X-ray detectors result from using n-type material.

The characteristic of the crystals that seems to be most correlated with detector quality is the dislocation density. We have seen exceptions only for crystals with obvious oxygen contamination or crystals grown in vacuum or non-reducing atmospheres.

As larger detectors are made, the crystal quality requirements become more stringent. Since spectral line widths are much more sensitive to differential than absolute charge collection efficiency, the inclusion of regions having a greater range of efficiencies in large devices makes their performance much poorer than small devices made from the same material. It has been our experience that practically all high-purity germanium makes high quality small detectors (say, 1/2 cm<sup>3</sup>), less than half of our crystals produce any high quality full area planars (approximately 10 cm<sup>3</sup>) and to make large coaxial detectors (about 50 cc) the material must be very carefully selected. Of course this is not an inherent feature of high-purity germanium, but simply a result of our present inability to control the dislocation density over greater lengths of our crystals without sacrificing purity.

In addition to the problem of material selection, coaxial detector fabrication presents more problems than do planar detectors due to the geometry of the surface barrier. Despite this, our group has made large coaxial detectors. Figure 8 shows a full energy spectrum of <sup>60</sup>Co made with a 43 cm<sup>3</sup> coax detector with an external surface barrier and a lithium-diffused core.

High-purity germanium detectors naturally contain very little undepleted germanium compared with lithium drift detectors so fewer pulses degraded by slow collection are observed. One might expect that the structural quality requirements for crystals used to make high-purity germanium detectors would be no more stringent than for lithium drift and probably somewhat less so. While regions of high dislocation density produce only trapping in high-purity detectors, they might also act as lithium precipitation centers and thus lower the local electric field precisely where it is most needed in lithium-drifted detectors.

## VIII. CONCLUSIONS

The principal source of contamination in much of our high-purity germanium has been shown to be aluminum in the starting material. Fourier Transform Spectroscopy permits analysis of polycrystalline germanium for very low concentrations of p-type impurities, so we are confident that the aluminum impurity can be controlled in the future.

The dominant trapping center in high-purity germanium in the absence of oxygen is produced by excess vacancies in dislocation free regions in the crystal. The presence of excess vacancies is always associated with vacancy-clusters which can be revealed by chemical etching. High concentrations of oxygen lead to oxygen complexes in germanium, which can also be revealed by etching. These also result in charge trapping. The oxygen concentration can be lowered below the level at which clusters form by growing the crystals in high purity hydrogen.

Dislocation densities greater than about 10<sup>4</sup>/cm<sup>2</sup> result in detectors with noticeable trapping; consequently crystals used to make high quality detectors should have a dislocation density of 500 to 5000/cm<sup>2</sup> with reasonably uniform distribution.

It is interesting to note that all the defects which give rise to trapping can be revealed by chemical etching. The character of the etching process which decorates defects is the accelerated chemical attack due to the local strain fields (bond stretchings) associated with point- and line-defects. The presence of these strain fields have been shown by anomalous X-ray transmission<sup>11</sup> and their spatial distribution visualized by optical birefringence.<sup>12</sup> Thus there is strong evidence that an important source of carrier trapping is due to the micro-strain fields associated with point- and line-defects producing deep energy levels. It is likely that Fourier Transform Spectroscopy can be expanded to higher frequencies so as to explore the entire band gap for optical transitions. The character of the trapping centers can then be established unequivocally.

As to detectors, the fabrication process presents no fundamental problems and the particular methods used are not by any means as critical as the choice of material. Excellent small detectors can be made from most high-purity germanium but routine production of large detectors such as coaxial units of >50 cc volume awaits sufficient supply of crystals with good structural perfection over large volumes.



While this paper attempts to delineate the main problems in producing high-purity germanium for high quality detectors, we do not wish to imply that the solution of the remaining problems will be easy. In fact, we anticipate that considerable work will be needed to develop processes capable of producing substantial quantities of large diameter material suitable for large (50 cm<sup>3</sup>) detectors.

