Lawrence Berkeley National Laboratory
Recent Work

Title
HIGH-PURITY GERMANIUM - OBSERVATIONS ON THE NATURE OF ACCEPTORS

Permalink
https://escholarship.org/uc/item/2n98f6d4

Author
Hansen, William L.

Publication Date
1971-11-01

eScholarship.org Powered by the California Digital Library
University of California

IEEE Nuclear Science Symposium
San Francisco, Ca. Nov. 3-5, 1971

RECEIVED
LAWRENCE
RADIATION LABORATORY

LIBRARY AND
DOCUMENTS SECTION

LBL-503
Preprint

HIGH-PURITY GERMENIUM — OBSERVATIONS ON THE NATURE OF ACCEPTORS

William L. Hansen and Eugene E. Haller

November 1971

AEC Contract No. W-7405-eng-48

For Reference

Not to be taken from this room

LBL-503

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

0 0 0 0 3 7 0 4 0 2 8

HIGH-PURITY GERMANIUM— OBSERVATIONS ON THE NATURE OF ACCEPTORS*

William L. Hansen and Eugene E. Haller†

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

SUMMARY

A critical examination of observations on high-purity germanium, exhibiting acceptor concentrations in the $10^{10}/cm^3$ range, indicates that the acceptors are probably due to lattice defects such as vacancy clusters. The paper presents evidence to support this contention.

INTRODUCTION

When attempting to grow high-purity crystals, it is natural to attribute variations in impurity concentration to uncontrolled chemical contaminants. We found, however, that the impurity concentration in our crystals seemed not to be affected by our cleaning procedures, and the impurity variation along the length of a crystal could not be represented by any reasonable distribution coefficient. In fact, the impurity variations seemed incompatible with any melt-solid distribution law. Furthermore, it was found that minute changes in the crystal growing conditions (pull-rate, diameter, etc.) led to large changes in acceptor concentration. Evidently we were seeing an effect due to the mechanical structure of the crystals, and not due to chemical impurities. An appreciation of these effects has allowed us to grow p-type germanium crystals, with high yield, with a net acceptor concentration of less than $10^{10}/cm^3$ over most of their length.

CRYSTAL ACCEPTOR-CONCENTRATION PROFILES

All the crystals reported here were grown in pure hydrogen; they were about 3 cm in diameter, 20 cm long and 800 gms in weight.[1] They had acceptor concentrations in the range 10^9 to $5 \times 10^{11}/cm^3$.* The crystal acceptor-concentration profiles can be naturally classed according to the distribution of dislocations in the crystals: a) dislocation free, b) uniformly dislocated, and c) crystals containing significant regions of each type. In Fig. 1, crystals typical of the first two classes are shown. The two upper profiles (150 and 152) are for dislocation free crystals, while the higher-purity profiles (153, 154, 157, 158, and 182) show crystals whose cross-sections exhibit almost uniform dislocation densities. The dislocations in the tail end of the higher-purity crystals show tension-compression ring structure to various degrees, due to the thermal strain introduced as the melts were depleted.

A noteworthy feature of these profiles is the long regions of almost constant acceptor concentration. Since the rate of pull from the melt is constant, this result is incompatible with the distribution of an impurity from a melt. We note also that the detectors made from these crystals show no detectable radial impurity gradient.

Figure 2 shows the acceptor-concentration profile of a crystal which is partially dislocated, and Fig. 3 shows the dislocation distributions of samples cut at 4 and 12 cm along this crystal. The slice that is dislocated over about half its area has about half the impurity concentration of a dislocation free crystal. The slice that is dislocated over its entire area has a much lower concentration ($2 \times 10^{10}/cm^3$).

Figure 4 shows the impurity distribution of a crystal that was examined in more detail. This crystal was sectioned in 5 mm thick slices and the etch pit distribution observed throughout the entire crystal. The head slice had a total of only four dislocations, and an impurity concentration of $2 \times 10^{11}/cm^3$. The dislocation density multiplied down the length of the crystal, leaving islands of dislocation free material which became progressively smaller until, by 10 cm, the whole area was dislocated and the impurity concentration was less than $10^{10}/cm^3$. The etch pit distribution of the slice at 3 cm from the head is

* This work was done under the auspices of the U. S. Atomic Energy Commission.

† Presently working with grants from Jangpen-Poehn Stiftung and the Kanton Basel-Stadt, Switzerland.

* All crystals grown in hydrogen have been p-type. Crystals grown in environments containing residual oxygen (forming gas, water vapor, nitrogen, and vacuum) have been p-type at the head end and n-type at the tail.

shown in Fig. 5. Five diodes (detectors) of 10 mm x 5 mm area were made as shown in this figure. Figure 6 shows the C-V characteristics of these five diodes. It is seen that the "impurity" concentration as measured by capacitance is strongly correlated with the absence of non-dislocated areas. Diode #1 is uniformly dislocated and has an "impurity" concentration of $6 \times 10^{10}/cm^3$, while #4 and #5, that have an impurity concentration of 4×10^{11}, are almost dislocation free. Diodes 2 and 3 have intermediate purity and have a few dislocations.

The effect of an axial distribution of dislocations can be seen. Figure 7 shows the acceptor profile of a crystal which was dislocation free for 14 cm, and then acquired dislocations which spread to cover the whole crystal cross-section by 20 cm. A 1 cm thick, full area detector made from a slice at 20 cm made a high quality detector.

