PHYSICAL REVIEW B VOLUME 51, NUMBER 17 1 MAY 1995-I

Defect clustering and self-healing of electron-irradiated boron-rich solids

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(Received 19 September 1994)

Transmission-electron-microscopy observations are used to evaluate damage produced by irradiating boron-rich metals, semimetals, and semiconductors of three different structure types with energetic electrons. The propensity for damage increases with decreasing carrier concentration except for borides based on twelve-atom icosahedral units. In these semiconducting icosahedral borides neither defect clusters nor amorphization were observed. In accord with studies of other icosahedral borides, we conclude that radiation-induced boron vacancies and interstitials self-heal in icosahedral borides. We explain this self-healing as having its origin in the unusual structural and electronic stability of fragments of boron-rich icosahedra, termed degraded icosahedra.

I. INTRODUCTION

Boron-rich solids often possess unique structures.[1] For example, many borides are based on 6-atom and 12-atom clusters in which boron atoms reside at the vertices of octahedra and icosahedra, respectively. Analogous octahedral and icosahedra units occur in boron-rich molecules, e.g., B_6H_6 and $B_{12}H_{12}$.[2] Each boron of an octahedral or icosahedral structure has five or six neighbors, respectively. These clusters form because boron atoms can bond in unconventional ways.[2–4] In these particular instances, each cluster is held together through electron-deficient (metallic) "internal" bonding while each of its atoms usually also bonds covalently to an atom outside of its cluster, e.g., to a hydrogen atom of B_6H_6 and $B_{12}H_{12}$. Thus, each boron atom engages in both metallic and covalent bonding.

These boron clusters have great affinity for additional electrons, often adding two electrons in their "internal" bonding states to act as dianions.[2–4] Thus, in solids these boron clusters generally accept electrons from atoms or larger structural units that serve as donors.[1] Although their electron-deficient internal bonding differentiates the boride clusters from their surroundings, these boron-rich solids differ from molecular solids in that the covalent bonding between boron-rich clusters is generally even stronger and stiffer than clusters' internal bonding.[1] As a result, unlike molecular solids, these borides are refractory with melting temperatures well above 2000 °C. These octahedral and icosahedral boron-rich solids are open structures in which the clusters occupy a small fraction of the volume. As such, these structures can support relatively rapid diffusion of interstitial atoms. Beyond their unconventional bondings and structures, boron-rich solids also possess many unusual properties.[1]

A general goal of research on boron-rich solids is to obtain a detailed understanding of how their unusual properties result from their distinctive structures and bonding. Here we address the striking resistance of some boron-rich solids to radiation damage. In particular, we study the tendency of radiation-induced interstitials and vacancies in some borides to spontaneously recombine with one another.

This study is motivated by experiments suggesting that radiation damage self-heals in some boron-rich solids. In particular, neither the condensation of defects nor the amorphization that is expected from large densities of point defects is found in these borides after they are subjected to heavy doses of ionizing radiation. For example, neither amalgamation of defects nor amorphization is observed in β-rhombohedral boron after a bombardment with nitrogen ions that is estimated to produce about 36 displacements per atom.[5] Similar radiation resistance is found in boron carbides that have been bombarded with large doses of lithium ions.[6] Comparable radiation tolerance is also found after boron carbides are irradiated with high doses of 1-MeV electrons in an electron microscope.[7] Amorphization and clustering of defects are not even observed when this electron bombardment of boron carbides is performed at very low temperatures, ~ 12 K.[7] This result suggests that the recombination of radiation-induced interstitials and vacancies that occurs in self-healing does not require thermally activated diffusion.

Radiation tolerance is not a property of all borides. In particular, radiation damage is readily produced in BN, a boride with conventional bonding.[8] Thus, one is led to ask a series of questions. First, noting that β-rhombohedral boron and boron carbides are both semi-

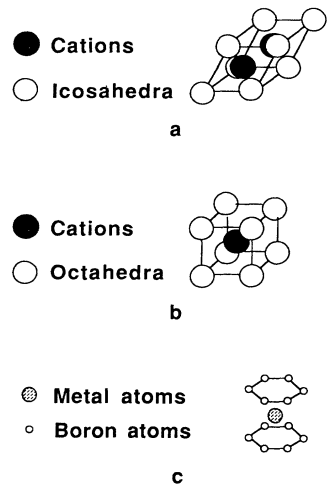

FIG. 1. The structures of the (a) icosahedral borides, (b) octahedral borides, and (c) diborides that we study here are schematically illustrated. The open circles depict 12-atom icosahedral and 6-atom octahedral units, as indicated. The solid circles represent atoms. The solid lines indicate conventional two-center covalent bonds.