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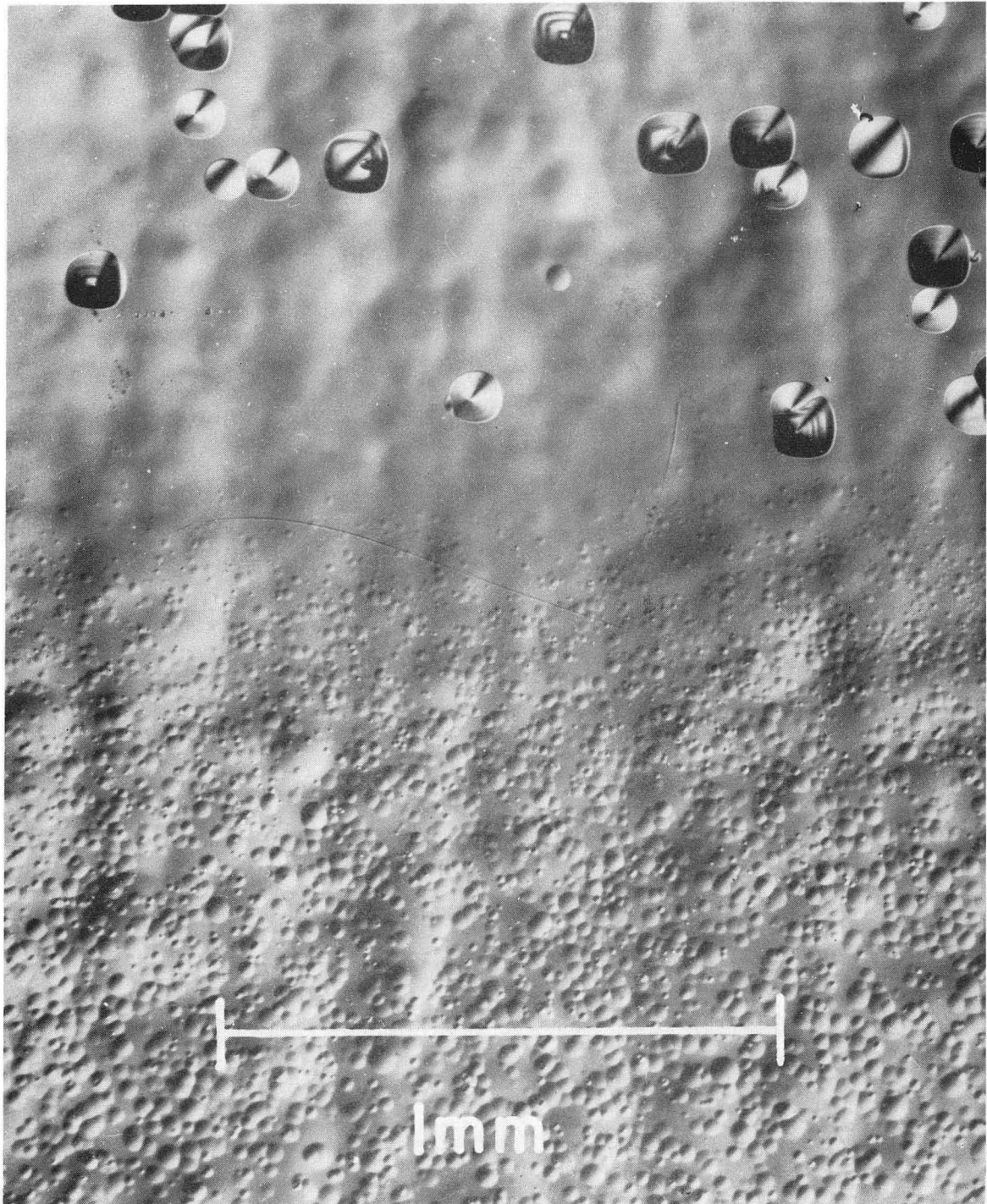
We gratefully acknowledge the contribution of R. Pehl and R. Cordi who are responsible for the group's detector evaluation and production, and also for supplying the <sup>60</sup>Co spectrum. M. Roach has also contributed by making crystal measurements, and R. Davis has constructed much of our apparatus. We thank P. Glasow, a short-term visitor to our Laboratory, for growing many recent crystals and thereby freeing our time to write this report. F. Goulding has contributed to every phase of this work and the manuscript has benefited greatly by his critical reading.

