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X-ray Scattering by Neutron-Irradiated Single Crystals of Boron Carbide. I

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Neutron irradiation of single crystals of boron carbide produces very strong X-ray diffraction effects. These effects are (*a*) *contraction* of the lattice in the c_0 direction and *expansion* in the a_0 direction, (*b*) an anisotropic artificial temperature factor which is six times as strong in the c_0 direction as in the a_0 direction, (*c*) changes in the average lattice positions of a number of the atoms, and (*d*) very heavy diffuse scattering surrounding many of the reciprocal-lattice points. Annealing experiments show that most of the X-ray effects are removed in the temperature range of 700 to 900° C. The present work shows that the effects are due to the production of the anisotropic defect in the lattice. This defect is produced by the selective removal of the central carbon atom in a chain of three carbon atoms which lies parallel to the c_0 axis. In the 700–900° C. range the selectively removed carbon atom becomes mobile and finds its way back to its normal position. The effects are interpreted qualitatively in terms of an elastic model of Huang. Work is in progress to extend the analysis of Huang to the case of anisotropic defects and to measure and interpret the diffuse scattering in detail.

Introduction

The qualitative nature of the X-ray effects found in neutron-irradiated single crystals of boron carbide, B_4C, has been described recently (Tucker & Senio, 1954). These effects are (*a*) large, highly anisotropic lattice parameter changes, (*b*) a highly anisotropic artificial temperature factor, (*c*) true structural changes, and (*d*) very heavy diffuse scattering surrounding many of the reciprocal-lattice points. Items (*a*), (*b*) and (*c*) have been studied in detail, including annealing experiments, and are now well understood. The results of these studies will be reported in the present paper, while detailed studies of the diffuse scattering will be given in a second paper.

The damaging reaction and the crystal structure of boron carbide

In most nuclear reactors, the radiation damage produced in boron carbide is overwhelmingly due to the reaction of the B–10 nucleus with thermal neutrons to form Li–7 and He–4 nuclei. According to Bethe (1950), these nuclei dissipate 0·84 and 1·47 MeV., respectively, in the lattice by ionization and bumping collisions. The effects of the B–10 reaction far outweigh those of fast neutron bumping collisions because

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the cross-section of the B–10 reaction is 4000 barns for thermal neutrons compared with a cross-section of only several barns for fast neutron bumping collisions. This difference is further accentuated by the fact that the slow neutron flux outweighs the fast flux in many nuclear reactors. Since the isotopic concentration of the B–10 nucleus is 15% of all atoms in boron carbide, the irradiations may be continued to very high burnups. Further, the high melting point and great strength of boron carbide lead one to expect that the damage once produced will tend to be stable at ordinary temperatures. Finally, the fact that the Li–7 and He–4 nuclei are stable isotopes means that boron carbide is virtually non-radioactive, even after very heavy irradiations, and all of the standard X-ray diffraction techniques can be applied. These factors make boron carbide admirably suited for radiation damage studies.

The crystal structure of boron carbide has been given independently by Zdanov & Sevastianov (1941) and by Clark & Hoard (1943). The structure is rhombohedral with

$$a_0 = 5{\cdot}19 \text{ Å}, \quad \alpha = 65° 18',$$

while the corresponding hexagonal unit cell has

$$a_0 = 5{\cdot}60, \quad c_0 = 12{\cdot}12 \text{ Å}.$$

The space group is D^5_{3d}–$R\bar{3}m$. The hexagonal unit cell contains 12 boron and 3 carbon atoms. Clark & Hoard (1943) give their position parameters (*Internationale Tabellen*, 1935) as:

6B in (h) with $x = \frac{1}{6}$, $y = -\frac{1}{6}$, $z = 0{\cdot}360$,
6B in (h) with $x = 0{\cdot}106$, $y = -0{\cdot}106$, $z = 0{\cdot}113$,
2C in (c) with $x = y = 0$, $z = 0{\cdot}385$,
1C in (b) with $x = y = 0$, $z = \frac{1}{2}$.

The boron atoms are linked together to form icosahedra while the carbons are linked to form a linear chain of three atoms parallel to the hexagonal c_0 axis. Each of the two end carbons is bound to three boron atoms and, of course, to the central carbon atom. The central carbon atom is bound only to the two end carbons in the chain of three carbons. Six of the borons in each icosahedron are linked to six other icosahedra while the other six borons are attached to the end carbons of six linear carbon chains. Thus the structure forms a three-dimensional network of boron icosahedra and linear carbon chains. Zdanov & Sevastianov (1941) show that the boron carbide structure may be viewed as a deformed rock salt structure in which the units are the boron icosahedra and the linear chains of three carbon atoms. To form the boron carbide structure, the cubic unit cell must be compressed 12% along the body diagonal to form the rhombohedral unit cell of boron carbide.

