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J. P. Kopasz, C. A. Seils, and C. E. Johnson

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Chemical Technology Division  
Argonne National Laboratory  
Argonne, IL 60439

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TRITIUM RELEASE FROM IRRADIATED LITHIUM ALUMINATE, CAN IT BE IMPROVED?

J. P. Kopasz, C. A. Seils, and C. E. Johnson  
Argonne National Laboratory,  
9700 South Cass Avenue  
Argonne, Il 60439

ABSTRACT

Lithium aluminate is an attractive material (in terms of its chemical, mechanical and irradiation properties) for breeding tritium in fusion reactors; however, its tritium release characteristics are not as good as those of other candidate materials. To investigate whether tritium release from lithium aluminate can be improved, we have studied the tritium release from irradiated samples of pure lithium aluminate, lithium aluminate doped with Mg, and lithium aluminate with a surface deposit of platinum. The release was studied by the temperature programmed desorption (TPD) method. Both the platinum coating and magnesium doping were found to improve the tritium release characteristics, as determined by TPD. Tritium release shifted to states with lower activation energies for the altered materials.

## 1. INTRODUCTION

For breeding tritium fuel in fusion reactors, lithium aluminate compares favorably with other candidate solid breeder materials in terms of chemical, mechanical, and irradiation properties; however, tritium release from lithium aluminate is much slower than that from lithium oxide or lithium zirconate. Thus, we are striving to improve the tritium release from lithium aluminate and gain a more thorough understanding of the mechanisms involved in the tritium release from this class of materials.

An earlier experiment (TRIO) demonstrated an improvement in tritium release from lithium aluminate by adding hydrogen to the purge gas[1]. The TRIO experiment also demonstrated the deleterious effect of adding oxygen to the purge stream[1]. If altering the gas phase above the solid can cause such drastic changes in the tritium release characteristics, it is possible that the solid itself can be modified to bring about similar changes in the tritium release behavior.

The key to improving tritium release from lithium aluminate is to alter the solid in such a way as to increase the rate of the slowest, or rate determining, step in the tritium release process. If diffusion is rate limiting, the tritium release rate can be increased by doping the material to increase the tritium diffusivity. Increased diffusion has been reported in  $Al_2O_3$  doped with Mg and in SiC doped with Al by Kitazawa and Coble[2]. The dopants reportedly increased the tritium diffusivity in these materials by several orders of magnitude. Calculations performed for lithium aluminate suggest that if diffusion is rate controlling the tritium release can be substantially improved by doping the material with Mg[3]. However, for lithium aluminate, tritium release may be desorption controlled. If surface desorption is rate controlling, the solid surface can be altered to provide low energy sites for desorption of tritium by substituting some surface sites or coating the surface with a catalyst for hydrogen or water desorption. Quanci has attributed an enhanced tritium desorption to the presence of platinum impurities on single crystals of lithium oxide[4].

In an attempt to improve the tritium release from lithium aluminate and to gain a better understanding of the mechanisms of tritium transport in lithium ceramics, we have investigated tritium release from modified lithium aluminate. Three types of lithium aluminate samples have been prepared and irradiated at the TRIGA reactor at the University of Illinois, Urbana-Champaign: pure single crystals, single crystals doped with Mg, and single crystals sputter coated with Pt. The Mg doped material should increase the tritium diffusivity by increasing the number of lithium vacancies[3]. The Pt-coated material is expected to alter the surface characteristics, and increase the desorption rate. Tritium release characteristics were determined by temperature programmed desorption (TPD) measurements.

