MASTER

GEAP-3743(Pt. III)

RADIATION EFFECTS IN BORIDES

Part III — Crystallographic Changes in Irradiated Borides

By
W. V. Cummings
W. I. Clark

May 1962

Vallecitos Atomic Laboratory
General Electric Company
San Jose, California

UNITED STATES ATOMIC ENERGY COMMISSION • DIVISION OF TECHNICAL INFORMATION

Printed in USA. Price $1.25. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

USAEC Division of Technical Information Extension, Oak Ridge, Tennessee

GEAP-3743 (Pt. III)
RADIATION EFFECTS ON MATERIALS

RADIATION EFFECTS IN BORIDES

PART III - CRYSTALLOGRAPHIC CHANGES IN IRRADIATED BORIDES

By

W. V. Cummings
General Electric Company
Vallecitos Atomic Laboratory

W. I. Clark
General Electric Company
Hanford Atomic Products Operation

May 31, 1962

U. S. Atomic Energy Commission
Contract No. AT(04-3)-189
Project Agreement #4

VALLECITOS ATOMIC LABORATORY

GENERAL ELECTRIC

ATOMIC POWER EQUIPMENT DEPARTMENT
SAN JOSE, CALIFORNIA

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

ABSTRACT

Crystallographic changes in several irradiated metal boride systems have been studied by x-ray diffraction techniques. Three structures were investigated quite extensively and a fourth examined in a cursory manner. Irradiation damage can be related to structure. The relationship does not depend primarily upon the crystal system, but rather upon the strength of the structure bonds. The metal diborides with their tightly bonded hexagonal structures are most resistant to radiation damage. The hexaborides on the other hand, have a loosely bonded cubic structure and are extensively damaged by radiation. The tetraborides are intermediate in bond lengths and also are intermediate in structure damage. A very limited study was made of irradiated dodecaborides. This face-centered cubic structure has an intermediate bond length between metal and boron atoms but a long bond length between metal atoms. The damage to this structure was apparently quite extensive as determined from the limited data available.

INTRODUCTION

Boron is one of the most widely used materials in reactor control systems. The high cross-section B-10 isotope has a natural abundance of 19.6 percent and since the cross-section varies in a 1/v manner, neutron absorption is most effective in the energy region of primary importance for reactor control. Applications of boron as a control material to date have included boron stainless steels, boron dispersions in various matrix systems, and a few of the more easily obtained compounds such as boron carbide. These applications however, are only a very small portion of the total boron containing materials that have potential use as reactor control materials. The borides of major interest in this field have been discussed at length by Holden.(1) These include the metal diborides, metal tetraborides, and metal hexaborides. In addition to these, some metal dodecaborides exist that have some potential reactor applications. These boride compounds vary in cross-section worth not only with boron content but also with the cross-section characteristics of the particular metal atom. The metal atoms that are found in the various borides have thermal neutron cross-sections that range from a few barns for titanium and yttrium to 38,000 barns for gadolinium. The total worth however, must be evaluated from considerations of the total cross-section versus neutron energy curve and the nature of the daughter products. Most of the metal nuclei after capturing a neutron either transmute to stable daughter products of low cross-section or to a chain of radioactive isotopes each of which have low neutron absorption cross-sections. The net result in nuclear control worth is essentially only that which is possessed by the parent metal atom. On the other hand, a few metal atoms such as europium have a chain of daughter products that have substantial cross-sections in addition to that of the parent isotope. This "breeding" process can grossly affect in a positive way the total life of a control material.

In the metal borides the nuclear properties of the boron, or specifically the B-10 isotope, is usually the principal criterion upon which the potential of the material as a reactor control is evaluated. The density of the boron in terms of atoms per unit volume is of primary importance and is dependent upon both the stoichiometry and crystallographic structure of the compound. The structures of the metal borides of interest are the hexagonal diborides, the tetragonal tetraborides, the simple cubic hexaborides and the face-centered dodecaborides.

The diboride structures include those of the transition metals Ti, Zr, Hf, V. The C-32 type structure is essentially hexagonal close-packed with the metal atoms situated at the points of the hexagonal lattice or in the 0,0,0 positions, and with the boron atoms occupying the 1/3, 2/3, 1/2 and 2/3, 1/3, 1/2 positions. This arrangement gives one formula weight per unit cell. The resulting structure is characterized by alternating layers of metal and boron atoms and a small c/a ratio. It can be seen from the basic structure shown in Figure 1(a) that no three-dimensional arrangement of boron atoms exist.

The hexaborides form a cubic structure of the CaB_6 $D2_1$ type but also can be visualized as a CsCl type. As seen in Figure 1(c) this structure is basically a framework of three dimensional boron octahedra with metal atoms occupying the relatively large interstitial positions that exist between the octahedra. Atom positions are one metal atom at 0,0,0 and six boron atoms at 1/2, 1/2, x and like positions where $x \simeq .207$. This unit cell also contains one formula weight. The rare earths and a few other atoms such as Ca, Y, Ba, and Th form this hexaboride structure.

The tetraborides form a tetragonal $D1_e$ type structure that exhibits some of the geometry found in both the diborides and hexaborides. The boron atoms in the hexagonal diborides form a layered structure and in the cubic hexaborides a three dimensional structure in the form of octohedra. A close study of the structures in Figure 1 reveals these basic features of each in the transitional tetraboride structure. The octahedra formed by the boron atoms can be seen in the center of the distorted cube outlined by the metal atoms. Other remaining boron atoms in the structure are in the form of layers between the metal atoms. These arrangements can best be seen by visualizing a (001) projection of several unit cells of the three structures. In the diboride projection, triangular prisms formed by the network of metal atoms are centered by a boron atom. In the cubic hexaboride projection, squares formed by the boron octahedra are centered within a square outlined by the metal atoms. Both of these basic configurations are present in the tetraboride (001) projection.

The MB_{12} dodecaboride structure is a $D2_f$ type and is also characterized by a three dimensional arrangement of boron atoms. The metal atoms have a face-centered cubic coordination and are surrounded by clusters of boron atoms that can be visualized as forming a fourteen sided polyhedron (truncated octahedron). Perhaps the most fundamental nature of this structure is represented if the boron atoms are visualized in their closest arrangement. In Figure 1(d) this is shown by the heavily outlined group of atoms that is midway between the metal atoms. This grouping represents the structure in a manner more nearly in line with structural tendencies of the other higher borides and also of elemental boron, i.e., a network composed basically of a three dimensional array of boron atoms, and, in the case of the compounds, with the metal atoms occupying the large interstitial positions. This method of representation gives the dodecaborides a sodium chloride type structure in the same sense that the hexaborides are a cesium chloride type structure.

Structure data for the borides of basic interest in this study are given in Table I. Not all of the materials listed in the table were given post-irradiation structure examinations, but all were given pre-irradiation structure characterization and are listed in the table to indicate the structural characteristics of each group. It can be seen that the metal-to-metal and metal-to-boron distances are least in the hexagonal diborides, intermediate in the tetragonal tetraborides, and greatest in the cubic hexaborides. This increasing inter-atomic spacing with boron content also continues for the metal-to-metal distance when the lone dodecaboride YB_{12} is included but the metal-to-boron spacing for this compound is less than for the hexaborides. The boron-to-boron distances do not vary greatly with structure and are not significantly different from that found in elemental boron.

Since the properties of a material are a unique function of the positions of the atoms, any changes in the described structures of the borides

TABLE I

CRYSTALLOGRAPHIC DATA FOR SOME BORIDES

	Lattice Parameters	Grams Boron per cc	r(M-M) (Å)	r(B-B) (Å)	r(M-B) (Å)
* TiB_2	Hex. a = 3.028 c = 3.228	1.40	3.028	1.77	2.38
* HfB_2	Hex. a = 3.14 c = 3.47	1.21	3.14	1.81	2.51
* ZrB_2	Hex. a = 3.17 c = 3.53	1.17	3.17	1.83	2.54
* YB_4	Tetr. a = 7.09 c = 4.01	1.43	3.31	1.60	2.59
DyB_4	Tetr. a = 7.23 c = 4.09	1.34	3.50	1.64	2.64
* B_4C	Rhomb. a = 5.19 α = 66°18'	1.98	--	--	--
* YB_6	Cubic - P a = 4.08	1.58	4.08	1.69	3.01
CaB_6	Cubic - P a = 4.153	1.51	4.15	1.72	3.06
DyB_6	Cubic - P a = 4.13	1.53	4.13	1.71	3.04
SmB_6	Cubic - P a = 4.129	1.53	4.129	1.71	3.04
* EuB_6	Cubic - P a = 4.175	1.48	4.175	1.73	3.08
* YB_{12}	Cubic - F a = 7.50	2.02	5.30	1.77	2.80

* Post-irradiation study of crystallographic changes

will affect its potential as a control material, or at least will affect the manner in which it can be used. The irradiation of a boron containing material with neutrons can cause structural changes in several ways. First, the fast neutrons produce damage by bumping collisions with atoms in the crystalline lattice. Second, thermal neutrons are captured by the high cross-section Boron-10 isotope and produces an (n,α) nuclear reaction. The result of this reaction is analogous to a nuclear fission since the products are He-4 and Li-7 nuclei which dissipate approximately 2.4 Mev of energy by collisions and ionization as they travel through the crystal lattice. The final form of damage to the structure is caused by these relatively large atoms of He and Li coming to rest in non-equilibrium positions and producing lattice strains.

The result of any of these damaging mechanisms is basically a disruption of the periodicity of the crystal lattice. Since the diffraction of x-rays depends upon this periodicity, the study of irradiated materials by x-ray diffraction should disclose information concerning the nature of the defect structure that is produced. This application of x-ray diffraction has received limited use primarily because of the experimental difficulties inherent in working with radioactive specimens.

Tucker and Senio(2) have made a rather extensive study of the effects of neutron irradiation on the structure of boron carbide. This study was of fundamental importance to the understanding of radiation damage in a boron containing material and in addition demonstrated the potential of x-ray diffraction in radiation damage studies. The results of this study showed that the B_4C rhombohedral structure became distorted during irradiation. An increase in c_o and a decrease in a_o was measured and in addition, central carbon atoms in the chain of three in the center of the structure were removed during the irradiation. However, the bulk stability of the material was quite good with only a small amount of spalling occurring. It was theorized that this stability was due to the ability of the relatively open boron carbide structure to accommodate the irradiation-generated helium atoms interstitially and that the spalling was a result of anisotropic thermal expansion. On the basis of these results, it has been rather generally concluded that the most radiation resistant borides would be those with both an open crystal structure and isotropic properties. From a reactor control viewpoint, boron density also is of primary importance. Using these criteria, one of the higher borides with an open cubic structure such as is possessed by the hexaborides should rate high in potential as a reactor control material.

The successful analysis of radiation damage in boron carbide described above depended to a large extent upon obtaining precise experimental data. In this case, the use of single crystals assured high diffracted intensities and the non-radioactive nature of the irradiation products of carbon and boron minimized background interference. In order to assure that investigations will not be limited to materials with these particular characteristics however, other experimental techniques should be available. Materials that are very radioactive may require the use of heavily shielded x-ray diffraction equipment that also utilizes other discriminating devices such as monochromators and pulse height selectors. In addition, the total radioactive intensity may be reduced by using very small specimens. The latter method is seldom successful unless single crystals are used so that a maximum intensity-to-background ratio is achieved. Of course, these techniques may be used in any combination. Because of the diverse nature of the radioactive spectra of the various borides included in this study, it was necessary to employ all of these techniques to a certain extent in order for successful x-ray examinations to be made.

EXPERIMENTAL PROCEDURE

A. Material Selection

The borides that were chosen for structure damage studies are indicated in Table I by an asterisk. Included are the diborides TiB_2, ZrB_2, and HfB_2; the tetraborides YB_4 and B_4C and the hexaborides YB_6 and EuB_6. The dodecaboride YB_{12} was also included but because of the delay in procuring this compound the examination was primarily of a cursory nature. Difficulty also was encountered in obtaining x-ray specimens of a second tetraboride of the tetragonal type structure (B_4C is rhombohedral). With the exception of TiB_2 and YB_{12}, samples of both dense self-bonded bodies (vacuum hot pressed) and fine powders were examined to determine the effect of open porosity on structure damage. In the case of TiB_2, vacuum hot pressed and single crystal bodies were examined. For YB_{12}, only vacuum hot pressed samples were irradiated.