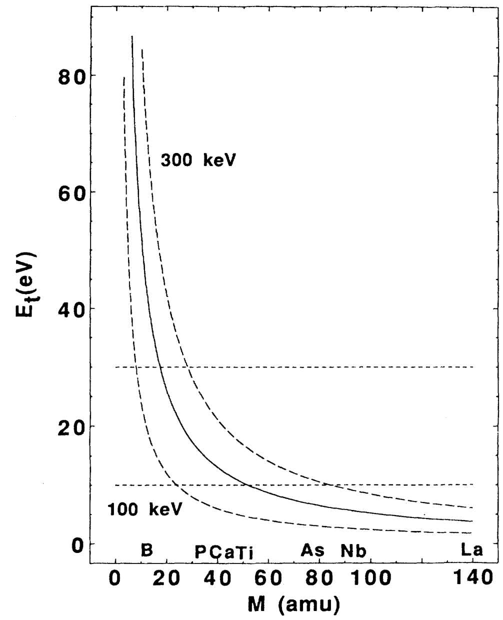

FIG. 2. The maximum energy transferred to a stationary atom in a collision with an electron, E_t, is plotted against the mass of the atom for three electronic kinetic energies. The solid curve is for an electronic energy used in our experiments, 200 keV. Dashed curves are of electronic energies of 100 and 300 keV. Threshold energies for the displacement of an atom in a solid, typically between 10 and 30 eV, are bracketed by the horizontal dashed lines. The masses of the atoms used in this study are indicated by their symbol's positions along the plots' abscissa.

conductors based on icosahedral boron-rich clusters, one asks whether self-healing also occurs in other semiconducting icosahedral borides. Second, one asks whether self-healing also occurs in octahedral borides, since these materials have structures and bonding that are similar to those of icosahedral borides. Finally, one may ask whether radiation tolerance also occurs in other boron-rich solids with different unconventional bonding.

The aim of this work is to systematically determine which classes of boron-rich solids manifest this self-healing effect. Specifically, we use TEM to compare the damage induced by electron irradiation of different types of boron-rich solid. We investigate semiconductors based on boron icosahedra whose radiation tolerance has not previously been studied: $B_{12}P_2$ and $B_{12}As_2$, illustrated in Fig. 1(a). We also examine insulators and conductors based on boron octahedra: CaB_6 and LaB_6, respectively, illustrated in Fig. 1(b). We also study radiation damage in some semimetallic and metallic diborides: TiB_2 and NbB_2, respectively, illustrated in Fig. 1(c). Our results indicate extensive self-healing only in semiconducting boron-rich solids based on icosahedral units. We base an explanation of this effect on the persistence of the unusually large bielectron affinity of boron icosahedra when they are "degraded" by the removal of some of their atoms.

II. EXPERIMENT

Here we report experiments in which atoms in solids are displaced from their equilibrium positions as a result of their being bombarded with energetic electrons. Figure 2 shows the maximum energy that can be transferred by a relativistic electron to an atom in a collision, E_t, plotted against the atom's mass, M, in amu, for electron energies of 100, 200, and 300 keV. The horizontal band on this figure indicates the typical range of threshold atomic energies above which atomic displacements occur.[9] Zuppiroli, Kormann, and Lesueur estimated the threshold energy for displacements of boron atoms in boron-rich compounds to be about 20 eV.[10] Therefore, bombardment of $B_{12}P_2$, $B_{12}As_2$, CaB_6, LaB_6, TiB_2, and NbB_2 with 200-keV electrons is expected to displace boron atoms and perhaps some phosphorus atoms. However, 200-keV electrons are not expected to displace these solids' calcium, titanium, arsenic, niobium, or lanthanum atoms.