a. Experimental

Single crystals of pure and Mg doped (0.3%) lithium aluminate were supplied by CEA. These crystals were grown using the Czochralski technique from a chemical bath containing  $\text{LiAlO}_2$  plus 3% by weight  $\text{Li}_2\text{O}$  (plus 0.5% Mg for the doped material) at 1973 K in an iridium crucible.[5] Crystal growth was accomplished on a seed crystal of  $\text{LiAlO}_2$  using a rotation speed of 10-15 rpm. Spark source spectrometry indicated that the Mg dopant level was 0.3%. Platinum was coated onto pure single crystals using a sputter chamber. All the crystals were dried at 1073 K under vacuum for 4 hours. They were then transferred to a helium atmosphere glovebox, where each individual crystal was placed in an aluminum capsule. The capsules were cold welded in the glovebox, then checked for leaks using a helium leak detector. The capsules were irradiated in the Cadmium Lined Neutron Activation Tube at the University of Illinois, Urbana Champaign, for 3 hours at a power level of 1500 kW. This cadmium-lined facility was employed to harden the neutron spectrum and ensure that the tritium production within the single crystals was spatially uniform. The calculated amount of tritium produced is 1  $\mu\text{Ci}$  per single crystal.

Tritium release from the  $\text{LiAlO}_2$  crystals was measured under a flow of helium plus 0.1% hydrogen in a stainless steel annealing apparatus. A schematic of the experimental arrangement used for this measurement is shown in Figure 1. A single crystal was transferred from the sealed aluminum capsule to a sample holder in the helium-filled glovebox. The sample holder isolated the sample from the atmosphere using a set of compression fittings. The compression fittings on either side of the sample were sealed, and the sample holder was removed from the glovebox and connected to the annealing apparatus with an O-ring seal. The apparatus was evacuated, then purged with  $\text{He} + 0.1\% \text{H}_2$ , and the furnace brought to the desired test temperature. The sample was then introduced into the heated zone by loosening the compression fitting just enough to slide the rod holding the sample through the fittings into the heated section of the apparatus. The tritium release was determined by a proportional counter downstream from the sample. During this measurement, methane gas was bled into the proportional counter at a rate that provided it with a gas mixture of approximately 85% purge gas and 15% methane. The temperature was controlled by an OMEGA temperature controller, to provide the desired constant heating rate. Feedback to the temperature controller was provided by a thermocouple positioned in the sample holder, and separated from the sample by approximately 1/4 in. of stainless steel.

#### b. Results and Discussion

Earlier experiments performed on single-crystal lithium aluminate by Botter et al. indicated that tritium release was not diffusion controlled, even for crystals as large as 2000  $\mu\text{m}$  in diameter[6]. Our experiments support that conclusion. Temperature programmed desorption measurements performed on single crystals (2 mm dia) of pure  $\text{LiAlO}_2$  at a heating rate of 0.75 K/min show several overlapping peaks (see Figure 2). This indicates that the tritium is released from several states. If diffusion were rate limiting, a single peak would have appeared.

Information on the energetics of release from the different states was obtained by a careful analysis of the TPD data. The normalized release for first-order desorption from one state with an activation energy  $E$  during a TPD experiment is given by[7]:

$$P = 1 - \exp(-\nu b E I / RT) \quad (1)$$

where

$$I = \frac{\exp(-E/RT)}{(E/RT)^2} \left[ 1 - \frac{2!}{E/RT} + \frac{3!}{(E/RT)^2} - \frac{4!}{(E/RT)^3} + \dots \right]$$

$\nu$  = desorption pre-exponential

$b$  = heating rate

$R$  = Boltzmann's constant

$T$  = the absolute temperature

A nonlinear least-squares optimization routine was used to fit a sum of curves given by equation 1 to the observed TPD curve. The results for a sample of pure  $\text{LiAlO}_2$  are shown in Figure 2. The analysis indicates five curves are present with activation energies of 60.8, 98.7, 128.6, 154.3 and 174.4 +/- 5 kJ/mol. These activation energies are in good agreement with those obtained by Botter et. al. using a different analysis technique[6]. The amount of tritium released from each state is proportional to the area under the curves determined by equation 1. The majority of the tritium for the pure  $\text{LiAlO}_2$  (roughly 60%) was released from the state with highest activation energy. Tritium release can be improved if the population of the lower energy peaks is increased at the expense of this higher energy peak.

