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### Abstract

Graphite moderated reactors are being operated in many countries including, the UK, Russia, Lithuania, Ukraine and Japan. Many of these reactors will operate well into the next century. New designs of High Temperature Graphite Moderated Reactors (HTRS) are being built in China and Japan.

The design life of these graphite-moderated reactors is governed by the ageing of the graphite core due to fast neutron damage, and also, in the case of carbon dioxide cooled reactors by the rate of oxidation of the graphite.

Nuclear graphites are polycrystalline in nature and it is the irradiation-induced damage to the individual graphite crystals that determines the material property changes with age. The life of a graphite component in a nuclear reactor can be related to the graphite irradiation induced dimensional changes. Graphites typically shrink with age until a point is reached where the shrinkage stops and the graphite starts to swell. This change from shrinkage to swelling is known as "turnaround".

It is well known that pre-oxidising graphite specimens caused "turnaround" to be delayed, thus extending the life of the graphite and hence the life of the reactor. However, there was no satisfactory explanation of this behaviour.

This paper presents a numerical crystal based model of dimensional change in graphite, which explains the delay in "turnaround" in the pre-oxidised specimens irradiated in a fast neutron flux, in terms of crystal accommodation and orientation and change in compliance due to radiolytic oxidation.

### Introduction

The graphite in a graphite moderated nuclear reactor not only acts as a moderator but is also a major structural component, which can not easily be replaced. The life of the graphite may therefore govern the life of the nuclear plant.

During operation the graphite components change size due to fast neutron damage. In addition there are also significant changes to many other graphite properties, most importantly to the strength and modulus, coefficient of thermal expansion and thermal conductivity. During reactor operation significant irradiation dose and temperature gradients in the large cross-sections of these graphite components leads to the generation of internal stresses, which may eventually result in component failure. However irradiation creep relieves these stresses. This is fortunate because it is irradiation creep coupled with suitable design that allows graphite to be successfully used as a moderator.

Whilst fast neutron induced physical changes to the graphite are of prime concern in helium cooled high temperature reactors and light water cooled graphite moderated reactors, in the case of carbon dioxide cooled graphite moderated reactors radiolytic oxidation leads to significant graphite weight loss. This weight loss occurs fairly uniformly throughout the accessible graphite porosity within the component reducing the graphite density. In addition weight loss also modifies some of the graphite properties, particularly the strength, modulus and thermal conductivity.

The fast neutron induced changes to the physical properties are primarily a function of the dimensional change within the well graphitised crystals that make up typical nuclear graphite components.

These crystal dimensional changes arise due to the formation of interstitial and vacancy loops within the graphite basal planes. The formation of these loops causes 'c' axis expansion and 'a' axis contraction, the magnitude of which is a function of fast neutron dose and irradiation temperature, see Fig. 1.

Typical nuclear graphite is manufactured from coke particles joined together by a pitch binder. After graphitisation the coke particles consists of well graphitised crystallites which contain a number of cracks of various sizes parallel to the basal plane. These filler coke particles are typically either needle shaped or spherical shaped. The first type of filler particles leads to anisotropic graphite component material properties, the second type of filler particle leads to almost isotropic material properties.

The binder consists of a conglomerate of much smaller graphite crystals and less well graphitised material and contains gas evolution pores. These gas evolution pores and the porosity within the graphite coke particles give the graphite component a much lower density than may be expected ( $\sim 1.7-1.9 \text{ g/cm}^3$ ) compared with  $2.26 \text{ g/cm}^3$  for pure graphite crystals.

At the temperatures of interest in modern graphite moderated reactors (greater than  $300^\circ\text{C}$ ) a typical nuclear graphite shrinks with irradiation dose, before "turning around" and swelling until the graphite reaches its original volume and beyond. At this point all of the graphite physical properties are rapidly deteriorating.

Various attempts [Simmons, 1965, Brocklehurst and Kelly, 1993, Sutton and Howard, 1962, Jenkins, 1964] have been made to model dimensional and other irradiation induced physical changes in graphite. In the first three of these references an attempt was made to relate the dimensional change to the accommodation offered by the small shrinkage cracks [Mrozowski, 1956] within the graphite crystal structure and the orientation of the crystals. However these models assume graphite to be a loose assembly of unconnected graphite crystals. [Jenkins, 1964] pointed out that this was not the case and attempted to devise a mathematical model which accounted for the compliance of the individual crystals and global polycrystalline compliance as well as the accommodation and crystal orientation. Unfortunately his model was very complex and did not readily lend itself to structural assessment of irradiated graphite behaviour. However, the development of modern computers and non-linear finite element analysis techniques now allow this behaviour to be assessed.

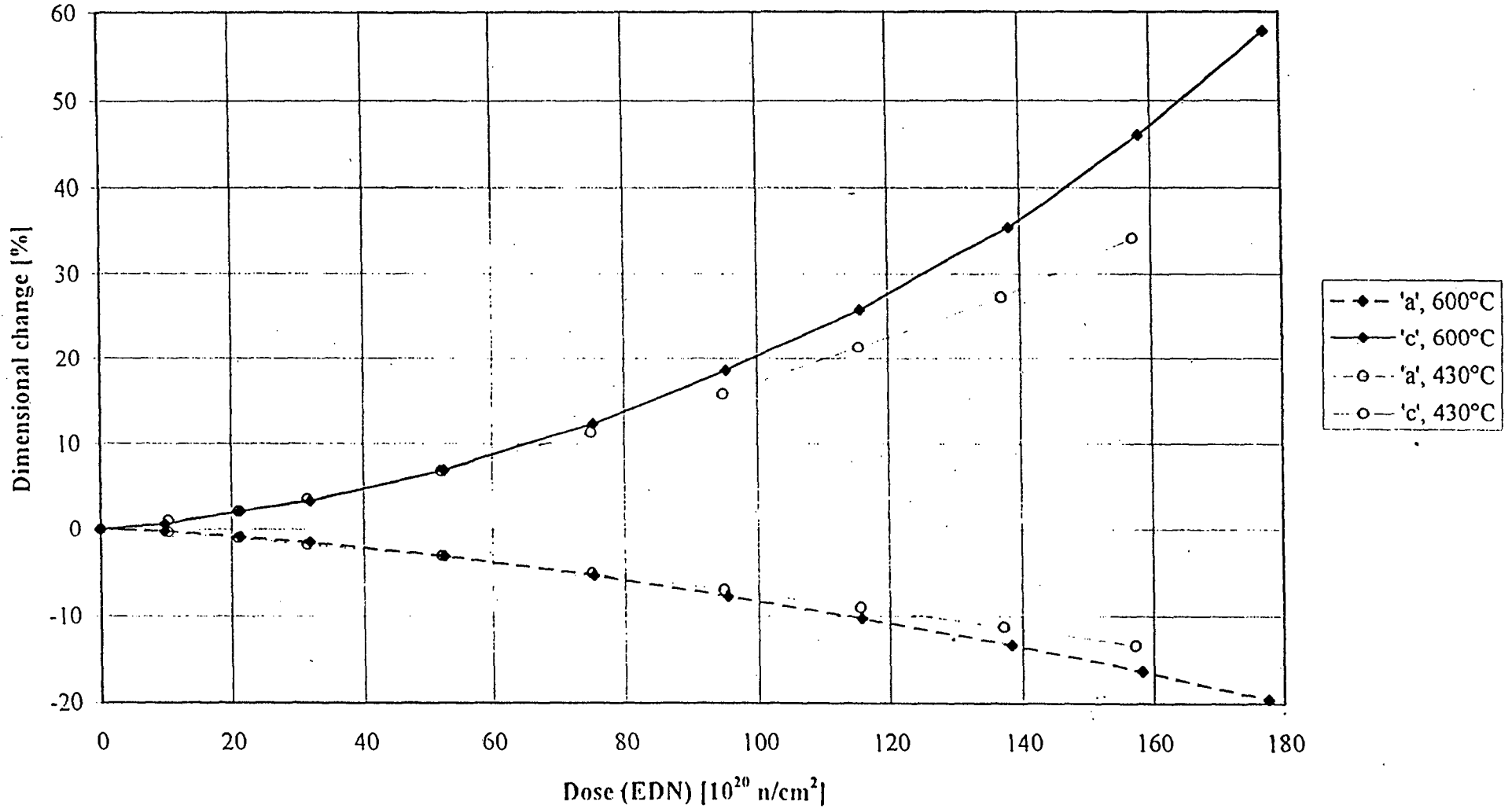


Figure 1 Dimensional changes in highly orientated pyrolytic graphite irradiated at 430°C and 600°C

An early attempt at modelling this behaviour [Marsden, 1998] using very elementary models of graphite crystals, joined together to form a polycrystalline material, clearly demonstrated that “turnaround” could be modelled using finite element methods. As this was the first time that “turnaround” had been modelled in polycrystalline graphite the authors decided to construct a more mathematical rigorous graphite crystal model and polycrystalline model of graphite irradiation ageing.