General description of the X-ray effects

Three irradiations of single crystals of boron carbide have thus far been performed. The integrated thermal neutron fluxes for these irradiations are $6{\cdot}4\times10^{18}$, $1{\cdot}4\times10^{19}$, and 3×10^{20} neutrons/cm.^{2}. Neglecting self-shielding, these irradiations correspond to burnups of 0·4, 0·8, and 15%, respectively, of all atoms present in boron carbide. These burnups should be reduced because of self-shielding. However, there is increased burnup due to the effect of epithermal neutrons. As a result, the burnups are somewhat uncertain but the figures certainly serve as a semi-quantitative index for the amount of damage each set of crystals received. The temperature of the crystals was not controlled during the irradiations but was known to be well below the levels required to anneal out the observed X-ray effects. These effects were observed to increase with increasing neutron exposure. The results reported will therefore deal largely with the crystals given the greatest exposure since the X-ray effects were very large and readily measured.

The most striking changes occurring in boron carbide on irradiation may be seen in Laue patterns of the single crystals. These changes are the decrease in intensity of the Laue spots and the increase in intensity of the diffuse scattering surrounding the reciprocal-lattice points, and are shown in Fig. 1(a)–(c). Fig. 1(a) is a Laue pattern of an unirradiated boron carbide single crystal using X-radiation from a copper target tube. Some weak thermal diffuse scattering can be seen adjacent to some of the spots at, or close to, the position for reflecting the copper K radiation. Fig. 1(b) is a Laue pattern from a similarly oriented single crystal which had been exposed to an integrated thermal neutron flux of $1{\cdot}4\times10^{19}$ neutrons/cm.^{2}. It is seen that the diffuse scattering has increased very greatly and actually is present around some of the spots which showed no diffuse scattering in the unirradiated crystal. It is also easily seen that the Laue pattern is much weaker relative to the pattern of diffuse spots for the irradiated crystal than for the unirradiated crystal. These effects are seen much more strongly in Fig. 1(c). The crystal shown in Fig. 1(c) is again a similarly oriented single crystal but which had been exposed to an integrated thermal neutron flux of 3×10^{20} neutrons/cm.^{2}. Here the effects are extremely pronounced. The Laue spots are still sharp but their intensities have been greatly reduced. The diffuse scattering, on the other hand, is very strong and in the low-angle region diffuse spots due to both the Cu $K\alpha$ and Cu $K\beta$ radiation are easily seen.

The changes in the diffuse and Bragg scattering were also evident in a zero-level Weissenberg pattern of the $h0.l$ reflections for the heavily irradiated crystal. In this pattern the changes in the Bragg intensities were clearly of two types. First, there was a strong, highly anisotropic, artificial temperature factor present. This factor was much stronger for the c_0 than for the a_0 direction. In addition, there were a few moderate or weak reflections (particularly the ($\bar{2}0{\cdot}2$) reflection) which actually *increased* in intensity due to the irradiation. These effects were also clearly apparent in a