Doping lithium aluminate with magnesium was expected to increase the tritium diffusivity by a factor of 2 or 3 in the lower temperature region (< 673 K)[3]. The magnesium doping did affect the tritium release, as can be seen by comparing the TPD curves for the pure material (Figure 2) and Mg doped material (Figure 3). However, this effect is much less than that expected if diffusion were rate limiting. In addition, several peaks were observed in the TPD data, suggesting that tritium is also released from several different

states for the doped material. Deconvolution of the TPD curve in Figure 3 indicates five peaks were present which correspond to activation energies of 47.0, 94.6, 113.4, 155.9, and 205.0 $\pm$ 5 kJ/mol. Doping with magnesium shifts the release to lower temperature in a TPD experiment. The peaks at about 650 K and 725 K (47 and 94.6 kJ/mol peaks) for the doped material are shifted slightly from those in the pure material and are increased in intensity. In the doped material these peaks account for roughly 25% of the detected tritium, while in the pure material they account for roughly 13% of the detected tritium. The activation energy of 94.6 kJ/mol is in excellent agreement with the 99.4 kJ/mol (23.8 kcal/mol) activation energy found by Ito et al. for desorption of hydrogen from MgO[8]. This suggests that doping LiAlO<sub>2</sub> with Mg provides a low energy site on the surface (surface MgO) from which the tritium desorbs.

Platinum was deposited on the surface of single crystals of pure LiAlO<sub>2</sub> in the hopes of increasing the desorption step in the tritium release process. The platinum coating did affect the tritium release from lithium aluminate (see Figure 4). Four peaks were determined corresponding to activation energies of 71, 99, 146 and 177  $\pm$ 5 kJ/mol. The platinum coating shifts the tritium release to lower temperatures. For the platinum-coated samples, approximately 40% of the tritium was released from peaks with activation energies below 150 kJ/mol, while for samples of the pure material only 25% was released from states with activation energies below 150 kJ/mol. In addition, the low temperature peak ( $\sim$ 800 K) is shifted slightly and now corresponds to an activation energy of 71 kJ/mol. This value is in excellent agreement with the reported value for desorption of H<sub>2</sub> from platinum of 67.5 kJ/mol[9]. Also the peak at approximately 1073 K, corresponding to an activation energy of 146 kJ/mol, is in good agreement with the observed activation energy for desorption of H<sub>2</sub>O from platinum[10].

The fact that the platinum coating shifted the tritium release peaks to lower activation energy states strongly suggests that the rate-controlling step in tritium release from lithium aluminate involves the surface and not

bulk diffusion. The platinum was sputtered onto the surface, and should not effect the bulk properties such as diffusion. If diffusion were the rate-limiting step in tritium release, the platinum would have had no effect on the TPD curves.

## 2. CONCLUSIONS

TPD experiments performed on lithium aluminate suggest that tritium release from this material is controlled by surface processes. The release occurs from several different energetic states, with the majority of tritium in the pure material trapped in a state with a high activation energy. Altering the material by doping with Mg or coating with Pt improves the tritium release by providing new states with lower activation energies. These new states are believed to be associated with MgO or Pt surface sites.