To test out this new model it was decided to apply it to irradiated graphite data in which the microstructure of various graphites had been changed by radiolytic oxidation [Kelly, 1972]. These experiments appeared to demonstrate that radiolytic oxidation delayed “turnaround” and increased shrinkage. However, all attempts to explain this behaviour in terms of increased porosity and accommodation have previously failed. If [Jenkins, 1964] was right and the change in crystal and polycrystalline compliance were important, this could be demonstrated using the new models.

This paper describes these new models and their application to modelling dimensional change in graphite and the effect radiolytic oxidation has.

### Graphite Crystal Behaviour

Perfect graphite crystals have two main axes ‘c’ and ‘a’ and the two properties of interest in this paper for the two principal directions are considerably different as shown below:

Property	‘c’	‘a’
Modulus (GPa)	36.5	1060
Coefficient of Thermal Expansion (20-120°C) ( $K^{-1} \times 10^{-6}$ )	26.5	-1.5

The temperature and irradiation behaviour of these properties and the crystal dimensional changes are described below:

#### Modulus

There is relatively little detailed information on the changes in the crystal modulus and compliance with irradiation. However what is known is that irradiation greatly increases the shear modulus between the basal planes and to a lesser extent reduces the ‘c’ axis compliance. There is some temperature dependence in modulus.

#### Thermal Expansion Coefficient (CTE)

It has been shown that at temperatures greater than 300°C the CTE in both the ‘c’ and ‘a’ direction is independent of irradiation dose. However the CTE is temperature dependent in both directions.

#### Dimensional Change

Dimensional change data for graphite crystals has been obtained in material test reactors over a wide range of doses and temperatures. However, some of this data is inconsistent and in some temperature ranges the data is limited. It has been

established that dimensional change rates are much larger in graphite crystals irradiated below 300°C than above this temperature and that above ~600°C the dimensional change rate is dependent on crystal size. For this study dimensional change data for irradiation temperatures of 430°C and 600°C was used [Brocklehurst and Kelly, 1992].

### The finite element graphite crystal model

This new model was developed, using the ABAQUS finite element program, to synthesise a volume of well-crystallised cracked material, surrounded by a volume of binder. The model was implemented in ABAQUS using a Fortran subroutine facility known as a UMAT that includes the anisotropic, irradiation dependent constitutive relationships for:

- a) The crystal dimensional changes  $[\Delta a/a]$ ,  $[\Delta c/c]$
- b) The crystal CTE (and changes with strain)  $\alpha_a$ ,  $\alpha_c$
- c) The crystal elastic modulus  $E_a$ ,  $E_c$
- d) The crystal Poisson's ratio  $\nu_c$
- e) Crystal irradiation creep  $\varepsilon_c$

The new model was studied in isolation in order to determine the effect of the binder boundary restraint upon:

- a) The apparent crystallite dimensional change  $[\Delta L_a/L_a]_{app}$  and  $[\Delta L_c/L_c]_{app}$
- b) The apparent crystallite CTE  $\alpha_{L_a}$  and  $\alpha_{L_c}$

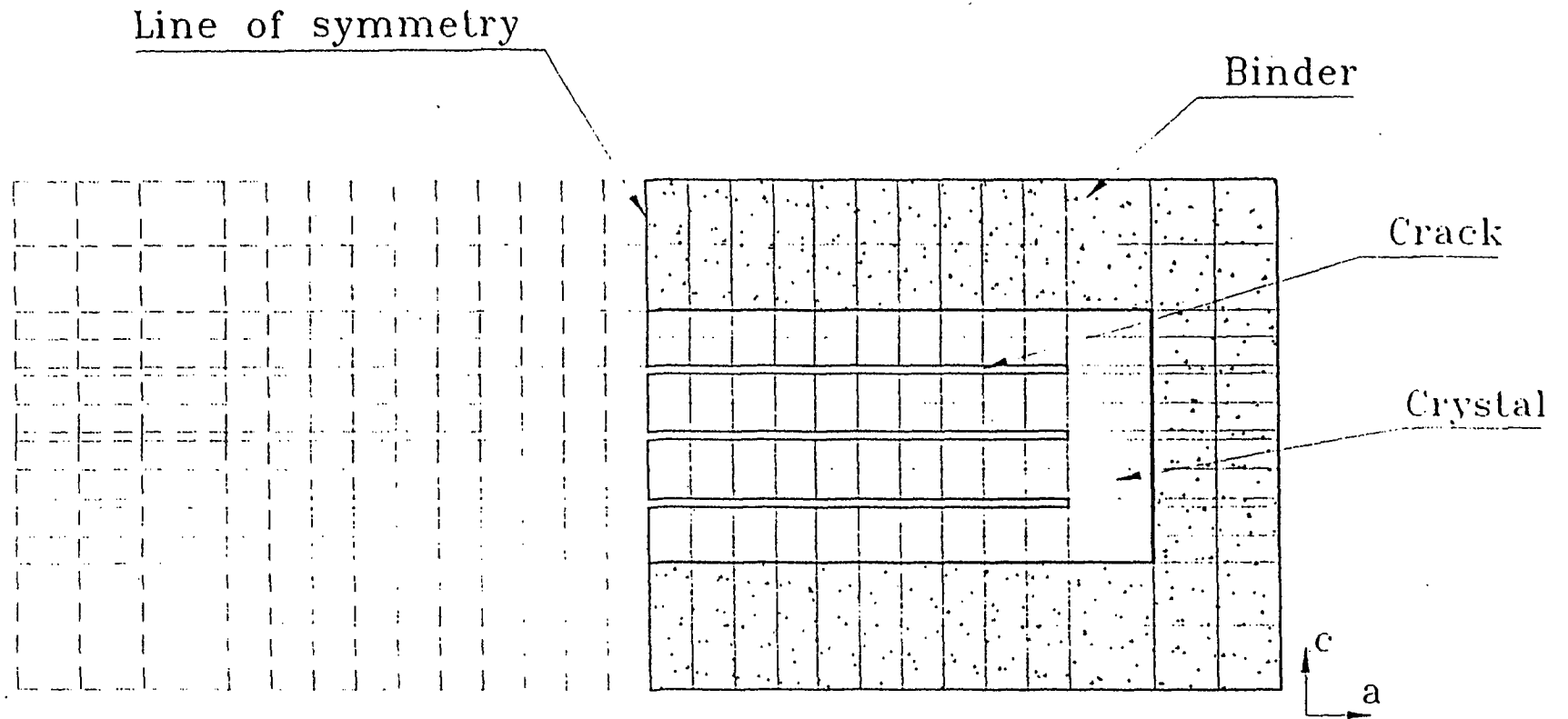
To examine the behaviour of a single graphite crystal, a finite element model of an idealised crystal based on work by [Sutton and Howard, 1962], 1.5  $\mu\text{m}$  wide by 6  $\mu\text{m}$  long, was created with three internal cracks 0.025  $\mu\text{m}$  wide. This work took account of the small "Mrozowski" type cracks. The surrounding binder was represented by a 0.75  $\mu\text{m}$  border around the whole crystal, see Fig. 2.

The ABAQUS graphite material property UMAT was utilised, using crystal data for irradiation at 450°C. The coefficient of thermal expansion for the crystal was calculated using the mean instantaneous value of the crystal CTE between the room temperature and the irradiation temperature. For the purposes of this initial analysis, it was decided to ignore the effect of creep.

The modulus in the basal plane 'a' is ~30 times greater than that for the 'c' direction, which has implications for the stresses and deformations within the crystallite. Large stresses are generated if the crystal is restrained in the 'a' direction, due to increases in dimensional change and thermal strains. The implications of this Poisson's effect are the subject of ongoing studies.

By cycling the graphite temperature between 20°C and 450°C at several intervals of dose, it is possible to attain the apparent dimensional change and change in CTE with irradiation.

To represent the restraint imposed on the crystal by the surrounding crystals and binder, a volume of material was evenly placed around the outer edges of the crystal.



**Figure 2 The finite element model of the single graphite crystal and binder**

This “binder” volume was given a modulus, that would allow it to simulate the effect of the surroundings within the polycrystalline material. Without this, the crystal would change according to the aspect ratio defined by the respective dimensional change and CTE for each direction. For the initial analysis, the binder was given a modulus that would represent a typical binder with 0% weight loss (10 GPa). The modulus was then adjusted in order to reflect the weight loss, using an empirical relationship between weight loss ( $x$ ) and modulus;  $E = e^{-3.6x}$ . Therefore, for a weight loss of 30% the modulus of the binder was 3.4 GPa. The analyses were run to a dose of  $80 \times 10^{20}$  n/cm<sup>2</sup> EDN at 450°C, returning to 20°C at various intervals. The resultant displacements for the varying parameters are given in Fig. 3 and Fig. 4. The change in the ‘a’ direction was the horizontal displacement of the centre of the crystal’s right hand edge, and the change in the ‘c’ direction was the vertical displacement of the centre of the crystal’s top edge.