For each crystal system a boride with both a low and a high cross-section metal atom were selected. In the diborides, titanium has a fairly low cross-section of 6.0 barns, zirconium has a cross-section of only 0.18 barns, and hafnium has a relatively high cross-section of 105.0 barns. In the tetraborides, the cross-section of yttrium is 1.3 barns. DyB_4 was irradiated and would have been examined except for unfortunate difficulties with handling and sampling in the Radioactive Materials Laboratory. Dysprosium has a cross-section of 1100 barns and also has a relatively unique chain of transmutation products that could result in interesting effects.

The nature of these effects is indicated by the results of x-ray diffraction studies of irradiated Dy_2O_3 which are reported separately.(3) The metal atoms in the hexaborides are represented by yttrium and by europium. Europium has a very high cross-section of 4300 barns.

In summary, the variables in this structure damage study are 1) crystal system - hexagonal, tetragonal, and cubic; 2) fabrication method - solid high density bodies and powders, and 3) the cross-section of the metal atom. Single crystals of one material also were included to refine the data. The release of the helium gas that is generated in the B-10 (n,α) reaction versus structure and structure damage also was of primary interest in this investigation. The results of gas release studies that have been reported in a previous document(4) will be related to crystallographic changes that have occurred in the various borides.

B. Irradiation and Examination

All of the borides in this study were irradiated in the General Electric Test Reactor at temperatures ranging from 200 to 500 C. The irradiations were divided into three groups classified according to type of materials and the related technique used in the post-irradiation study.

1. Group I - High Burn-Up

The first group consisted of ZrB_2, HfB_2, YB_4, YB_6, and EuB_6 and were part of the high burn-up (up to 99.8 percent of the B-10 isotope) irradiation test described in Part I of these series of reports.(4) Both hot pressed self-bonded and powder specimens of each boride were included in this group.

The x-ray samples were a part of the same series of specimens that were used for helium release measurements, metallography, and boron-10 burn-up determinations. The method of fabrication and encapsulation are reported in detail in the above mentioned report and since these details are mainly irrelevant as far as x-ray examinations are concerned will not be reiterated here. The irradiated specimens that were in solid form were cylinders 0.44" by 0.375" in size. In preparation for examination by x-ray diffractometer techniques, these samples were pressed into metallurgical mounts and then sectioned longitudinally. The surfaces were prepared for x-ray examination by grinding, polishing, and etching. The powder specimens were loaded into special plastic holders with the surface to be examined covered by 0.00025" Mylar film.

Because of the very high radioactivity levels, these specimens could not be examined with conventional x-ray diffraction facilities. The irradiation-induced activity of the EuB_6 samples for example was 180 rad/hr at 10 inches. The only way samples of this activity level could be examined was by using the heavily shielded and modified diffraction facilities at the Hanford Laboratories.(5) The yttrium and zirconium borides possibly could have been examined using conventional equipment and electronic discrimination but to eliminate unnecessary variables all of the borides of this high burn-up series were investigated using the Hanford facilities. Diffraction data from unirradiated controls also were obtained with this equipment in order to correctly characterize the pre-irradiation structures.

2. Group II - Selected Metal Atoms

A second group of boride samples were selected and experimentally designed so that post-irradiation x-ray examination could be accomplished using slightly modified Vallecitos facilities. These modifications consisted only of shielding the sample at its normal position on the diffractometer and of using electronic discrimination in the form of a pulse height selector in the detector system. The metal atom in each of the borides was selected so as to minimize the radioactivity in the irradiated specimen. This selection was made on the basis of cross-section and half-lives. The mass of the specimen was reduced as much as was practical to minimize radioactivity. These specimens were formed by hot pressing thin wafers to high density. The irradiation time was artifically accelerated by using boron enriched to 92 percent in the B-10 isotope. The purpose of this enrichment was to increase the ratio of the number of damage producing B-10 (n,α) reactions to the number of metal atom nuclear reactions. This technique should decrease the radioactivity of the specimen for a given amount of structure damage because the irradiation-produced products of the metal atoms are, in general, radioactive, while those of the $B(n,\alpha)$ reaction are non-radioactive, stable isotopes. The samples were encapsulated as shown in Figure 2 and irradiated to approximately 40 percent burnup of the B-10. The borides comprising this group were TiB_2, YB_4, YB_6, YB_{12}, and B_4C. These irradiated samples were studied using the Vallecitos x-ray diffraction equipment. The radioactivity levels were in the range of 100-200 mr/hr at 10 inches. In order to decrease the background in the diffraction patterns and to provide personnel shielding, a pulse height selector was employed in the detector system and a lead cell with a maximum thickness of 2 inches was placed around a modified sample holder. These modifications are shown in Figure 3. This arrangement reduced the background in the diffraction patterns by a factor of 10 and provided adequate shielding for laboratory personnel.

3. Group III - Single Crystals

The third irradiation of x-ray specimens consisted of two TiB_2 single crystals approximately 0.2 mm by 0.4 mm in size. Encapsulation was by holding these crystals in small cavities between the flat surfaces of two cylindrical shaped aluminum blocks held firmly together by three screws, and then loading this assembly into a slightly modified capsule. These crystals were then irradiated to a burn-up of 14 percent of the B-10 isotope. Following irradiation, the aluminum insert was removed from the capsule in the Radioactive Materials Laboratory and transferred to the x-ray diffraction laboratory where the final removal of the small crystals was accomplished. Because of the minute size of the crystals, the radioactive intensity from the specimens was quite low. Little trouble was encountered in mounting the crystals on quartz fibers by conventional techniques for examination. A single crystal orienter using direct intensity recording and both Laue and rotation cameras were used for post-irradiation examination of these crystals.

EXPERIMENTAL RESULTS

A. High Burn-Up Samples

Most of this group of samples were irradiated to B-10 burnups of 60 to 100 percent. Two vacuum hot pressed hexaborides, YB_6 and EuB_6, with burnups of 42 and 37 percent respectively, were below this irradiation level. As stated previously, most of the samples had radioactivity intensities well above the maximum limit that would permit examination with Vallecitos facilities and consequently were studied by use of the hot cell facilities at HAPO. The samples examined and the related pertinent information on each are listed in Table II.

It can be seen that the hexagonal structure of the diborides of zirconium and hafnium were distorted rather severely on an absolute scale. The unit cells in general expanded in the a_o direction and contracted in the c_o direction. In each type of sample, these effects in both expansion and contraction increased with burnup. The diffraction patterns were characterized by very broad lines that showed displacement to both higher and lower angles when compared to patterns from unirradiated controls. Even though the backgrounds were not excessive and did not contribute appreciably to the effect, the peaks were too broad and diffuse to be discernable above 90^o-2θ. Diffraction patterns of both unirradiated and irradiated ZrB_2 are shown in Figure 4. These patterns are typical for the diborides.

The structure of the tetragonal YB_4 was disrupted to a greater extent than that of the diborides. The solid specimen of this type received an exposure of 62 percent burnup and a lattice shrinkage of 1.5 percent was measured in the c_o direction. A change of + 0.40 percent occurred in the a_o direction. The diffraction peaks were very broad indicating that rather extensive microstrains are present and/or crystallite fragmentation has occurred in the structure. The powder specimen was exposed to a

TABLE II

IRRADIATION DATA FOR GROUP I BORIDES

Material	Sample Type	% Burn-Up		Structure	Dimensional Changes (%)			Helium Release (%)		Max. Irrad. Temp. (°C)
		B-10	Total		Δa_o	Δc_o	ΔV	During Irrad.	During Anneals to 1000 C	
ZrB_2-05	Solid	83	10.4	Hex.	+1.6	-0.30	+2.9	3.6	--	200
HfB_2-04	Solid	87	10.9	Hex.	+1.6	-0.20	+2.9	0.3	31.6	250
YB_4-05	Solid	62	9.3	Tetr.	+0.40	-1.5	-0.7	4.9	55.9	250
YB_6-16	Solid	42	6.3	Cubic	--	--	--	14	100.	200
EuB_6-14	Solid	37	6.0	Cubic	--	--	--	19	70.	250
ZrB_2	Powder	99	12.4	Hex.	+1.7	-1.2	+2.2	9		400
HfB_2-0Z	Powder	93	11.5	Hex.	+1.9	-0.60	+3.2	13		500
YB_4	Powder	94	14.1	Tetr.	+0.76	-1.7	+0.50	28		500
YB_6	Powder	91	14.6	Cubic	--	--	--	47		500
EuB_6-01	Powder	68	10.9	Cubic	--	--	--	61		550

burnup of 94 percent of the B-10 and the lattice distortion was greater than for the solid specimen. Shrinkage in the c_o direction increased in magnitude to a value of 1.7 percent and in addition, the unit cell increased in the a_o direction by 0.76 percent. The diffraction pattern obtained from the irradiated solid sample of YB_4 is compared to that from the unirradiated material in Figure 5.

Only one bit of information can be extracted from the cubic hexaboride diffraction patterns. Both the solid and powder samples suffered such extensive structure damage during irradiation that no peaks are discernable in the diffraction pattern. This effect indicates that the structures are approaching an amorphous state. The structure must damage quite rapidly since one of the solid samples reached an exposure of only 37 percent burnup. These effects are illustrated by the diffraction patterns of EuB_6 shown in Figure 6.

These results show no apparent differences in structure damage in the two types of fabricated samples, i.e., dense self-bonded or compacted powders. It is also apparent that the greatest damage occurs in the cubic hexaborides and the least in the hexagonal diborides.

B. Selected Metal Atom Samples

This group of samples is characterized by the selection of low radioactive metal atoms. In addition, all samples except the YB_4 were increased in B-10 content to 92 percent of the total boron. The YB_4 was of normal isotopic content. Although these samples were loaded into the irradiation capsules as dense self-bonded wafers with approximate dimensions of 0.440 inch diameter by 0.125 inch thick, three of the five fragmented to powders during irradiation. Initial examination of the as-exposed surfaces of the two solid wafers by x-ray diffraction showed that the structures had deteriorated to a non-crystalline state. These two specimens were YB_6 and YB_{12}. The surfaces were then ground away to a depth of several mils and this new surface examined. The structure at this depth was essentially undamaged. Even though the total burnup of B-10 was calculated to be 40 percent, gross self-shielding was shown to have occurred in these samples. The burnup evidently approached 100 percent near the surfaces and zero percent in the center. This means that essentially all of the damage to the central volume of these borides was that caused by high energy neutrons. As mentioned previously, only very small changes were measured in the diffraction patterns obtained from the central portions of the specimens. Essentially no broadening of the lines occurred and only subtle changes in lattice parameters were observed. The lattice of YB_{12} expanded by 0.08% but that for YB_6 contracted by 0.02 percent.

The powdered samples were thoroughly homogenized before examination. The hexagonal TiB_2 lattice expanded in both the a_o and c_o directions. The tetragonal YB_4 structure also behaved qualitatively in this manner. However, the B_4C expanded in the a_o direction and contracted in the c_o direction in the manner reported by Tucker.(2) The results of the measurements on this group of samples are given in Table III. With the exception of the data for the YB_4, the results given for this group of samples must be considered as purely qualitative data since the burnup is very inhomogeneous. The burnup gradient is very steep because of the 92 percent enrichment and no means of establishing an exact value at the point of x-ray examination was possible.