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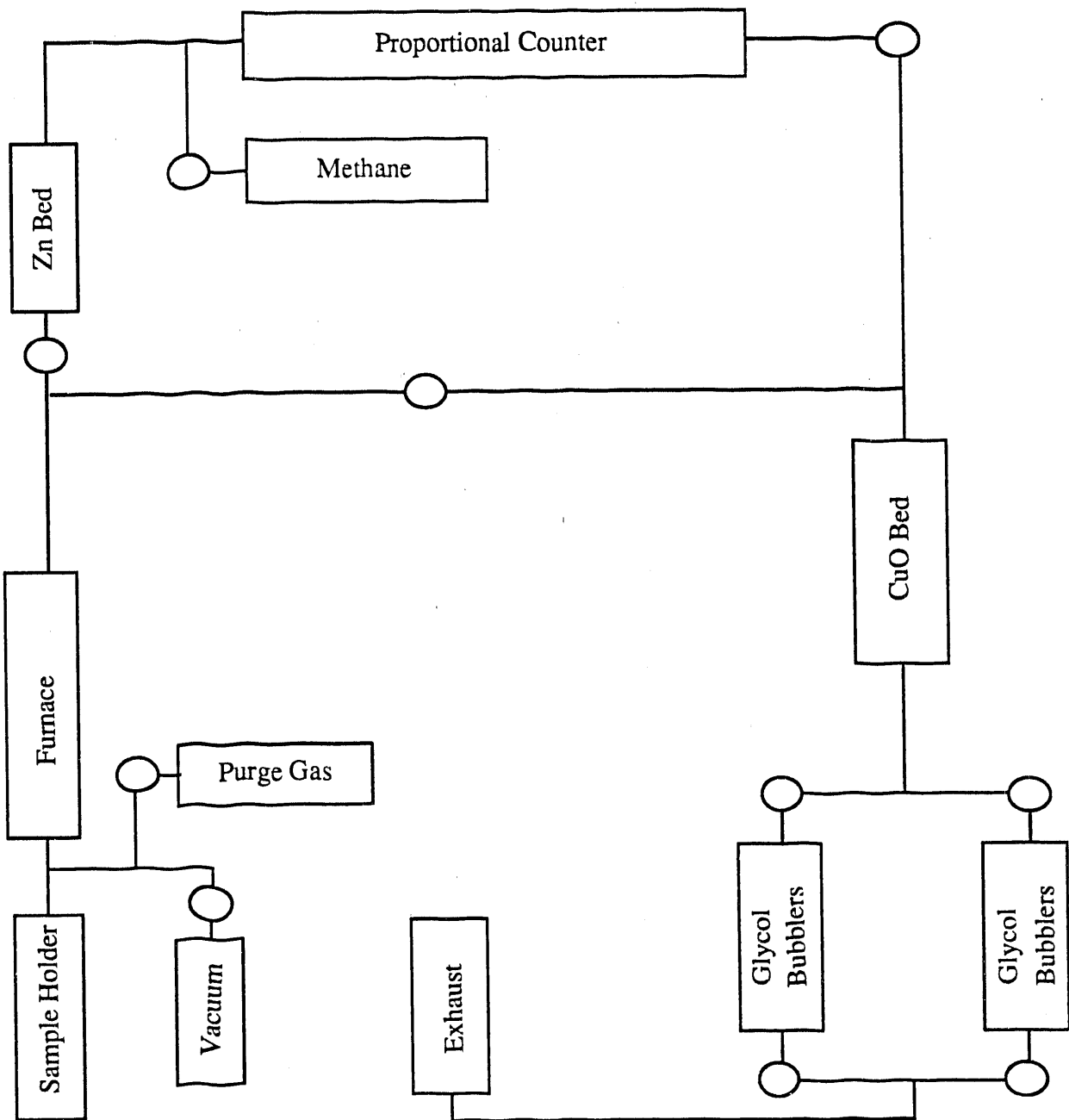
## FIGURE CAPTIONS

Figure 1. Schematic of Annealing System Used for Measurements of Tritium Release from Lithium Ceramics

