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# The interaction of P atoms and radiation defects with grain boundaries in an $\alpha$ -Fe matrix

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## Abstract

Classical molecular dynamics simulations have been employed to investigate the influence of P impurity atoms close to grain boundaries in  $\alpha$ -Fe. Static calculations have been performed to determine the energetics of P and Fe defects in the grain boundary region for three symmetrical tilt grain boundaries,  $\Sigma 5(310)[001]$ ,  $\Sigma 41(910)[001]$  and  $\Sigma 25(430)[001]$ . Additionally, collision cascades have been simulated both in the bulk and also close to the grain boundaries in order to investigate the influence of the grain boundaries on the damage formation. The simulations are carried using two different embedded atom Fe potentials, one of which includes the effect of second nearest neighbours. Both potentials produce quantitatively and qualitatively similar results for the static calculations, but the predicted number of defects during collision cascades is higher for the second nearest neighbour potential. It has been shown that P atoms preferentially segregate to the free volume region in the grain boundary plane. These sites are also preferred by the Fe interstitials. This and the tendency of grain boundaries to block the expansion of the collision cascade lead to an accumulation of defects at the grain boundaries.

*Key words:* Molecular dynamics, phosphorous, iron, computer simulation, radiation defects.

*PACS:* 61.72.-y, 61.82.-d

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## 1 Introduction

Radiation damage done to the nuclear pressure vessel (NPV) steel microstructure during service its time can seriously undermine the safe running and

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therefore the lifetime of the NPV. In order to get a proper understanding of the causes responsible for NPV failure key factors such as the energetics of defects in the grain boundary (GB) region and also the interaction of collision cascades with GB's need to be investigated. Due to the disruption of the crystalline periodicity at the GB's much of the material properties such as its ability to withstand brittle fracture can be dependent on the nature of atomic bonding in the GB regions. The presence of impurity and alloying elements in the grain boundary, in particular P, C and H, is known to weaken the cohesion between the atoms in the GB, thus causing embrittlement (1).

Experimental and theoretical studies have suggested that radiation events in the NPV lead to the segregation of P atoms to GB's (2; 3; 4). Recent computer simulations of radiation induced defects involving P atoms have illustrated mechanisms by which the P atoms can diffuse through the lattice (5; 6). There have been a number of previous atomistic simulations carried for symmetric tilt and twist GB's in pure Fe, which have illustrated the ability for the GB's to act as a sink to radiation induced defects (7; 8). However, it was not clear from the simulations which sites the interstitial Fe defects preferred to occupy and no calculations had been performed for P atoms in the GB regions. This study considers the energetics of P and Fe atoms in the GB by considering three different GB's.

We employ classical Molecular dynamics (MD) to study the energetics of P and Fe atoms near GB's. The aim is to obtain a better understanding of the energetically preferred sites for these defects in the GB regions. In addition to a first neighbour embedded-atom potential (9), we have employed a second-nearest neighbour interatomic potential (2NN MEAM) to describe the interactions between Fe atoms (10; 11).

We have also performed a set of collision cascades near GB's in  $\alpha$ -Fe to investigate the influence of the GB's on the interstitials generated in cascades; with cascade energies higher than 1 keV. In the next section we present the methodology employed for the above studies and then present the results obtained from the simulations.

## 2 Methodology

Symmetric tilt GB's of three different misorientation angles and  $\Sigma$  factor are considered. The GB's were constructed using the coincidence-site lattice (CSL) misorientation scheme as described in (12; 7). The size of the computational box was varied according to whether we were performing static energy calculations or collision cascades. In all the simulations we have performed, periodic boundary conditions were applied but only on the edges which are parallel to

the GB planes. Atoms in layers, up to a width of 8.0 Å, on the edges normal to the GB, were kept fixed. GB's constructed from the CSL scheme are in general not stable. A stable structure was sought by applying a rigid-body translation parallel to the GB plane and then performing a conjugate gradient (CG) minimisation.