C. Single Crystals

The only single crystals available for this study were those of TiB_2. Two small crystals approximately 0.2 mm x 0.4 mm in size were chosen for study on the basis of their perfection and geometry and were irradiated in the same capsule. Both crystals fragmented during irradiation, one into two pieces and the other into four pieces. In each case, the pieces were of nearly equal

TABLE III

IRRADIATION DATA FOR GROUP II BORIDES

Material	Sample Type	% of Burn-up B-10	Total	Structure	Dimensional Changes (1%) Δa_o	Δc_o	ΔV	B-10Conc. (%)
TiB_2	Powdered	40	5.0	Hex.	+0.73	+0.37	+1.8	92
YB_6	Powdered	40	6.4	Cubic	-0.02	--	-0.6	92
YB_{12}	Solid-Surface Removed	40	6.9	Cubic	+0.08	--	+0.2	92
B_4C	Solid-Surface Removed	36	5.4	Rhomb.	+0.28	-0.44	+2.6	92
YB_4	Powdered	9	1.35	Tetr.	+0.35	+0.80	+1.5	18.8
TiB_2	Single Crystal	14	1.75	Hex.	+1.49	+0.74	+4.01	18.8

size and no experimental difficulties were introduced by the fragmentation phenomenon. The crystals were first oriented by use of a single crystal orienter and then Laue and rotation photographs obtained for both the a_o and c_o axes alignments. During this process it was determined that the plane of fracture was within a few degrees of the c_o axis. It was immediately evident from both types of photographs that gross changes had occurred in the hexagonal structure. Preferential broadening of the spots and changes of intensity had occurred and in addition, the c/a axial ratio had changed from 1.063 to 1.058. The Laue and rotation photographs are shown in Figures 7, 8, 9 and 10. The structural changes that have occurred are illustrated by comparison with photographs of the unirradiated crystals.

In view of the increased precision in measurements that is possible with the single crystal orienter, the crystals were transferred to this instrument for detailed study. Very good diffraction data was obtained compared to that obtained with the other techniques or with polycrystalline specimens. The peak intensities diffracted from these crystals were increased by at least an order of magnitude over those from polycrystalline samples and background interference from radioactivity was only a few counts per second. With polycrystalline specimens, discernable peaks were almost nonexistant above 90^o-2θ and overlapping reflections could not be separated. With the single crystal technique, peaks were recorded over the full 2θ range and reflections with either identical or nearly identical 2θ positions were readily separated. A portion of the diffractometer tracings obtained from these crystals can be seen in Figure 11.

Data obtained by use of the single crystal orienter revealed that the TiB_2 lattice had expanded in both the a_o and c_o directions. The expansion in the a_o dimension was 1.49 percent and the expansion of c_o was 0.74 percent. These data are shown at the bottom of Table III. Line intensities and line breadths were also measured and compared with corresponding data obtained from the crystals in the unirradiated state. Comparisons of the unirradiated and irradiated values for the planes studied are shown by ratios in Table IV. The reflections recorded were chosen not only to represent various orders of the same reflection, but also to represent a diverse number of crystal directions. The various directions were obtained by choosing the planes of the zone [100].

DISCUSSION

Radiation damage from fast neutrons undoubtedly produces lattice defects in crystalline materials. However, results of this test show that damage from this mechanism is almost negligible when compared with the damage caused by the (n,α) reaction and the presence of foreign atoms in the lattice. These conclusions are based upon the experimental results obtained from the irradiated borides that were enriched to 92 percent in the B-10 isotope. In the YB_6 and YB_{12} samples it was determined that gross self-shielding from thermal neutrons occurred. The outer portions of the solid specimens were damaged to such an extent that no crystalline structure was detectable by x-ray diffraction; however, only minor damage to the crystalline structure was measured in the inner portions of the specimens. Since these inner portions were shielded from thermal neutrons, no (n,α) reactions occurred and consequently no foreign atoms were introduced. The damage in this region then was caused by fast neutron bombardment alone. On the basis of this evidence the small contribution from fast neutrons to the total structure damage will be ignored.

Rather than expressing burnup as a percent of the B-10 isotope that undergoes an (n,α) reaction, the more realistic and descriptive value of percent burnup of total atoms will be used. These values are shown in the fourth column of Table II and represent the percent of the original atoms that have been converted to helium and lithium by the nuclear reaction. It follows that the percent of foreign atoms that have been introduced into the material is twice this total burnup value. These atoms must come to rest in interstitial positions, grain boundaries, or at some defect site in the lattice. Of course, only one vacancy is generated at the original

TABLE IV

LINE BROADENING AND INTENSITY DATA FOR TiB_2 SINGLE CRYSTAL

(hkl)	Io/Ii	Bi/Bo
100	12.	6.4
200	17.	9.7
300	40.	13.
001	2.2	3.4
002	1.7	3.4
003	2.4	3.0
004	7.1	4.9
201	2.9	8.3
101	3.8	3.2
102	1.3	5.3
103	14.	5.2
110	10.	4.3
111	28.	2.3

lattice site of the B-10 atom and the ratio of interstitials-to-vacancies is 2 to 1.

Both of the atoms that are produced by the B-10 reaction are larger than the original boron atom and must be accommodated someplace within the material either at an interstitial position or defect site or must move to grain boundaries or surfaces by diffusion through the lattice. If these atoms are retained within the lattice as interstitials the gross misfit will cause large lattice strains. The nature of the strains will vary with structure since both the size of the interstitial positions and strength of the bonding are structure dependent. When the characteristics of the bonding and the interatomic distances are considered for the crystal structures included in this study it is strongly indicated that bond strengths are greatest in the diborides, intermediate in the tetraborides, and least in the hexaborides. As would be expected, the size of the interstices also decrease as the bond lengths decrease.

If only the sizes of the interstitial positions are considered, it would seem that the hexaborides would be able to accommodate the helium and lithium atoms with the least amount of distortion. In addition, the large number of such positions that are available should permit high levels of burnup to be obtained before the structure would be appreciably disrupted. For instance, in MB_6 of normal isotopic content, 100 percent burnup of the B-10 isotope produces on the average 2.26 foreign atoms per unit cell plus 1.13 boron vacancies. Large interstitial holes exist in the unit cell that are comparable in size to the helium atom. In fact, for each B-10 reaction per unit cell a total of three large interstitial sites and a vacancy are available to assimilate the two atoms of helium and lithium. One B-10 reaction per unit cell is equivalent to 88.5 percent burnup of the B-10 atoms or 14.3 percent burnup of the total atoms.

If the accommodation of these atoms within the lattice was the only parameter to consider in evaluating structure damage, then the hexaborides should rank high as a radiation resistant structure and nearly all of the gas that is generated during irradiation should be retained within the structure with very little change in dimensions occurring. In addition, no problem concerning the disposition of evolved gas would arise and the cubic structure would assure that the small effects that are produced would be isotropic in nature.

The tetraboride structure has a number of interstitial positions in the lattice, but these are considerably smaller than those for the hexaborides and cannot readily accommodate the helium and lithium atoms without a large distortion of the lattice. The inherently anisotropic nature of the tetragonal structure also can be expected to be reflected in the distortion. Again considering only the effects on the lattice produced by the disposition of the helium and lithium atoms, the tetraboride structure should be grossly distorted in an anisotropic manner and should retain only a limited amount of gas within the lattice. The radiation resistance of the tetraborides based upon this criterion should not only be limited, but also should be less than that for the hexaborides.

The hexagonal close packed structure is generally described as a tightly bonded structure with very small interstitial positions. In the hexagonal diboride structure the atoms are in the close packed positions as shown in Figure 1. The interstices vary in relative size from those in the close packed structures of pure elements because of the large differences in size between the metal and boron atoms. The largest interstitial site and the only one of significance is at 1/2, 0, 1/2 and like positions. Since this is the center of the (100) face, two such positions exist per unit cell. These interstices are smaller than those in the hexaborides and tetraborides but they can conceivably contain the atoms produced by the (n,α) reaction. Large strains in the lattice will result however, and the degree of damage to this structure caused by the presence of the helium and lithium atoms should be greater than for either the tetraborides or the hexaborides.

The concentration of foreign atoms that is retained within the lattice can be deduced by measuring the amount of helium that is released during irradiation. These values were obtained for a number of specimens and were reported in the first report of this series.$^{(4)}$ The pertinent values are shown in Table II along with the total gas that could be released by heating to 1000 C. In spite of the fact that the hexaborides have the largest interstices in which the foreign atoms may be trapped, this structure has retained the smallest amount of helium gas both during irradiation and during annealing treatments to 1000 C. On the other hand the diborides have retained nearly all of the helium atoms during irradiation and even after the series of annealing treatments well over half of the gas remains within the material, and very probably a large portion of this is within the crystalline lattice. Again, the tetraborides occupy an intermediate position in this respect. Even though the interstitial positions in the hexaborides are quite large, it is very unlikely that the interstitial atom can be removed from these posititions by normal diffusion processes at the temperature of irradiation. In addition, no "channels" for low activation migration exist in this structure. From considerations based upon relative sizes of the interstices and the interstitial atoms it would appear that the hexaboride interstitials would be more stable than those in either the tetraboride or diboride structures. Roughly the sizes of the interstices range from 0.9 Å by 2.0 Å in the cubic hexaborides to about 0.4 Å by 1.1 Å in the diborides. These are only approximate values since they vary with the particular metal atom of the structure and are based upon spherical atom models. The accepted values for the diamters of the helium and the neutral lithium atoms are 1.86 Å and 3.04 Å respectively so it would appear that the "hole" in the hexaboride structure would be the more effective trapping site. It should be pointed out here that the disposition of the lithium atoms within these materials was not completely determined in these tests. Large amounts of lithium were found at free surfaces however, and the data on bulk volume changes$^{(4)}$ indicate that these large atoms diffuse to defect sites and surfaces.

Unfortunately, damage to the various structures cannot be evaluated solely from the effects caused by the nature of the final disposition within the lattice of the interstitial atoms. The mechanism by which these atoms reach their final position must be evaluated. When the B-10 isotope "fissions", the helium and lithium nuclei are propelled through the lattice in opposite directions with a total energy of approximately 2.4 Mev. The magnitude of the structure damage would be dependent upon both the number of such fissions and the nature of the structure. As pointed out by Samsonov,(6) the bonding between the atoms in the various boride structures differ to a large degree. The layered structure of the hexagonal diborides form strong metal-to-metal and metal-to-boron bonds. These bonds are much weaker in the tetragonal tetraborides and cubic hexaborides primarily because of the three dimensional nature of the boron clusters. Insufficient numbers of valence electrons are available to form both the covalent boron-boron links and the metal-boron bonds. As a result the strength of the structure bonds are greatest for the diborides as would be surmised from the bond lengths as tabulated in Table I. The strongest bonds are undoubtedly most resistant to breakage by the passage of high energy particles through the lattice. Based upon this criterion, resistance to radiation damage should be greatest for the diborides and least for the hexaborides with the tetraborides again in an intermediate position.

From the above considerations of structural characteristics and the observations of both the relative damage to the various structures and the ability of these structures to retain radiation-generated foreign atoms within the lattice, it becomes quite apparent that the fission gas release does not depend primarily upon the size or number of trapping sites but rather upon the damage to the structure. In turn, the magnitude of structure damage is inversely proportional to the strength of the interatomic bonding. The weakly bonded cubic structure of the hexaborides damage extensively at relatively low exposures and this damage is almost entirely the result of the passage of the high energy helium (or alpha particles) and lithium nuclei through the lattice. The resulting interactions disrupt the structure to such an extent that very early in the exposure interstitial sites are destroyed and diffusion barriers are drastically lowered.

The data also indicate that grain boundaries play an important role in the disposition of the helium gas. As seen in Table II, the amount of gas released by the diborides during irradiation is several times greater for the powdered samples than for the solid samples. Since no differences in diffusion characteristics should occur within the lattice or crystallites, then the additional helium that is released by the powders should be nearly equal to that which is retained within the grain boundaries of the solid specimens. The x-ray data strongly indicate that this is the case. No significant differences in the diffraction patterns from the two types of diboride samples were measured. This indicates that lattice distortions are the same and implies that equal numbers of interstitials are retained within the lattice.

