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ANALYTICAL DESCRIPTION OF GROWTH OF BERYLLIUM OXIDE DURING NEUTRON IRRADIATION

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ABSTRACT

A simple analytical model is developed which adequately describes the available data on the lattice and macroscopic growth of beryllium oxide under neutron irradiation. This model is then used for interpolation and extrapolation of existing data. The model has a large number of adjustable parameters and it is emphasised that it does not necessarily bear any direct relation to the actual defect structure.

CONTENTS

1. INTRODUCTION

In this note we attempt to derive a simple analytical expression which adequately describes the available data on the growth of beryllium oxide under neutron irradiation. The justification for doing this is simply to allow interpolation and extrapolation of existing results over a wider range of temperature, dose, and dose rate as such information is required for reactor design purposes. Ideally, such an analytical expression should be based on knowledge of the defect structure and defect production mechanisms, and the ability of the model to predict behaviour then provides confirmation of the defect models. However, the situation in beryllium oxide is too complex to allow this to be done at this stage.

Two earlier attempts have been made to describe analytically the variation of the growth of beryllium oxide under neutron irradiation as a function of irradiation temperature and dose rate.

In a previous publication (Hickman and Pryor 1964) we assumed that the damage was a result of competition between production of defects at a constant rate and annealing with a spectrum of activation energies. At that time, results were only available at doses up to 8×10^{20} nvt >1 MeV at temperatures below 700°C and the treatment was found to describe these results reasonably well. Subsequently more experimental data became available which showed that the original treatment failed to give reasonable predictions under some conditions, particularly in relation to the macroscopic growth at temperatures above 700°C.

An alternative treatment of the same problem by Collins (1964) assumed that the in-pile annealing process had a unique activation energy. Although this treatment gave a somewhat better fit to the results at high temperatures, it failed to predict the effect of dose rate and it predicted saturation of the growth at far lower doses than is observed in practice, particularly at low dose rates. The values for the constants which Collins had to use to fit the data were also open to criticism (Hickman (1966).

In this note we take account of recent data and modify our original treatment in such a way as to produce the simplest model which

is compatible with most of the data.

2. THEORY

Information which must be taken into account in addition to that considered previously is :

(i) Dose rate does not appear to have any significant effect on the damage at temperatures up to 700°C (Hickman and Chute 1964).

(ii) The lattice growth as measured by changes in the lattice parameters decreases steadily with increasing temperature and becomes negligible at 1000°C (Hickman and Chute 1964).

(iii) The macroscopic growth and the lattice growth are equal within experimental error up to 550°C (Hickman and Walker 1966).

(iv) At 900°C to 1100°C considerable macroscopic growth is observed (General Electric workers 1965a, 1965b; J.G. Napier unpublished) although the X-ray growth is negligible.

(v) At least at 900-1000°C little of this growth can be attributed to helium bubble formation (J.G. Napier unpublished).

Neglecting the effects of volume changes due to helium bubble formation the macroscopic and X-ray growths will be given by :

$$G_M = C_i \Delta v_i + C_v \Delta v_v + C_v \Delta V - C_i \Delta V \quad ,$$

$$G_X = C_i \Delta v_i + C_v \Delta v_v \quad ,$$

where Δv_i = lattice distortion per interstitial

Δv_v = " " " vacancy

C_i = concentration of interstitials

C_v = " " vacancies

ΔV = atomic volume .

The macroscopic growth G_M will equal the X-ray growth G_X if $C_i = C_v$ but $G_M > G_X$ if $C_v > C_i$. We then require equations for C_i and C_v as a function of dose rate and temperature such that C_i becomes negligible by 1000°C

whilst C_v is still significant.