The displacement at the end of the crystal is representative of the graphite crystal dimensional changes and crystal dimensional changes due to the CTE, as it is essentially solid material at this point. However, in the centre of the crystal there is a delay in the onset of dimensional change due to the absorption of growth by the cracks. The delayed change in the rate of displacement in the ‘c’ direction highlights the points at which the cracks have closed. Comparison of dimensional changes between varying weight losses (see Fig. 4) indicates that an increase in weight loss, increases the dimensional change. This was to be expected as an increase in weight loss reduces the binder’s modulus, thus making the restraining material more compliant.

The apparent mean CTE for the ‘c’ direction at 20°C was obtained using the vertical displacement of the centre of the crystal (see Fig. 5). For the crystal surrounded by a binder with 0% weight loss, the apparent CTE is approximately zero at low doses, with a steady increase starting at  $20 \times 10^{20}$  n/cm<sup>2</sup> EDN, reaching a maximum positive value of  $\sim 21 \times 10^{-6}$  K<sup>-1</sup> at  $60 \times 10^{20}$  n/cm<sup>2</sup> EDN. The value then remains approximately constant. When the binder has 30% weight loss, the apparent CTE in the ‘c’ direction has the same basic shape as the 0% weight loss, except the initial increase begins at  $30 \times 10^{20}$  n/cm<sup>2</sup> EDN, peaking at  $\sim 24.5 \times 10^{-6}$  K<sup>-1</sup> at  $65 \times 10^{20}$  n/cm<sup>2</sup> EDN.

The apparent mean CTE for the ‘a’ direction was based upon the horizontal displacement of the end of the crystal (see Fig. 6). With respect to the binder with 0% weight loss, the apparent CTE starts at a positive value ( $0.43 \times 10^{-6}$  K<sup>-1</sup>) and then gradually increases to  $0.71 \times 10^{-6}$  K<sup>-1</sup> at  $40 \times 10^{20}$  n/cm<sup>2</sup> EDN. The apparent CTE then decreases to  $-0.09 \times 10^{-6}$  K<sup>-1</sup> at  $60 \times 10^{20}$  n/cm<sup>2</sup> EDN, remains constant until  $80 \times 10^{20}$  n/cm<sup>2</sup> EDN, where there is another decrease to  $-0.17 \times 10^{-6}$  K<sup>-1</sup>. When the binder has 30% weight loss, the apparent CTE in the ‘a’ direction is of the same basic shape with the peaks and troughs occurring at approximately the same dosage, but being of a different amplitude. The initial value is  $0.34 \times 10^{-6}$  K<sup>-1</sup>, rising to a maximum of  $0.48 \times 10^{-6}$  K<sup>-1</sup> at  $40 \times 10^{20}$  n/cm<sup>2</sup> EDN. The value then drops to  $-0.25 \times 10^{-6}$  K<sup>-1</sup> at  $65 \times 10^{20}$  n/cm<sup>2</sup> EDN, from which it remains constant.

From this analysis it is obvious that the crystal and binder modulus are an important factor in the way crystallites will interact in an overall polycrystalline structure, especially when the latter undergoes some degree of weight loss. The large difference