It is also of interest to note that the radiation damage resistance of the diboride structure can be extrapolated to show that for 100 percent burnup of the B-10 atoms (12.5 percent of total atoms) the structure should remain sufficiently intact to assure the retention of a large portion of the generated helium gas. Of course, the diffusion of the helium atoms through the lattice is temperature dependent and these data apply for irradiations at temperatures below 250 C. It also would seem possible to extend the useful life of the diborides as far as structure is concerned by a limited amount of B-10 enrichment. No similar burnup versus damage relationship can be established for the hexaborides since even at the relatively low B-10 burnup of 37 percent (6.0 percent of total atoms) the structure has deteriorated to nearly an amorphous state.

No quantitative measurements could be obtained from the hexaboride diffraction data. It is obvious from the diffraction patterns shown in Figure 6 that the hexaboride structures are extensively damaged by neutron irradiation. The structure is simple cubic as shown in Figure 1 and consequently reflections are possible for all combinations of (hkl). Diffracted intensities are practically zero for all reflections in the yttrium and europium hexaborides for both the powdered and densely-bonded samples. The burnup of total atoms range from 6.0 to 14.6 percent for the four samples, but even at the lowest burnup, the structure approaches an amorphous state.

A small number of measurements of limited precision were obtained from the yttrium tetraboride diffraction patterns. From Tables II and III it is seen that for an exposure of 1.35 percent burnup of the total atoms the lattice has expanded +0.35 and +0.80 percent in the a_o and c_o directions respectively. For a burnup of 9.3 percent, the changes in a_o and c_o are

+0.40 and -1.5 percent. This decrease in c_o continues to a value of -1.7 percent at for a burnup of 14.1 percent of the total atoms, but the change in a_o remains positive and has a value of +0.76 percent. This data indicates that during irradiation the tetragonal structure initially expands in both major crystallographic directions but as irradiation continues, c_o begins to decrease and a net contraction in this direction results at the higher exposure levels. The irradiation effects in the boron carbide will be mentioned here only to state that in general the same effects noted by Tucker and Senio(2) were observed in this study. The contraction in the c_o direction was measured to be -0.44 percent and the expansion in the a_o direction +0.28 percent but the extent of burnup cannot be determined for these B-10 enriched samples. These unit cell dimensional changes compare to values of -1.38 and +0.89 percent respectively from Tucker's work for a burnup of 15 percent of the total atoms. An approximate factor of 3 exists between both of the corresponding values for lattice dimension changes.

Sufficient data is available from the irradiated diborides however for an evaluation of radiation damage in this crystal structure to be made. In addition to the diffraction data from the polycrystalline samples of this material, the Laue and rotation photographs of the TiB_2 single crystals show general damage to this hexagonal structure. Both a_o and c_o axis shots are shown in Figures 7 to 10. It can be seen that not only have the reflections broadened and shifted in position but also that the relative intensities have changed. Diffractometer tracings of the reflections were obtained by use of a single crystal orienter. This technique gives quantitative measurements of these changes. Even though these specimens had received an exposure of only 1.75 percent burnup of the total atoms, relatively large changes in lattice parameters were measured. The lattice expanded in both major crystallographic directions. The a_o dimension increased by 1.49 percent and c_o increased by 0.74 percent for a total volume increase of 4.01 percent. Table VI also shows the large changes in relative intensities and some anisotropic broadening of the refelctions. These measurements were made on both a set of reflections of the type (00ℓ) and the type (h00). In addition, reflections from planes of the [100] zone were included so that a number of crystallographic directions would be represented. It is immediately apparent that the broadening increases more rapidly with the order of the reflection in the a_o direction or (h00) reflections than in the c_o direction or (00ℓ) type reflections. Broadening of the x-ray reflections from crystals is, of course, an indication of structure damage. This damage can be of two general types, either fragmentation of the crystallites, or microstrains (distortion) within the lattice. It has been shown by Warren and Averbach(7) that line broadening caused by microstrains or distortion of the lattice is dependent upon the order of the reflection but that caused by fragmentation is independent of order. This relationship and the observed broadening strongly suggests that distortion of the lattice is much greater in the a_o direction than in the c_o direction. It is seen in Table IV that broadening increases much more with the order of reflection in the a_o direction than in the c_o direction. Since the largest interstices are in the (100) faces, nucleation and clustering of the atoms along these planes would cause the observed effect. In addition, this could partially account for the weakening and fracture in this direction during irradiation. An examination of the Laue photographs in Figures 9 and 10 reveals definite and characteristic distortion of some of the reflections in the photograph taken with the x-ray beam parallel to the a_o axis. The shape of these reflection spots are typical of those from distorted planes.

A study of the measured lattice dimensional changes in all of the metal diborides as shown in Tables II and III show that the expansion in the a_o direction occurs at all exposures. On the other hand, the c_o dimension initially expands, then reverses and contracts as the exposure increases. The net effect at all exposures is an increase in volume. The diffraction data definitely indicates that the various diborides behave in the same general manner during irradiation. This similarity should be expected since the structures are isomorphous and the bonding is identical in all cases. The magnitude of the lattice dimension changes in the single crystals might be greater than for solid polycrystalline specimens of the same exposure because of the absence of anisotropic forces that undoubtedly occur between neighboring crystallites. The small differences in structural changes that were measured in the polycrystalline and unrestrained powdered specimens indicate that this variation in magnitude, if it exists, is not great. The data obtained from the TiB_2 sample that was enriched to 92 percent of the B-10 isotope cannot be compared with that obtained from the other diborides because the self-shielding effects preclude a determination of burnup. It is reasonably certain however, that the burnup at the point where the x-ray diffraction data was obtained is low and probably less than that for the single crystal. Both a_o and c_o increased for this specimen. The data points for the remainder of the diboride specimens should be more widely dispersed for a good description of distortion versus burnup to be obtained, but a relationship definitely exists as is shown in Figure 12.

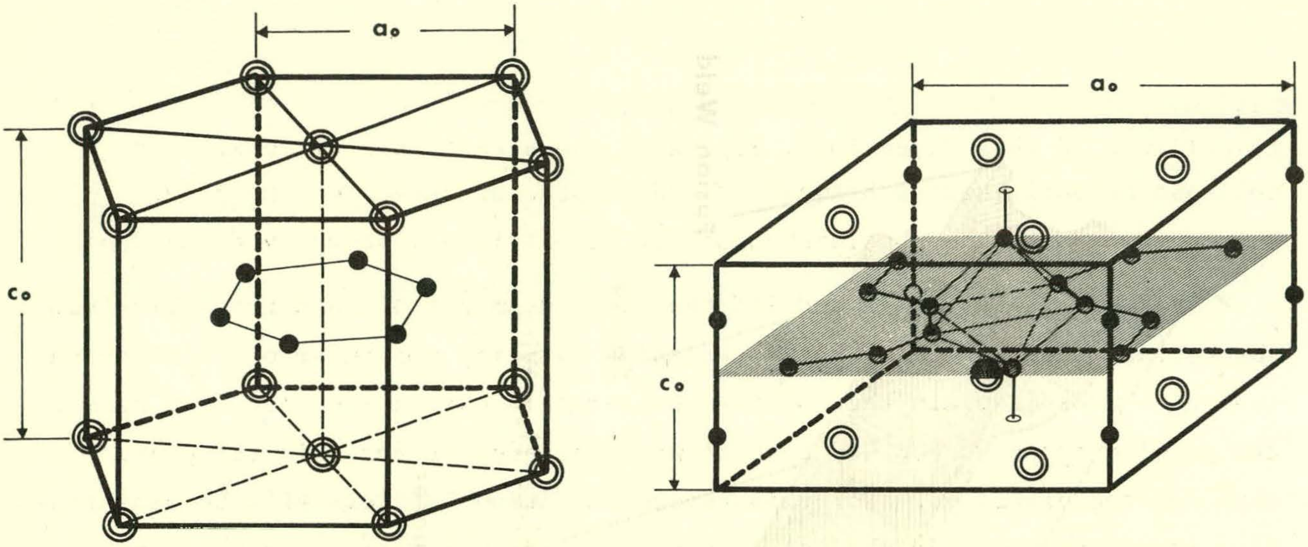
SUMMARY AND CONCLUSIONS

On the basis of the wide variety of data that has been accumulated for the diborides, it is felt that a model for the radiation-induced changes in this structure can be proposed. The diffraction data gives information concerning the changes in the structure that are caused by the B-10 (n,α) reaction and the disposition within the lattice of the atoms of helium and lithium produced by this reaction. The measurements of the amount of helium that is released indicates the efficiency of the trapping sites within this structure.

Initially an expansion of the hexagonal lattice in both directions occurs as a result of the trapping of helium and lithium atoms in interstitial positions. During the early stages of the irradiation, damage to the lattice is insufficient to disrupt an appreciable number of trapping sites and very little diffusion of the impurity atoms occur at the temperature of irradiation. The lattice strains that are produced by the misfit of the relatively large interstitials provide nucleation sites for clustering of the lithium and helium atoms along the (100) planes. As irradiation continues, the lattice is disrupted to the extent that trapping sites are gradually destroyed and the diffusion of the interstitials is enhanced. As damage to the structure increases, diffusion barriers are lowered, first for the point defects and then to a lesser extent for the clusters. Since boron is being removed from the layers perpendicular to the c_o direction, the removal of interstitials from the structure will permit the structure to collapse in this direction. Figure 12 shows that this diffusion and collapse probably begins between 20 and 30 percent burnup of the B-10. Beyond this point the absolute number of interstitials steadily diminishes.

As shown in Tables II and III the limited amount of data available from the tetraborides indicate that a radiation damaging mechanism of this general type also would explain the observed behavior in this structure. The rate of damage with boron burnup has been shown to be greater for this structure than for the diborides. For this reason diffusion barriers will be diminished at a lower exposure and the concentration of interstitials, and therefore the initial expansion of the lattice, will always be less than for the diborides. It also is felt that the radiation effects in the cubic hexaborides would follow this model but since the rate of damage to this structure is much greater than for the other structures it would be possible to obtain a damage versus burnup function only by examining specimens of very low burnups.

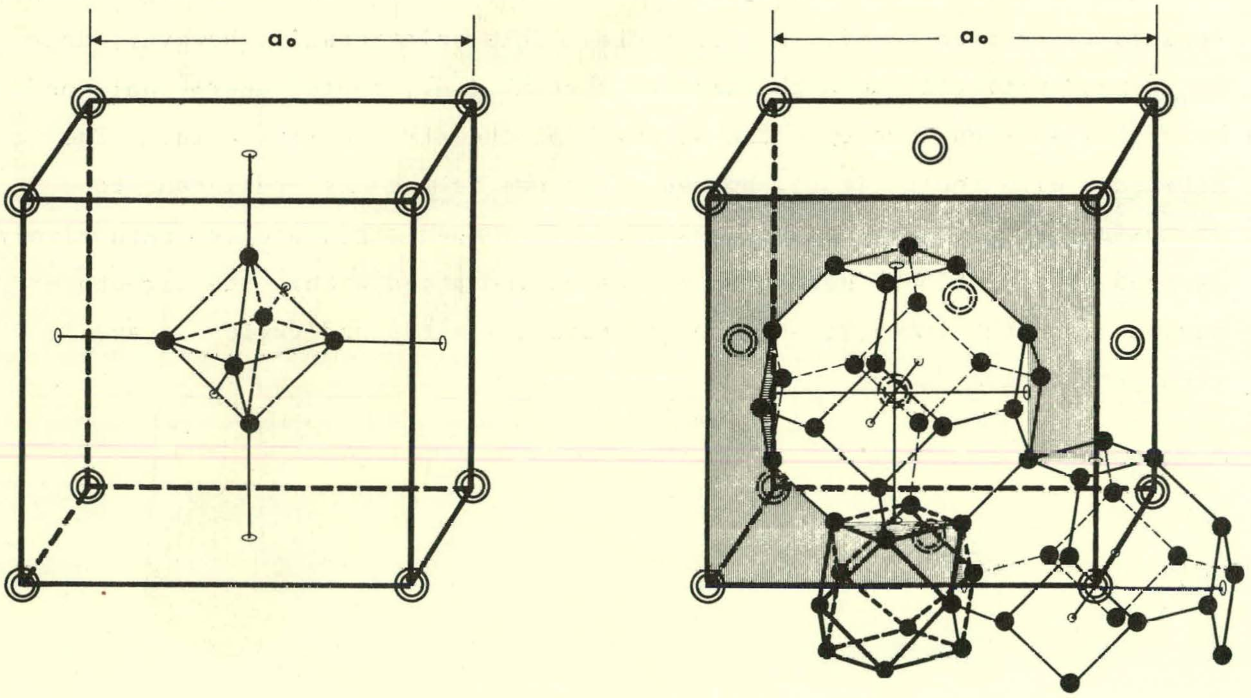
It has been established from this study that irradiation damage to the borides is related to crystal structure. This relationship, however, does not depend primarily upon the crystal system, i.e., cubic, tetrabonal, or hexagonal as such, but upon the strength of the structural bonding. The diborides with their tightly bonded structure is the most resistant to radiation damage. The hexaborides with their open structure are extensively damaged by radiation. Retention of the helium atoms within the structure depends upon the integrity of the interstitial sites and varies inversely with irradiation damage.