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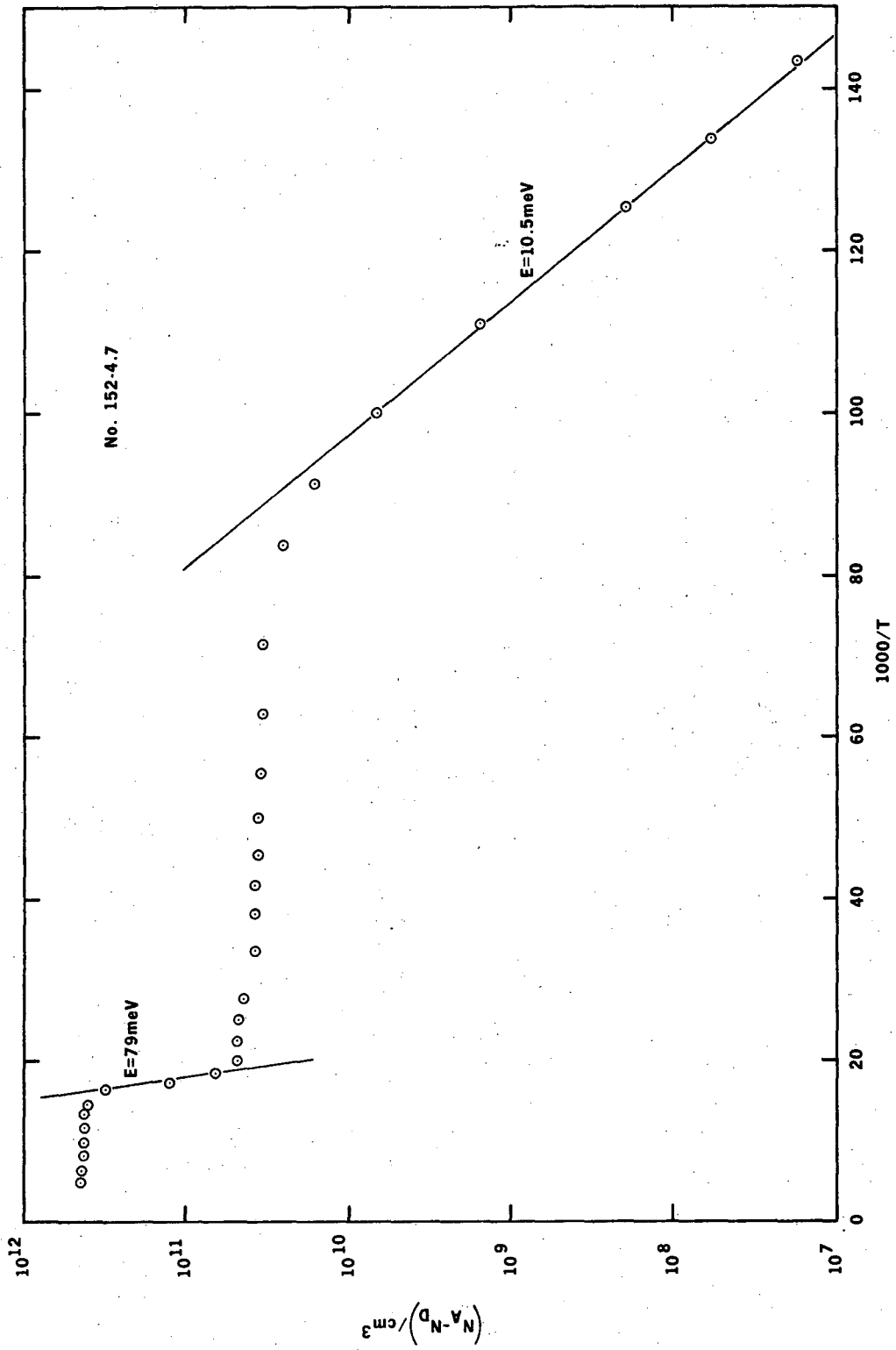
## FIGURE CAPTIONS

- Fig. 1. Photograph of etch pits at the boundary of a dislocated and undislocated region of a crystal slice. In the upper portion are large pits due to dislocations and the lower, small pits due to vacancy clusters. The boundary region is free of pits.
- Fig. 2. Acceptor concentration vs temperature for a dislocation free crystal. The energy level at 79 meV is associated with vacancy clusters and the level at 10.5 meV has been determined by FTS as being due to aluminum.
- Fig. 2a. Expansion of the higher temperature portion of Fig. 2 showing the effect of annealing on the population of the 79 meV level. The level at 44 meV, probably due to substitutional copper, is not effected by this annealing.
- Fig. 3. Annealing behavior of dislocation free germanium. The net acceptor concentration has been determined by Hall effect measurement at 77°K and the population of the shallow level by measuring conductivity at helium temperatures.
- Fig. 4. A selection of crystal profiles which show the common constant impurity concentrations which have been shown by FTS as due to aluminum. The n-type portions are not shown. The lower dashed profile is of an n-type crystal which apparently contains little aluminum.
- Fig. 5. Best fit obtained in attempting to fit "normal freezing" curves to the data of Fig. 4. The effective segregation coefficient was chosen to be 1.0.
- Fig. 6. Schematic representation of the distribution of impurities during zone refining and of impurity profiles of crystals grown from sections of the refined bar. Boron is an occasional impurity while aluminum is almost always dominant.
- Fig. 7a. Gas circulation patterns while crystal growing as revealed by GeO smoke.
- Fig. 7b. Change in gas circulation pattern as a result of increasing hydrogen gas flow from 1ℓ./min to 5ℓ./min.
- Fig. 8. Portion of a  $^{60}\text{Co}$  spectrum taken with a 43 cm<sup>3</sup> coaxial high-purity germanium detector. Resolution and peak-to-Compton ratio were determined from expanded plots of this spectrum.