In our previous treatment no distinction was made between interstitials and vacancies. Both were assumed to be produced by the irradiation at constant concentration in a band with activation energies for annealing from Q_1 to Q_2. We now modify this assumption so that the maximum annealing energy for the interstitials produced by irradiation is Q_{2i} and the maximum energy for the vacancies is a lower value, Q_{2v}. We retain the assumption that the total production rates of interstitials and vacancies are the same, and those vacancies which do not anneal between Q_{2i} and Q_{2v} are assumed to be produced in a stable configuration with a single high activation energy for annealing, Q_{vs} . This is illustrated in Figure 1. A hypothesis along these lines seems to be demanded by the data, but there seems to be little point in speculating on possible phenomenological explanations.

The equations governing the concentration of interstitials and vacancies follow from those of our previous paper.

$$C_i = K\emptyset t_i \frac{KT}{Q_{2i} - Q_1} \left[\beta (A_{2i} t_i) - \beta (A_1 t_i) \right]$$

$$C_v = K\emptyset t_i \left[\frac{KT}{Q_{2v} - Q_1} \left\{ \beta (A_{2v} t_i) - \beta (A_1 t_i \right\} \left(\frac{Q_{2v} - Q_1}{Q_{2i} - Q_1} \right) + \left(\frac{Q_{2i} - Q_{2v}}{Q_{2i} - Q_1} \right) \frac{1 - \exp (-A_{vs} t_i)}{A_{vs} t_i} \right] ,$$

where $A_1 = D_o \exp (-Q_1/KT)$ and similarly for A_{2v}, A_{2i} and A_{vs}. (The pre-exponential D_o is assumed the same for all annealing processes); $K\emptyset$ is the total production rate of interstitials or vacancies; KT is Boltzmann's constant by absolute temperature; t_i is the irradiation time and the function β is defined by :

$$\beta(z) = (1-e^{-z})/z - Ei(-z) \quad ,$$

where Ei is the exponential integral function.

The pre-exponential D_o is assumed to be 2×10^7 sec^{-1} (This corresponds to diffusion over about 100-1000Å. This figure was previously quoted erroneously at 3×10^{10} sec^{-1}). The production rate $K\emptyset$ is obtained

from the mean of all low temperature results. The value of Q_1 is of no great significance; it is only introduced to give a levelling off of growth rate in the "pile temperature" region. The theory could be formulated with $Q_1 = 0$. So, essentially, only the three activation energies Q_{2i}, Q_{2v} and Q_{vs} are available to fit all results. The ratio $\Delta V/\Delta v_i$ is assumed to be 0.7 (Sabine et al. 1963) and ΔV_v is assumed to be zero.

3. COMPARISON WITH RESULTS

The best fit to the experimental data was obtained with the following constants:

$Q_1 = 1.0$ eV

$Q_{2i} = 3.2$ eV

$Q_{2v} = 2.6$ eV

$Q_{vs} = 3.8$ eV

$K\emptyset t_i = 0.38\%$ growth per 10^{20} nvt when $C_i = C_v$. (single crystal value)

The growth curves at various temperatures obtained using these constants are shown in Figure 2 for a dose rate of 2.5×10^{13} nv > 1 MeV corresponding to HIFAR irradiations, and in Figure 3 for a dose rate of 2.0×10^{14} nv > 1 MeV corresponding to E.T.R. irradiations.

Note that these curves apply to single crystals. The same curves will apply to lattice growth of polycrystalline material but to obtain the macroscopic growth of high density polycrystalline material a value for $K\emptyset t_i$ of 0.46% per 10^{20} nvt should be used.

It will be noted that the curves meet all the requirements listed above, namely :

(i) The X-ray and macroscopic growth only diverge at temperatures above 600°C.

(ii) The effect of dose rate is small below 700°C.

(iii) Significant macroscopic growth is still observed at 1000°C although X-ray growth is negligible.

In Table 1 all Lucas Heights observations on X-ray growth are compared with predictions. It can be seen that with one or two exceptions there is reasonable agreement over a wide range of temperatures and doses. Errors in dose measurement (± 10-15%), temperature estimation (± 25°C), growth measurements (up to ± 10%), can easily account for the discrepancies. In Table 2 some comparisons are made with macroscopic growth measurements at 900-1100°C obtained by General Electric workers (1965a, 1965b). These measurements were on polycrystalline samples which other techniques showed to be free of microcracking. The growths predicted from the equations have been multiplied by a factor of 1.2 to account for the fact that the macroscopic growth of polycrystalline materials at elevated temperatures appears to be about 20% greater than in single crystals.

