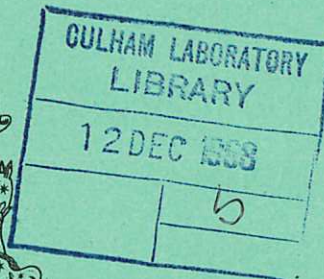


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# THE TEMPERATURE DEPENDENCE OF DEUTERIUM ION TRAPPING IN NIOBIUM, TITANIUM, ZIRCONIUM AND ERBIUM

G. M. McCracken

D. K. Jefferies

P. Goldsmith

Culham Laboratory  
Abingdon Berkshire

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by

G.M. McCracken  
D.K. Jefferies  
P. Goldsmith

U.K.A.E.A. Research Group,  
Culham Laboratory,  
Abingdon,  
Berks.

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## A B S T R A C T

Measurements have been made of the trapping of 18 keV deuterium ions in these chemically active metals with a view to finding out under what conditions high trapping efficiencies can be achieved. In particular the role of the hydrogen-metal binding energy has been investigated and found to be a major factor in determining whether a metal will trap ions at very large doses.

The number of incident ions re-emitted during bombardment is measured using a quadrupole mass filter, and the trapping efficiency is taken directly from this measurement. Thus trapping efficiency can be measured continuously during the period of bombardment. Measurements have been made as a function of time at fixed temperatures for a range of temperatures from 77<sup>o</sup> to 1000<sup>o</sup>K. These show that a high trapping efficiency is maintained for high doses at intermediate temperatures in the metals studied, whereas at high temperatures and also at low temperatures the trapping efficiency falls off for high doses. A physical model is proposed which explains these results in terms of (a) the diffusion of the trapped deuterium in the metal and (b) the potential barrier determined by the heat of solution of the deuterium in the metal.

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## 1. Introduction

The trapping of energetic ions in metals, and their subsequent release has been the subject of many investigations in recent years (Colligon and Leck (1962), Brown and Davies (1963), Kornelson (1964)). Most investigations have been concerned with the rare gas ions in order to eliminate the complications of chemical interactions between the incident ions and the metal lattice, but recently interest has been shown in chemically active gases (Borovik et al. (1965)) and some evidence obtained that chemical binding effects play a role in these cases (McCracken and Maple (1967)). It has been shown, for example, that under some circumstances the trapping efficiency of hydrogen ions in reactive metals can be extremely high, and remain high for very large doses arriving at the surface. It has also been shown in the case of titanium that this trapping is very temperature dependent (Borovik et al. (1966), Freeman et al. (1966), McCracken and Maple, (1967)). The purpose of the present study was to investigate a number of metals which reacted chemically with hydrogen to form hydrides, and thus to investigate the role which the hydrogen-metal binding energy played. For this purpose a group of four metals, Nb, Ti, Zr and Er were chosen, which had a wide range in their hydride heat of formation. Measurements have been made of their trapping efficiency  $\eta$  directly, by the partial pressure rise technique used in earlier work (McCracken and Maple, (1967)). From a series of measurements of  $\eta$  as a function of time at a number of definite temperatures, curves have been obtained showing the temperature dependence of the trapping efficiency at any arbitrary time and how the trapping efficiency of a metal can be correlated with the heat of formation of the hydride.

## 2. Experimental

The apparatus has previously been described in detail (McCracken, Maple and Watson (1966)). A beam of deuterium ions from an r.f. source is accelerated to an energy of about 20 keV, mass analysed and focussed onto a target, in a



target chamber within which an ultra high vacuum is maintained. The rise in deuterium partial pressure when the beam strikes the target is measured with a quadrupole mass filter, and this partial pressure rise is a measure of the ions re-emitted from the surface under bombardment. The four principal targets are mounted on a re-entrant stainless steel tube as shown in Fig.1. The tube can be moved up and down by means of bellows so that each target in turn can be brought into the beam and can be maintained at any fixed temperature between  $77^{\circ}\text{K}$  and  $1100^{\circ}\text{K}$  by means either of cooling liquids or a simple electric heater inside it. The inside of the tube is evacuated when heated to temperatures above  $500^{\circ}\text{K}$ .