Samples of $B_{12}P_2$, $B_{12}As_2$, and NbB_2 were produced by and obtained from Aselage of Sandia National Laboratories. Commercial samples of TiB_2 from Atomergic (Plainview, New York) and of CaB_6 and LaB_6 from CERAC (Milwaukee, Wisconsin) were obtained from Morosin of Sandia National Laboratories. Powders produced by crushing these samples in a boron carbide mortar were deposited on thin carbon films supported on copper grids for use in the TEM measurements. TEM measurements with 200-keV electrons were made at room temperature with a Hitachi H700 H and at 91 K with a Philips EM430ST. Combining Zuppirolli's estimate of the boron displacement cross section, 18 b,[10] with the measured electron flux of the Hitachi machine, $6\times10^{19}/cm^2$ sec, yields a rate of boron displacements of about 1×10^{-3} dpa/sec. Thus bombardments of up to 2 h produce about seven displacements per boron atom.

III. RESULTS

The boron-rich solids studied here differ among themselves in their electrical properties as well as in their structures and bondings. LaB_6 and NbB_2 are n-type metals with about one electron per unit cell. By contrast, CaB_6 and TiB_2 have relatively low carrier densities. This difference presumably occurs because the valences of the nonboron elements of CaB_6 and TiB_2 (from groups II and IV of the Periodic Table, respectively) are lower than those of LaB_6 and NbB_2, whose corresponding nonboron elements are from groups III and V. Thus, CaB_6 is a semiconductor and TiB_2 is a semimetallic conductor. The two icosahedral borides investigated here, $B_{12}P_2$ and $B_{12}As_2$, are both wide-gap semiconductors.

Damage in our metallic borides accumulates relatively slowly. In fact, no damage was observed in our TEM measurements of NbB_2 after 2 h of irradiation at room temperature. The absence of defect clusters can result from the diffusion of point defects to the sample's surfaces. To investigate the plausibility of this explanation, our experiment was also performed at 91 K. As shown in Fig. 3, small clusters of defects were then observed. Similarly, our electron irradiation of LaB_6 indicates small (<10 nm) defect clusters after an hour of irradiation. Figure 4 shows that the TEM for the LaB_6 sample has the black/white contrast of Frank loops with $\{100\}$ habit planes.

The group-IV diborides, represented by TiB_2, are semimetallic conductors. As illustrated by the dark field image of Fig. 5, significant defect clustering occurs in TiB_2 within minutes of the onset of irradiation. The nearly vertical straight line in these three micrographs is the edge of the carbon film that supports the sample grain. The defect clusters appear as small (<10 nm) lobes suggestive of Frank loops. The direction of the border between black and white regions gives (with $\pm 10°$) the trace of the loops' habit plane. The loops all have the (001) ha-

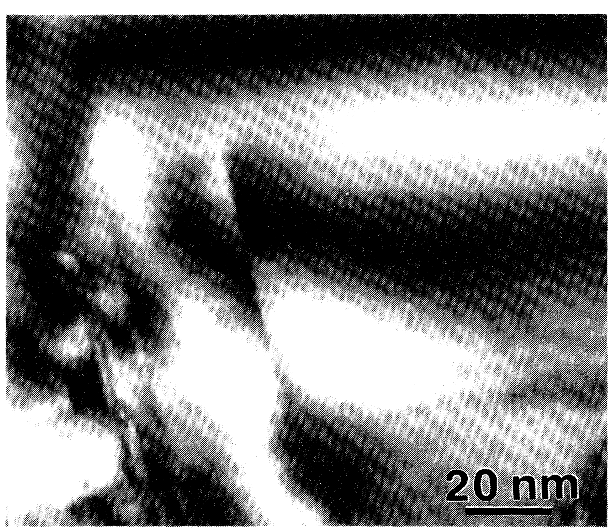

FIG. 3. A dark-field TEM micrograph of NbB_2 after an 82-min bombardment with 200-keV electrons at 91 K shows small defect clusters.