Again reasonable agreement is observed although the theory appears to overestimate the growth at high neutron doses at 1000°C.

In summary it must be emphasised that the derived equations and constants must not be taken too literally, that is, although they are found to describe the available data reasonably well we do not claim that this agreement is evidence that the defect model on which they are based is necessarily correct, particularly when the many adjustable parameters are taken into account. In fact, in some respects it is contrary to recent ideas on the defect structure (see for instance Hickman 1966). There are also two aspects of the behaviour which the equations do not predict:

(i) Saturation of the volume changes has been observed to occur after irradiation at 100°C at a value of approximately 4 to 4.2 per cent. This is not predicted and is presumably due to some defect interaction processes. The equations therefore do not apply to dose-temperature conditions which predict volume changes greater than 4%.

(ii) Volume changes due to helium bubble formation are not allowed for. As stated earlier, in some materials at least these are not thought to be significant up to 1000°C but at higher temperatures significant volume changes due to helium bubbles will probably occur. In the absence of experimental data in this region and in view of the likelihood that these changes will be very structure sensitive we do not feel that they can be allowed for at this stage.

4. REFERENCES

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T A B L E 1.

COMPARISON OF PREDICTED AND MEASURED X-RAY GROWTH IN A.A.E.C. EXPERIMENTS

Reference to Rig	Material*	Dose nvt > 1 MeV	Temp. °C	$\frac{\Delta V}{V}$ (Measured)	$\frac{\Delta V}{V}$ (Predicted)	Variation %
X-127	P.C.	7×10^{20}	630	0.9	0.8	-11
X-97 A	S.C.	2.5×10^{20}	400	0.53	0.56	+ 8
C	S.C.	4×10^{20}	390	0.95	0.92	- 3
D	S.C.	5×10^{20}	470	0.82	0.92	+12
E	S.C.	5×10^{20}	475	0.89	0.92	+ 3
X-73 A	P.C.	3.9×10^{20}	520	0.60	0.60	-
B	P.C.	4.5×10^{20}	670	0.50	0.40	-20
C	P.C.	3.2×10^{20}	590	0.51	0.44	-12
X-83 A	P.C.	7×10^{20}	500	1.42	1.20	-15
B	P.C.	8.4×10^{20}	690	1.00	0.70	-30
C	P.C.	7.7×10^{20}	590	1.20	1.0	-17
X-96 A	P.C.	1×10^{21}	300	2.66	2.64	-
C	P.C.	1.7×10^{21}	530	2.09	2.5	+20
F	P.C.	1.3×10^{21}	380	2.80	3.0	+ 8

*P.C. = polycrystalline, S.C. = single crystal

T A B L E 2.

COMPARISON OF PREDICTED MACROSCOPIC GROWTH WITH RESULTS QUOTED BY GENERAL ELECTRIC WORKERS (1965a, 1965b)

Dose nvt > 1 MeV	Temp. °C.	$\frac{\Delta V}{V}$ (Measured)	$\frac{\Delta V}{V}$ (Predicted)	Variation %
1×10^{21}	900	1.2	0.9	-25
5.5×10^{20}	950	0.6	0.54	-10
1×10^{21}	1000	0.9	0.85	- 5
2.7×10^{21}	11	1.6	2.0	+30
4.4×10^{21}	11	2.1	3.0	+40
5.5×10^{21}	1100	0.3	0.35	+16