Diboride Structure (MB_2)

Tetraboride Structure (MB_4)

◎ Metal Atom ● Boron Atom



Hexaboride Structure (MB_6)

Dodecaboride Structure (MB_{12})

Figure 1. STRUCTURES OF THE METAL BORIDES

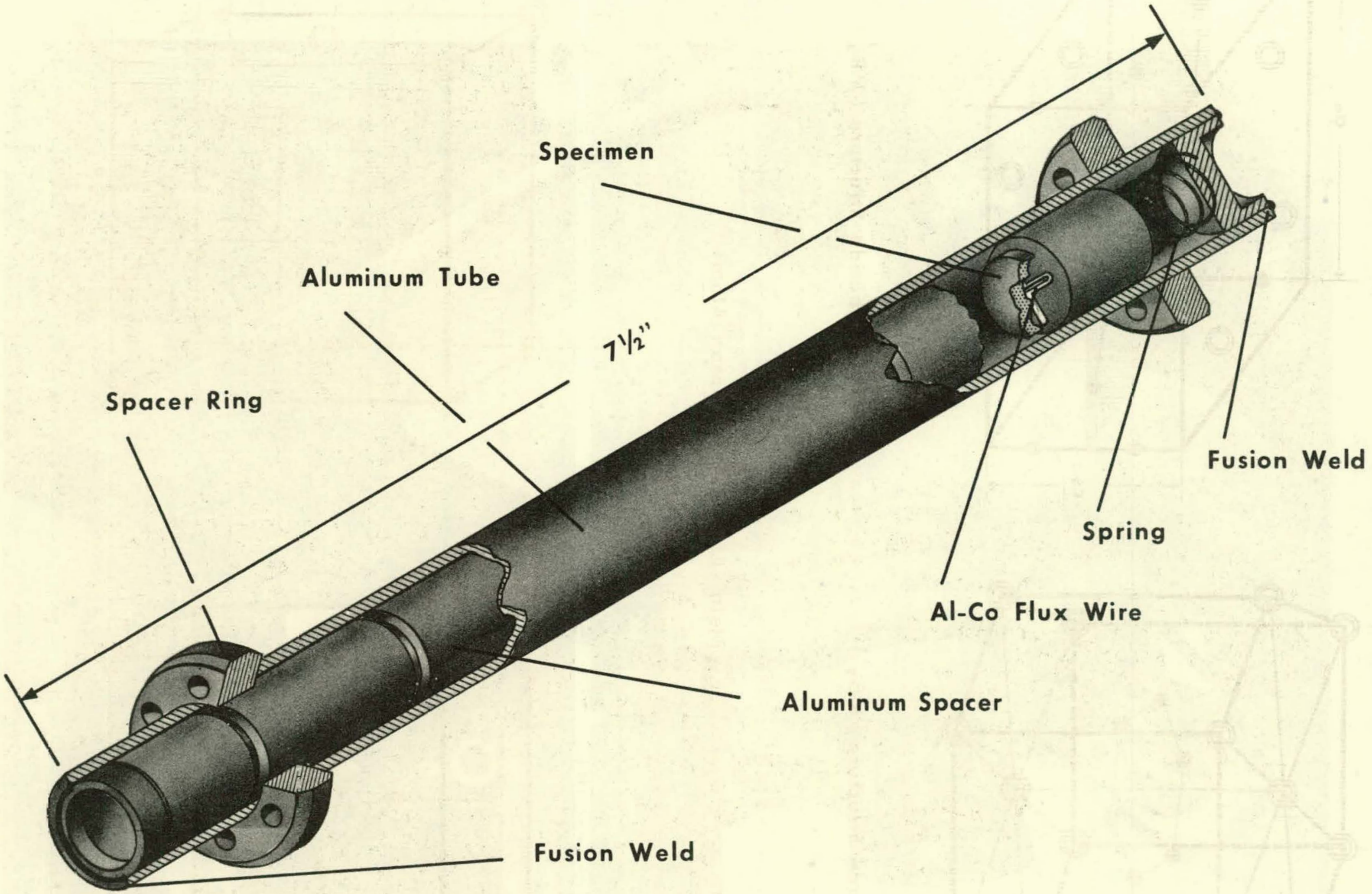


Figure 2. IRRADIATION CAPSULE

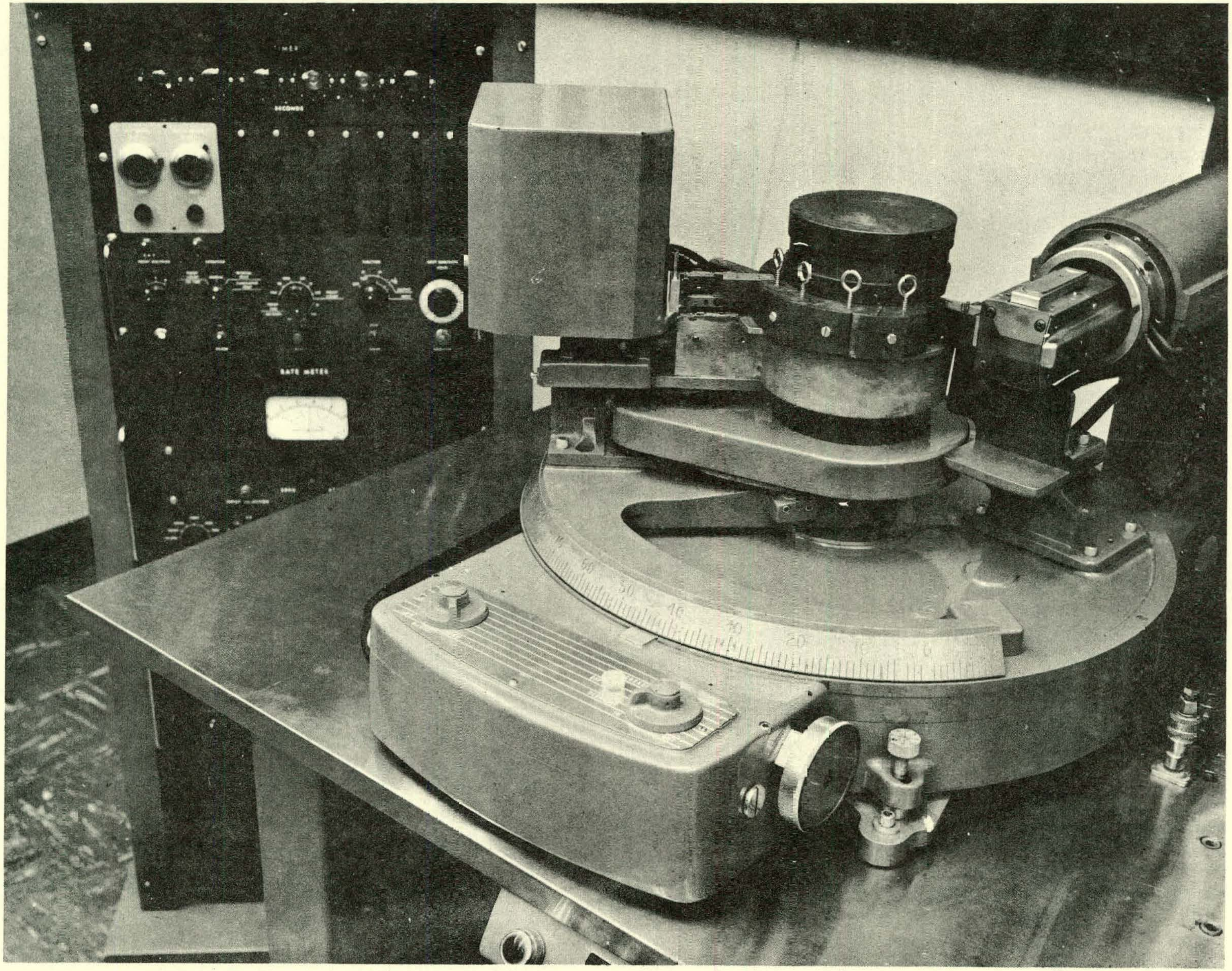


Figure 3. INSTRUMENT MODIFICATIONS. LEAD CELL ON DIFFRACTOMETER AND PULSE HEIGHT SELECTOR IN DETECTOR INSTRUMENT RACK.

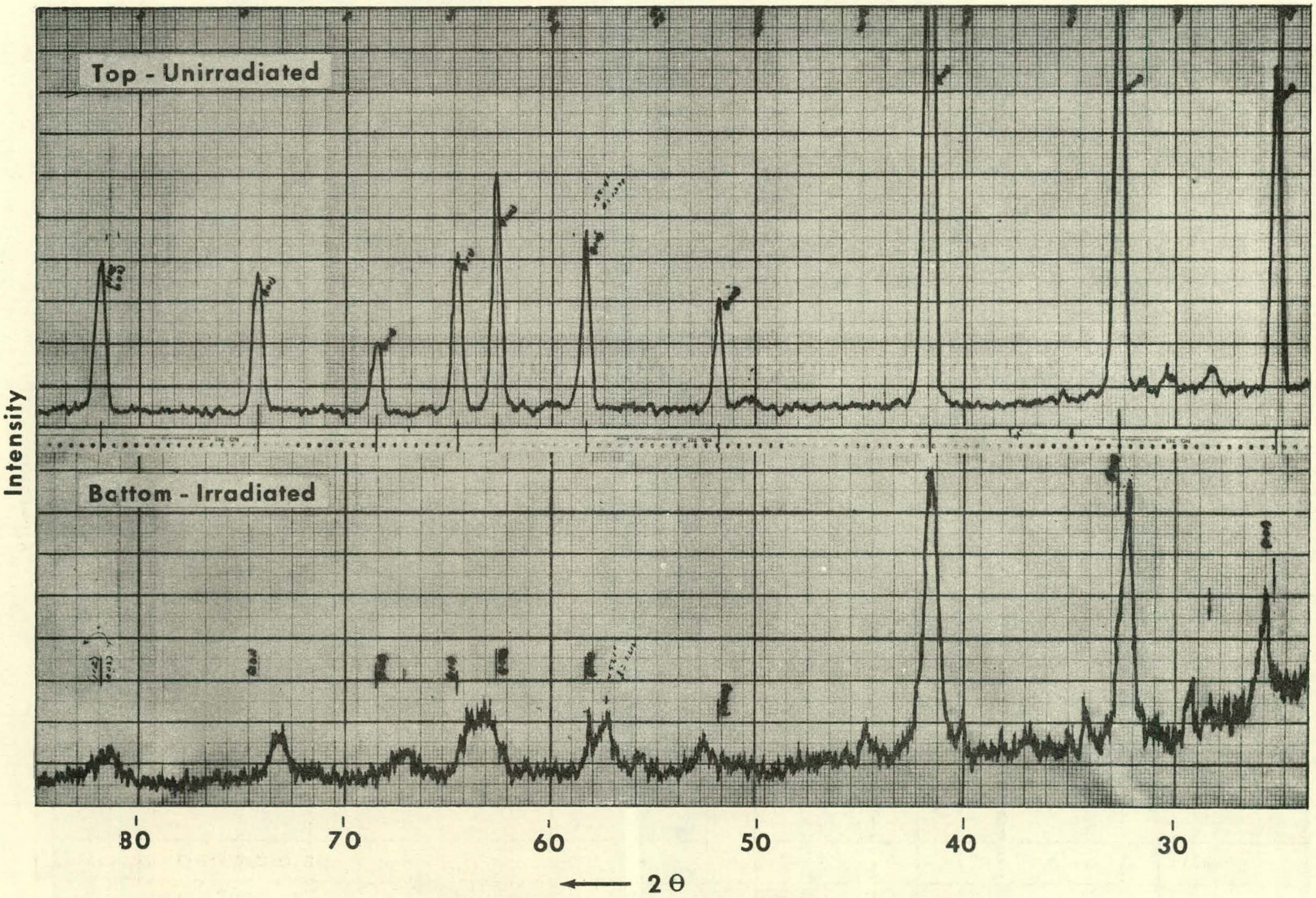


Figure 4. X-RAY DIFFRACTION PATTERNS OF ZrB_2.