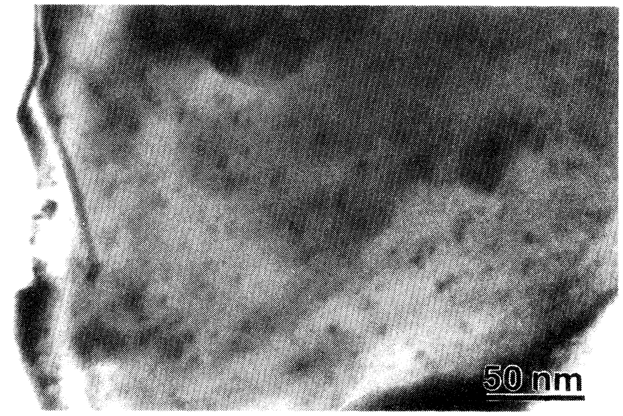

FIG. 4. A bright-field TEM micrograph of LaB_6 after an 84-min bombardment with 200-keV electrons at 300 K shows small defect clusters.

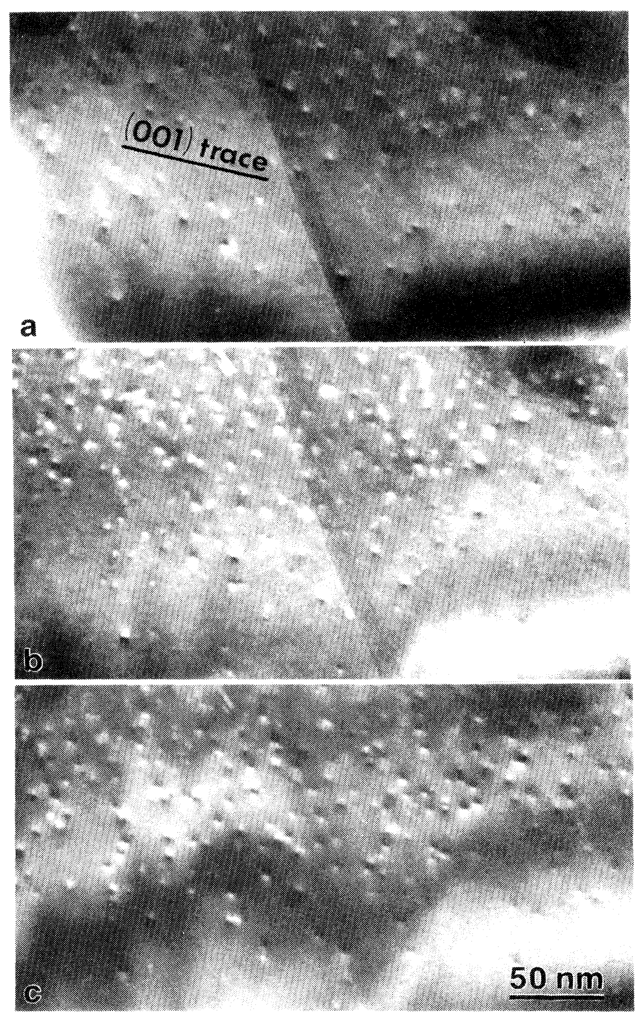

FIG. 5. A succession of dark-field TEM micrographs of TiB_2 taken during bombardment with 200-keV electrons at 300 K shows rapid growth of defect clusters. These micrographs were taken after (a) 4, (b) 9, and (c) 13 min of bombardment.

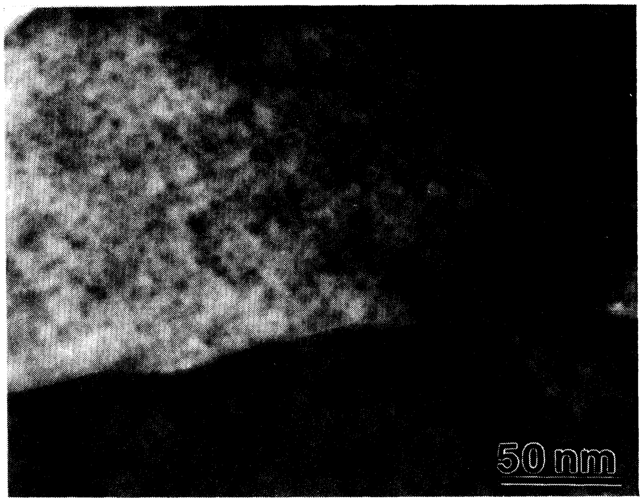

FIG. 6. A dark-field TEM micrograph of CaB_6 after a 37-min bombardment with 200-keV electrons at 300 K shows a very high density of small defect clusters.

bit plane.