The purities of the samples used were Nb, 99.9%; Ti, 99.7%; Zr, 99.8%; Er, 99.8%. Sample preparation initially consisted simply of degreasing the rolled sheet supplied by the manufacturer and then vacuum brazing to the stainless steel tube using nickel gold eutectic at a temperature of  $1223^{\circ}\text{K}$ . Later samples were mechanically polished to  $0.1\ \mu\text{m}$  surface finish before brazing, but no difference in trapping behaviour was observed as a result. Surface erosion due to sputtering is expected to clean the targets and to be the principal factor controlling surface conditions during the experiments. The target temperatures were measured by chromel alumel thermocouples which were directly spotwelded to them.

In addition to the four principal targets, a fifth target - made of molybdenum - was mounted on a bellows operated cantilever. In earlier work (McCracken and Maple (1967)) it has been shown by measurements of trapping followed by measurements of thermal desorption, that at all temperatures above about  $400^{\circ}\text{K}$  molybdenum rapidly saturates and has a trapping efficiency of zero. The partial pressure rise observed when the beam strikes this target can thus be taken as a measure of beam intensity and used as an in situ calibration of the mass filter used to make all partial pressure measurements. The trapping efficiency of any target is given by:



$$\eta = \frac{I_{Mo} - I_T}{I_{Mo}}$$

where  $I_{Mo}$  is the signal detected by the mass filter when a primary ion current of a given value strikes the molybdenum target, and  $I_T$  the signal when the same primary beam strikes the target under investigation. Effects due to adsorption and desorption of the deuterium released from the target on the target chamber walls have been shown to be negligible (McCracken and Maple (1967)).

### 3. Results

The four targets have been bombarded by deuterium ions of 18 keV, using ion currents of about  $700 \mu\text{A}/\text{cm}^2$ . The target area bombarded was  $0.07 \text{ cm}^2$ . Direct measurements of the trapping efficiency were made as a function of time at a variety of fixed temperatures. The results obtained for niobium are shown in Fig.2. These results indicate the same trends as observed for Ti (Freeman et al. (1966)); high trapping is observed at intermediate temperatures from  $300^\circ - 500^\circ\text{K}$  for all doses, while at low temperatures and at high temperatures the trapping efficiency decreases with dose. The results obtained for the other three metals are similar except that the upper temperature at which the trapping efficiency decreases gets progressively higher in the four metals in the order Nb, Ti, Zr, Er. Results for erbium, the metal which trapped at the highest temperatures, are shown in Fig.3.

If the trapping efficiency measured after a fixed arbitrary bombardment time (18 minutes or a dose of  $5 \times 10^{18}$  ions/ $\text{cm}^2$ ) is plotted against temperature, from a series of runs at different temperatures, a clear pattern emerges as shown in Fig.4. The high trapping efficiency is observed in a different temperature range for each of the four metals.

#### 4. Discussion

The variation in the trapping efficiency for hydrogen of these metals can be explained in terms of the model briefly discussed previously (McCracken and Maple (1967)). After the ions have slowed down and reached thermal energies (they have a mean range  $\sim 2.0 \times 10^{-5}$  cm, Schjøtt (1966)) they may then diffuse through the lattice. However the positive heat of solution of hydrogen in the metal implies that ions which reach the metal surface encounter a potential barrier inhibiting escape. The probability of escape will be given simply by the usual rate process term  $e^{-Q/RT}$ , where  $Q$  is the heat of solution. Since the activation energies for diffusion are much lower (typically 5 kcal/mole e.g. Sawatsky (1963); Zamir and Cotts (1964); Marshall (1965)) than the heat of solution (20-50 kcal/mole e.g. Morton and Stark (1960); Albrecht et al. (1959); Jones et al. (1964)) the implanted hydrogen ions will be able to diffuse through the lattice, without being able to escape from the surface, over a wide range of temperatures. At higher temperatures, however, the diffusing atoms will have an increasing probability of getting over the potential barrier thus leading to decreasing trapping efficiencies.