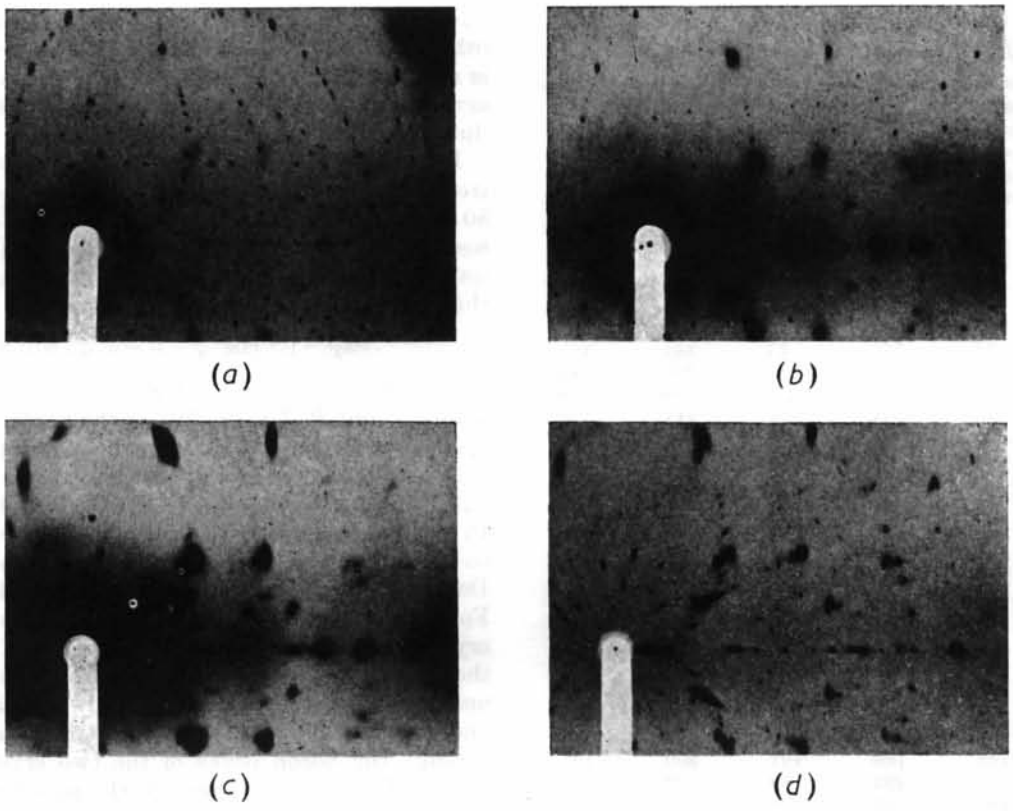


Fig. 1. (*a*) Laue pattern of unirradiated single crystal of boron carbide. (*b*) Laue pattern of irradiated single crystal of boron carbide (integrated thermal neutron flux of $1{\cdot}4\times10^{19}$ neutrons/cm.^{2}). (*c*) Laue pattern of irradiated single crystal of boron carbide (integrated thermal neutron flux of 3×10^{20} neutrons/cm.^{2}). (*d*) Laue pattern of irradiated single crystal of boron carbide (integrated thermal neutron flux of 3×10^{20} neutrons/cm.^{2}) after vacuum annealing for 15-hr. periods from 200–1200° C.

powder pattern of polycrystalline material given the same irradiation. Here the first line, the (01·1) reflection, had *increased* in intensity whereas the effect of the artificial temperature factor is always to *decrease* intensities. Therefore, one concludes that, in addition to the artificial temperature factor, there are actual changes in the average positions of the lattice atoms due to the irradiation.

Both the single-crystal and powder patterns also showed large changes in the lattice parameters of the irradiated material. For the heaviest irradiation the c_0 axis was found to have *contracted* 1·38% while the a_0 axis *expanded* 0·89%.

Thus, there are large and very unusual X-ray effects found in neutron-irradiated boron carbide. These effects will first be discussed in detail and then interpreted in a general way by theory.

Changes in Bragg intensities

Examination of the zero-level Weissenberg pattern of the $h0.l$ reflections for the crystal given the heaviest irradiation showed that the biggest effect on the intensities was the large anisotropic artificial temperature. The first step, therefore, was to determine this factor. For this purpose, zero-level Weissenberg patterns of the $h0.l$ reflections were prepared using Cu $K\alpha$ radiation and the multiple-film technique for both irradiated and unirradiated single crystals.

Column (2) of Table 1 gives the calculated structure factors based on the atomic position parameters of Clark & Hoard (1943), using the calculated atomic scattering factors for carbon and boron given by McWeeny (1951). Column (3) gives the observed structure factors for the unirradiated crystal. Lorentz and polarization corrections have been made, but no absorption or temperature corrections since absorption is very low in boron carbide and its melting point extremely high. The squares of the structure factors in the two columns have been normalized to the same value. Since neither Zdanov & Sevastianov (1941) nor Clark & Hoard (1943) give a detailed comparison of observed and calculated structure factors it seemed worthwhile to make this comparison for the $h0.l$ reflections. The reliability factor for the 53 $h0.l$ reflections in Table 1 is 18%. Thus, the structure of Clark & Hoard (1943) is satisfactorily confirmed by the present data.

Column (4) of Table 1 gives the structure factors obtained from the irradiated single crystal. These

Table 1. *Structure factors for boron carbide $h0.l$ reflections under various conditions*

Column (1): $h0.l$
Column (2): $|F|$ calculated
Column (3): $|F|$ unirradiated
Column (4): $|F|$ irradiated
Column (5): $|F|$ irradiated, corrected
Column (6): $|F|$ annealed, corrected