Semiconducting borides based on boron octahedra, represented by CaB_6, and boron icosahedra, $B_{12}P_2$ and $B_{12}As_2$, were studied. As indicated in Fig. 6, large densities of small (< 5 nm) defect clusters appeared within a few minutes of irradiation of the octahedral boride, CaB_6. By contrast, our TEM of the icosahedral borides showed no indication of damage after hours of irradiation. Measurements at 91 K also showed no indication of damage clusters in the icosahedral borides. This result is consistent with prior studies of other icosahedral boride semiconductors, β-rhombohedral boron, and boron carbides, finding that irradiation did not produce either defect clusters or amorphization.

Our results are summarized in Table I. The growth of defect clusters tends to be much more rapid in nonicosahedral borides with low carrier densities, TiB_2 and CaB_6, than in our metallic nonicosahedral borides, NbB_2 and LaB_6. However, no evidence of the amalgamation of defects was found in icosahedral semiconducting borides even when the measurements were performed at low temperatures, 91 K.

IV. DISCUSSION

In this work we have extended studies of radiation damage in boron-rich solids to semiconducting icosahedral borides other than β-rhombohedral boron and boron carbides,[5-7] $B_{12}P_2$ and $B_{12}As_2$. In all of these icosahedral borides, the failure to observe defect clusters or amorphization implies the self-healing of radiation-induced defects. Furthermore, the persistence of this self-healing when the damage is created at low temperatures implies that the self-healing does not involve a thermally assisted process.[7]

While the structures and bondings of icosahedral borides, $B_{12}P_2$ and $B_{12}As_2$, are distinctive, they are not qualitatively different from those of a semiconducting octahedral boride, CaB_6, as depicted in Figs. 1(a) and 1(b). In particular, in both sets of solids the closoboride units, B_{12} and B_6, have a large bielectron affinity through which they garner two additional electrons.[1-4] These electrons reside in molecular orbitals that encompass the boron atoms of the icosahedral or octahedral structures.[1-4] The two electrons per unit cell required to occupy these states are contributed by the cations that are represented by solid circles in Figs. 1(a) and 1(b). In the icosahedral borides, $B_{12}P_2$ and $B_{12}As_2$, each unit cell has two donor cations: P^+ and As^+, respectively. In the octahedral boride, CaB_6, the two donor electrons are donated by a single dication, Ca^{2+}. In both icosahedral and octahedral borides, the "external" covalent boron-boron bonds [depicted as solid straight lines in Figs. 1(a) and 1(b)] provide strong links between the closoboride structures.

Motivated by the strong similarities between semiconducting icosahedral and octahedral borides, we have compared the responses of both types of solids to damage induced by electron irradiation. Strikingly, we find rapid growth of defect clusters in the semiconducting octahedral boride but no evidence of such clusters in the icosahedral borides. Thus, we ask why self-healing would occur in icosahedral borides but not octahedral borides.

To address this question, we consider how self-healing of radiation-induced damage can occur in icosahedral semiconducting borides. We first note that electron bombardment will initially produce interstitial boron atoms and damaged icosahedral structures. In particular, knocking a boron atom from an icosahedron (1) "degrades" that icosahedron by removing an atom from it and (2) breaks the external covalent bond that emanates from that atom. The breaking of this covalent bond enables its two electrons to be deployed elsewhere. In particular, these two second-shell electrons can remain with the boron interstitial. Then, these two electrons together with the two 1*s* core electrons comprise the four electrons required of a B^+ ion.

In addition, the $2(n+1)$ electrons that fill the internal bonding orbitals of an n-atom closoboron structure may be envisioned to remain with the icosahedral fragment even though it loses an atom. Indeed, this is just what

TABLE I. Irradiation-induced damage rates in borides.