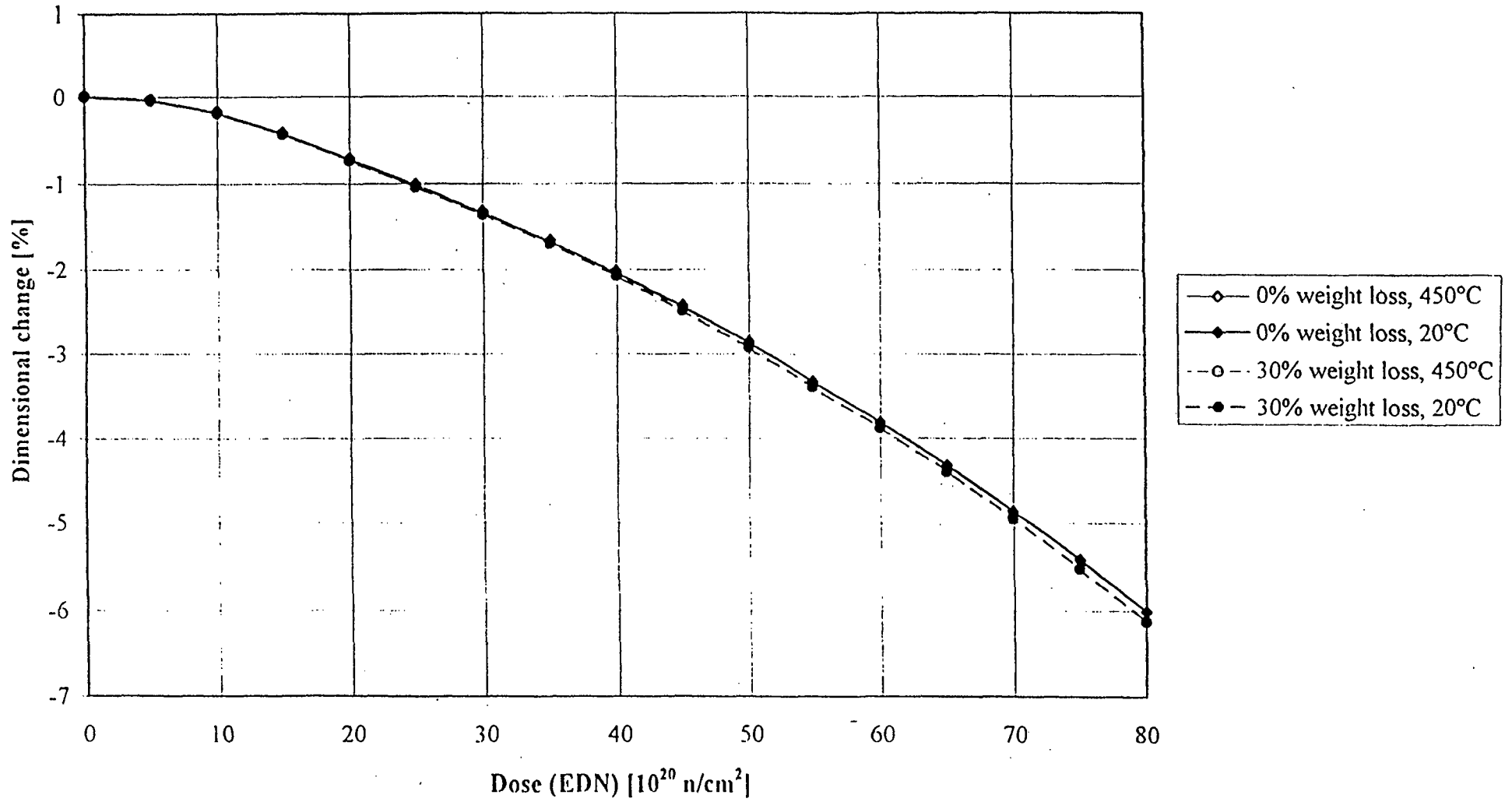


Figure 3 Displacement of graphite crystal in the horizontal ('a') direction



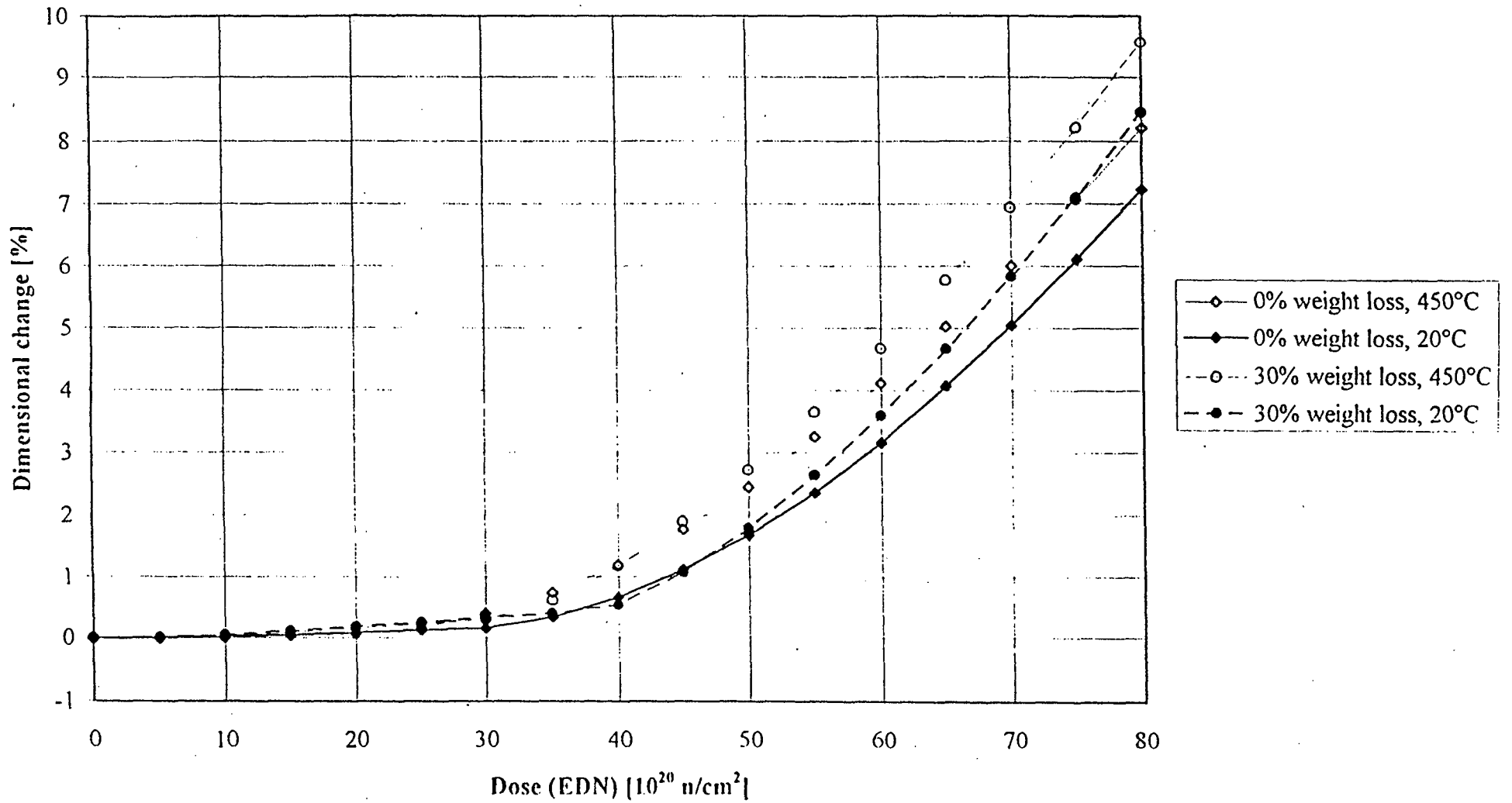


Figure 4 Displacement of graphite crystal in the vertical ('c') direction

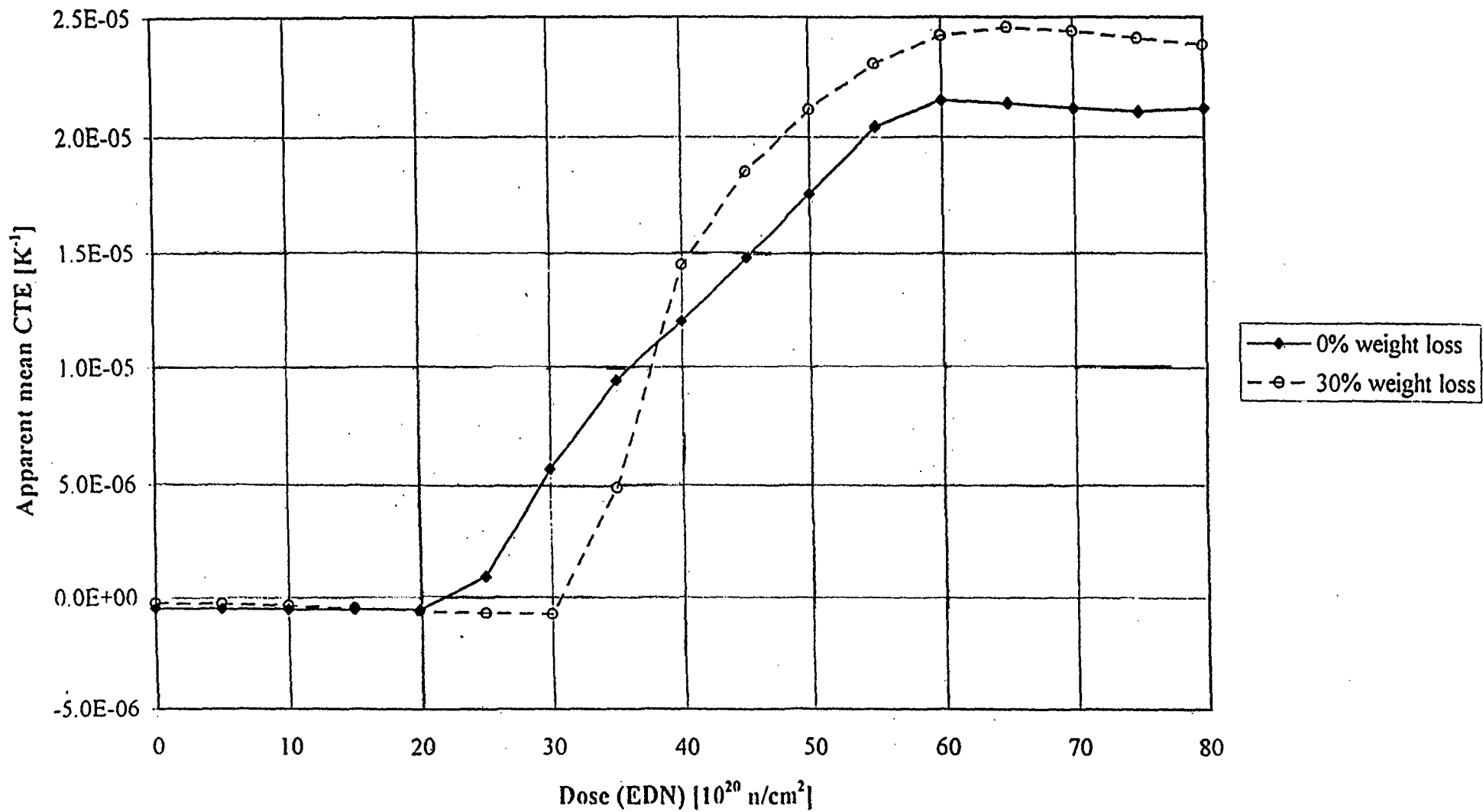


Figure 5 Apparent mean CTE in the vertical ('c') direction

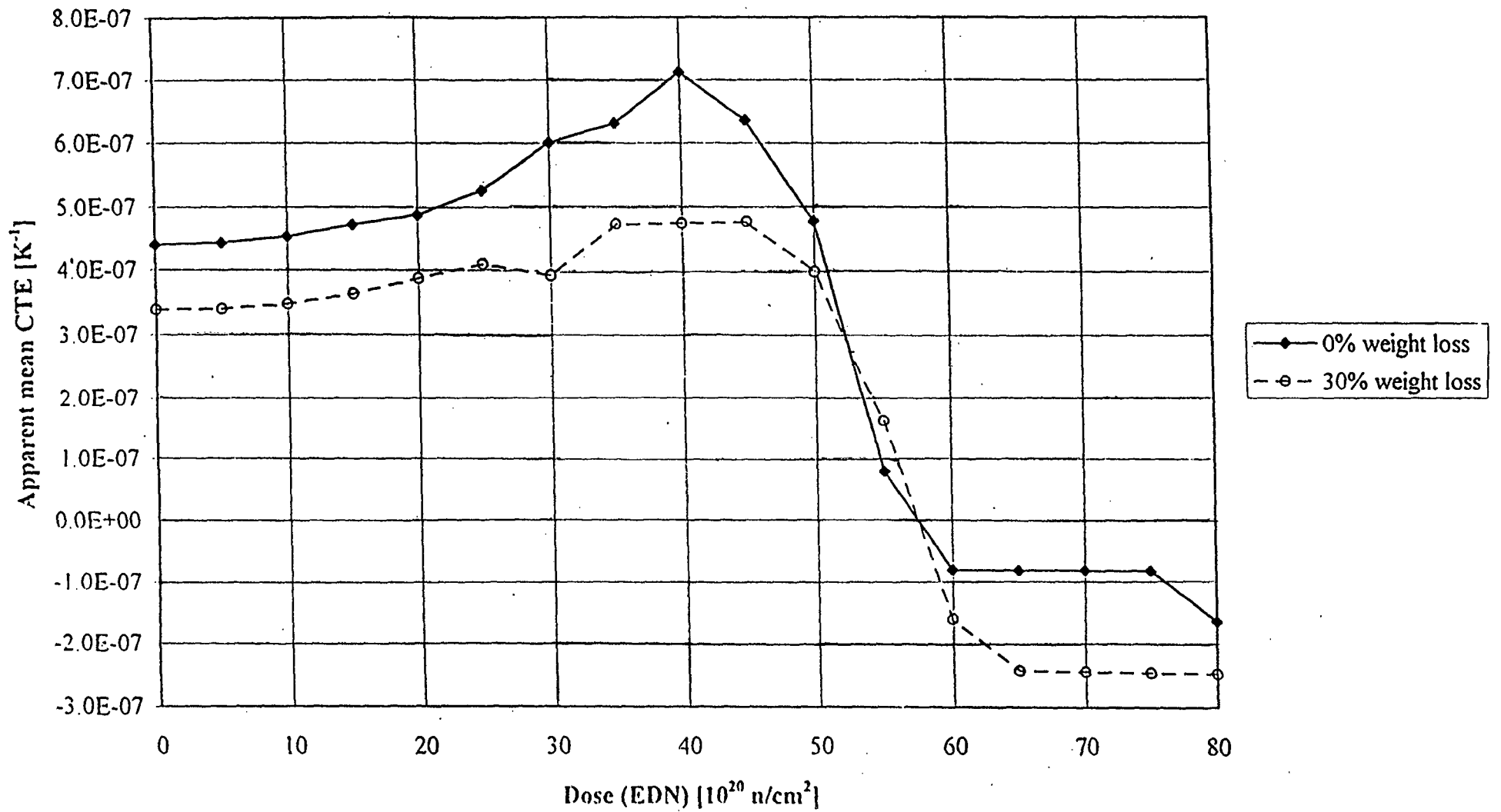


Figure 6 Apparent mean CTE in the horizontal ('a') direction

in crystal modulus between the 'a' and 'c' directions have significant implications for the creation of stress and displacements due to the effect of Poisson's ratio. These stresses and displacements may lead to the creation of basal plane cracks with irradiation and thermal cycling.

### The polycrystalline graphite model

The data obtained from the analysis of the single crystal model was then used in a polycrystalline model. This model comprises of a rectangle with two axes of symmetry, made up from individual elements, see Fig. 7. Each individual element may represent:

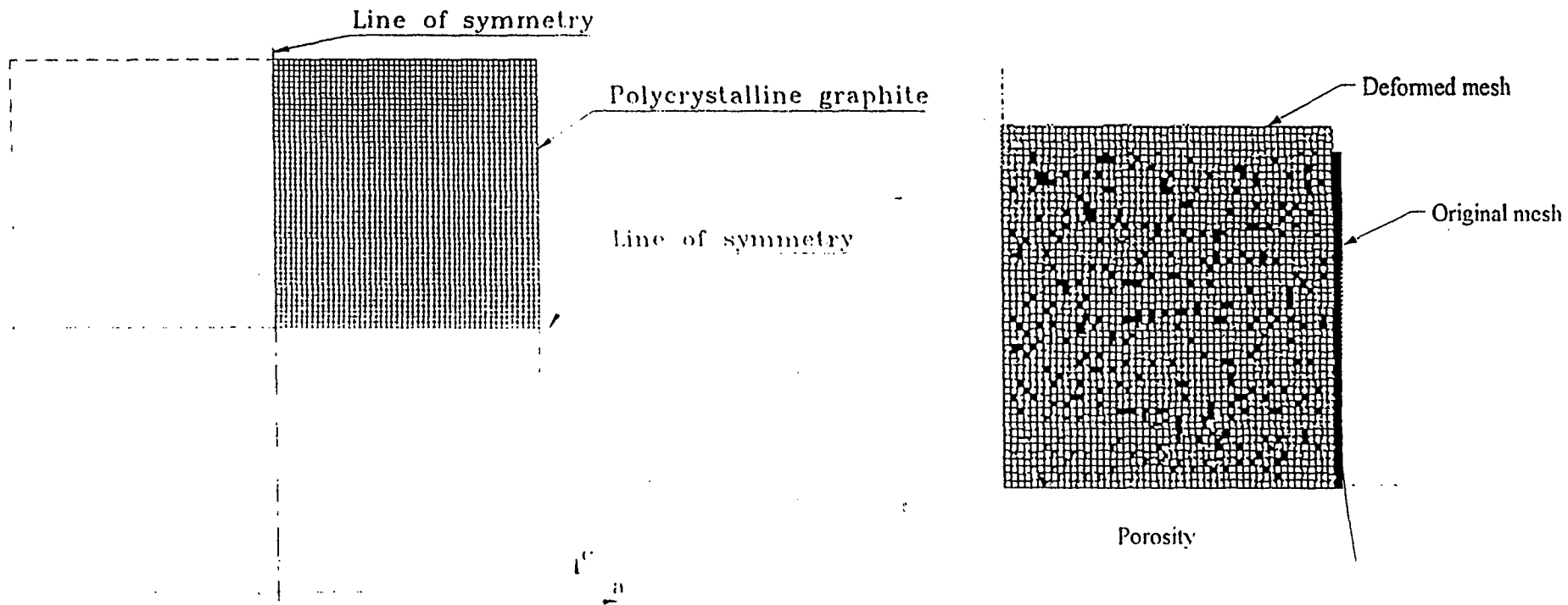
- a) Crystalline graphite material containing cracks, surrounded by binder material, giving an apparent CTE and dimensional change
- b) Holes to represent inter-crystalline porosity and gas evolution pores

To simulate the possibility of varying orientation within the structure, it was possible to orient the individual crystallites (the 'c' crystallite axis of a non-orientated crystal corresponds to the vertical axis of the mesh). In this study only 0° and 90° orientation was considered.

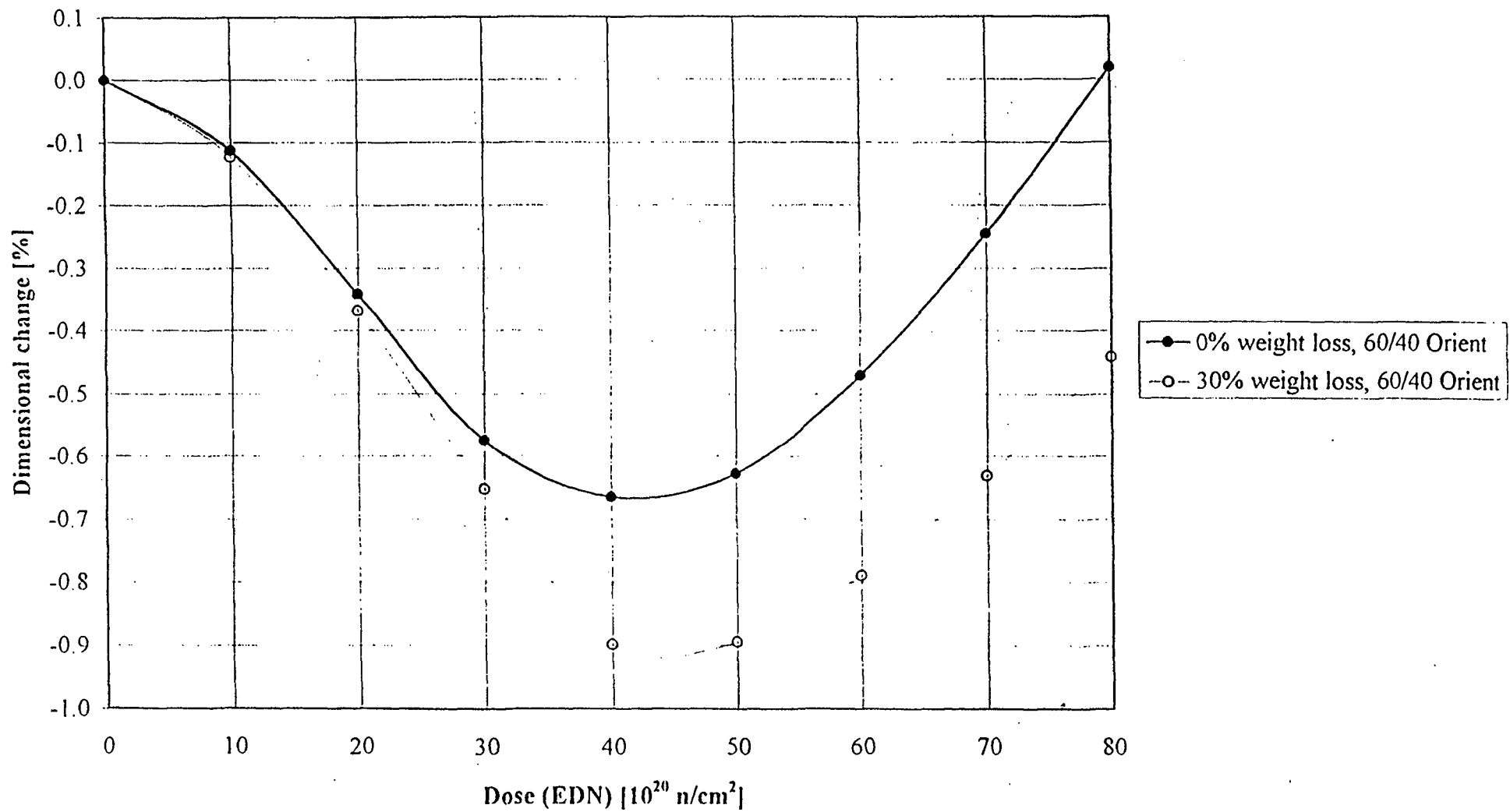
The distribution of the graphitic materials and the porosity can be generated randomly, although there is the possibility to generate groups of similar crystal, porosity or other binder type material.