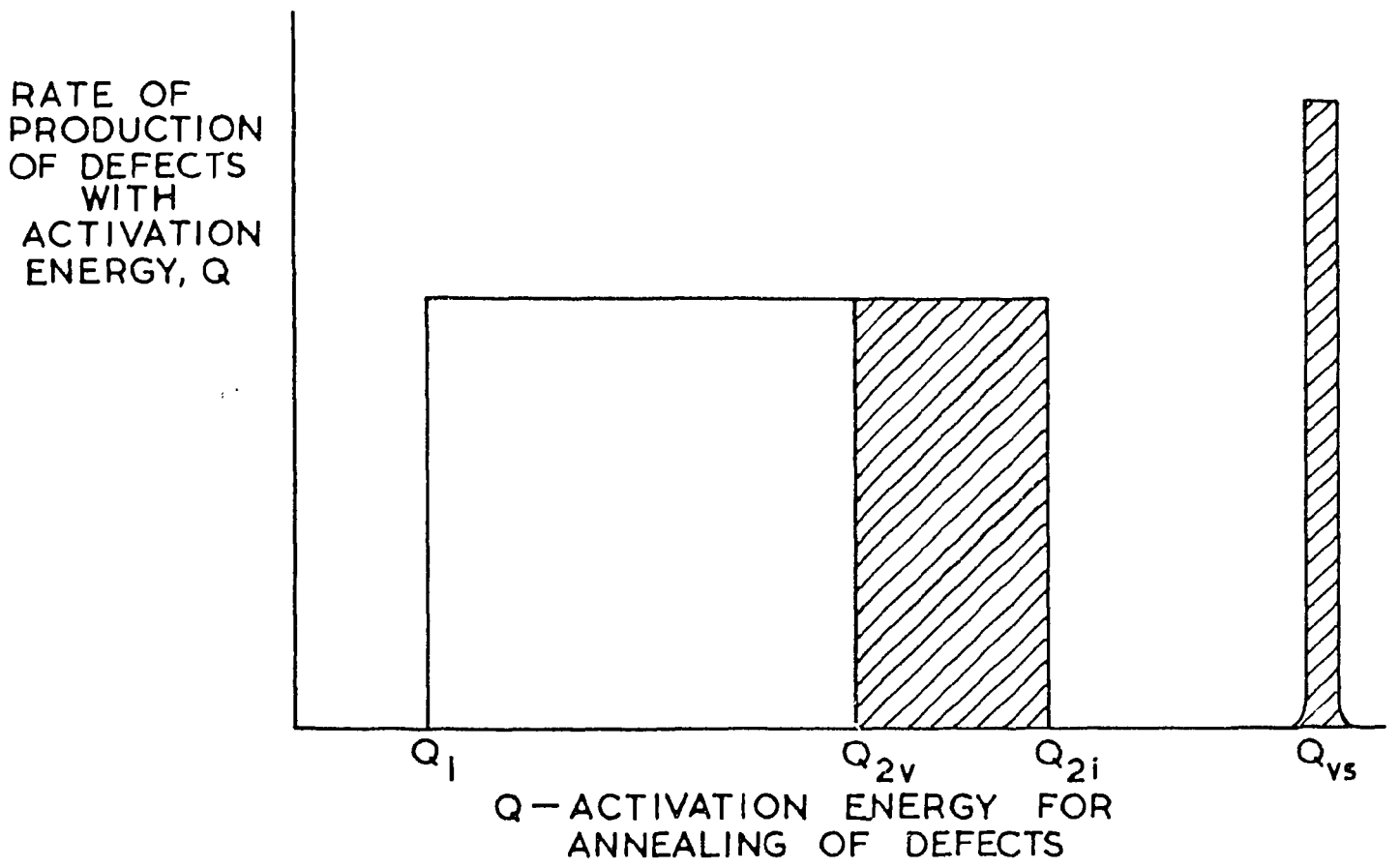

FIGURE 1. SCHEMATIC DIAGRAM OF ACTIVATION ENERGY SPECTRUM MODEL USED IN THE CALCULATIONS (The shaded areas are equal)