This mechanism immediately predicts a close correlation between the potential barrier  $Q$  and the temperature at which the trapping efficiency decreases. The experimental results give good confirmation of this as illustrated in Fig.5, where the heat of formation of the hydride is plotted against the temperature at which the trapping efficiency decreases to two arbitrary values. The heat of formation of the complete hydride has been used to illustrate this correlation, but as the heat of solution is concentration dependent and the concentration at the surface cannot be directly determined, no quantitative conclusions can be directly drawn. However, the variation of trapping efficiency with time and temperature can be calculated on the basis of the model discussed by solving the diffusion equation with appropriate boundary conditions. It is intended to discuss the comparison of such a solution with experimental results in a later publication.



At low temperatures,  $\sim 77^{\circ}\text{K}$ , the thermal diffusion rate will be reduced to a negligible amount and thus with the high initial trapping efficiency the concentration near the surface, within the range of the incident ions, will increase rapidly. It is found that for all metals the decrease in  $\eta$  comes at a dose equivalent to  $10^{18}$  ions/cm<sup>2</sup> which, if distributed throughout the solid to a depth equivalent to the initial median range of the ions in the metal, would correspond to a deuterium/metal atom ratio of the order of 1.0. Clearly at this concentration some bombardment induced release process, similar to physical sputtering, could take place and explain the sudden decrease in  $\eta$  despite the potential barrier at the surface.

If the foregoing argument is correct, then the reason why trapping is maintained beyond doses of  $10^{18}$  ions/cm<sup>2</sup> at higher temperatures is not simply that there is a barrier at the surface, but also because the diffusion coefficient is sufficiently large to prevent a high concentration occurring near the surface within the range of subsequent ions.

The temperature at which  $\eta$  increases is thus an indication of the diffusion coefficient of hydrogen in the metal. Although absolute values of diffusion coefficient are not available for all the metals, the activation energies for diffusion for Nb, Zr, and Ti are in the same order as the temperature at which  $\eta$  increases. Provided the pre-exponential factor  $D_0$  in the expression for the diffusion coefficient is approximately the same for all the metals, as is normally the case, the activation energy will determine the relative order of the diffusion coefficients. The trapping at low temperatures by niobium is consistent with the results obtained for the high sorption capacity of niobium films for hydrogen gas at low temperatures, which also implies a high diffusion coefficient (della Porta and Giorgi (1966)). No information is available on the diffusion coefficient for erbium but it is interesting to note that the results imply that the diffusion coefficient of deuterium in erbium is very much lower at  $300^{\circ}\text{K}$  than the diffusion coefficient of deuterium in the other three metals.



## 5. Conclusions

The most obvious application of the information obtained about the trapping of ions in metals is in the design of beam traps for high current density ion beams, particularly in the field of nuclear fusion research. However the understanding obtained of the physical processes involved in trapping should also be of importance in many vacuum devices, particularly ion pumps.

The success of the physical model proposed in explaining the experimental results implies that it could be used for predicting the trapping behaviour of other metals, provided the surface potential barrier and the diffusion constants are known. On the basis of the model one would expect that for other active gases where the activation energy for diffusion is higher, much higher temperatures would be required to maintain high trapping efficiencies at high doses. However, it does not follow that trapping will occur for all metals having positive heats of formation of the hydride. If for a particular gas-metal combination the activation energy for diffusion is of the same order or higher than the heat of formation of the hydride, then no trapping will occur beyond the point at which a saturated solution is built up within the range of incident ions.