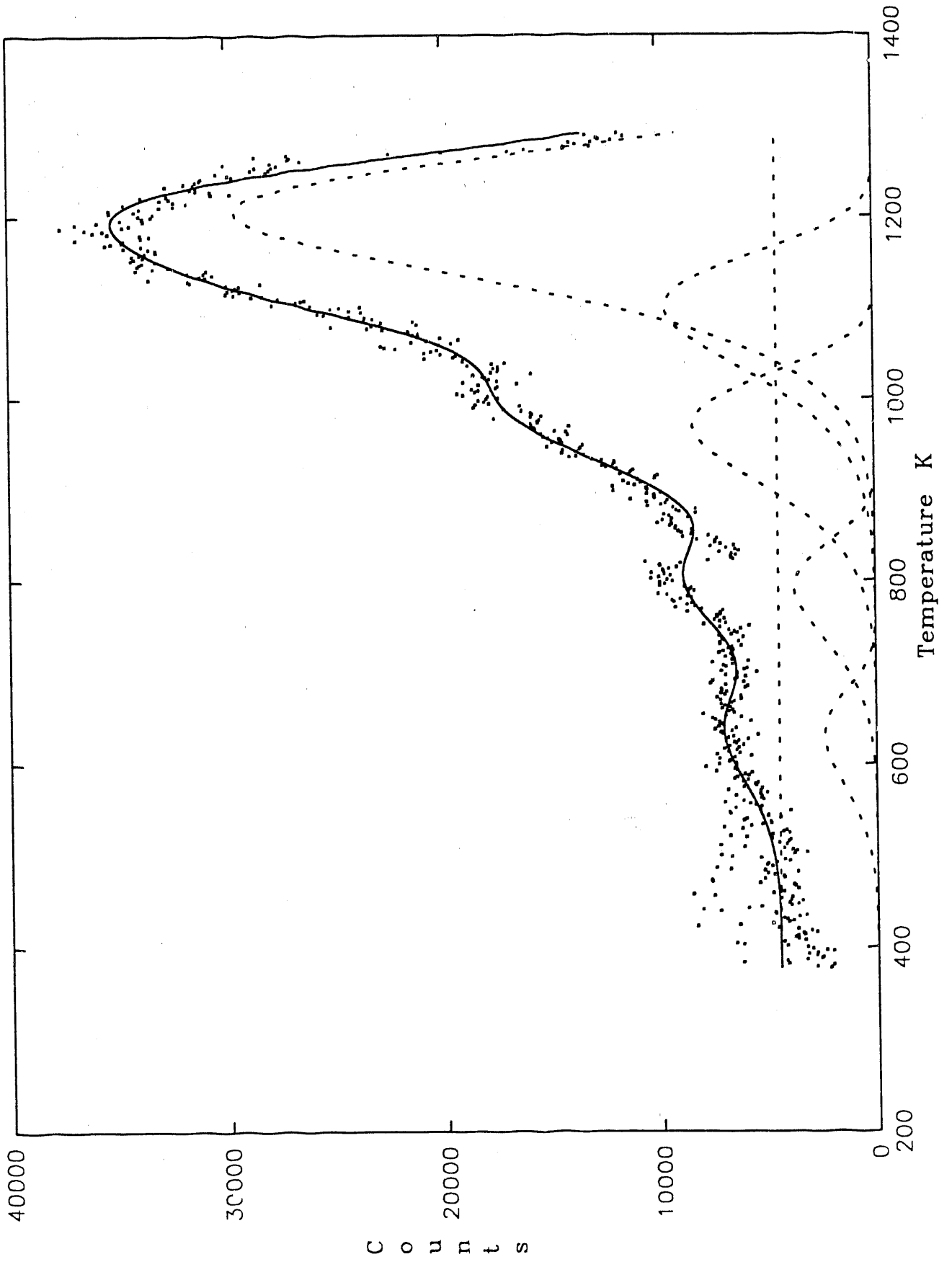
Figure 2. TPD Curve for Pure  $\text{LiAlO}_2$  at Heating Rate of  $0.75^\circ/\text{min}$ . Dashed curves indicate calculated values for individual peaks; solid curve represents total calculated curve; points represent observed data.

Figure 3. TPD Curve for Mg Doped  $\text{LiAlO}_2$  at Heating Rate of  $0.75^\circ/\text{min}$ . Dashed curves indicate calculated values for individual peaks; solid curve represents total calculated curve; points represent observed data.