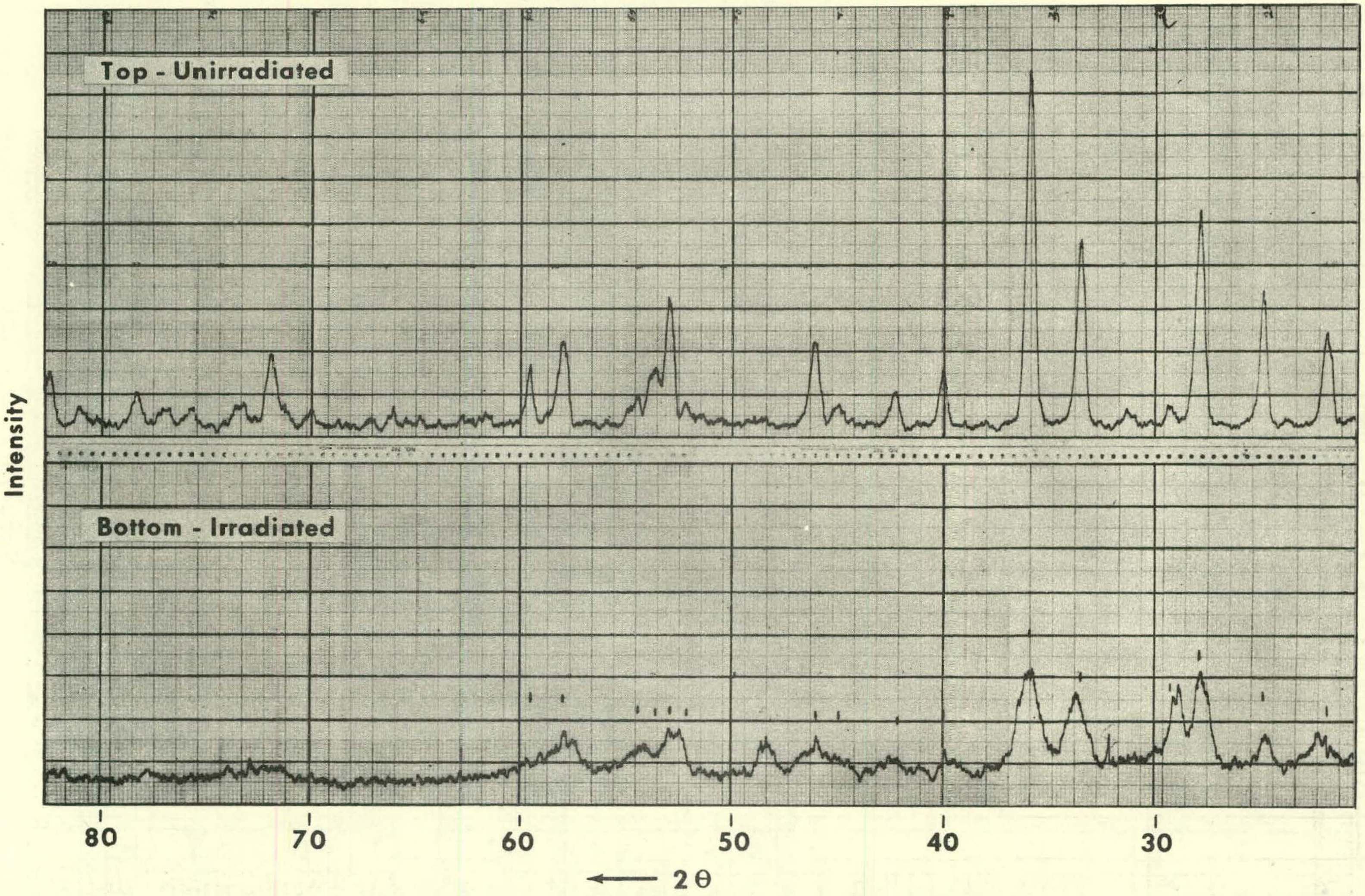


Figure 5. X-RAY DIFFRACTION PATTERNS OF YB_4.

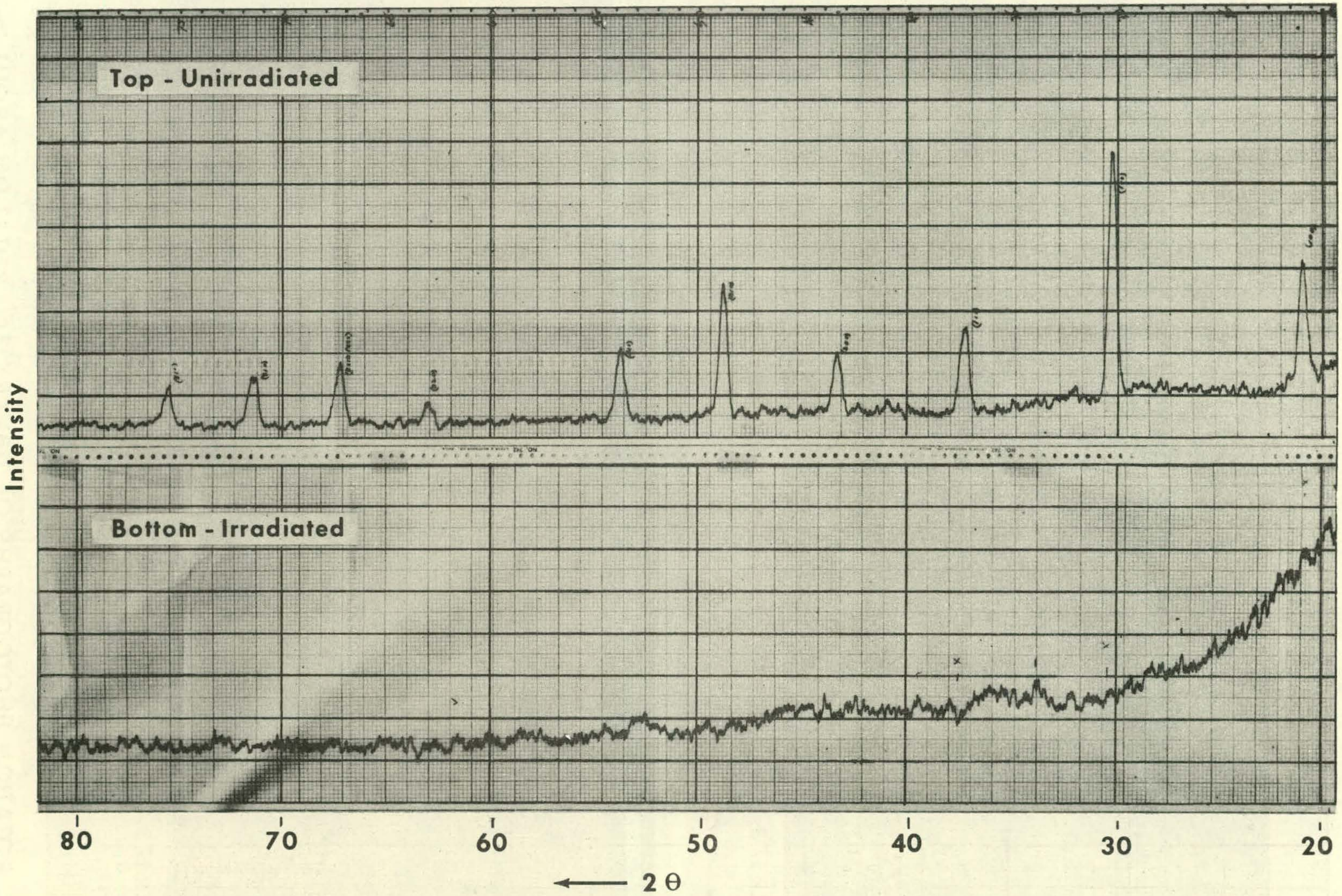
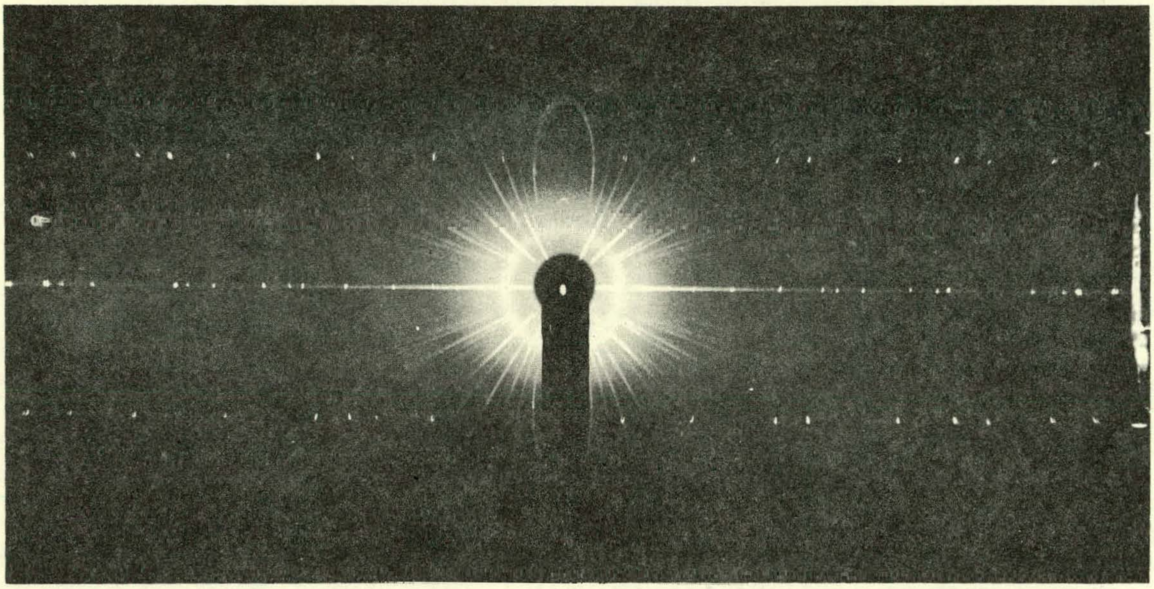
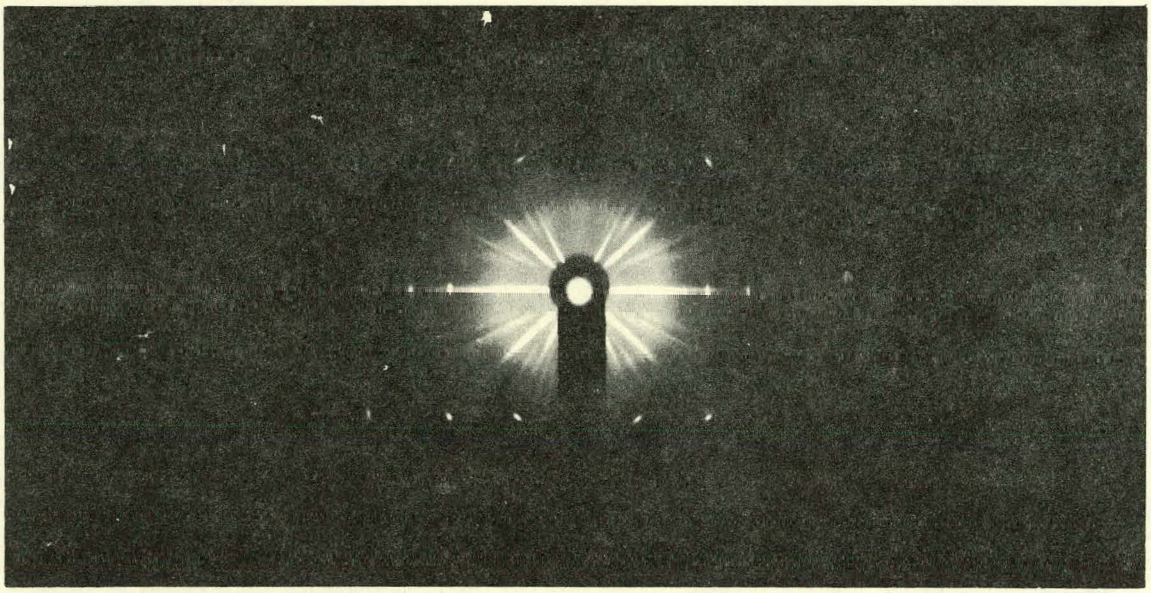


Figure 6. X-RAY DIFFRACTION PATTERNS OF EuB_6.