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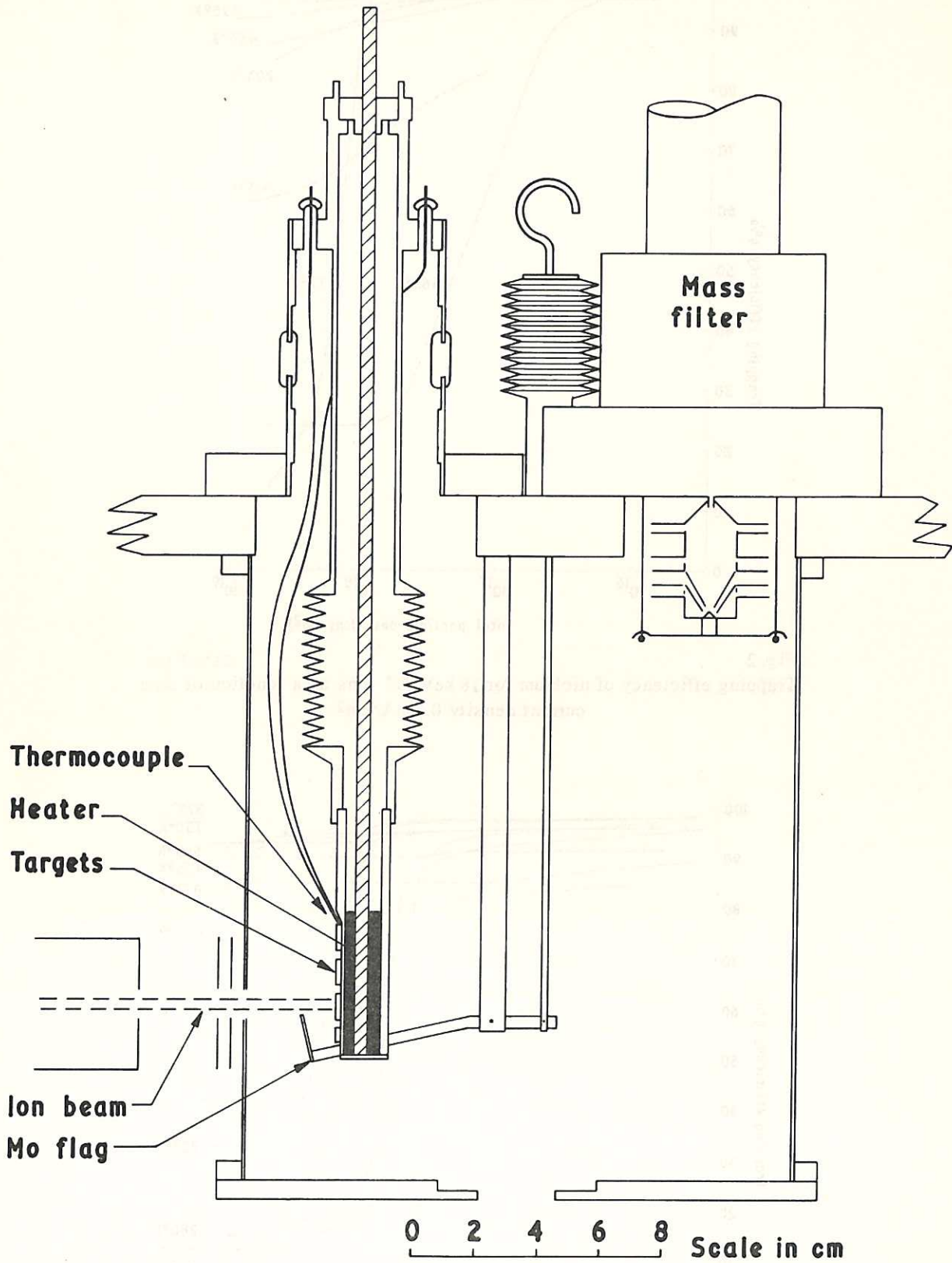


Fig. 1 Target assembly for trapping measurements (CLM-P 166)