XBB 7310-6167

Fig. 1



XBL 7310-1380

Fig. 2

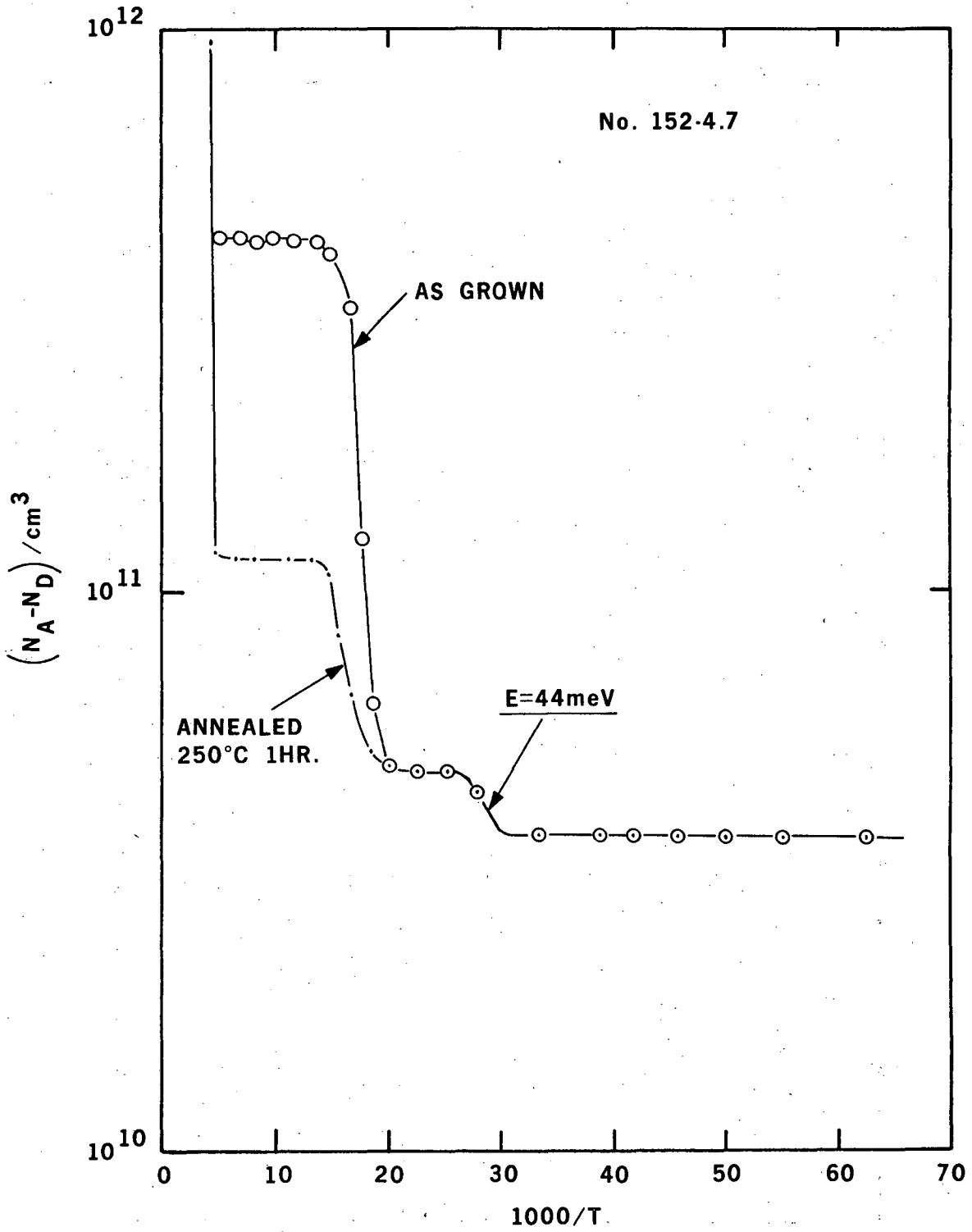