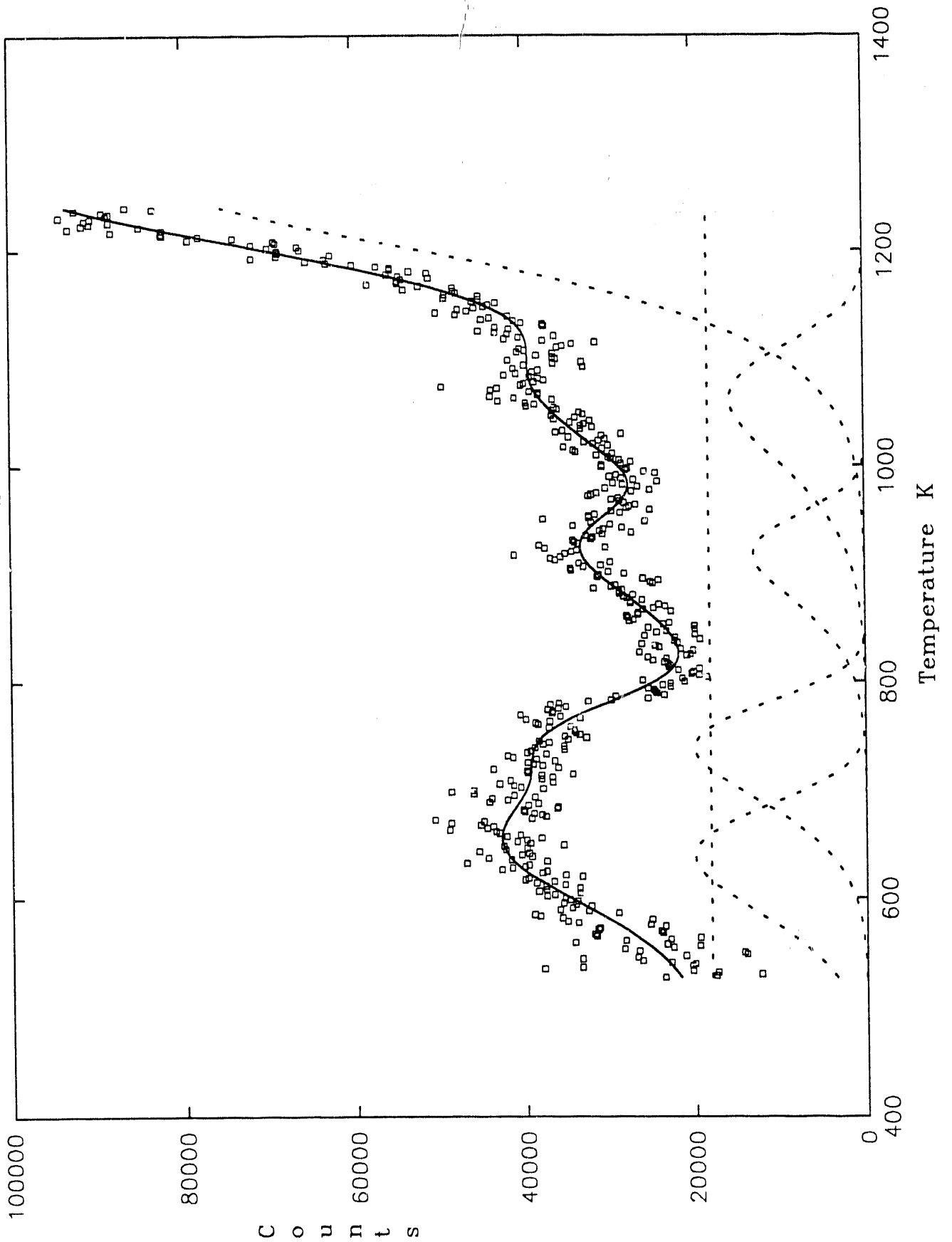
Figure 4. TPD Curve for Pt-Coated  $\text{LiAlO}_2$ , at Heating Rate of  $0.75^\circ/\text{min}$ . Dashed curves indicate calculated values for individual peaks; solid curve represents total calculated curve; points represent observed data.