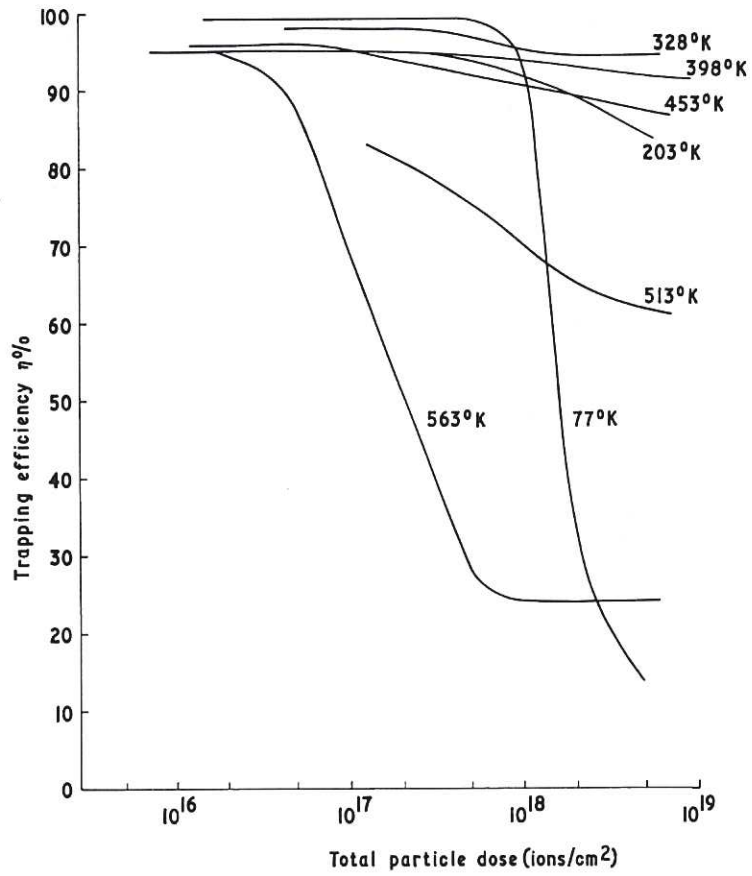


Fig. 2 (CLM-P 166)  
 Trapping efficiency of niobium for 18 keV  $D^+$  ions as a function of time  
 current density 0.7 mA/cm<sup>2</sup>

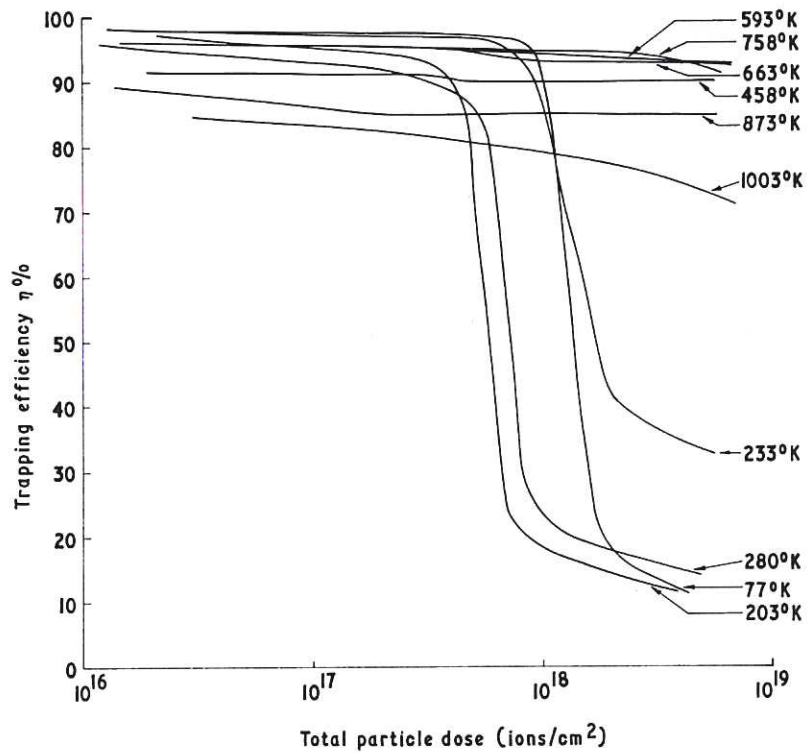


Fig. 3 (CLM-P 166)  
 Trapping efficiency of erbium for 18 keV  $D^+$  ions as a function of time  
 current density 0.7 mA/cm<sup>2</sup>