TEMPERATURE DEPENDENCE OF ACCEPTOR CONCENTRATION

The temperature dependence of the acceptor concentration, as derived from conductivity measurements, is shown for a dislocation-free crystal in Fig. 8, and for a dislocated crystal in Fig. 9. Also shown in Fig. 9 is the carrier concentration derived from a measurement of the resistivity of the undepleted material in a detector made from another section of the same crystal. In this very low temperature region the two types of material appear similar. The acceptor concentration begins to decrease at about 20°K at too fast a rate to be characterized by a simple acceptor level such as would be produced by a chemical impurity.

For the dislocation free material, another more populous level exists which deionizes or disappears between 100°K and 50°K.[2]

DISCUSSION

It is tempting to try to explain away the absence of any observable effect of impurities as being due to some constant and secondary phenomena such as compensation by levels near the middle of the band-gap or by precipitation of impurity atoms at dislocations.

The degree of compensation by deep levels may be studied by measuring the capacitance-voltage characteristic, and the charge collection in detectors made from these crystals at 77°K. If deep levels were present, they would show up as a higher impurity concentration derived from the capacity-voltage measurement over that from conductivity, as the former measures the net fixed change in the lattice, while the latter measures the equilibrium free-carrier concentration. In our high-purity crystals, the acceptor concentrations derived from capacity, and from conductivity, agree within experimental error in the temperature range above 20°K. This applies even to crystals in the low $10^9/cm^3$ range of impurity concentration, so the concentration of deep levels must be very low.

The possibility of precipitation of an impurity at dislocations explaining these results is considered negligible for the following reasons:

a) Since precipitation at dislocations is not possible in dislocation-free crystals, the impurity concentration must be less than the constant minimum of $4 \times 10^{11}/cm^3$ observed in these crystals.

b) Figure 8 shows that the acceptors present at a concentration of 4×10^{11} begins to disappear just below 100°K, a behavior not explainable in terms of a normal acceptor.

c) Impurities producing levels near the middle of the band-gap have been ruled out by comparing capacity-voltage measurement with resistivity measurement.

The long regions of constant acceptor concentration make any attempt to attribute these acceptors to chemical impurities very unlikely. Czochralski growth is incompatible with constant impurity concentration along the length of a crystal, except for the unique case of unity segregation coefficient. (No such impurities are known to exist in germanium.) Furthermore, the temperature behavior of the acceptor-concentration data indicates that the acceptor levels are more complex than simple impurity deionization.

Thermodynamic considerations require that the dislocation-free material be saturated with vacancies. A possible explanation of the level which disappears below 100°K in dislocation-free material is that a change in the nature of vacancy clusters takes place, so as to change the activation energy at this temperature. It is also possible that the level which begins to freeze out at 20°K in both dislocation-free and in dislocated material, is simply another configuration of vacancies which changes its activation energy at this temperature. The rapid change of hole concentration with temperature that occurs below 20°K is not consistent with simple deionization of an acceptor.

0 0 0 0 5 7 0 4 3 2 9

CONCLUSION

All the features we see in the "impurity" profiles of our high-purity germanium crystals can be understood as arising from regions of zero dislocation density, or from stress due to melt-liquid interface curvature. Within the range of acceptor concentrations in our crystals (10^9 to $10^{12}/cm^3$), no observations support the presence of chemical impurities. Recognizing the role of mechanical features in producing acceptor centers, we can now reproducibly grow long lengths of crystals with a net acceptor concentration of less than $10^{10}/cm^3$.

ACKNOWLEDGMENTS

R. H. Pehl and R. C. Cordi have continually supplied us with results of their measurements on detectors made from these crystals. F. S. Goulding has been interested in all phases of this investigation, and has provided many valuable comments and suggestions.

REFERENCES

1. W. L. Hansen, Nucl. Inst. and Methods 94, No. 2, 377 (1971).

2. R. N. Hall and T. J. Soltys, IEEE Trans. Nucl. Sci. NS-18, No. 1, 160 (1971).

FIGURE CAPTIONS

Fig. 1. Acceptor profiles of dislocated and dislocation-free crystals. The two upper curves are for dislocation-free crystals while the lower five are for crystals dislocated throughout their cross-section. The rise in acceptor concentration at the tail end is attributed to unrelieved thermal stress.

Fig. 2. Acceptor profile of a crystal containing dislocation-free regions.

Fig. 3. Dislocation distribution of samples cut at points A and B on the crystal shown in Fig. 2.

Fig. 4. Acceptor profile of a crystal that was cut into 5 mm sections. The crystal contains only four dislocations at the head end, but by 10 cm its cross-section is completely dislocated.