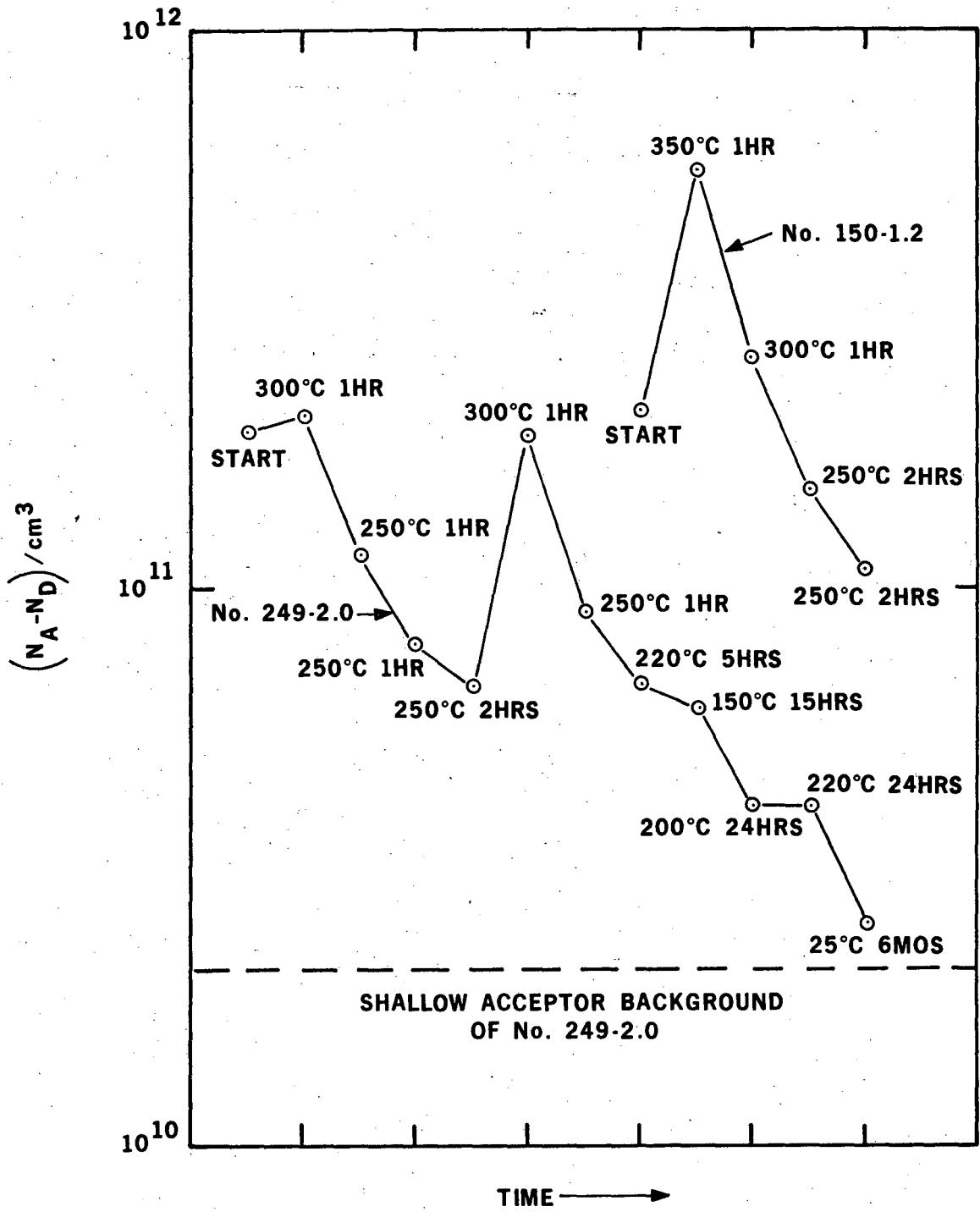
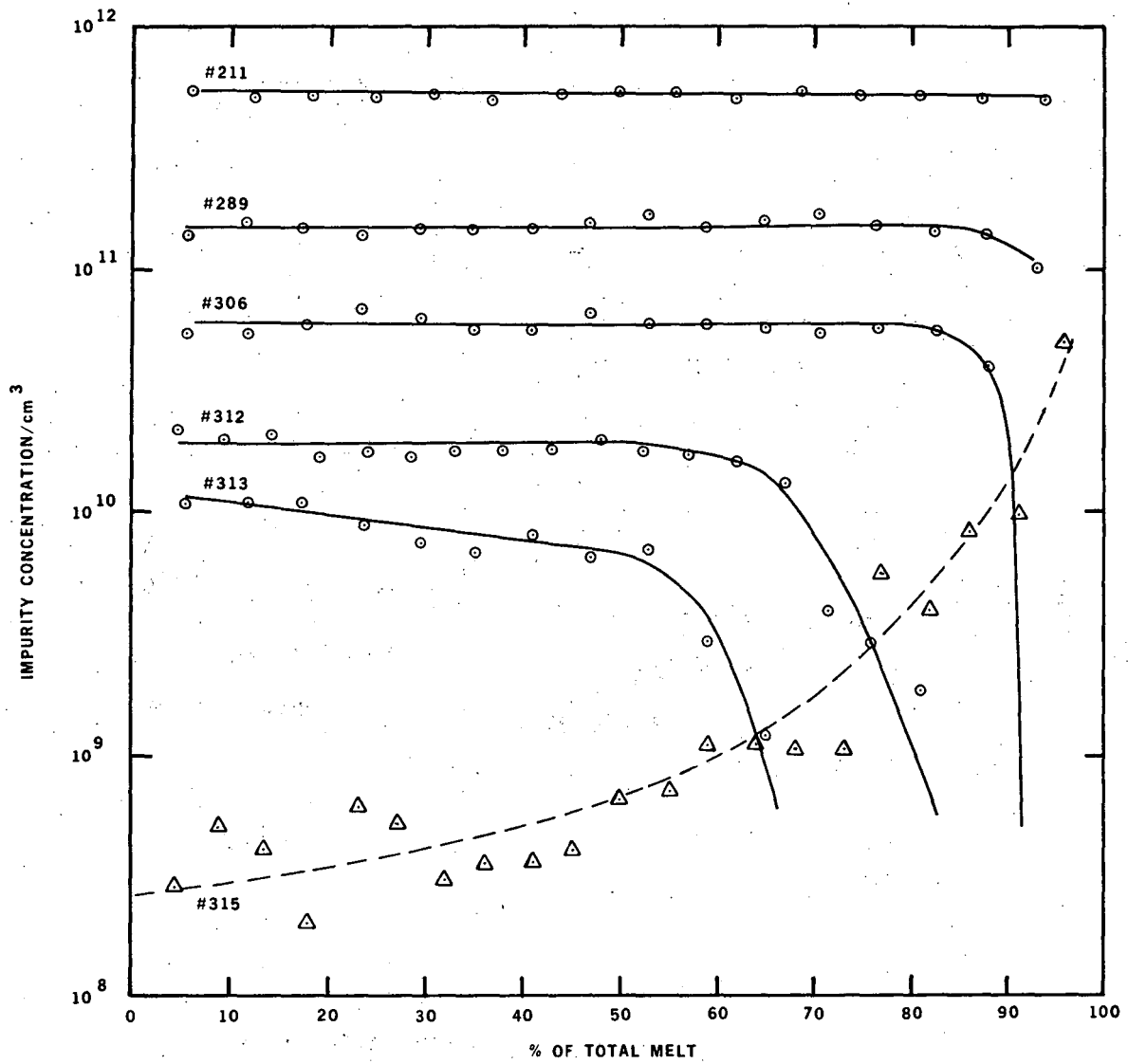