Two assessments were conducted; the first having 0% weight loss and 60% - 40% orientation (0° - 90°), and the second having 30% weight loss and 60% - 40% orientation (0° - 90°). The apparent displacement plots for these are given in Fig. 8 and Fig. 9. The apparent dimensional changes in the 'a' direction exhibit "turnaround" for both weight losses, with the 30% weight loss having greater displacements and a delayed "turnaround" with respect to the 0% weight loss. In the 'c' direction, the apparent dimensional changes for the 0% weight loss initially shrink at the lower doses (up to  $\sim 30 \times 10^{20}$  n/cm<sup>2</sup> EDN), and then grow at the remaining doses. The 30% weight loss case has similar trends with initially no movement until  $\sim 30 \times 10^{20}$  n/cm<sup>2</sup> EDN, at which point it begins to grow, reaching a greater displacement than the 0% weight loss model. This is behaviour that had been observed experimentally in virgin and pre-oxidised polycrystalline anisotropic needle coke graphite specimens irradiated in the Dounreay Fast Reactor, see Fig. 10, giving some confidence in the new methodology.

The apparent mean CTE in the 'a' and 'c' directions (see Fig. 11 and Fig. 12 respectively) highlights a delayed response in the increase of CTE for the 30% weight loss ( $\sim 30 \times 10^{20}$  n/cm<sup>2</sup> EDN), when compared to the 0% weight loss ( $\sim 20 \times 10^{20}$  n/cm<sup>2</sup> EDN). In the 'a' direction the apparent CTE of both cases are initially the same, there is then an increase in the 0% and then 30% model. Between 40 and 50  $\times 10^{20}$  n/cm<sup>2</sup> EDN the 30% weight loss model is approximately equivalent to that of the 0% weight loss model, and then slightly less at higher doses. In the 'c' direction, a similar process occurs at the lower doses and then after 40  $\times 10^{20}$  n/cm<sup>2</sup> EDN the 30% weight loss case has a greater apparent CTE. In a true polycrystalline graphite there would also be a component of CTE associated with the binder phase. If this binder



**Figure 7 The finite element model of the polycrystalline graphite**



**Figure 8 Apparent horizontal displacement of a polycrystalline graphite block (mostly 'a')**

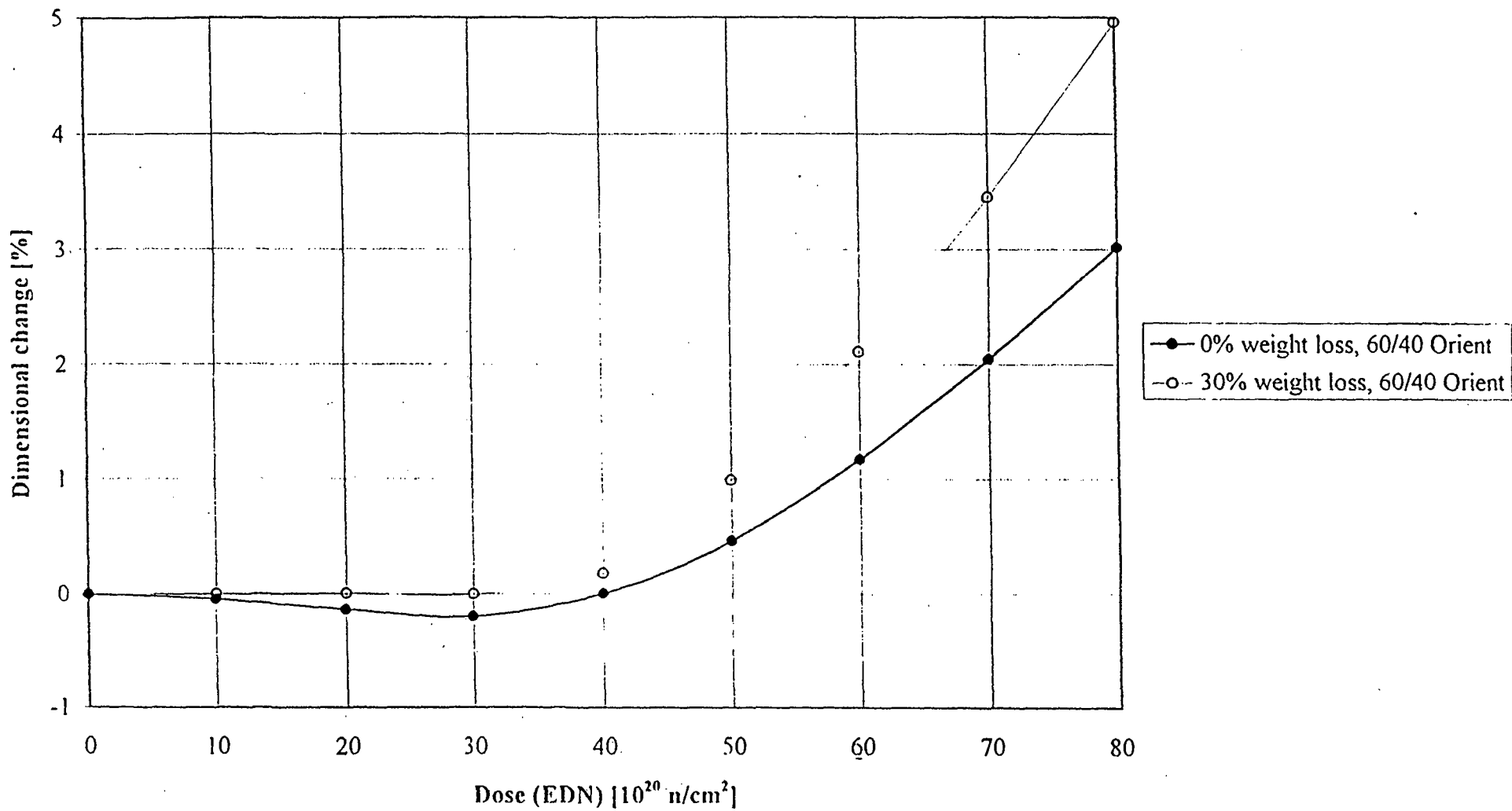


Figure 9 Apparent vertical displacement of a polycrystalline graphite block (mostly 'c')