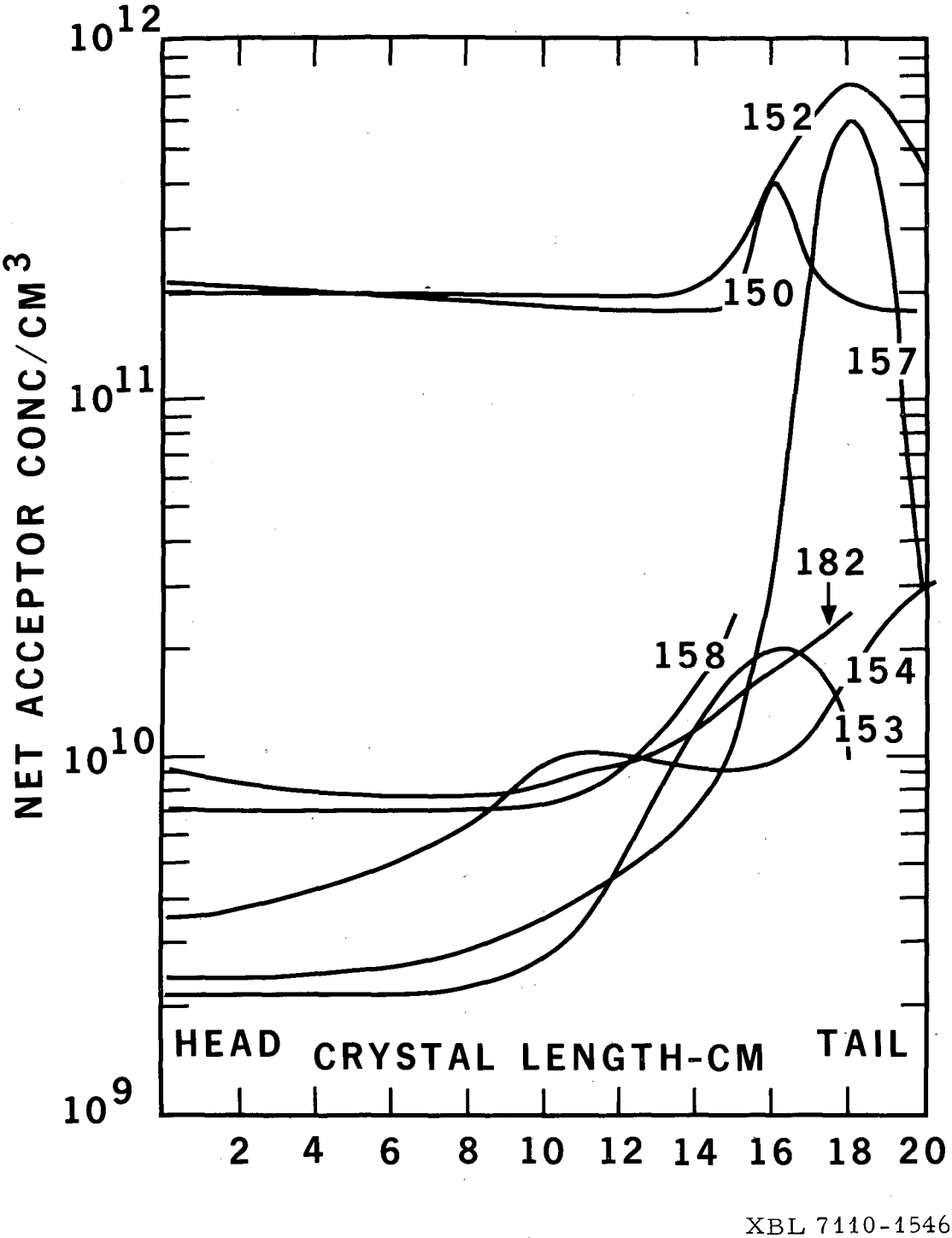
Fig. 5. The dislocation distribution, and the configuration of the diode array made from a slice of the crystal shown in Fig. 4 cut at 3.5 cm. The cut between the diodes 1 and 2 has been aligned with the boundary of the dislocated region.

Fig. 6. Capacity-voltage characteristic of the five diodes shown in Fig. 5. Diode No. 1 is almost uniformly dislocated while 4 and 5 are almost dislocation-free.

Fig. 7. Acceptor profile of a crystal which is dislocation-free for most of its length. The cross-section is completely dislocated by 20 cm.

Fig. 8. Acceptor concentration vs. temperature determined from conductivity measure ments on a full area slice of a dislocation-free crystal. The rapid fall in acceptor concentration near 70°K is attributed to a sudden change in the nature of vacancy clusters.

Fig. 9. Acceptor concentration vs. temperature determined from conductivity measurements on a full area slice of a uniformly dislocated crystal. The rate of deionization of the acceptor centers in this crystal below 20°K, and also of the crystal in Fig. 8, is too rapid to be characteristic of a simple acceptor impurity. It is believed to be associated with a sudden change in the acceptor energy level at this temperature.