(1)	(2)	(3)	(4)	(5)	(6)
00·3	257	293	262	242	301
00·6	65	110	0	0	122
00·9	147	186	117	247	220
00·12	311	296	105	467	343
00·15	332	376	33	385	315
10·2	355	299	327	292	244
10·5	9	0	0	0	0
10·8	469	503	178	314	399
10·11	6	47	0	0	42
10·14	128	73	17	143	87
20·1	647	501	501	445	597
20·4	30	81	30	32	81
20·7	227	182	182	291	236
20·10	245	188	52	150	235
20·13	318	419	42	287	347
30·0	68	104	116	107	113
30·3	243	219	198	209	222
30·6	264	217	140	208	267
30·9	321	421	119	309	380
30·12	81	128	0	0	124
40·2	342	292	292	313	349
40·5	69	66	30	42	67
40·8	124	156	127	300	197
40·11	375	393	88	432	298
50·1	118	64	28	32	76
50·4	59	85	26	39	118
50·7	216	184	106	238	254
60·0	274	269	135	174	289
60·3	486	469	406	606	364
$\bar{1}$0·1	84	103	174	149	110
$\bar{1}$0·4	411	415	415	426	446
$\bar{1}$0·7	173	147	82	123	206
$\bar{1}$0·10	117	147	30	81	158
$\bar{1}$0·13	194	189	46	288	234
$\bar{2}$0·2	7	20	65	60	14
$\bar{2}$0·5	323	446	223	269	277
$\bar{2}$0·8	226	214	195	376	286
$\bar{2}$0·11	107	75	0	0	76
$\bar{2}$0·14	136	122	14	127	185
$\bar{3}$0·0	68	103	116	107	113
$\bar{3}$0·3	242	300	219	232	272
$\bar{3}$0·6	209	177	125	186	206
$\bar{3}$0·9	270	210	51	137	287
$\bar{3}$0·12	272	234	83	476	278
$\bar{4}$0·1	223	181	143	147	279
$\bar{4}$0·4	152	163	105	134	187
$\bar{4}$0·7	101	130	0	0	171
$\bar{4}$0·10	269	406	105	402	331
$\bar{5}$0·2	49	45	20	25	44
$\bar{5}$0·5	233	234	131	212	325
$\bar{5}$0·8	174	139	35	94	189
$\bar{6}$0·0	274	268	134	173	288
$\bar{6}$0·3	108	128	59	88	163

structure factors have not been normalized but are based on setting the intensities of the (20·1) reflection (the strongest reflection) equal for the irradiated and unirradiated crystal. The very strong effect of the artificial temperature factor in the c_0 direction is seen in the (00·15) reflection whose structure factor is reduced by a factor of ten by the irradiation. On the other hand, the structure factor of the (60·0) reflection is reduced only by a factor of two, showing that the artificial temperature factor is much less for the a_0 direction than for the c_0 direction.

In order to determine the magnitude of the anisotropic artificial temperature factor, a series of Fourier $h0.l$ projections were computed, using IBM equipment, for a variety of anisotropy ratios. The artificial temperature factor was assumed to be equivalent to that given by Hughes (1941), namely,

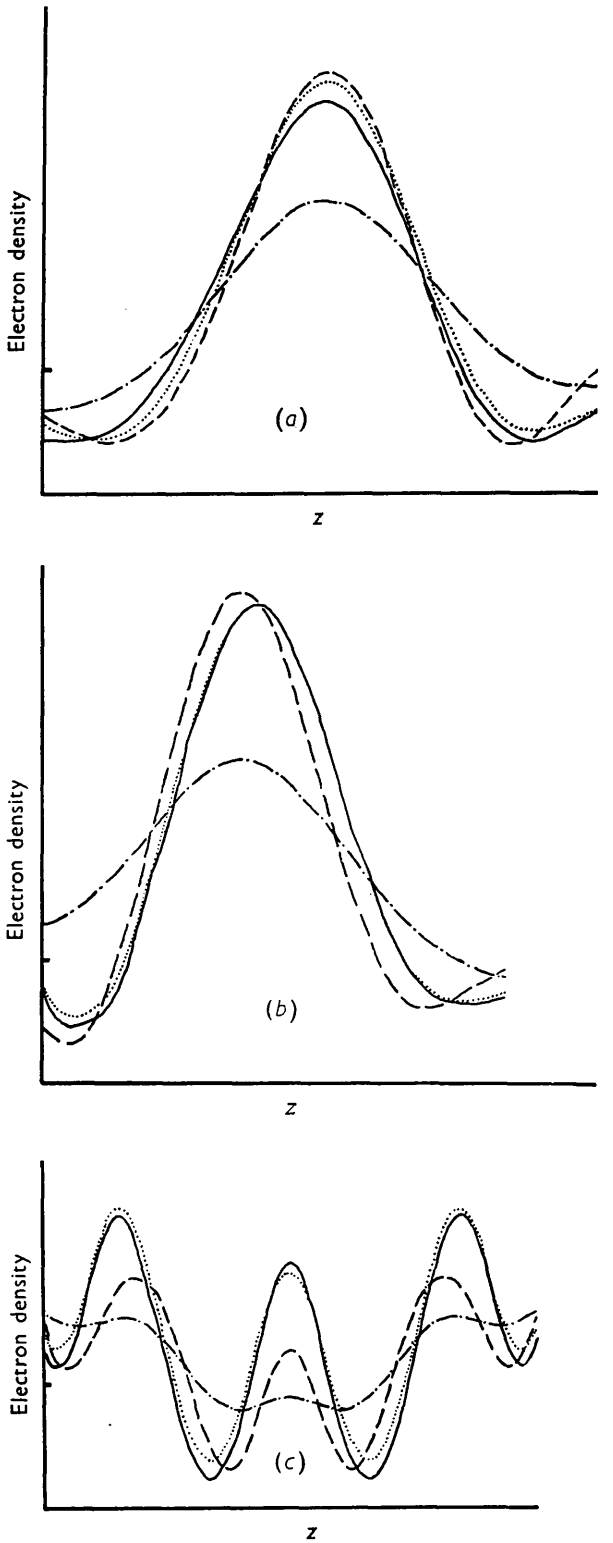
$$\exp -[A\cos^2\varphi + B\sin^2\varphi]\sin^2\theta\,, \qquad (1)$$