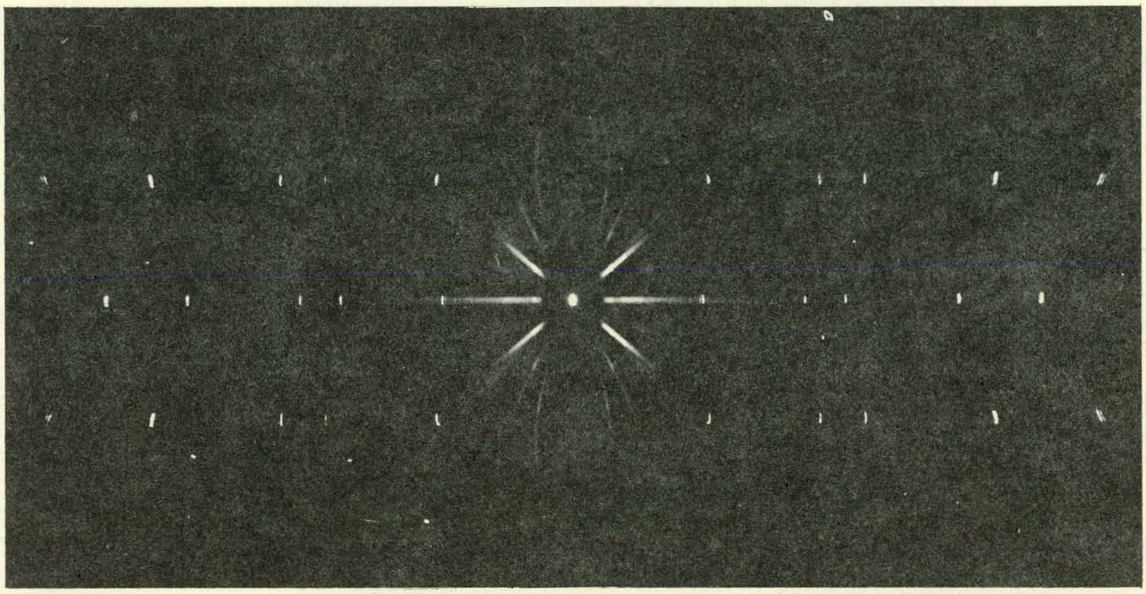


XR 173-1 (a) Unirradiated

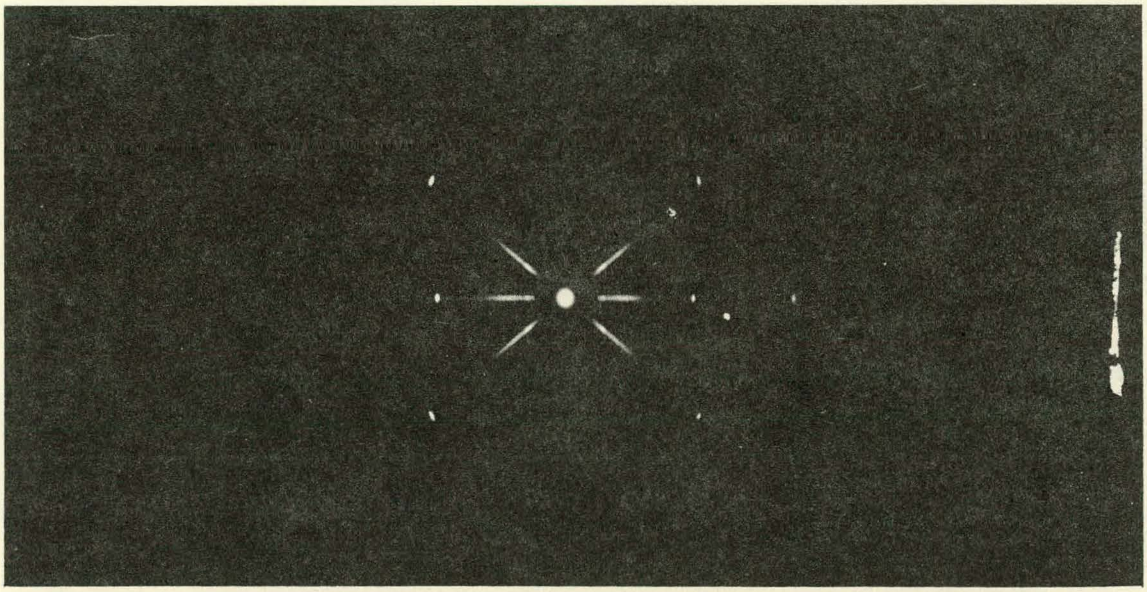


XR 173-2 (b) Irradiated

Figure 7. ROTATION PHOTOGRAPHS OF TiB_2 CRYSTAL. ROTATION ABOUT "a" AXIS.