XBL 7110-1546

Fig. 1

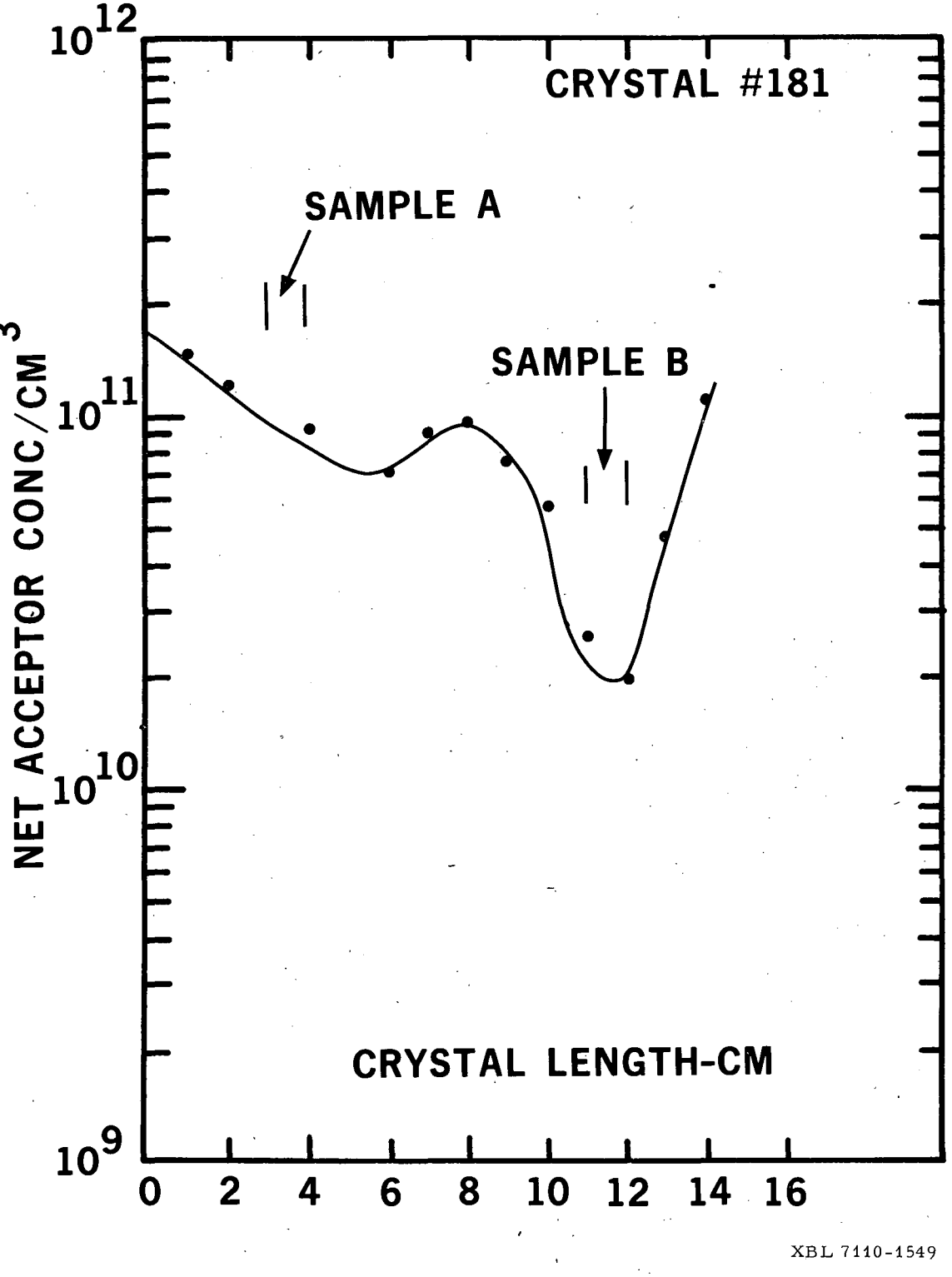
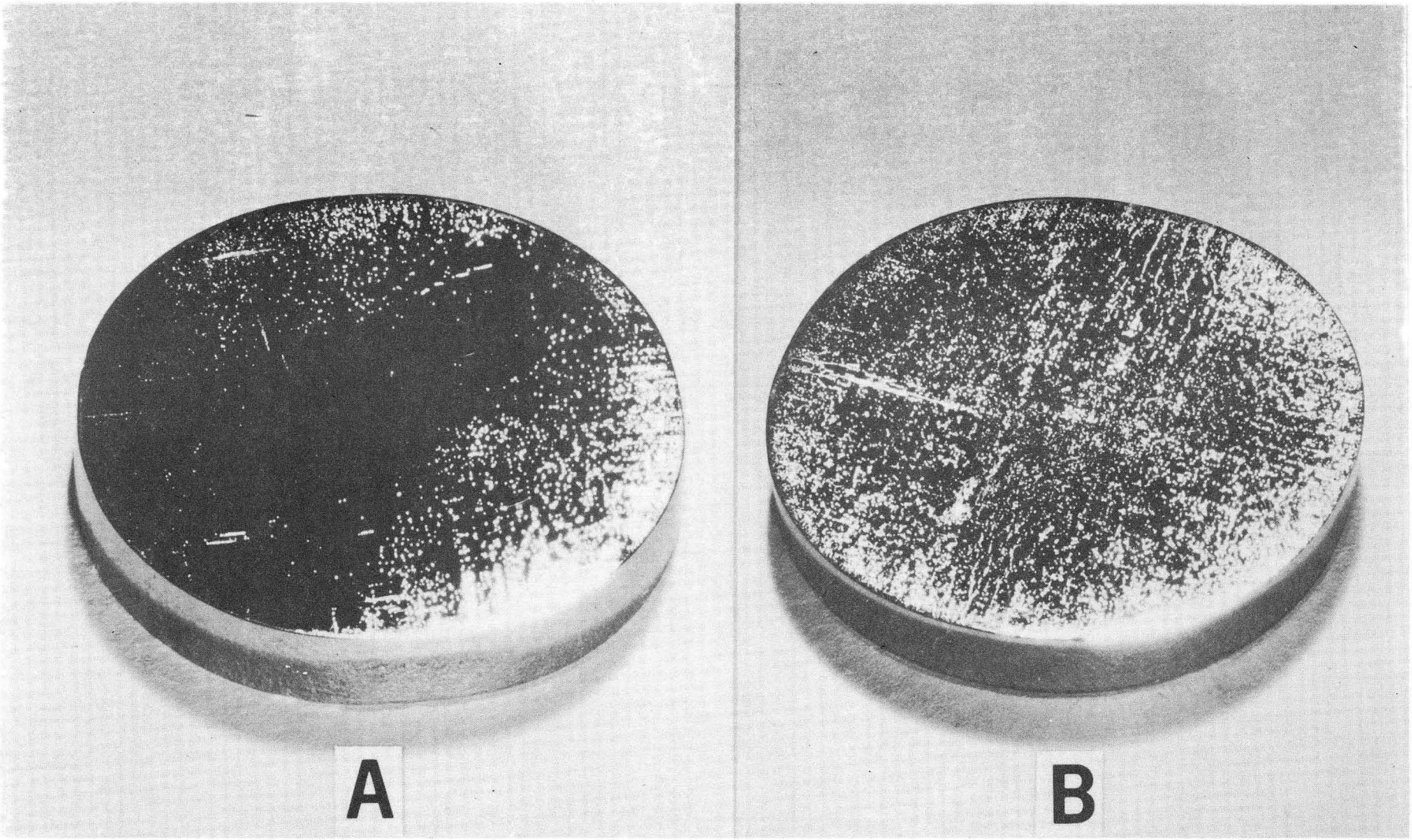