The static calculations were performed at 0K using the CG minimisation whereas the radiation cascades were run in systems whose initial temperature was 450 K. The collision cascades were performed in the energy range of 2-16 keV, and were initiated by providing some excess energy to a lattice atom (the primary knock-on atom, pka) on one side of the GB. The effect of the initial pka position with respect to the GB plane is studied by performing two sets of simulations, in which the cascades are initiated at 30 and 40 Å respectively from the GB plane. The pka directions were chosen to be directed towards the GB.

The interaction between the Fe atoms has been modelled primarily by the Ackland embedded-atom (EAM) potential (9). In a bcc lattice, the contribution of the second NN on bond energies is important. The influence of this 2NN on defect production and the energetics of defects is tested with the 2NN MEAM potential (11) which accounts for the 2NN contribution. To cater for short range ion-ion interactions in collision cascades the pair part,  $V(r)$ , of the 2NN MEAM is joined to the screened Coulomb potential (ZBL) (13). A quintic spline is employed for this purpose, connecting  $V(r)$  (at  $r = 1.85$  Å) to the ZBL part at ( $r = 0.85$  Å) such that the pair part and its first and second derivatives are continuous. The quintic is given by  $\exp(9.41 - 5.74r + 4.69r^2 - 8.57r^3 + 6.78r^4 - 1.78r^5)$ , the units of  $A_i$  are Å<sup>-i</sup> for  $i = 0 \dots 5$ .

The Fe-P and P-P interactions are described using Morse-like pair potentials, obtained from (14). This potential has been used to calculate the energetics of a P atom in a pure iron lattice (15) and to study the interactions of a P atom with radiation defects in Fe (5).

For a detailed analysis, the concept of GB width and GB energy is needed. The GB width is defined here as the region about the GB plane, in which the average potential energy of the atoms differs by more than 0.2 % from the cohesive energy,  $E_{coh}$ , of an iron atom in a perfect lattice, (-4.32 eV for the Ackland potential and -4.29 eV for the 2NN MEAM). It is then possible to calculate the grain boundary energy, which is defined as the formation energy of one square unit of the GB,  $E_\gamma$ . Assuming that in the GB region we have  $n$  atoms then  $E_\gamma = (E_{inter} - nE_{coh})/A$ , where  $A$  is the GB area and,  $E_{inter}$  is the potential energy of the region containing the GB.

In order to measure the affinity for the P atom to occupy a site near the GB

the segregation energy,  $Q_s$ , is determined. If we define  $E_{gb}(qFe + 1P)$ , where  $q$  is the number of Fe atoms, as the system's energy when we have one P atom near the GB (in an interstitial or substitutional position) and  $E_{bulk}(rFe + 1P)$  as the corresponding energy when the P atom is in a substitutional site in the same cell but far away from the GB plane, then  $Q_s = E_{gb}(qFe + 1P) - E_{bulk}(rFe + 1P) + (q - r)E_{coh}$ . In our case,  $q = r$  when the P atom is in a substitutional site and  $q = r + 1$ , when the P atom is in an interstitial position. A negative sign for  $Q_s$  means that the P atom prefers this site rather than a substitutional site in the bulk, whereas a positive one implies that the bulk substitutional site is more favourable.

The formation energy of defects (interstitials and vacancies) in the lattice has also been computed in this work. The formation energy of a pure Fe interstitial and the vacancy formation energy at sites near the GB is defined as  $E_f^\alpha = E_{gb}^\alpha - E_{gb} \pm E_{coh}$  where  $E_{gb}^\alpha$  is the energy of the system with the defect at the GB; the plus sign corresponds to the vacancy and the minus sign to the interstitial.

### 3 Energetics of P and Fe atoms in the GB region

The relaxed structures of the three GB's considered is given in Fig. 1. The GB's were relaxed with the Ackland and the 2NN MEAM potential. In both cases similar structures are obtained at the interface. The GB width and the GB energy associated with the three systems are shown in Table 1. Both interatomic potentials predict similar values for the width of the GB region and the GB energy. It is observed that the complexity of the GB structure affects the width, with the  $\Sigma 25$  (430)[001] having the greatest boundary width.