except that the value of $1/\lambda^2$ is included in the constants A and B. The angle φ is the angle between the c_0 axis and the normal to the plane in question. Fourier $h0.l$ projections were then calculated for values of A and B, respectively, of 2, 1; 4, 1; 6, 1; 8, 1; and 10, 1. In each case the corrected intensities were normalized to the same value as that for the unirradiated crystal. Detailed comparison of the boron peaks of these Fourier projections with those of the unirradiated crystal showed that the anisotropy ratio of six restored the peaks to essentially the same shape as for the unirradiated crystal. This is readily seen in Figs. 2(*a*) and (*b*). These figures show the electron-density profiles through the boron peaks of the two crystallographically different boron atoms in the structure (actually two of the same kind are superimposed in the cases chosen). It is clear that the peaks for the unirradiated crystal and the irradiated (corrected—using an anisotropy ratio of six) crystal are very nearly the same. There is a displacement of the irradiated (corrected) peak in Fig. 2(*b*) but this will be considered later.

Fig. 2(*c*) shows the electron-density profile through the linear chain of three carbon atoms in the structure. Comparing the curves for the unirradiated crystal and the irradiated (corrected) crystal one sees immediately that the peak for the central carbon atom is reduced approximately 50% in height. Actually, relative to the areas under the curves for the end carbon atoms and to the unirradiated crystal peaks, one finds that the peak of the central carbon atom has been reduced 47% owing to the irradiation. Further, the two end carbons are each displaced 0·12 Å toward the central carbon atom. The reason for the displacement of the boron peak in Fig. 2(*b*) of 0·06 Å is now clear, for this boron atom is attached to the end carbon atom and its displacement is in the same direction as the carbon atom to which it is attached.

These changes may be interpreted in the following way. Owing to collision events, the central carbon atom is occasionally knocked into a stable interstitial position. On other occasions, the end carbon atoms may be similarly dislodged. However, when an end carbon is removed the central carbon atom moves into approximately the position previously occupied by the end carbon atom, where it can form bonds with the three surrounding boron atoms rather than remaining

bonded to a single carbon atom. Between the two end carbon atoms (with the missing central carbon atom) there must still be considerable attraction as they are each displaced 0·12 Å toward each other and displace the boron atoms to which they are bonded 0·06 Å in the same direction. This condition prevails in about 47% of the linear chains of carbon atoms in the structure.



The removal of 47% of the central carbon atoms and the motion of the end carbon atoms and the boron atoms to which they are bonded can be confirmed in a very striking way. It has been observed previously that the ($\bar{2}$0·2) and (01·1) reflections *increase* in intensity owing to irradiation whereas the effect of the artificial temperature factor is always to *decrease* intensities. Since both of these reflections are of rather weak or at most moderate intensity, it is clear that their increase in intensity due to irradiation is not due to a reduction of extinction due to the irradiation. Rather, if one examines the structure factor for these reflections it turns out that the boron and carbon atoms are scattering very strongly but with opposite phase, thus producing weak reflections. When 47% of the central carbon atoms are removed and the end carbon atoms and half the boron atoms are displaced according to the figures given above, the intensities of the ($\bar{2}$0·2) and (01·1) reflections are increased, giving quite reasonable agreement with the observed intensities in the irradiated material. Thus the results given by Fourier analysis receive critical and sensitive confirmation by the increase in intensity of the ($\bar{2}$0·2) and (01·1) reflections due to irradiation.