CRYSTAL #181
SAMPLE A
SAMPLE B
NET ACCEPTOR CONC/CM 3
10 12
10 11
10 10
10 9
CRYSTAL LENGTH-CM
0 2 4 6 8 10 12 14 16
XBL 7110-1549

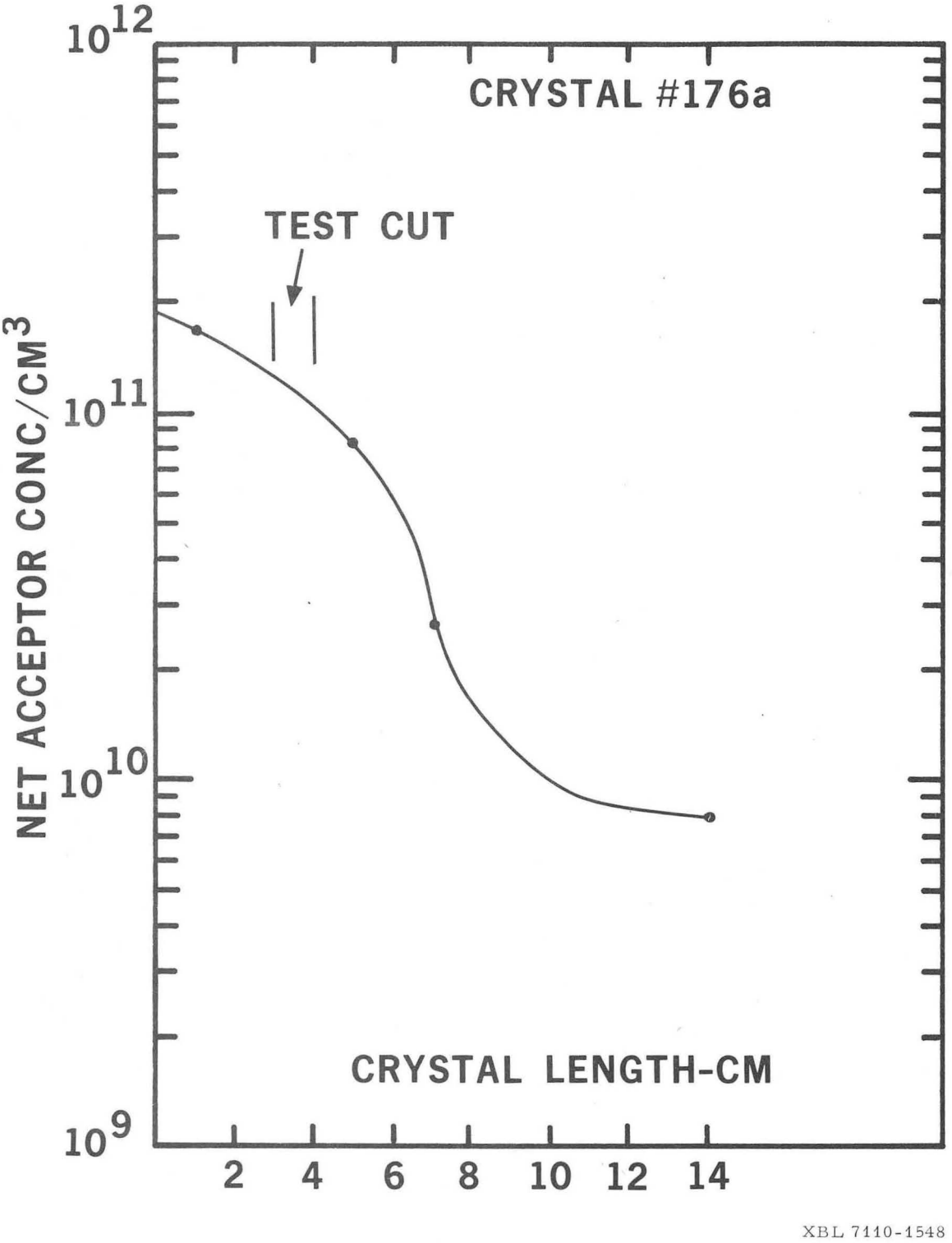
Fig. 2



CRYSTAL 181