Fig. 2a



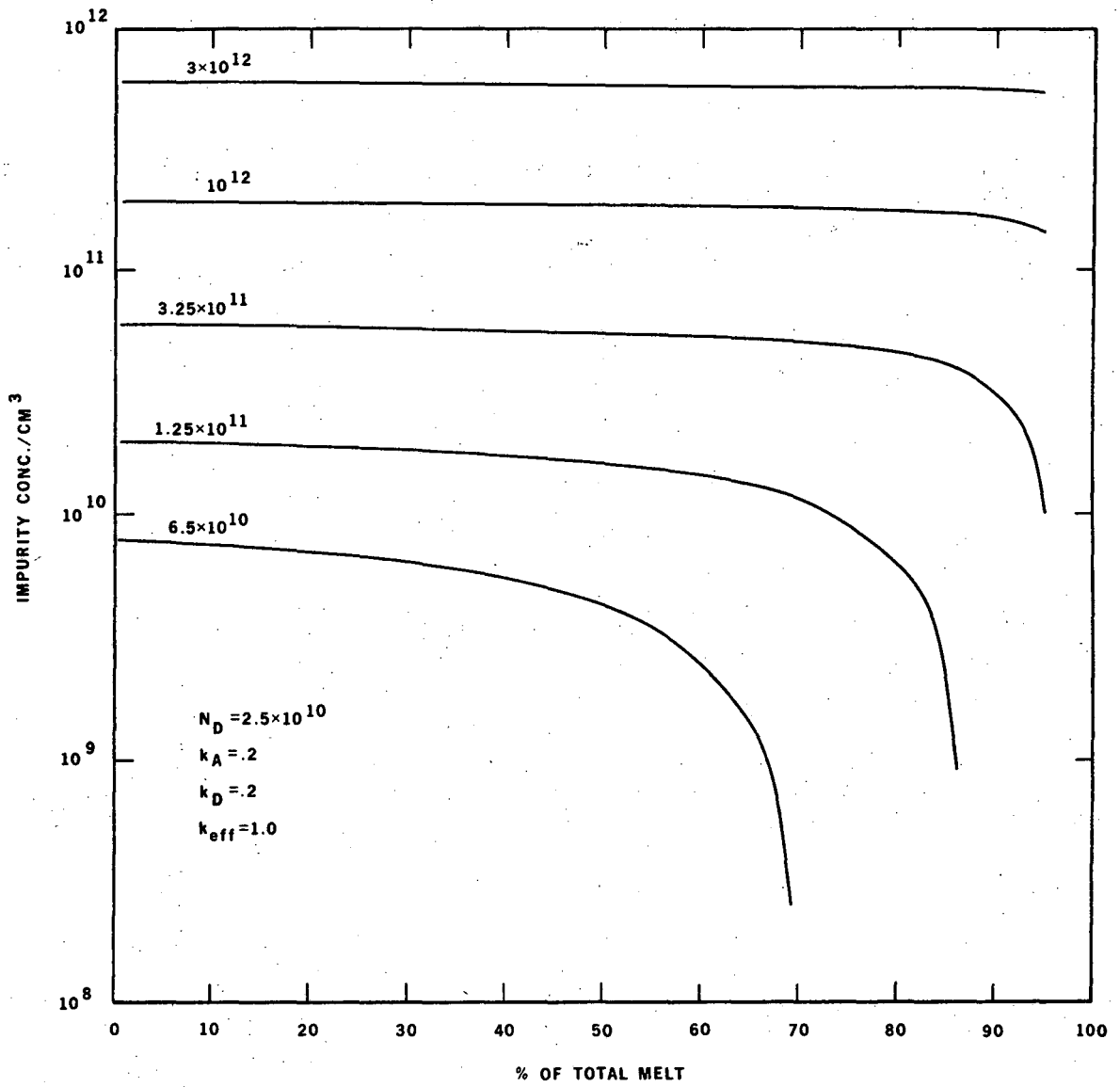
XBL 7310-1379

Fig. 3



XBL 7310-1341

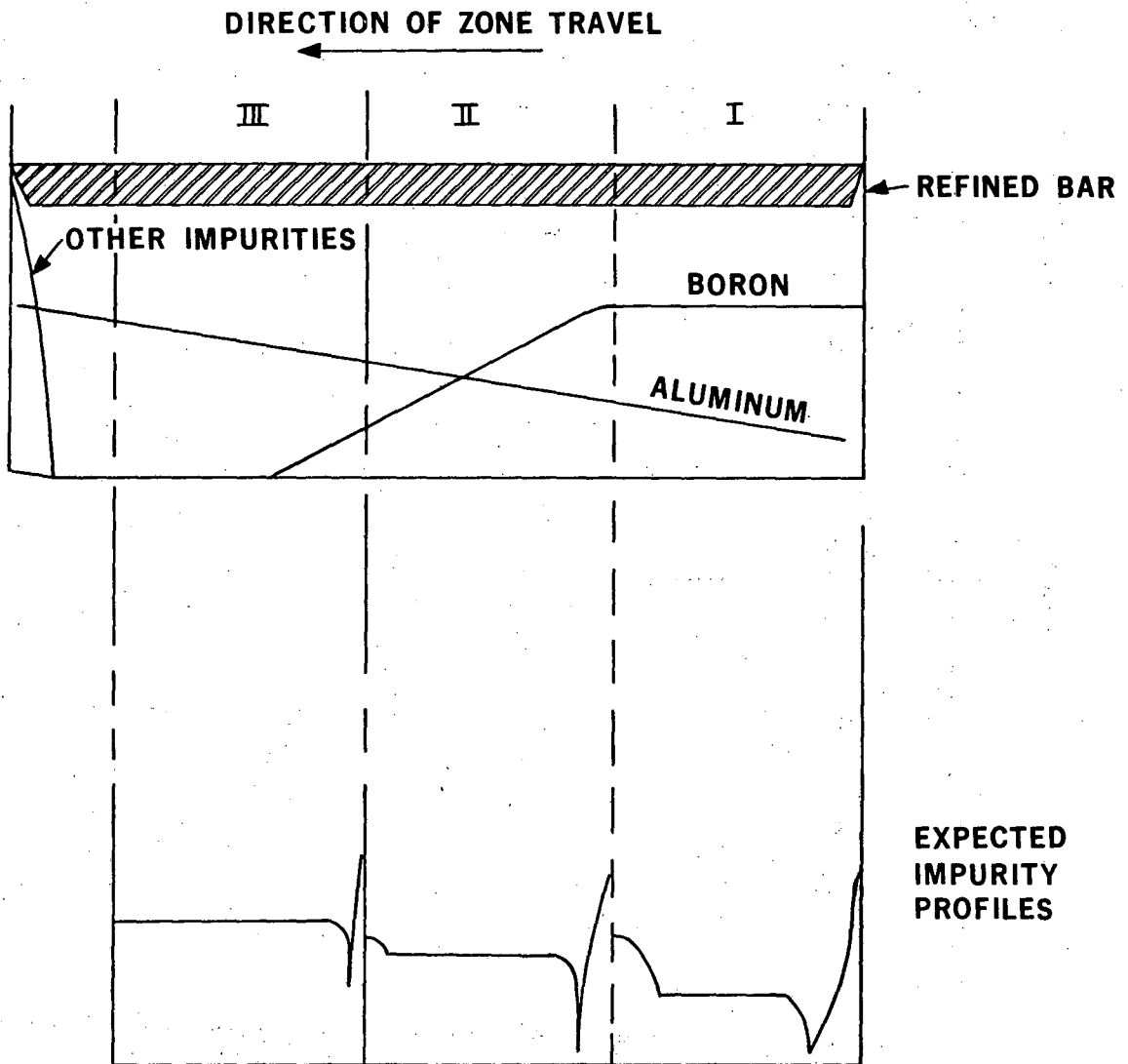
Fig. 4



XBL 7310-1348