The segregation energy,  $Q_s$ , at different sites about the GB plane for all the three systems above has been computed. The structure of the GB influences which sites are energetically favourable for the P atom, giving no discernible pattern by which the favourable sites are distributed in the GB region. For example, some sites which lie on the GB plane itself appear unlikely to host a P atom, as they have positive segregation energies, but for the  $\Sigma 41$  (910)[001] GB there are also sites with negative segregation energies. The segregation energy general has a oscillatory behaviour away from GB plane, which is shown in Fig. 2. It is clear that the most preferential sites are located within a few layers of the GB (typically, within 3.0 Å). The most likely substitutional site for a P atom in the GB regions considered is indicated by E' in Fig. 1.

Sites which have the lowest segregation energies were also found to have a relatively low vacancy formation energy. In the  $\Sigma 41$  (910)[001] GB for instance the site with lowest  $Q_s$  (-0.99 eV) has a vacancy formation energy which is

lower than the bulk vacancy formation energy by 0.29 eV. In addition, the minimum in the vacancy formation energy corresponds to a site with negative segregation energy. In Fig. 2, the vacancy formation energies at sites in the GB region is depicted.

Although some substitutional sites in the GB region are more favourable for P atoms than a bulk site the calculations show that the most preferable site for a P atom is an interstitial one at the GB plane. For all the GB's considered, the P atom is found to prefer the region with more free volume as illustrated in Fig. 1, by sites marked by 'I'. The segregation energy of the P atom to these sites were -1.62 eV, -1.93 eV and -1.84 eV for the  $\Sigma 5$ ,  $\Sigma 41$  and  $\Sigma 25$  GB's respectively. It can be seen that the  $\Sigma 41(910)[001]$  has other available pockets of free volume but the P atom was found to be metastable in these regions.

The iron atoms similarly prefer these sites in the GB core. The formation energy for these defects is of the order of 1 eV for all the three GB's. Comparatively, the most likely configuration of an interstitial atom in an  $\alpha$ -Fe lattice, the  $\langle 110 \rangle$  dumbbell, has a formation energy of the order of 5.0 eV and 4.0 eV for the Ackland and the 2NN MEAM potentials respectively.

#### 4 Simulation of collision cascades

The calculated threshold energy at 0K for the 2NN MEAM in the  $\langle 110 \rangle$  and  $\langle 111 \rangle$  directions is lower than those predicted by the Ackland potential, as shown in Table 2. Collision cascades performed in a perfect lattice at 0 K at a pka energy of 1 keV show that the mean number of vacant sites are 6.9 and 10.4, with standard deviations of 2.2 and 3.2 for the Ackland and the 2NN MEAM potentials respectively. For a 2 keV pka energy this trend is repeated, with the mean number of vacant sites at this energy being 9.6 (2.5) and 15.1 (3.6) respectively for the Ackland and the 2NN MEAM potentials.

In the pure Fe lattice, the Fe dumbbell interstitials are found to diffuse through in the lattice over MD timescales, since they have low activation energies (0.16 eV) (5) . However, GB's act as sinks to interstitial Fe atoms and the defects are found to accumulate there. The tendency for the defects to accumulate at the GB is controlled by several factors.

First, the distance at which we initiate the cascade away from the GB is important. For cascades initiated 30 Å away from the GB, nearly 80% of the interstitials agglomerated in the GB plane. This fraction was independent of the choice of GB. With increasing pka energy there was a gradual decrease in the fraction of interstitials at the GB plane for the  $\Sigma 5(310)[001]$  GB. When the pka was initiated 40 Å away from the GB plane, the  $\Sigma 5(310)[001]$

boundary accumulated only 40% of the interstitials from the 2 keV cascade. The same trend, though less pronounced, is noted with the remaining two GB's ( $\Sigma 41$  and  $\Sigma 25$ ). However, for these two GB's the difference in the fraction of accumulated defects in the 30 and 40 Å cases becomes indistinguishable at higher energies as shown by the histogram in Fig. 3.

Secondly, cascades in the  $\Sigma 5$  (310)[001] system tend to penetrate the GB plane and cross to the other side of the boundary for the 8 and 16 keV cascades. The interstitials created there take longer to reach the GB plane. For the  $\Sigma 41$ (910)[001] GB penetration of the boundary plane by the developing cascade was observed for some high pka energies, however, it was not observed as often as in the  $\Sigma 5$  (310)[001] case. For the  $\Sigma 25$  (430)[001] GB the cascade rarely penetrated the GB; the denser arrangement of the GB structure is the reason for this behaviour.