XBB 7110-5090

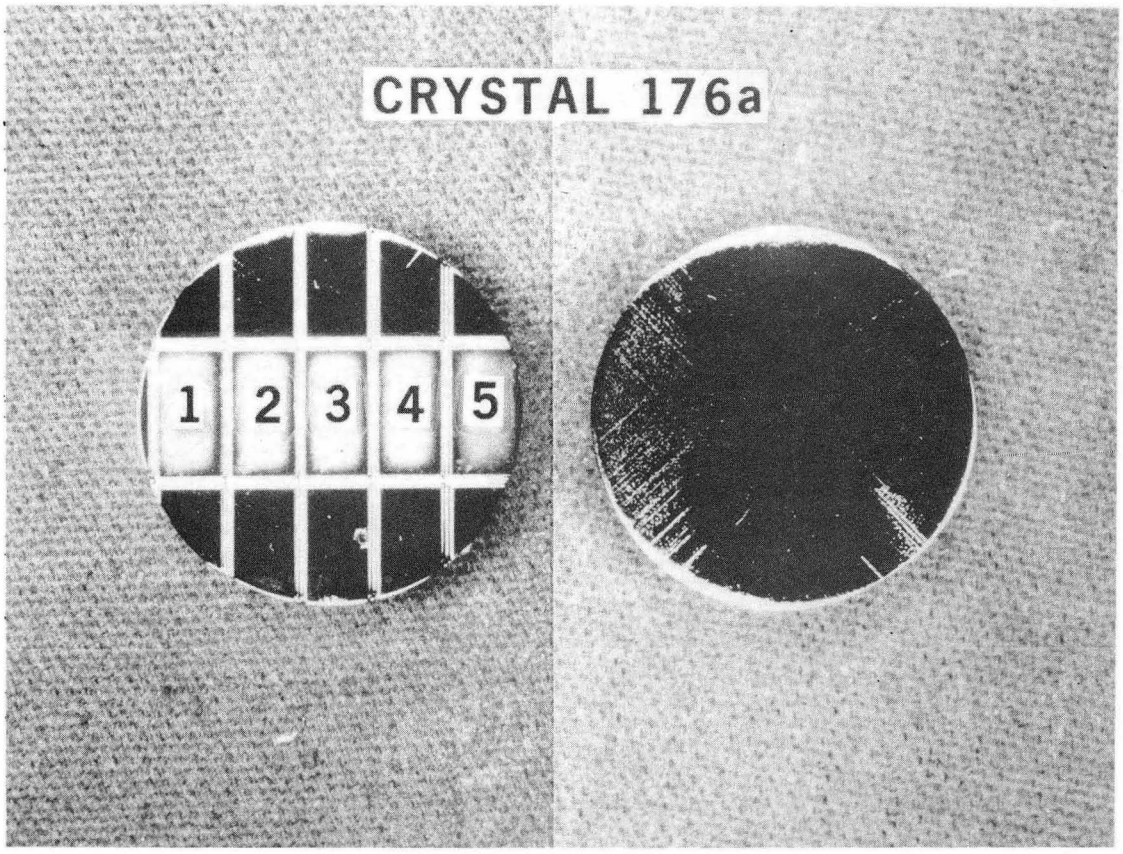
Fig. 3



XBL 7110-1548

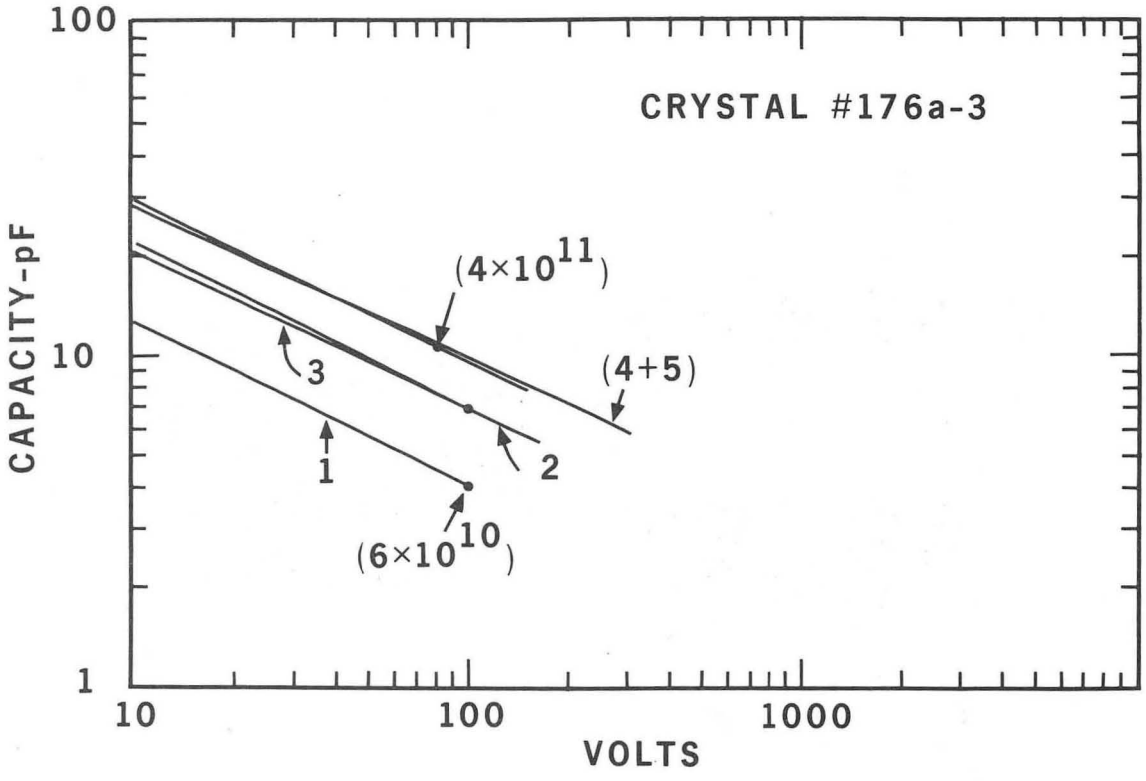
Fig. 4

0 0 0 0 3 7 0 4 3 3 1



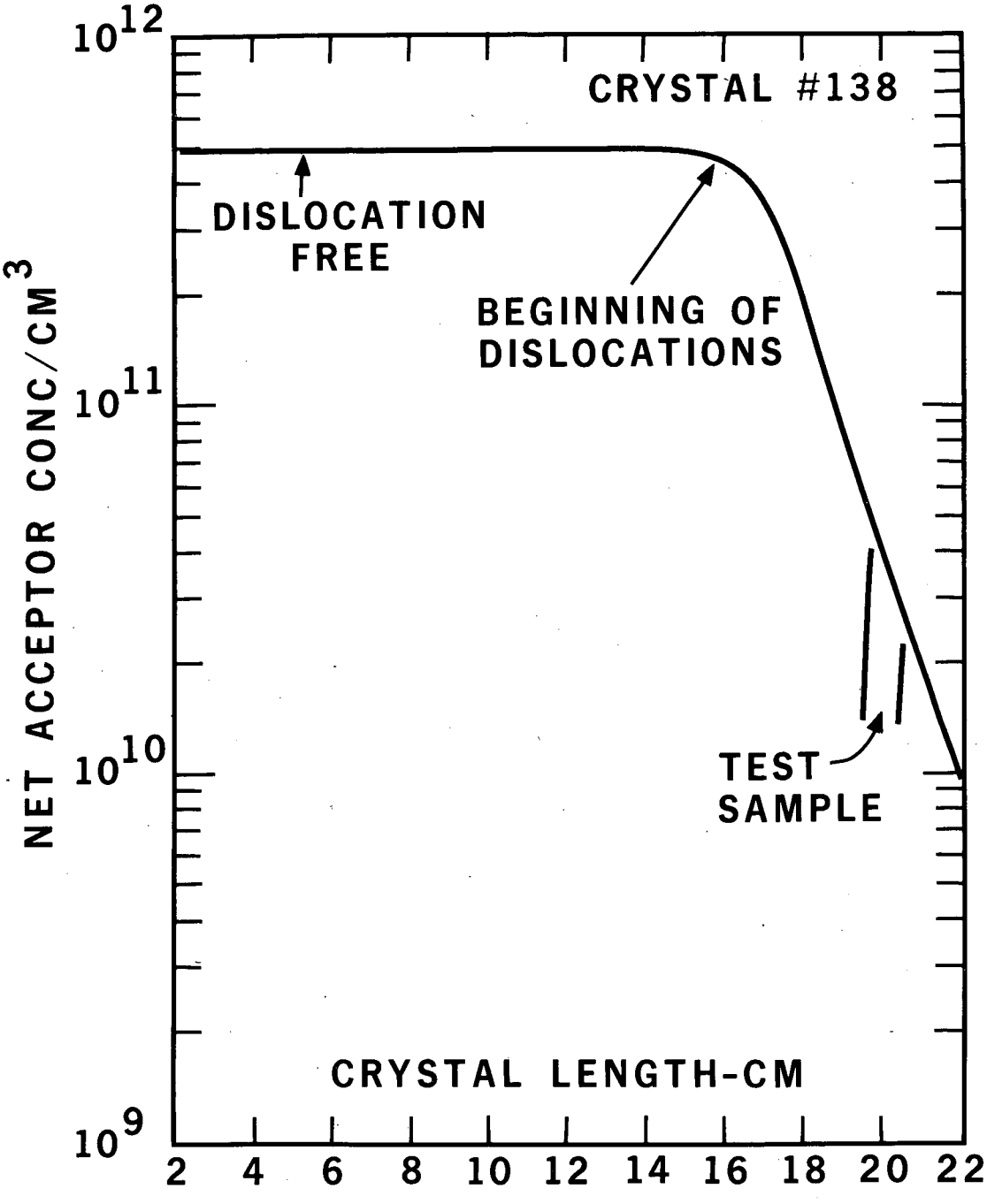
XBB 7110-5091