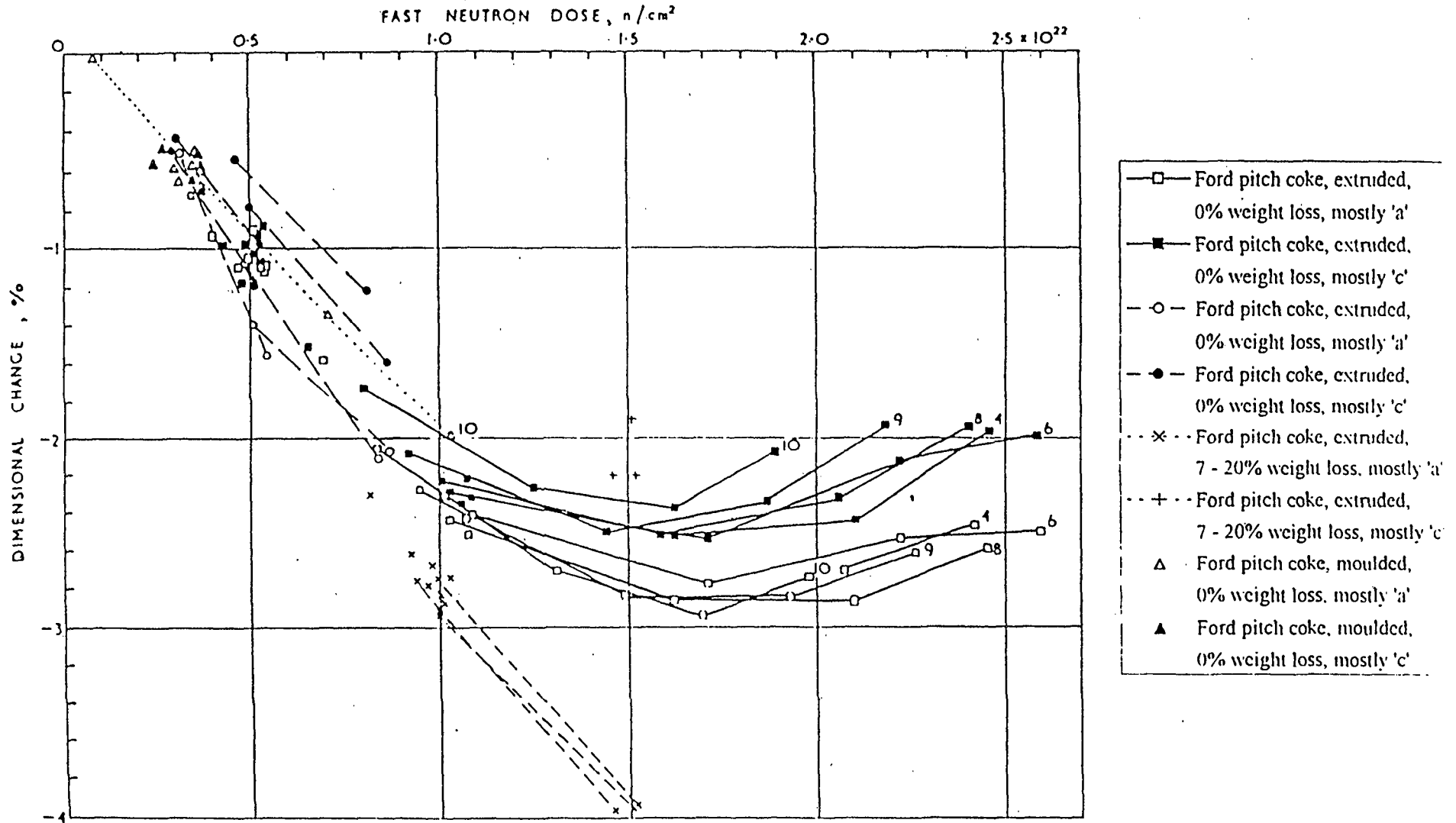


Figure 10 Dimensional changes in BAEL pitch coke graphite irradiated in DFR



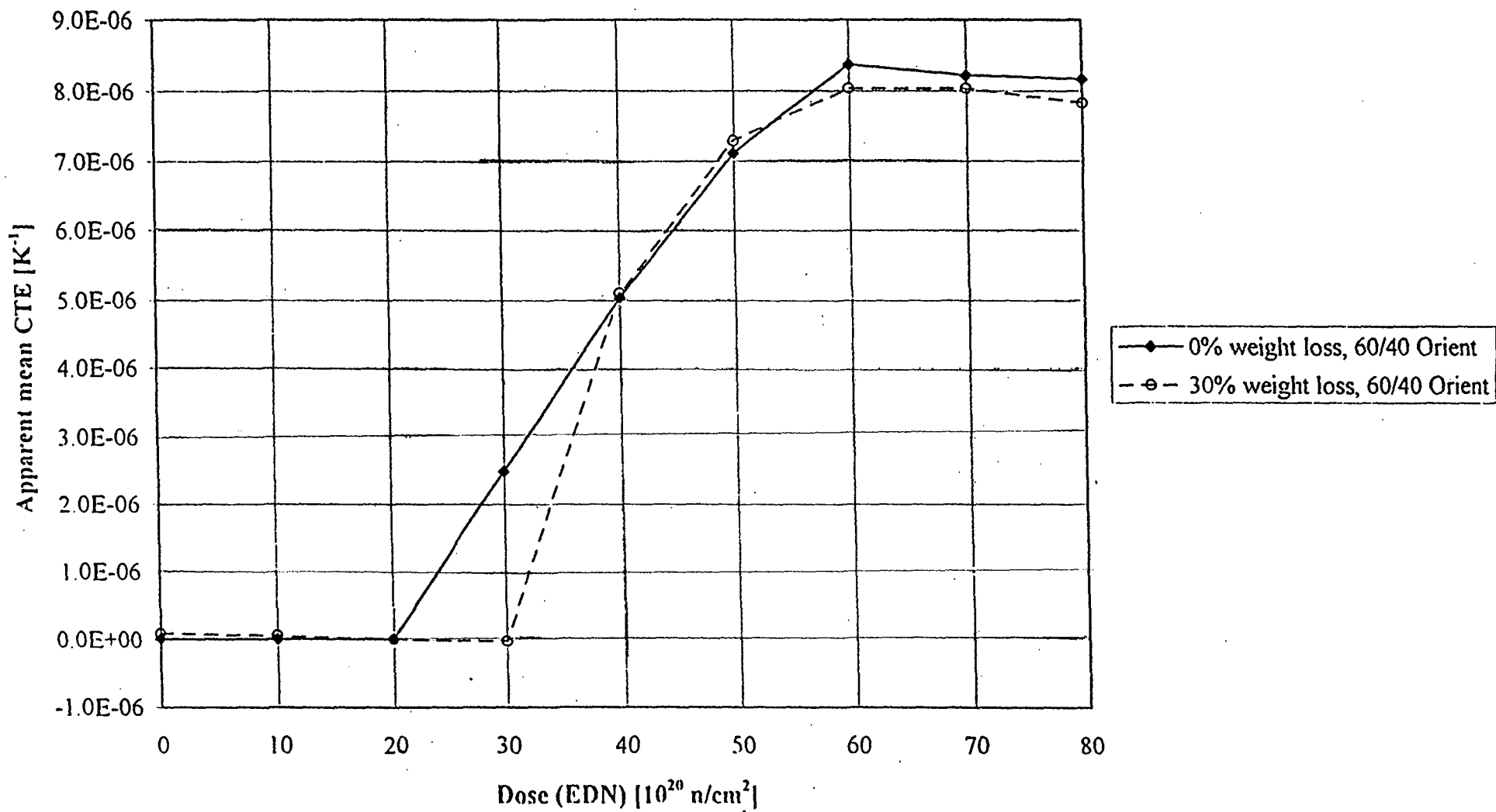


Figure 11 Apparent horizontal mean CTE of a polycrystalline graphite block (mostly 'a')