	Metals		Semimetals		Semiconductors	
Diborides	NbB_2	Slow	TiB_2	Rapid		
Octahedral borides	LaB_6	Slow			CaB_6	Rapid
Icosahedral borides					$B_{12}As_2$	None
Icosahedral borides					$B_{12}P_2$	None

happens when B and H atoms are removed from an icosahedron of a carborane molecule, $B_{10}C_2H_{12}$, thereby forming the doubly charged icosahedral fragment ("degraded" icosahedron), termed a dicarbollide ion, $(B_9C_2H_{11})^{2-}$.[11,12]

Thus, consistent with the strong bielectron affinity of boron-rich icosahedra, we envision electrons remaining bound within icosahedra's internal bonding orbitals as a boron nucleus is removed from it. Then, the interstitial boron only has sufficient electrons to form a cation. Concomitantly, the region from which the boron atom is removed garners an additional negative charge. Written as a chemical equation, this damage process is described by $[(B_{12})-(B_{12})]^{4-} \rightarrow [(B_{11}) \cdots (B_{12})]^{5-} + B^+$. In this notation the breaking of the intericosahedral covalent bond is indicated by replacing the solid horizontal line by a dashed horizontal line.

An analogous process can occur if the displacement of an icosahedral boron atom breaks a bond to a non-icosahedral cation (e.g., a fourfold coordinated P^+ or As^+ cation of $B_{12}P_2$ or $B_{12}As_2$). The electrons liberated by the breaking of the covalent bond to the degraded icosahedron can remain with the interstitial boron cation. This damage process may be described by the chemical formula $[(B_{12})-P]^- \rightarrow [(B_{11}) \cdots P]^{2-} + B^+$.

For these reasons, we suggest that the self-healing of radiation-induced damage in icosahedral semiconducting borides is driven by Coulomb attractions between positively charged boron interstitial ions, B^+, and regions of increased negative charge associated with boron vacancies. Furthermore, the persistence of self-healing even when samples are kept at a low temperature indicates that the energy barriers for the diffusion of B^+ ions are small enough to be overwhelmed by these Coulomb attractions.

Our model of the self-healing of an icosahedral boride presumes the electronic and structural stability of a (degraded) icosahedron, an icosahedron devoid of a boron atom. As noted above, this presumption of our model is supported by the existence of electronically and structurally stable degraded icosahedral molecules.[11,12] However, degraded octahedral molecules are not known to exist.[2,12] Rather, new molecules form when one of the atoms of an octahedral boride is removed. Thus, a boron-rich icosahedron can survive the loss of one of its 12 atoms while a boron-rich octahedron is destroyed by the loss of one of its six atoms. We ascribe the presence of self-healing in semiconducting icosahedral borides and its absence in semiconducting octahedral borides to this effect.

ACKNOWLEDGMENTS

We are grateful to T. L. Aselage and B. Morosin of Sandia National Laboratories for the samples used in these measurements. The Swiss contribution to this work was performed under the auspices of the Fonds National Suisse de la Recherche Scientifique under Contract No. 27-32106.91. David Emin's work was performed under the auspices of the U.S. Department of Energy and was funded in part by the Office of Basic Energy Sciences, Division of Materials Sciences under Contract No. DE-AC04-94AL85000.

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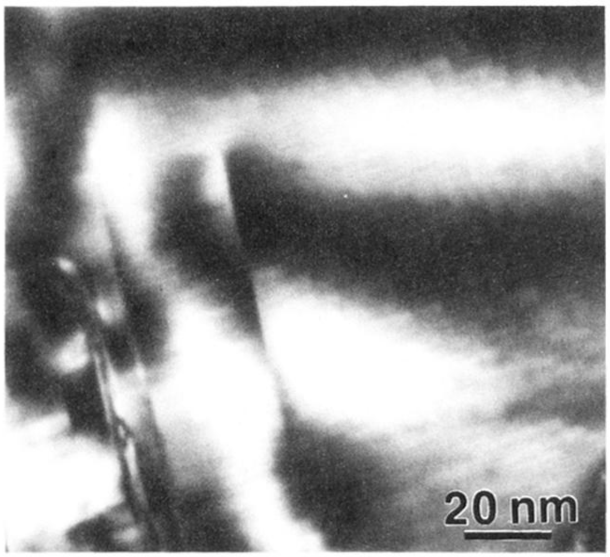