The changes in position involving the carbon atom chains and the boron atoms attached to them also account for the very unusual lattice-parameter changes which occur. The strong attraction of the end carbon atoms (with the missing central atom) contracts the lattice in the c_0 direction (since the carbon atom chains are parallel to the c_0 axis of the crystal). The observed expansion in the a_0 direction is probably mostly a compensation for the contraction in the c_0 direction.

There is one remaining point concerning the carbon atoms which is given by Fig. 2(*c*). That is the slight broadening of the end carbon peaks for the irradiated (corrected) curve. This broadening may be due to the fact that about half of the end carbons are in their normal positions and the other half are displaced somewhat more than 0·12 Å toward the missing central carbon atom. It might also indicate that a still stronger anisotropic artificial temperature factor should be applied to these atoms. The former interpretation seems rather more probable but, in any case, the effect

Fig. 2. (*a*) Section parallel to *z* axis through boron atom bonded only to other boron atoms. (*b*) Section parallel to *z* axis through boron atom bonded to end carbon atom. (*c*) Section parallel to *z* axis through linear chain of three carbon atoms.

Full line: unirradiated.
Chain line: irradiated.
Broken line: irradiated (corrected).
Dotted line: irradiated (annealed).

is small and does not seriously influence any of the conclusions or interpretations given above.

Lattice parameter and diffuse scattering changes

As mentioned previously, the single-crystal and powder pattern data show that the exposure of 3×10^{20} thermal neutrons/cm.^{2} causes the c_0 axis of boron carbide to shrink and the a_0 axis to expand. Measurements on the (20·1) and (01·4) reflections of polycrystalline material gave a *contraction* of 1·38% in the c_0 direction and an *expansion* of 0·89% in the a_0 direction. As a check on the c_0 contraction the (00·3) reflection was also measured and gave a contraction of 1·41%, very good confirmation of the previous value. The zero-level $h0.l$ Weissenberg patterns of irradiated and unirradiated single crystals also show the anisotropic nature of the lattice-parameter changes. These patterns exhibit not only the contraction in the c_0 direction and expansion in the a_0 direction, but also the gradual change from one to the other with zero expansion in approximately the expected direction.

No quantitative measurements have yet been made of the very strong diffuse scattering produced in boron carbide by thermal neutron irradiation, but a number of qualitative experiments have been performed. It was clear at the outset that the heavy diffuse scattering in the irradiated crystals might either be due to a degradation of the lattice-vibration spectrum to lower frequencies or to static lattice defects in the crystals. In the former case, the intensity of the diffuse scattering should be reduced on lowering the crystal temperature to that of liquid nitrogen but should be temperature insensitive in the latter case. Laue patterns of the heavily irradiated crystals at room and liquid-nitrogen temperatures showed no detectable change in intensity of the diffuse scattering. It was therefore concluded that the diffuse scattering is due to static lattice defects.

Quite a number of experiments have been performed to establish the behavior of the diffuse spots. Rocking curves have been obtained, the effect of filters has been used to identify certain diffuse spots as due to characteristic α or β radiation, and careful comparisons have been made of Laue patterns from similarly oriented irradiated and unirradiated crystals. From this work it is clear that the diffuse scattering surrounds the reciprocal-lattice points. In the heavily irradiated material the diffuse scattering is extremely strong—in integrated intensity exceeding that of the corresponding Bragg reflections. The shapes of the diffuse spots are not, in general, spherical but they do not have the fine structure observed in some thermal diffuse spots. While some weak thermal diffuse spots are observed in unirradiated single crystals, the diffuse scattering due to irradiation completely submerges these spots and also appears in many other positions.

It is planned to make quantitative measurements of the intensity and shape of the diffuse scattering around the reciprocal-lattice points. These measurements and their interpretation will be given in a second paper.

Annealing experiments

We have determined the temperature range in which the very pronounced X-ray effects found in irradiated boron carbide are annealed. Lattice-parameter measurements and Laue patterns have been made of polycrystalline and single-crystal samples of the most heavily irradiated material after successive 15-hr. vacuum anneals at 100° C. intervals from 200 to 1200° C. The lattice-parameter measurements show that in the temperature range of 700–900° C. the lattice parameters return, within experimental error, to the values for unirradiated boron carbide. This result has also been observed for less heavily irradiated samples. The Laue and powder patterns show that the artificial temperature factor and the diffuse scattering are very largely removed in the same temperature range (700–900° C.). Fig. 1(*d*) shows a Laue pattern of a single crystal after the annealing treatments up to 1200° C. It is readily seen that, relative to Fig. 1(*c*) of a heavily irradiated single crystal, the Laue spots have increased in strength whereas the diffuse spots are much smaller. Comparison with Fig. 1(*a*) of an unirradiated single crystal, however, shows that the annealed crystal has not returned to normal. The remaining diffuse scattering observed in Fig. 1(*d*) will be discussed in the next section.