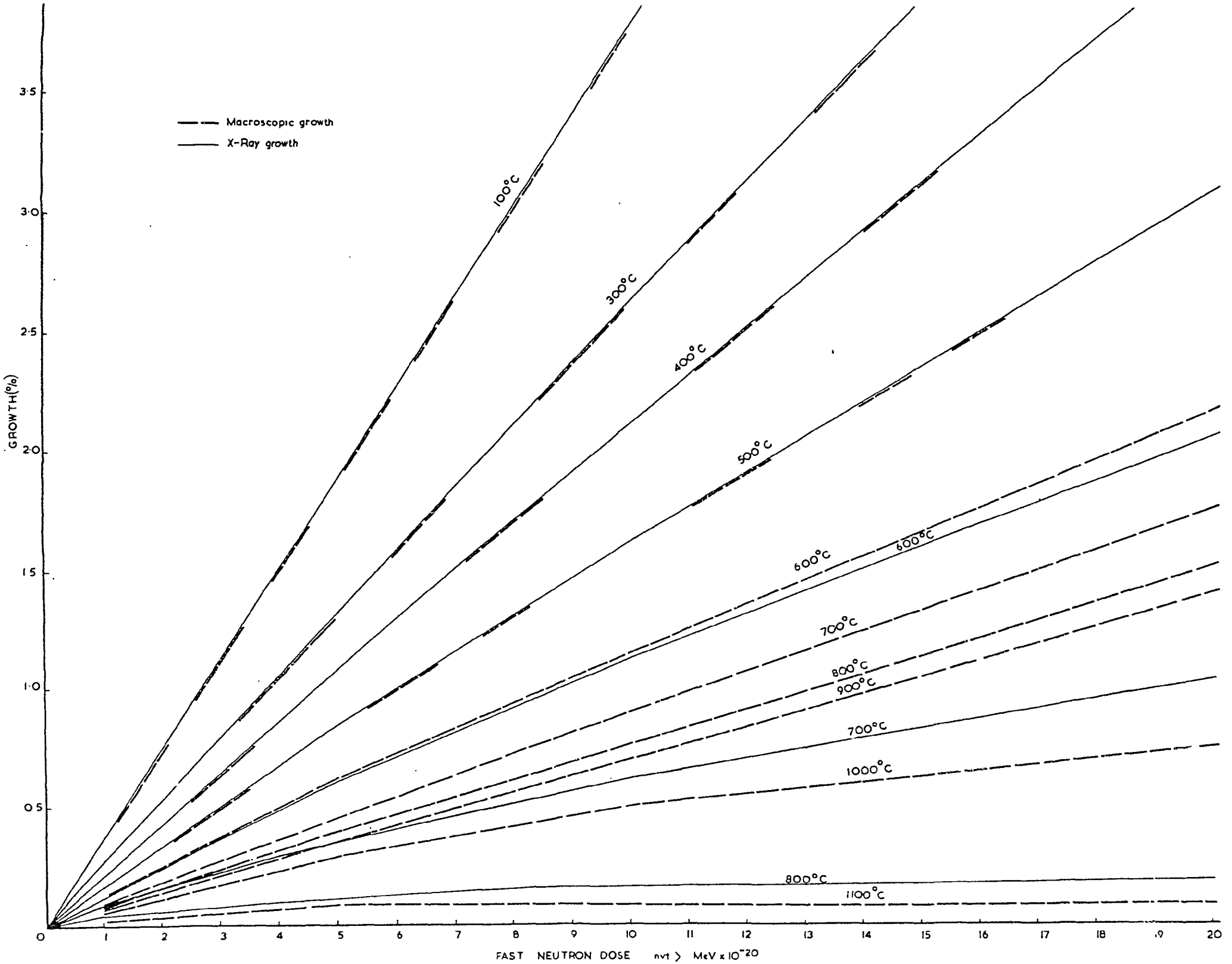

FIGURE 2. PREDICTED GROWTH OF BERYLLIUM OXIDE SINGLE CRYSTALS AT A DOSE RATE OF 2.5×10^{13} nv