The GB width can also affect the fraction of interstitials at the GB, especially for the case of low energy cascades. It can be seen from Fig. 3 that the  $\Sigma 41$  and  $\Sigma 25$ , which have similar GB width (14.4 and 19 Å respectively), show a similar trend with regard to defect accumulation at the interface. The  $\Sigma 5$  GB with a GB width which is narrower, has a comparatively lower number of interstitials in the interface after a cascade.

As predicted from the energetic calculations the iron interstitials from the cascade also lie in the regions where more free volume is available in the GB core region. Fig. 5 shows a typical picture of the columns of interstitial defects that are formed at the end of a 16 keV cascade in a  $\Sigma 41$  (910) GB.

## 5 Discussion and Conclusions

We have shown that there are a number of substitutional and interstitial sites in the GB region that are preferentially occupied by P atoms. This provides a driving force for P segregation to the GB region. However it has also been shown that many of these sites are also favourable for Fe defects which will lead to site competition when collision cascades interact with GB planes.

It is found that the proportion of defects accumulating at the GB depends on the arrangement of the atoms in the core of the GB. The open structures, such as  $\Sigma 5$  (310)[001] and the  $\Sigma 41$  (910)[001], are found to provide a less resistant barrier for the energetic cascades, than the more densely packed  $\Sigma 25$  (430)[001]. For the 8 and 16 keV pka energies, the cascade penetrated these open structures and developed on the other side of the GB. Few of the interstitial clusters that penetrate the GB plane recoil, hence reducing the proportion of defects that accumulate in the GB.



Although the spatial extent and the number of defects formed in a collision cascade in Fe depends critically on the potential used both potentials studied show that similar defect types occur. Furthermore, the GB structures and energies agree closely.

## 6 Acknowledgements

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GB	Ackland EAM		2NN MEAM	
	$E_\gamma(\text{eV}/\text{\AA}^2)$	Width(\text{\AA})	$E_\gamma(\text{eV}/\text{\AA}^2)$	Width(\text{\AA})
$\Sigma 5(310)[001]$	0.076	7.0	0.073	8.0
$\Sigma 41(910)[001]$	0.056	14.4	0.050	14.7
$\Sigma 25(430)[001]$	0.072	19.0	0.061	19.2

Table 1

Comparison of the grain boundary width and energies as calculated by the Ackland and the 2NN MEAM potential.

pka direction	Ackland EAM	2NN MEAM
$\langle 100 \rangle$	$20.0 \pm 1.0$	$16.0 \pm 1.0$
$\langle 110 \rangle$	$32.0 \pm 1.0$	$26.0 \pm 1.0$
$\langle 111 \rangle$	$> 50.0$	$> 50.0$

Table 2

A comparison of the threshold displacement energies (in eV) obtained with the two potentials at 0K, along the principal crystallographic directions of the bcc lattice.

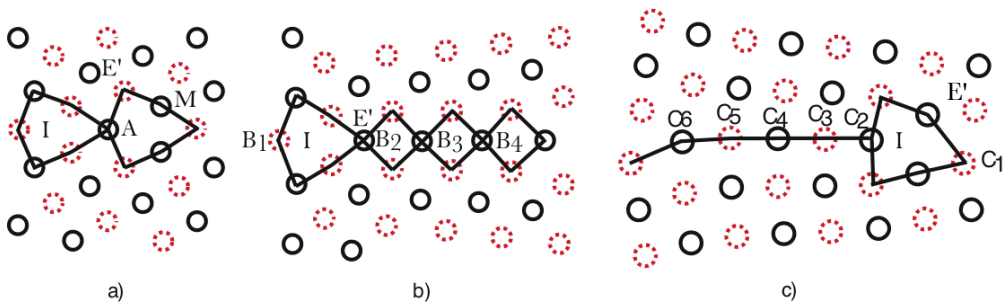


Fig. 1. The relaxed structures of the  $\Sigma 5(310)$ ,  $41(910)$  and  $25(430)$  GB's. The A, B's and C's label sites on the grain boundary plane. E' is the energetically most favourable substitutional site in the GB region and 'I' is the most preferential site in the GB region.