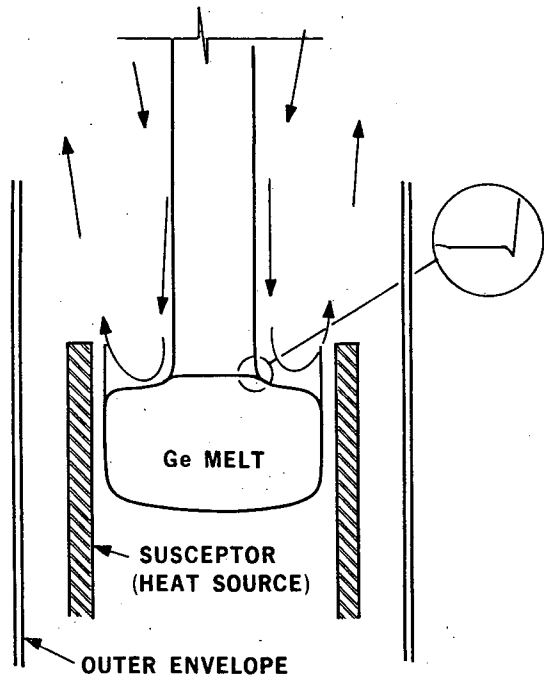
Fig. 5



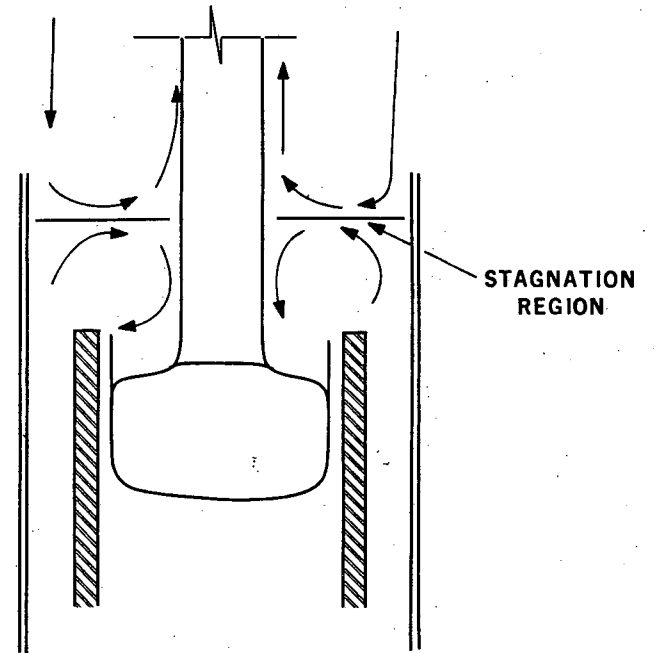


XBL 7310-1351

Fig. 6



a  
GAS CIRCULATION  
AT LOW FLOW RATE  
(1 li/min)



b  