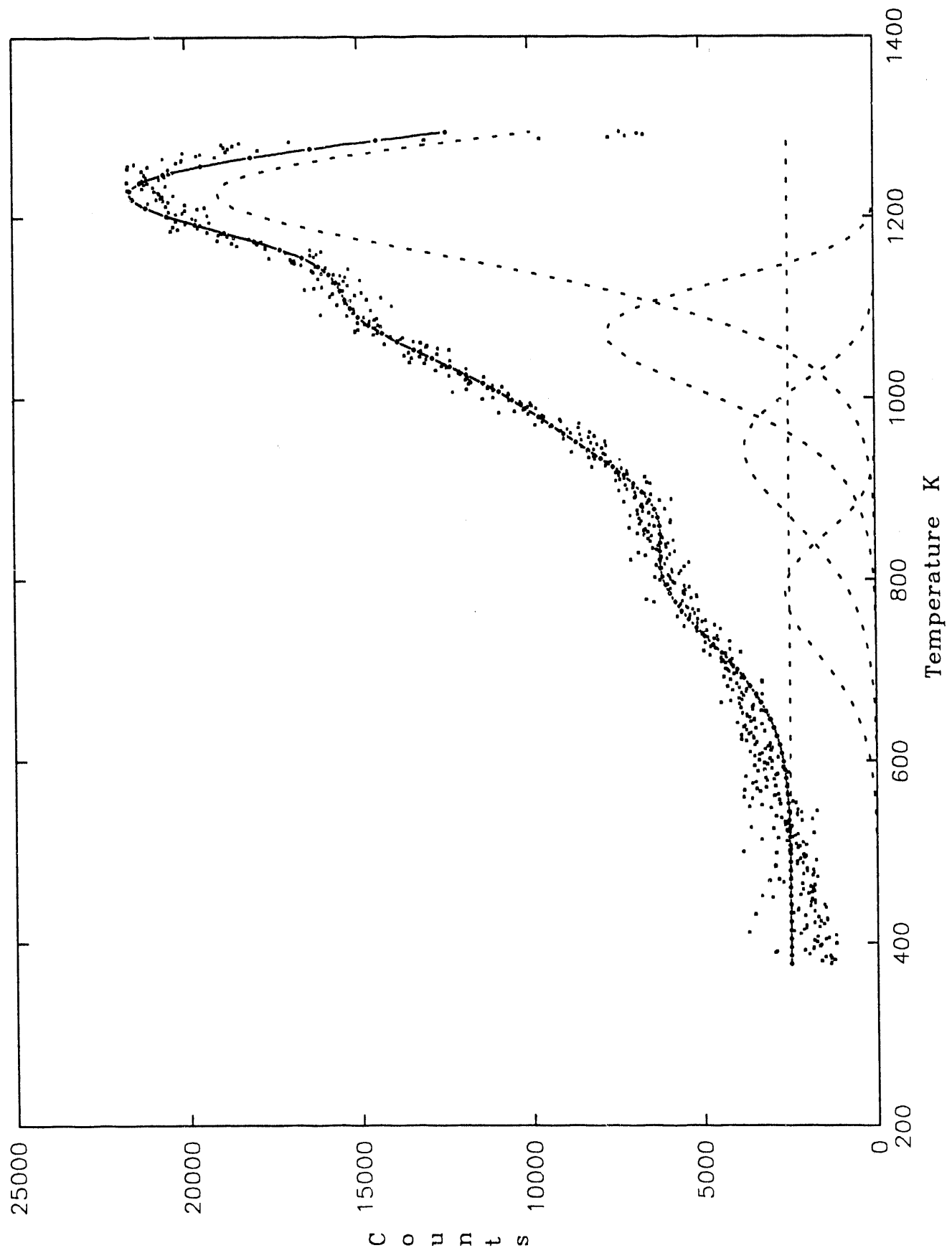
Pure  $\text{LiAlO}_2$



Mg doped  $\text{LiAlO}_2$



Pt coated  $\text{LiAlO}_2$



## SUBJECT INDEX

The editors will prepare a subject index for the proceedings of ICFRM-5. To simplify that task and to ensure that each paper is indexed properly, all authors are asked to submit five key words (or more if appropriate) that describe the subject of the paper. As an aid in this process, a list of words from the subject index of a previous ICFRM conference is attached. Please use this list as a guide to pick appropriate key words for the index, but you may, if necessary, use words not on the list. Submit your chosen key words on the form on the bottom of this page when you submit your manuscript.

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release, kinetics tritium behavior Diffusion in ceramic breeder materials.

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