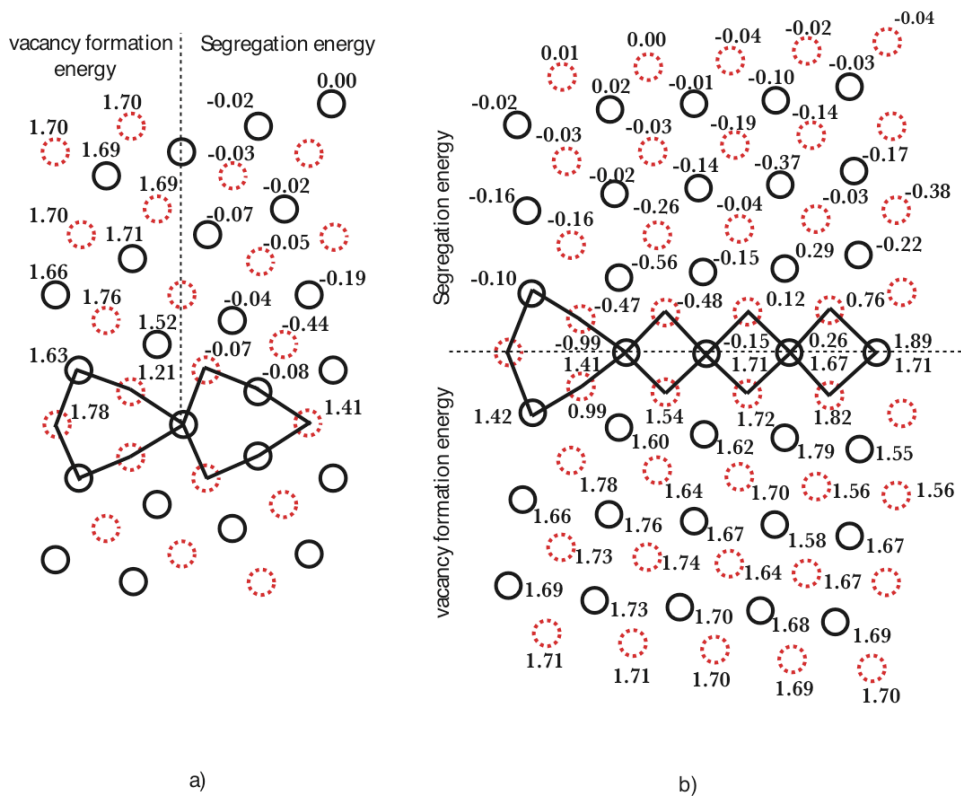


Fig. 2. The segregation energy and vacancy formation energy distribution, given in eV, near the (a)  $\Sigma 5(310)$  and the (b)  $\Sigma 41(910)$  GB's. In (a) the numbers on the left of the dotted line represent the vacancy formation energies and the numbers on the right the segregation energies. In (b) the numbers above the dotted line represent the vacancy formation energies and the numbers below the segregation energies.