The single crystal annealed up to 1200° C. was oriented, a zero-level $h0.l$ Weissenberg pattern was prepared, and the $h0.l$ intensities were measured. Examination of these intensities showed that although the anisotropic artificial temperature factor was removed there was still evidence for a small isotropic artificial temperature factor. Accordingly, a correction of the form $\exp[-\sin^2\theta]$ was applied. This correction corresponds to values of unity for the constants A and B in equation (1). A Fourier $h0.l$ projection was then computed from these structure factors (listed in the last column of Table 1) and sections through the boron and carbon atoms are included in Figs. 2(*a*)–(*c*). From these curves, it is clear that as regards peak positions and intensities the crystal has returned to normal. It is particularly interesting to note in Table 1 that the critical ($\bar{2}0{\cdot}2$) reflection returns to its normal intensity owing to the annealing. In this connection it is important to point out that the equally critical (01·1) reflection returns to its normal intensity in the range of 700–900° C., so it may be presumed that the ($\bar{2}0{\cdot}2$) reflection also returns to its normal intensity at the same temperature. Thus, it is clear that the interstitial carbon atoms become mobile in the temperature range of 700–900° C. and find their way to their normal lattice positions.

From the annealing experiments two very important conclusions can be reached. First, the carbon atoms in

irradiated boron carbide become mobile in the temperature range of 700–900° C. Second, all of the observed X-ray effects (lattice parameter changes, Bragg and Laue intensity changes, and diffuse scattering) are due to the anisotropic defect formed by removing the central carbon atom from the linear chain of three carbon atoms. The basis for these conclusions is the following. The motion of carbon atoms is proved by the Fourier $h0.l$ projection of the annealed crystal and by the facts that at 700–900° C. the lattice-parameter changes and the intensity of the critical (01·1) reflection return to normal. The interrelation of all of the X-ray effects is proven by the fact that, except for some of the diffuse scattering and a fairly small isotropic artificial temperature factor, all of the X-ray effects are removed simultaneously in the 700–900° C. temperature range.

Theoretical interpretation of the X-ray effects

The X-ray effects which have been found in neutron-irradiated boron carbide are highly anisotropic lattice-parameter changes, a highly anisotropic artificial temperature factor, changes in the average positions of certain lattice atoms, and heavy diffuse scattering surrounding many of the reciprocal-lattice points. These effects have been found to be interrelated; they anneal in the temperature range of 700–900° C., and are in fact due to an anisotropic static defect formed by removing the central carbon atom from the linear chain of three which occurs in the structure. Qualitative understanding of these effects is not difficult to achieve.

A number of calculations have been made of the X-ray scattering produced by localized static lattice defects in crystals. The most general approach seems to be that of Zachariasen (1945). He gives a general theory of displacement disorders (i.e. disorders in which the atoms are not located precisely at the sites of an ideal lattice) from which the effect of temperature, for example, can be calculated as a special case. This theory shows that the scattering divides into two terms. The first term gives the usual Laue–Bragg scattering except that the structure factors for the various atoms in the lattice are altered, depending on the detailed nature of their displacements. In the case of thermal motion this leads to the familiar temperature factor, but in the general case one may expect somewhat different intensity changes. It is important to note that the theory predicts no change in the breadth of Laue–Bragg maxima due to the displacement disorder. The second term of the scattering leads to diffuse maxima around the reciprocal-lattice points. The shape and intensity of this scattering depends on the detailed nature of the atomic displacements, but in the boron-carbide case will undoubtedly lead to diffuse spots of various shapes surrounding the reciprocal-lattice points. This theory predicts qualitatively many of the X-ray effects observed in irradiated boron carbide, except for the lattice-parameter changes, and it may well be useful eventually to use the observed atomic displacements in boron carbide to calculate the X-ray effects predicted by this theory.

Calculations of X-ray scattering by lattice defects have also been made by Ekstein (1945), Warren, Averbach & Roberts (1951), and Matsubara (1952). It is worthy of note that all of these authors predict diffuse maxima surrounding the reciprocal-lattice points. While the work of these authors might be used in interpreting the boron carbide results, the most promising approach seems to be that of Huang (1947), who has given a detailed treatment of the X-ray effects to be expected from spherically symmetric elastic singularities in a face-centered cubic lattice. Huang was concerned with X-ray effects from dilute substitutional solid solutions. He considered the case of a random distribution of elastic singularities which produce radial displacements of the form $u = c/r^2$. Here u is the radial elastic displacement at a point which is a distance r from the singularity. The constant c is proportional to the 'strength' of the singularity.