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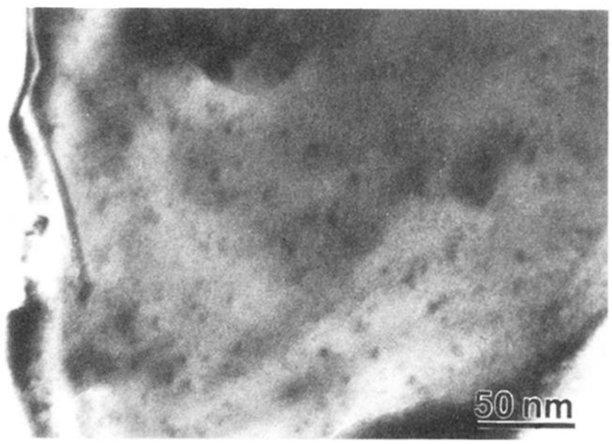

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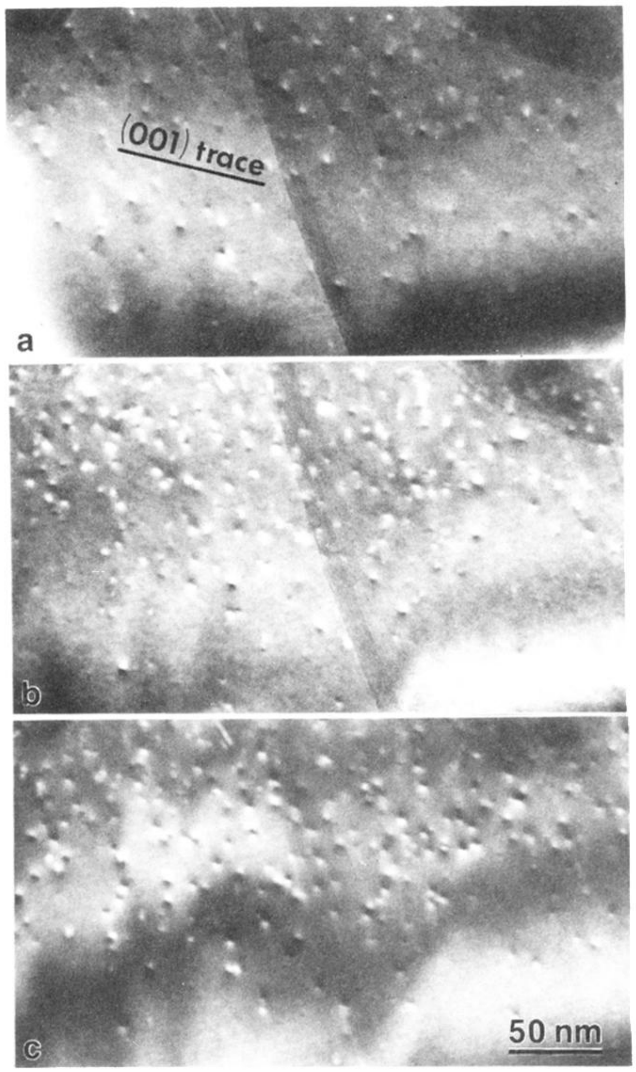

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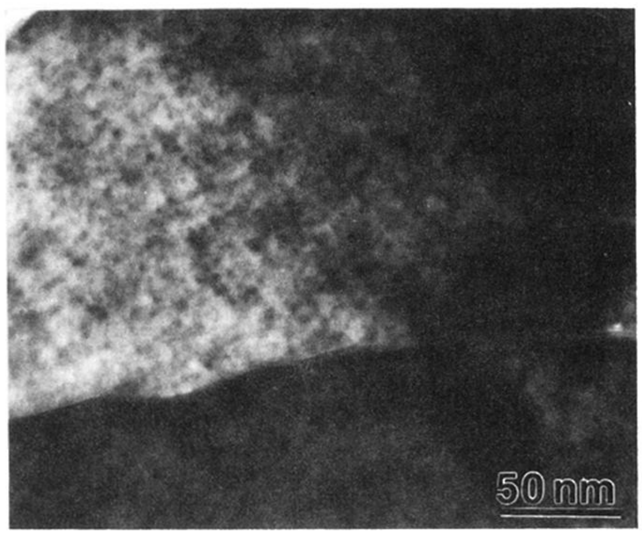

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