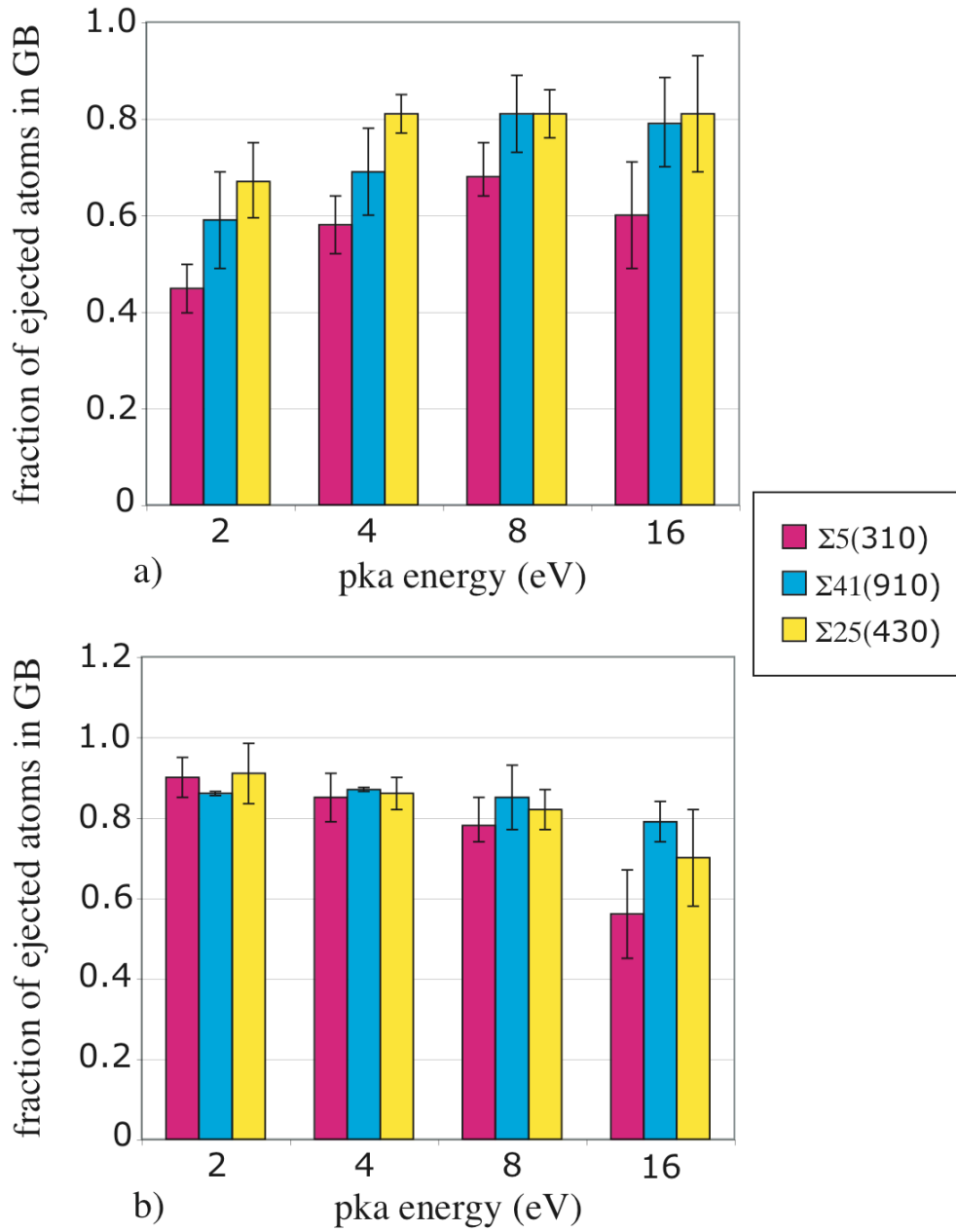


Fig. 3. The fraction of interstitials in the GB plane as a function of energy with the pka initially (a) 40 Å away from the GB plane and (b) 30 Å away from the GB plane.

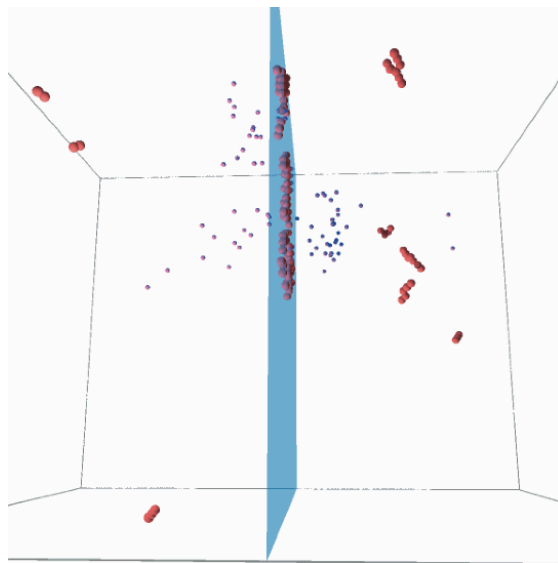


Fig. 4. The tendency for interstitials to agglomerate in the GB plane is shown here, at the end of a 16 keV cascade in a  $\Sigma 41(910)[001]$  GB