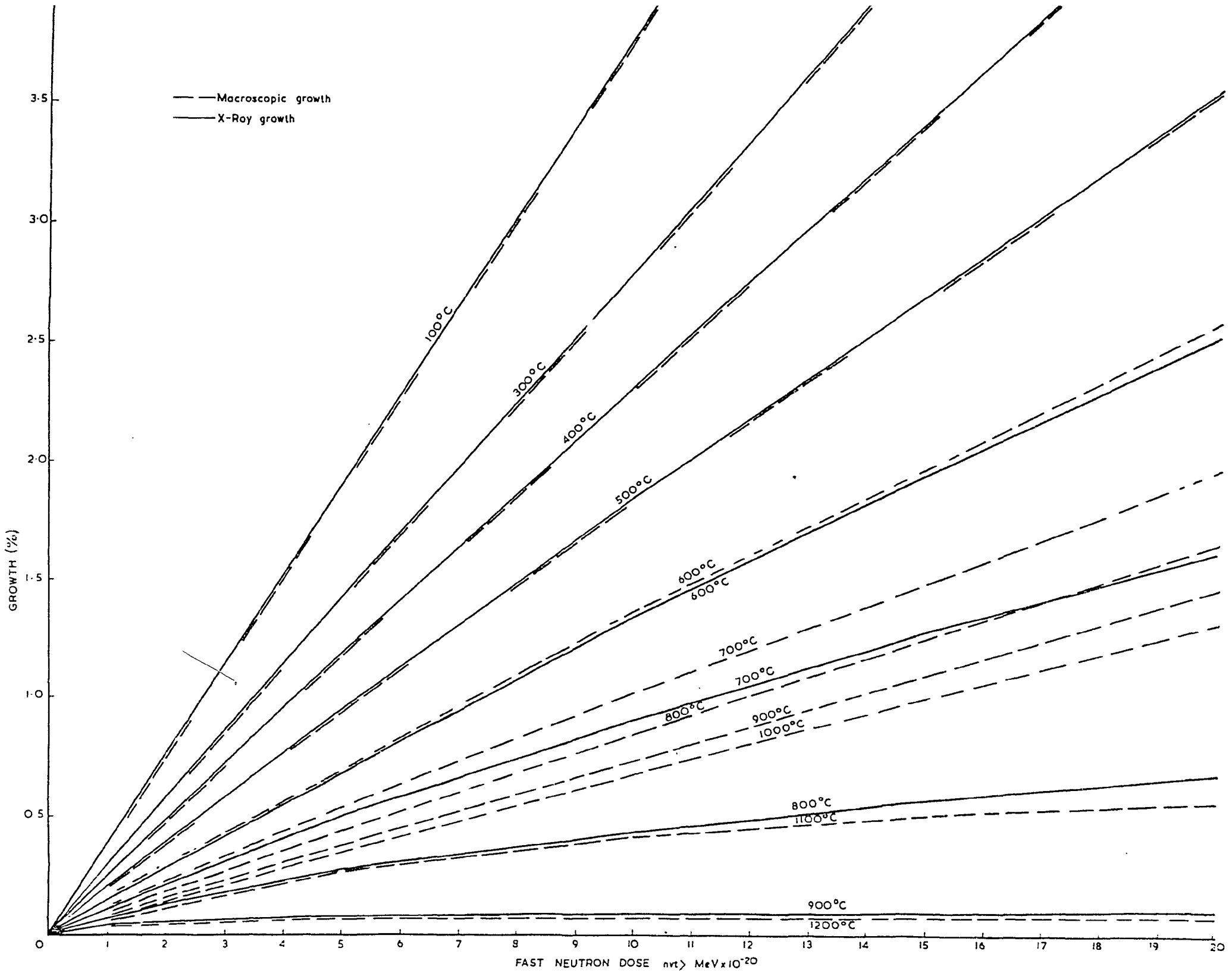

FIGURE 3. PREDICTED GROWTH OF BERYLLIUM OXIDE SINGLE CRYSTALS AT A DOSE RATE OF 2.0×10^{14} nv