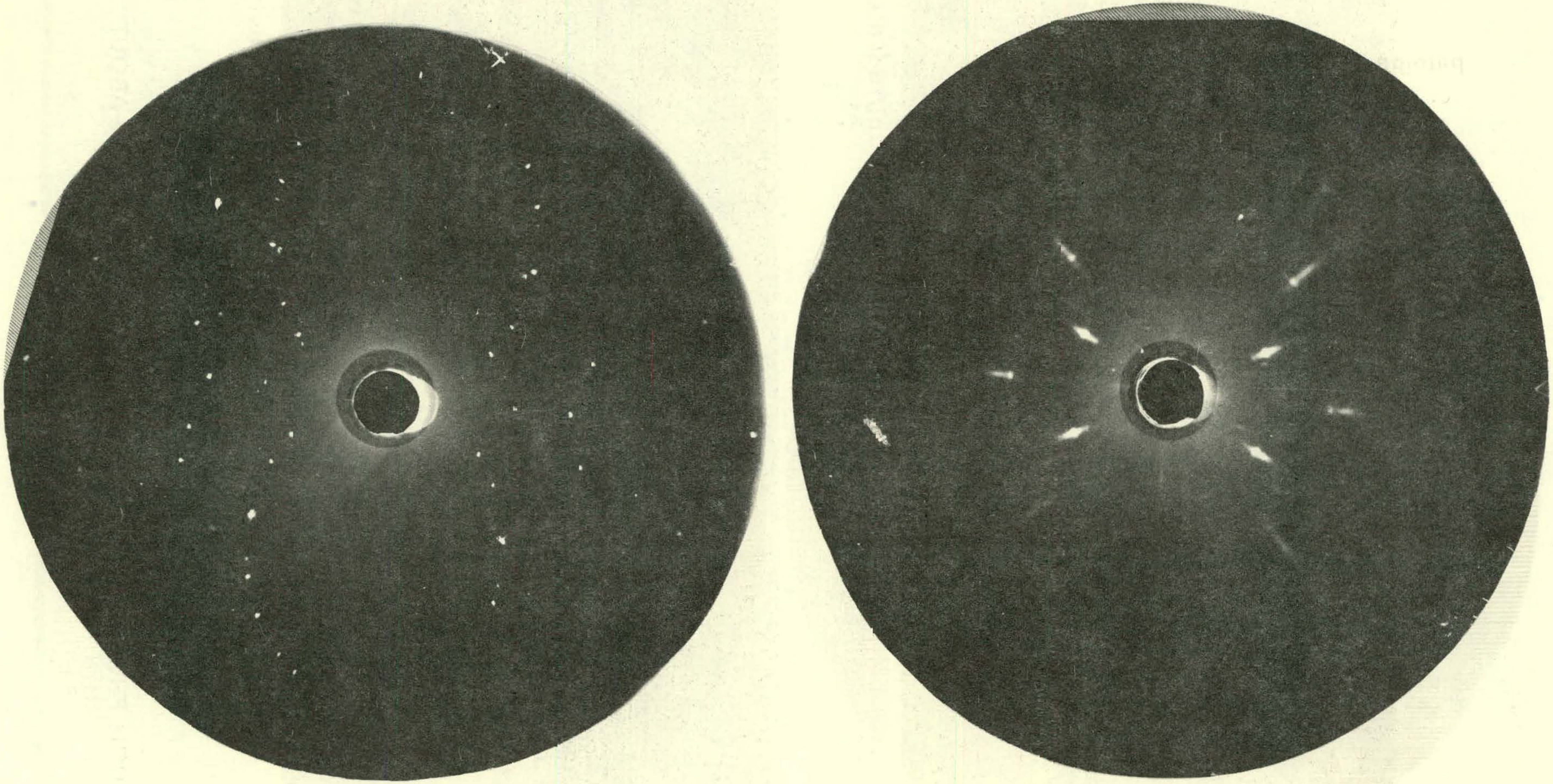


XR 173-3 (a) Unirradiated



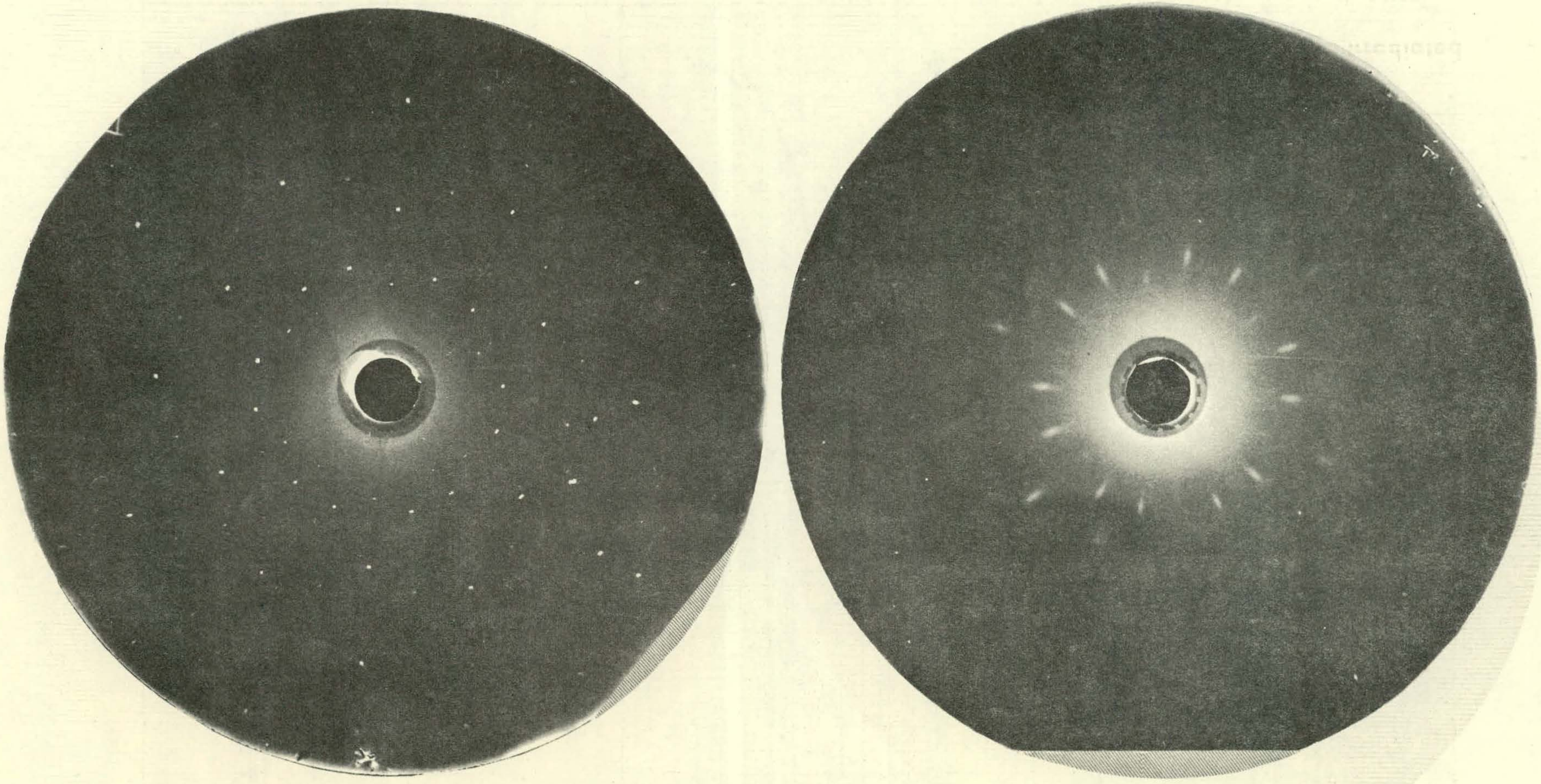
XR 173-4 (b) Irradiated

Figure 8. ROTATION PHOTOGRAPHS OF TiB_2 CRYSTAL. ROTATION ABOUT "c" AXIS.



XL173-1 (a) Unirradiated XL173-2 (b) Irradiated

Figure 9. TRANSMISSION LAUE PHOTOGRAPHS OF TiB_2 CRYSTAL. INCIDENT BEAM PARALLEL TO "a" AXIS.



XL 173-3 (a) Unirradiated

XL 173-4 (b) Irradiated

Figure 10. TRANSMISSION LAUE PHOTOGRAPH OF TiB_2 CRYSTAL. INCIDENT BEAM PARALLEL TO "c" AXIS.

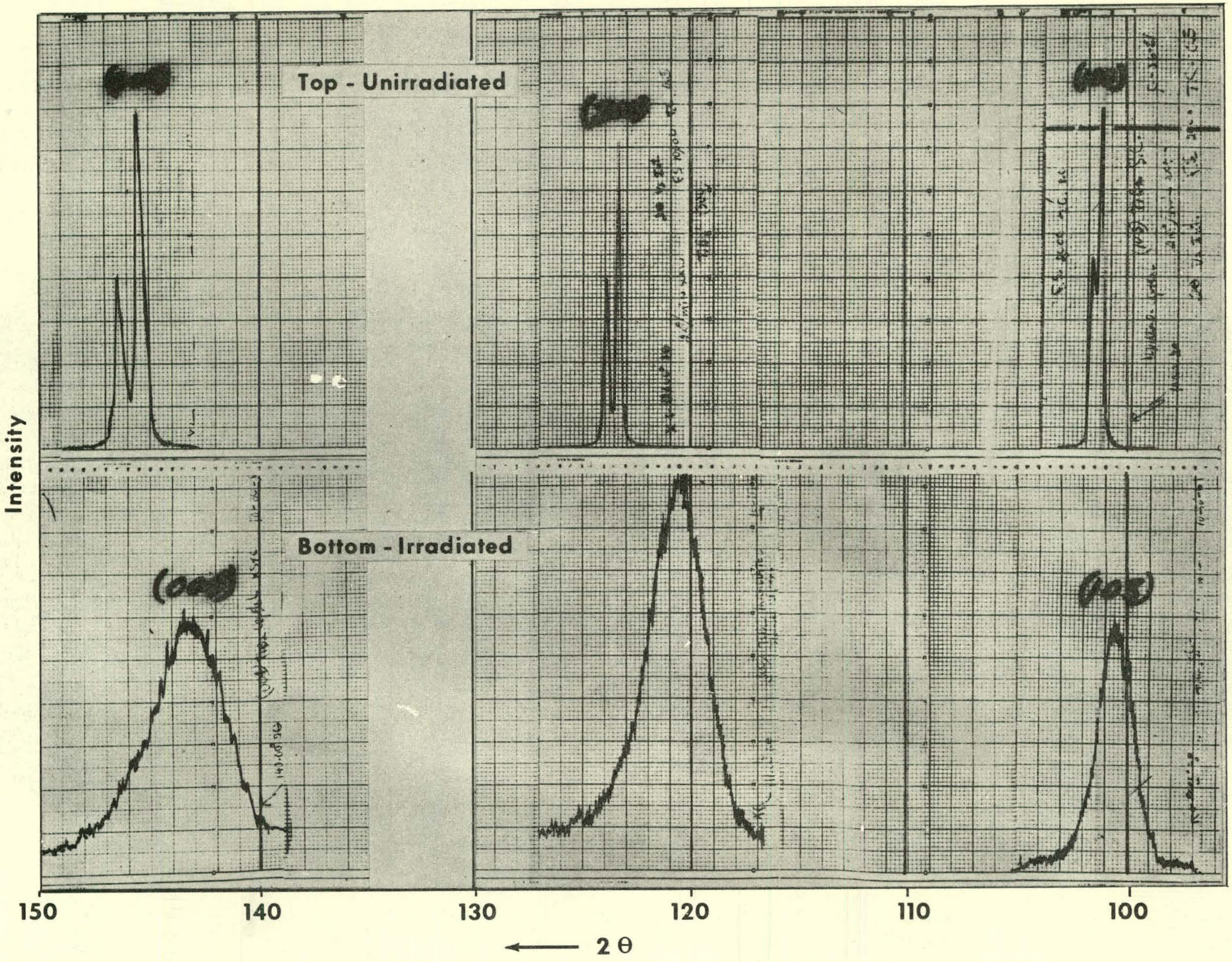


Figure 11. X-RAY DIFFRACTION PEAKS FROM A SINGLE CRYSTAL OF TiB_2.

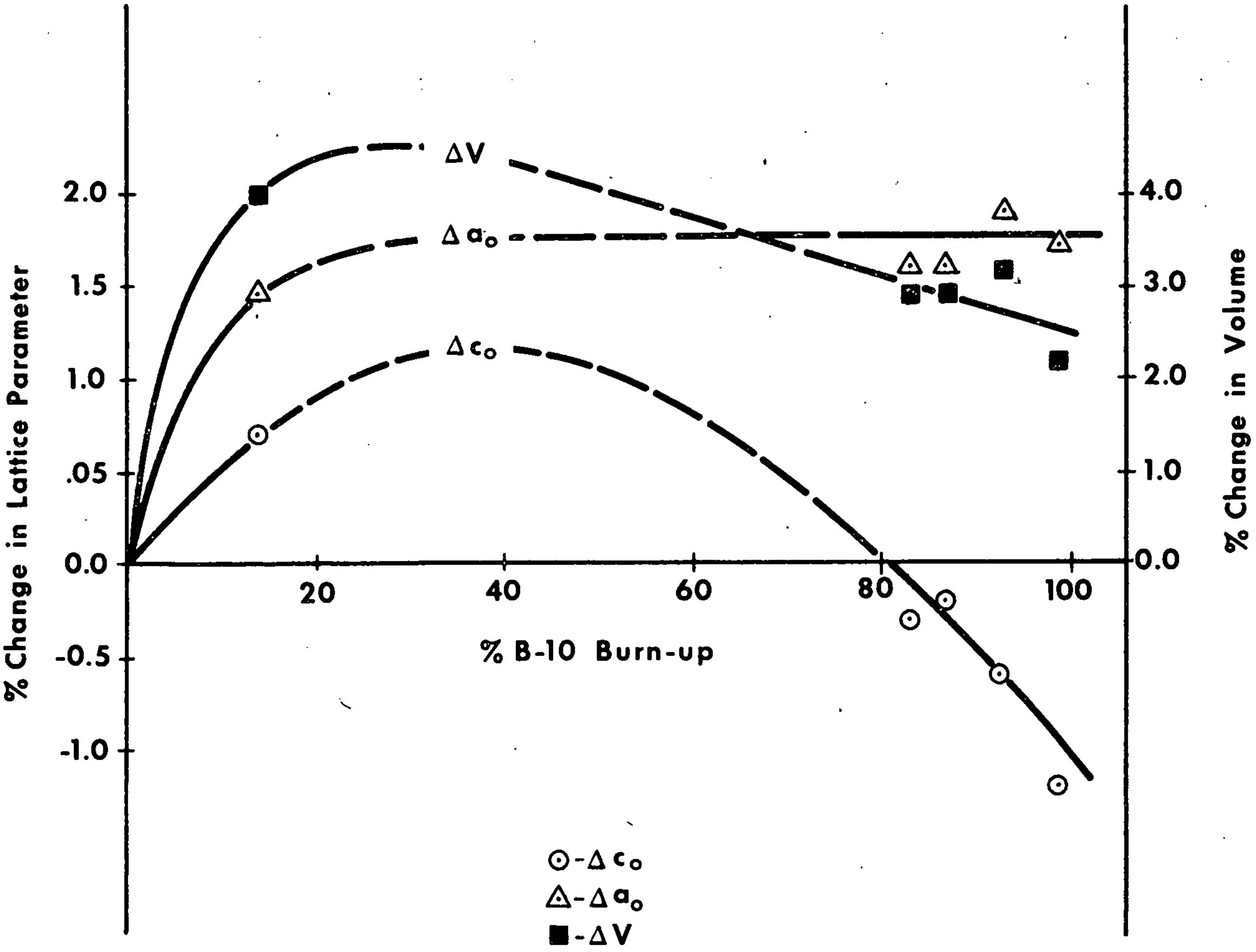


Figure 12. LATTICE PARAMETER AND UNIT CELL VOLUME CHANGES IN IRRADIATED DIBORIDES

ACKNOWLEDGEMENT

The authors wish to acknowledge the continued encouragement of Dr. B. Weidenbaum and Dr. H. H. Klepfer in the performance of this work and also the special contribution of A. N. Holden for his original suggestions on the scope of these crystallographic studies. Other Vallecitos personnel who receive our thanks for invaluable contributions include E. W. Hoyt, D. L. Zimmerman, E. S. Darlin, and J. E. Lewis. We also express our gratitude for the cooperation received from the personnel of the Radiometallurgy Laboratory at Hanford. Special thanks are extended to R. E. Olson, Manager of the Laboratory who made the x-ray facilities available for our use and to W. J. Gruber for his valuable technical assistance.

REFERENCES

1. Holden, A. N., "Borides of Interest for Control Materials", GEAP-3117, January 29, 1959.

2. Tucker, C. W. and Senio, P., "X-Ray Scattering by Neutron Irradiated Single Crystals of Boron Carbide", Acta Cryst., 7, 456 (1954).

3. Hoyt, E. W., Cummings, W. V., Zimmerman, D. L., "Rare Earth Oxides and Rare Earth Borates - Corrosion Compatibility and Radiation Effects", GEAP-3909, (1962).

4. Hoyt, E. W., Zimmerman, D. L., "Radiation Effects in Borides, Part I - Helium Release and Swelling in Irradiated Borides", GEAP-3743, February 13, 1962.

5. Cummings, W. V., Kaulitz, D. C., Sanderson, M. J., "Double Diffracting X-Ray Spectrometer for Study of Irradiated Materials", Rev. Sci. Instr., 26, No. 1, January 1955.

6. Samsonov, G. V., "Rare Earth Metal Borides", Uspekhi Khimii, 28, 189-217, 1959.

7. Warren, B. E., Averbach, B. L., "The Separation of Cold-Work Distortion and Particle Size Broadening in X-Ray Patterns", J. Appl. Phys., 23, 497 (1952).