Huang finds that the X-ray scattering divides into two terms. The first term gives the Laue–Bragg scattering with the following features. The intensities are altered as if by an artificial (isotropic) temperature factor, there is no broadening of the Laue–Bragg maxima, and their positions change corresponding to an isotropic expansion of the lattice. The second term of Huang's calculated scattering gives rise to diffuse maxima surrounding the reciprocal-lattice points. For the case of solid solutions Huang finds that the diffuse maxima are of the same order of magnitude in size and intensity (but not shape) as thermal diffuse maxima. Two of Huang's predicted effects may be tested experimentally. By correcting Huang's analysis to include the effect of the surface term (Eshelby, 1954), it can be shown (Tucker & Sampson, 1954) that the isotropic expansion of the lattice given by Huang is simply Vegard's law, which is known to be a reasonable first approximation for a number of solid-solution systems. In addition, the observed lack of line broadening in solid solutions, in spite of large local deformations around solute atoms, provides a second successful test of Huang's analysis. By comparison of the above effects with those found in irradiated boron carbide, it is seen that Huang's elastic model of solid solutions predicts qualitatively the X-ray effects found in irradiated boron carbide.

In order to apply Huang's approach to irradiated boron carbide, however, the anisotropic artificial temperature factor and anisotropic lattice expansion must be taken into account. For this purpose we are presently attempting to extend Huang's analysis to the case of anisotropic defects, for in boron carbide the carbon atom chain with the missing central atom is surely the anisotropic defect responsible for the ob-

served X-ray effects. The elastic concept being used is the double force without moment (Love, 1927). Two models are being considered: (*a*) a compressive double force along the c_0 axis and tensile double forces of equal absolute magnitude along the a_0 axis; and (*b*) a single compressive double force along the c_0 axis. Thus far only case (*a*) has been examined in any detail and it predicts the correct anisotropy of the lattice parameter change. Work is in progress on the artificial temperature factor. It is planned to carry through the necessary calculations mentioned above for these models and also to make quantitative measurements of the diffuse scattering in irradiated boron carbide to compare with the model. This work will be reported in a second paper.

From the discussion of this section it is also possible to understand why there is still some diffuse scattering present in Fig. 1(*d*) of the annealed irradiated crystal. This diffuse scattering is probably due to the defects remaining in the crystal after the interstitial carbon atoms have returned to their normal positions. These defects would be missing boron atoms (since approximately 10–15% of all boron atoms have disintegrated) and the helium and lithium formed by these disintegrations. The two effects apparently balance as far as effect on the lattice parameter is concerned, but the diffuse scattering and the artificial isotropic temperature factor are still observed. This interpretation is further supported by comparison of Fig. 1(*c*) and (*d*), which show that the diffuse scattering differs in detail between the irradiated and annealed crystals. Work on the diffuse scattering of these crystals, as well as experiments designed to discover the fate of the helium and lithium atoms during annealing, will be presented in a second paper.

Conclusions

Neutron irradiation of boron carbide produces very strong X-ray diffraction effects. An exposure to an integrated thermal neutron flux of 3×10^{20} neutrons/cm.^{2} produces (*a*) a *contraction* of the c_0 axis of 1·38% and an *expansion* of the a_0 axis of 0·89%; (*b*) an artificial anisotropic temperature factor which is six times as strong in the c_0 direction as in the a_0 direction; (*c*) changes in the average positions of certain of the lattice atoms; and (*d*) very heavy diffuse scattering surrounding many of the reciprocal lattice points.

It is shown that the X-ray effects are due to an anisotropic lattice defect produced from a chain of three carbon atoms which is parallel to the c_0 axis of the crystal. During the irradiation the center carbon atom of this chain is selectively removed to an interstitial position. To compensate for the removal of this atom the two end carbon atoms move toward each other, pulling the boron atoms to which they are attached in the same direction. This produces an anisotropic defect which contracts the lattice in the c_0 direction and expands it in the a_0 direction.

Annealing experiments have shown that in the range of 700–900° C. the interstitial carbon atoms become mobile and return to their normal lattice sites. Accompanying this, almost all of the observed X-ray effects disappear, thus proving that the effects are due to the anisotropic defect. The remaining diffuse scattering and small isotropic artificial temperature factor is attributed to vacant boron positions and helium and lithium atoms produced by the boron disintegrations.

The observed X-ray effects may be understood qualitatively in terms of an elastic model for isotropic lattice defects given by Huang (1947). Work is in progress to extend this theory to the case of anisotropic defects, and to measure and interpret the diffuse scattering in detail. The results of this work will be given in a second paper.

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