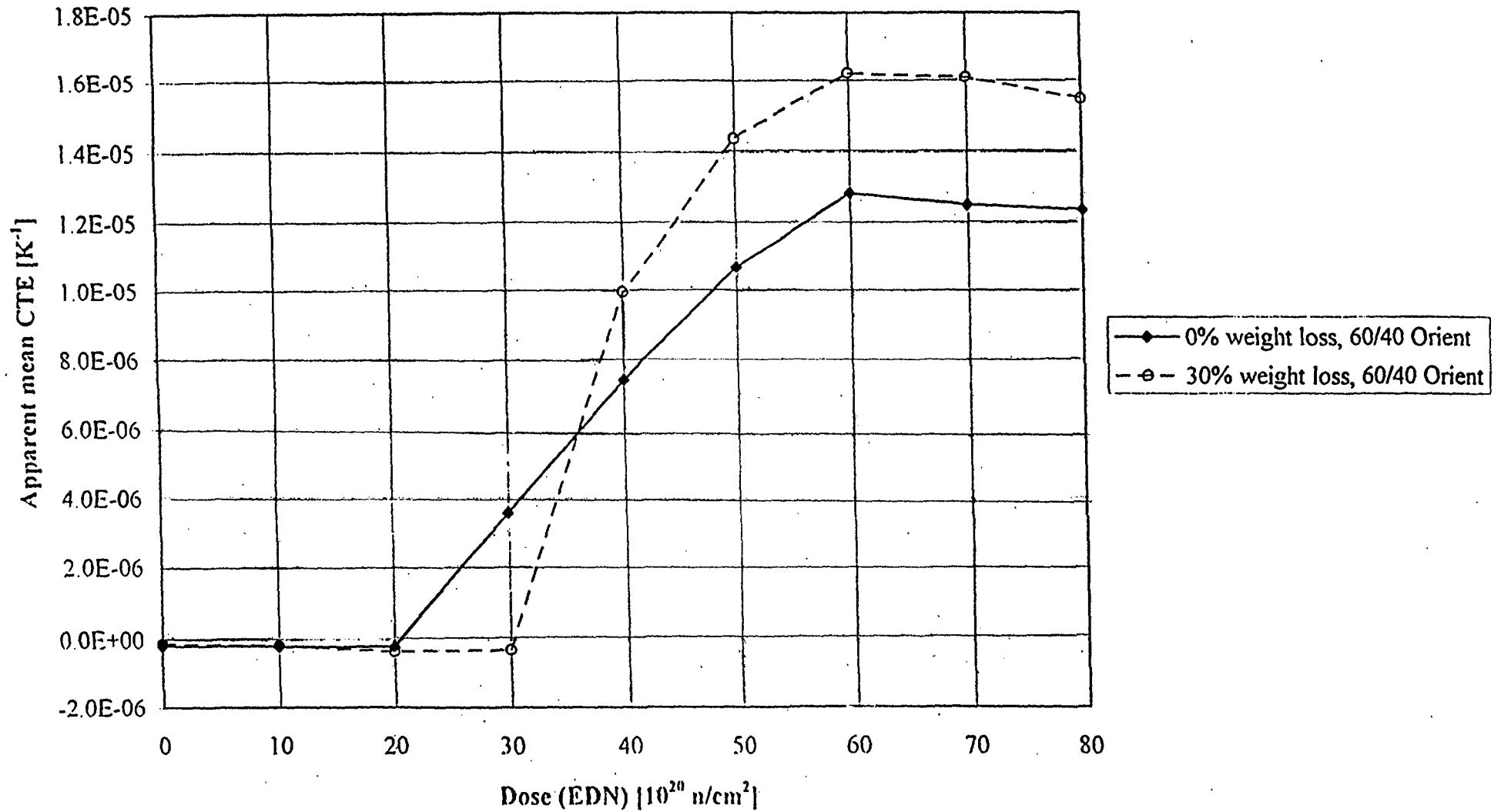


Figure 12 Apparent vertical mean CTE of a polycrystalline graphite block (mostly 'c')

phase CTE were included similar changes to CTE as predicted in Pile Grade A graphite by [Brocklehurst and Kelly, 1993], would be expected, again giving some confidence to the method.

The results indicate that “turnaround” can be explained by crystal growth, accommodation and compliance without the necessity of simulating the generation of new cracks. The phenomenon of delay in “turnaround” may be explained by the decrease of compliance within the structure, caused by weight loss.

## Discussion

Previously, the models considered graphite as a single-phase, well crystalline graphitic material. These were only applicable to relatively low irradiation doses, as at higher doses binder filler interaction becomes more predominant. Therefore, it was suggested that a two-phase analytical model would simulate the graphite more accurately.

Initially the polycrystalline graphite’s dimensional change is dominated by the ‘a’ direction shrinkage, as the ‘c’ direction growth is absorbed by the inter-crystalline accommodation.

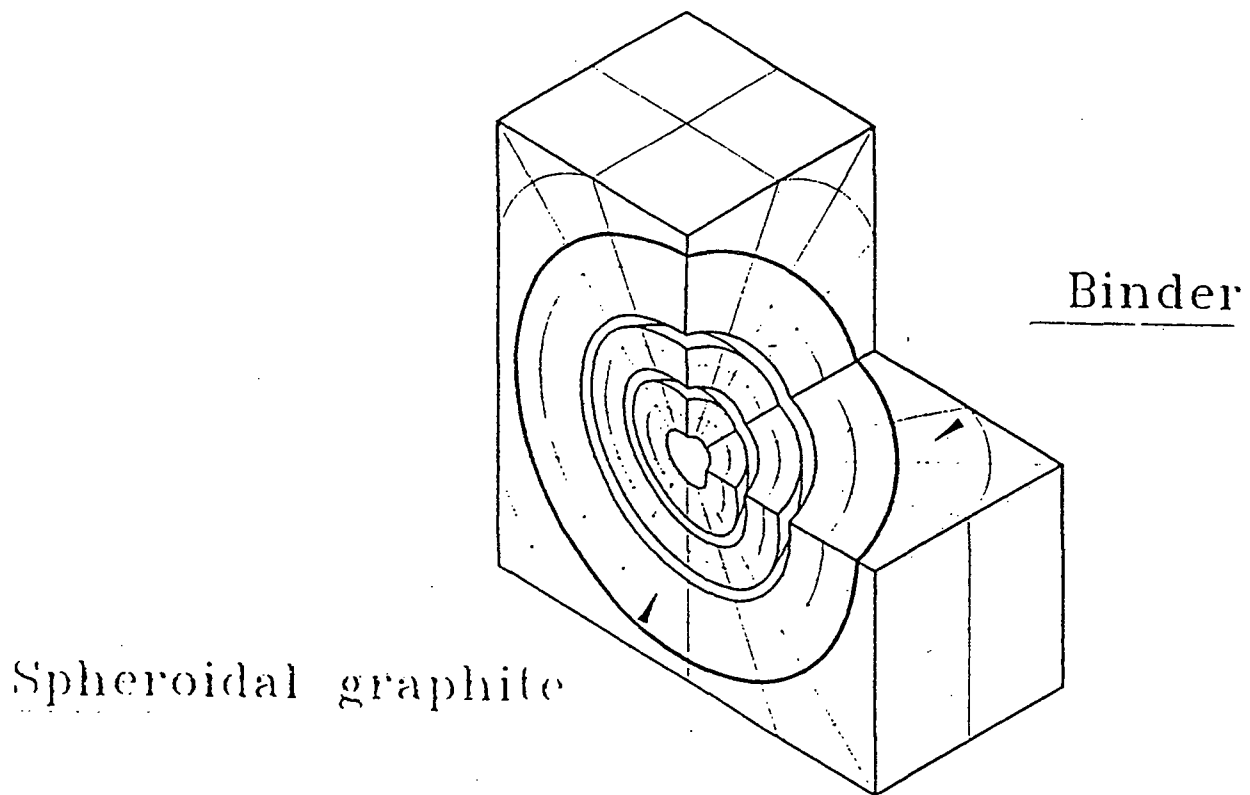
At “turnaround” the ‘c’ direction expansion becomes the dominant driving force, and the polycrystalline graphite begins to expand in both directions. This growth will continue until the final failure of the structure through inter crystalline cracking.

The delay in “turnaround” with weight loss has been demonstrated to be primarily a function of the increase in compliance due to weight loss. Earlier work [Marsden, 1998] has shown that changing the modulus by adding porosity in the polycrystalline model did not significantly affect the change in dimension behaviour. The reason for this is that it did not account for the change in the individual crystal behaviour due the change in the global compliance.

After “turnaround” large stresses due to crystal growth will lead to inter crystalline cracks and deterioration of the properties such as thermal and electrical conductivity, modulus, and failure strength [Shtrombakh, 1995].

It is also true that the overall modulus will change with irradiation due to pinning of the dislocations in the basal plane. However this will apply to both virgin and non-oxidised material. In addition irradiation creep will also have an effect on “turnaround” and property changes as this will affect the inter crystalline stresses. Both of these phenomena are currently under further investigation (the model has the capability of simulating both these types of behaviour).

The model is also capable of assessing three-dimensional needle coke particles and spheroidal graphite particles, see Fig. 13.



**Figure 13 Finite element model of spheroidal graphite**

#### Conclusions

- 1 A two-phase finite element model of a single graphite crystal containing Mrozowski type cracks, surrounding by a binder region, has been developed. This model can account for crystallite behaviour including apparent changes in CTE and dimensional changes due to fast neutron irradiation.
- 2 The single crystallite model has been included in a larger polycrystalline finite element model, which has demonstrated the mechanism of shrinkage and “turnaround”.
- 3 The model has been used to explain experimental results of virgin and pre-oxidised graphites.
- 4 Dimensional changes in graphite are initially governed by:
  - a) Crystal dimensional change in the ‘a’ and ‘c’ directions, where ‘a’ is predominant
  - b) Accommodation within inter-crystalline cracking
  - c) Crystal orientation
  - d) The restraint of the crystallite within the polycrystalline graphite
  - e) The crystallite compliance
  - f) The polycrystalline compliance, which can be affected by the weight loss
- 5 Dimensional changes at and after “turnaround” are governed by:
  - a) Crystal dimensional change in the ‘a’ and ‘c’ directions, where ‘c’ becomes predominant

- b) The loss of inter-crystalline porosity
  - c) Crystal orientation
  - d) The crystallite compliance
  - e) The polycrystalline compliance, which can be affected by the weight loss
- 6 Generation of inter-crystalline stresses at and after "turnaround" may also be governed by the generation of new cracks between crystals and particles. This will lead to a deterioration of thermal conductivity, modulus and failure strength.
  - 7 The change in polycrystalline compliance due to radiolytic weight loss is a major contributing factor to the delay in "turnaround" and the increase in dimensional change.
  - 8 The model can be further enhanced to account for other polycrystalline behaviours such as dimensional and CTE changes for three dimensional needle and spheroid geometries, caused by fast neutron damage and radiolytic oxidation.

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