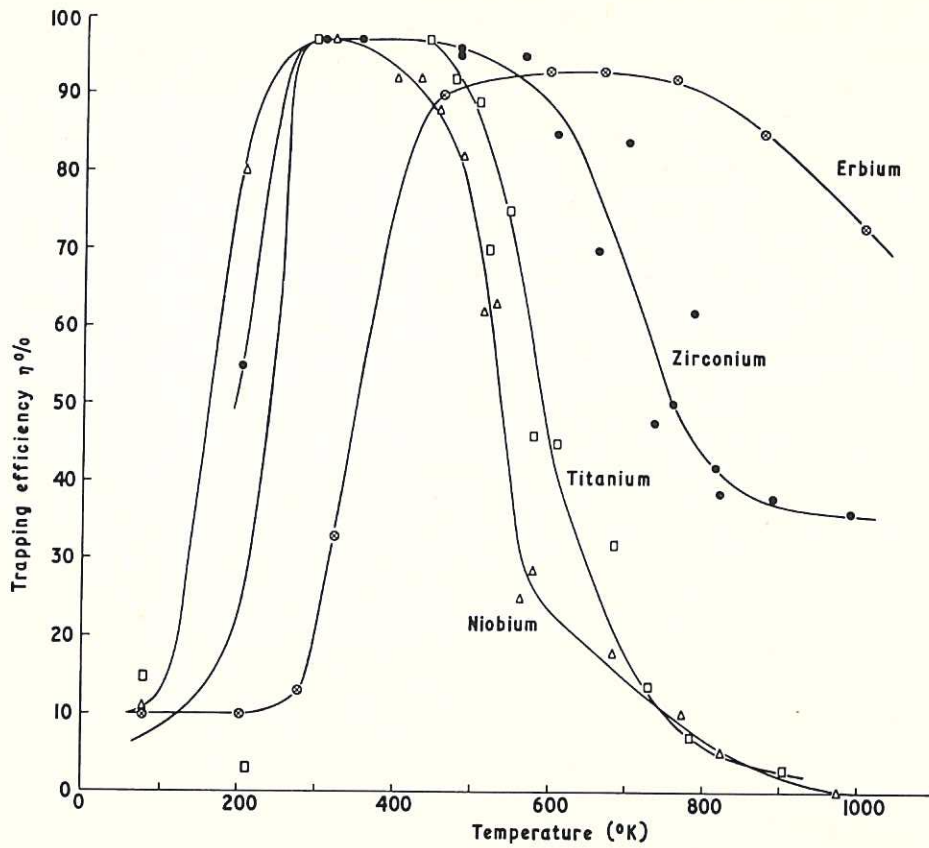


Fig. 4 (CLM-P166)  
 Trapping efficiency of Nb, Ti, Zr and Er for 18 keV D<sup>+</sup> ions as a function of temperature. Total ion dose  $5 \times 10^{18}$  ions/cm<sup>2</sup>

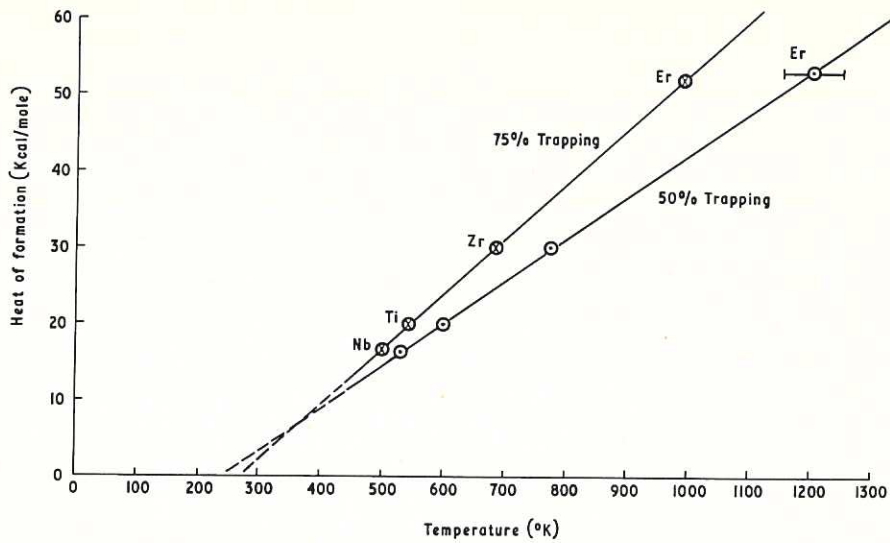


Fig. 5 (CLM-P166)  
 Variation of temperature at which trapping efficiency decreases, with the heat of formation of the hydride