GAS CIRCULATION  
AT HIGH FLOW RATE  
(5 li/min)

XBL 7310-1352

Fig. 7

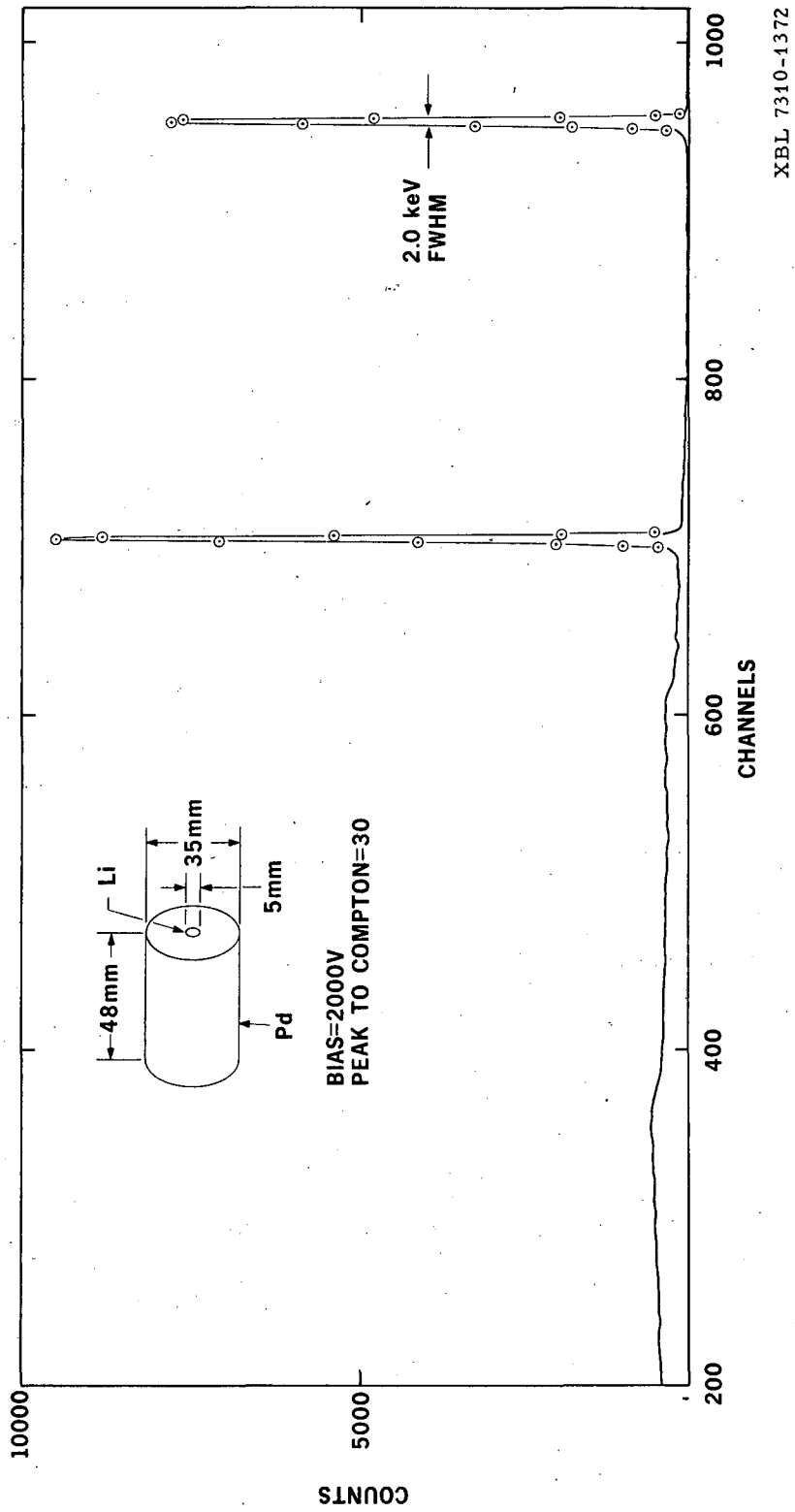


Fig. 8

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