Fig. 5



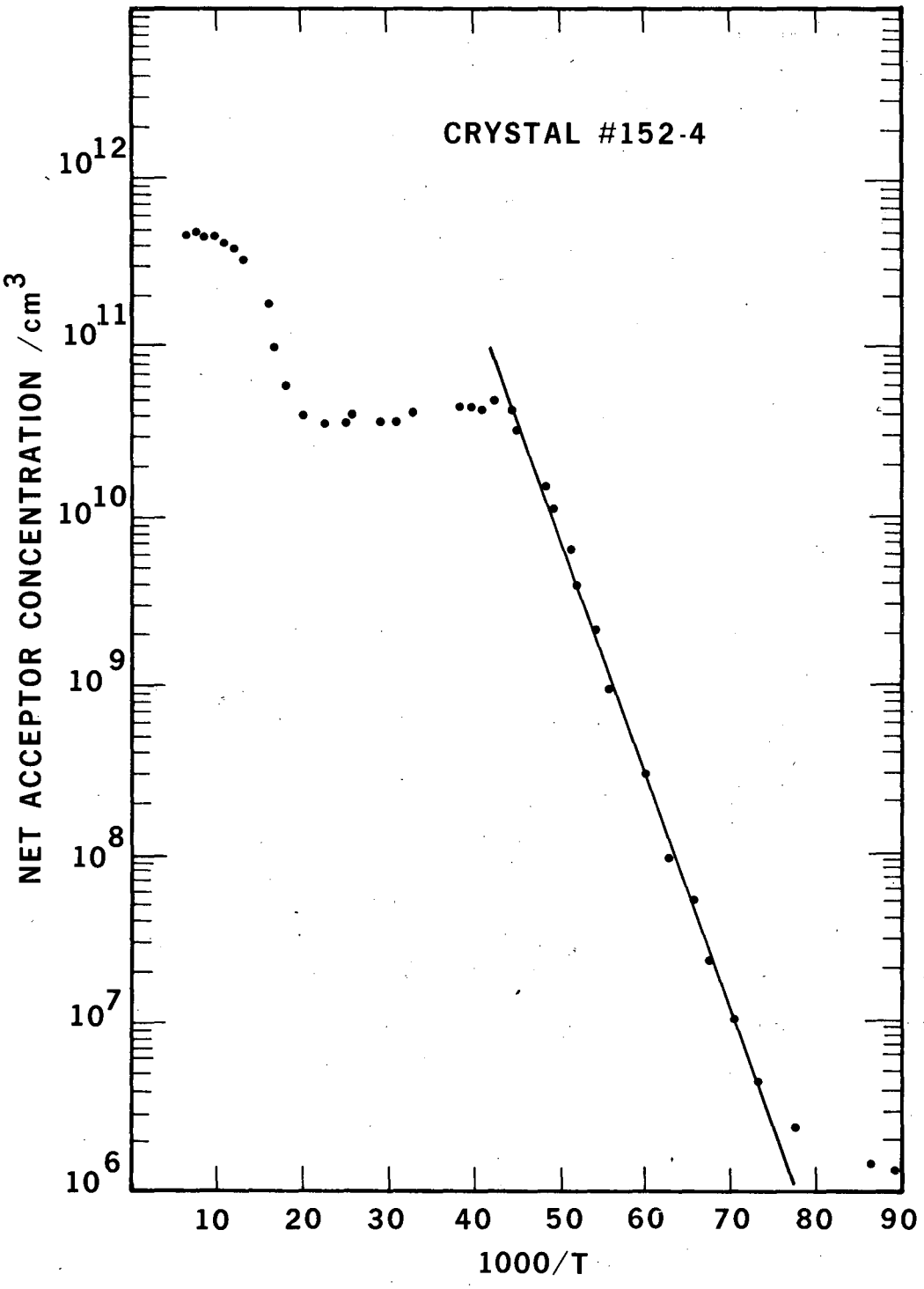
XBL 7110-1547

Fig. 6



XBL 7110-1545

Fig. 7



XBL 7110-1562

Fig. 8

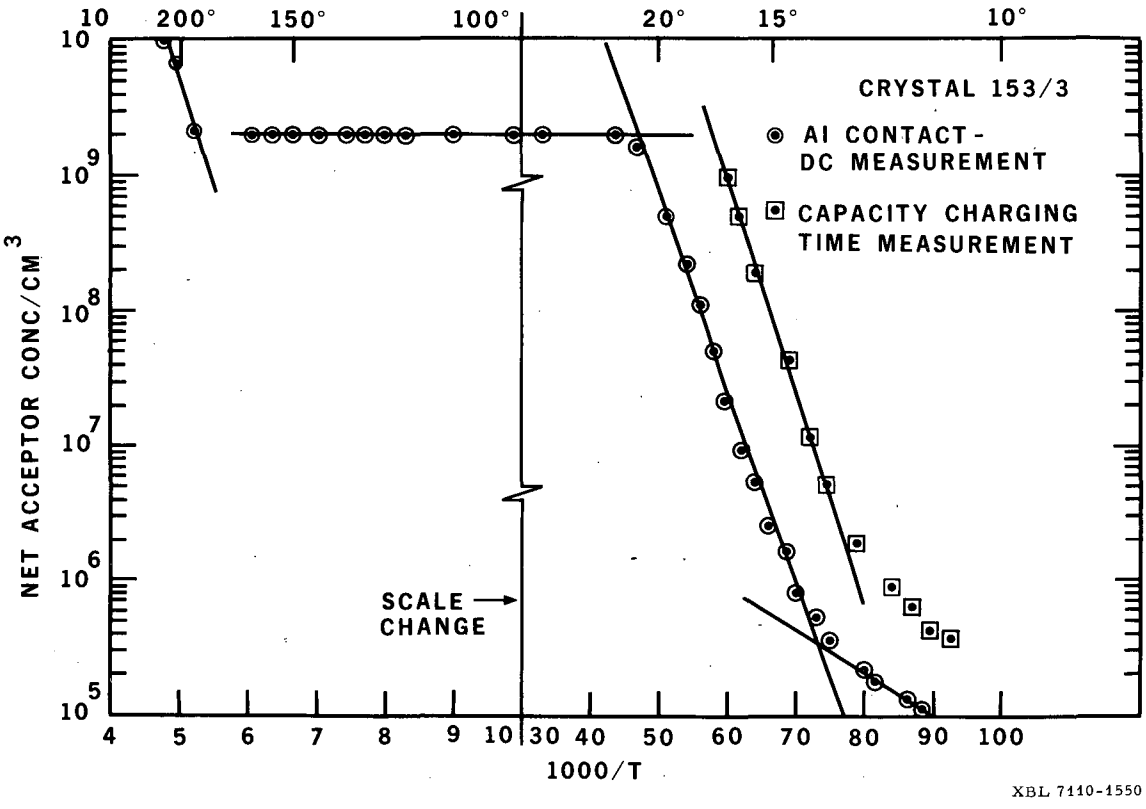

10
200°
150°
100°
20°
15°
10°
CRYSTAL 153/3
Al CONTACT - DC MEASUREMENT
CAPACITY CHARGING TIME MEASUREMENT
NET ACCEPTOR CONC/CM3
SCALE CHANGE
1000/T
XBL 7110-1550

Fig. 9

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720