

**FOREWORD**

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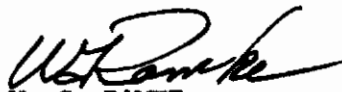
This report covers work conducted from May 1962 to September 1963.

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**ABSTRACT**

A study was made of the high-temperature phase change that occurs in  $\text{LiAl}_5\text{O}_8$ . The reaction has been reported to be either an order-disorder transformation or a reconstructive polymorphic inversion. Kinetics of the phase change with respect to compositional, temperature, and time variables were studied. The spinel structure was found to exist over wide compositional ranges in both lithia-rich and lithia-poor regions. The degree of the defectiveness of the structures affected the transformation rates. The transformation process is diffusion controlled and required a small activation energy. Insufficient evidence was obtained to resolve the question of the type of change that occurs.

This technical documentary report has been reviewed and is approved.



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# Contrails

## TABLE OF CONTENTS

	PAGE
I. Introduction-----	1
II. Experimental Procedure-----	2
III. Results-----	4
IV. Discussion-----	5
V. Conclusions-----	8
VI. References-----	9

A STUDY OF THE CRYSTALLINE  
TRANSFORMATION IN  $\text{LiAl}_5\text{O}_8$

I INTRODUCTION

In 1935 Kordes<sup>(1)</sup> proposed a spinel structure for the compound  $\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$  in which the lattice parameter was 7.903Å. Further investigation of the compound by Braun<sup>(2)</sup> led to the conclusion that the crystal structure of the lithium aluminate underwent an order-disorder transformation similar to that found in  $\text{Li}_2\text{O} \cdot 5\text{Fe}_2\text{O}_3$ . The appearance of (110), (210) and (211) x-ray diffraction peaks in the low-temperature phase and the absence of these peaks in the high-temperature phase was taken as an indication of an order-disorder transformation in the  $P4_13$  space group. More recently Datta and Roy<sup>(3)</sup> have cast doubt on the existence of an order-disorder reaction in lithium aluminates. On the basis of infrared absorption spectra, thermal expansion data, and the transition temperature range, they conclude that a reconstructive transformation takes place at  $1295 \pm 5^\circ\text{C}$ . Further, Datta and Roy propose the following structural formulae: High temperature phase,  $(\text{Li}_{0.35}\text{Al}_{1.65}) (\text{Li}_{0.65}\text{Al}_{3.35}) \text{O}_8$ ; low-temperature phase,  $(\text{Li}_{0.13}\text{Al}_{1.87}) (\text{Li}_{0.87}\text{Al}_{3.13}) \text{O}_8$ . Neither phase is thought to be ordered. Tarte<sup>(4)</sup> explained the differences in the infrared spectra of the high and low-temperature phases of  $\text{LiAl}_5\text{O}_8$  as resulting from the fact that there were cations of largely different radius and charge distributed on crystallographically equivalent sites. He considers the reaction to be of the order-disorder type.

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Lejus and Collongues(5) have studied the properties of  $\text{LiAl}_5\text{O}_8$ . They present thermal expansion data which show an expansion of about 0.2% at the transition temperature (which they term an order-disorder reaction). According to a lithia-alumina phase diagram which is also shown, Lejus and Collongues found considerable solid solution existing between  $\text{LiAl}_5\text{O}_8$  and  $\text{Al}_2\text{O}_3$  at high temperatures. The limits of solubility decrease with decreasing temperature. At  $1900^\circ\text{C}$ . for instance, the limit of solubility corresponds to a composition of approximately  $\text{Li}_2\text{O}\cdot 8.71 \text{ Al}_2\text{O}_3$  ( $\text{Li}_{0.58}\text{Al}_{5.13} \square_{0.29}\text{O}_8$ ) and at  $1400^\circ\text{C}$ . a composition of  $\text{Li}_2\text{O}\cdot 6\text{Al}_2\text{O}_3$  ( $\text{Li}_{0.84}\text{Al}_{5.05} \square_{0.11}\text{O}_8$ ). No solid solution of  $\text{LiAlO}_2$  and  $\text{LiAl}_5\text{O}_8$  was found.

This investigation was initiated to further study the properties of lithium aluminate. The kinetics of the transition process and the effect of variable composition have not been previously studied.

## II EXPERIMENTAL PROCEDURE

The materials used to form the desired compositions were Alcoa A-11 aluminum oxide and reagent grade lithium carbonate. The proper mixtures were ground together, pressed into pellets, and fired in an electric furnace at  $1450^\circ\text{C}$ . The pellets were ground and heated three times to obtain homogeneous mixtures. The following compositions were prepared and studied:  $\text{Li}_2\text{O}\cdot 4 \text{ Al}_2\text{O}_3$ ;  $\text{Li}_2\text{O}\cdot 4.5\text{Al}_2\text{O}_3$ ;  $\text{Li}_2\text{O}\cdot 5\text{Al}_2\text{O}_3$ ;  $\text{Li}_2\text{O}\cdot 5.5\text{Al}_2\text{O}_3$ ; and  $\text{Li}_2\text{O}\cdot 6\text{Al}_2\text{O}_3$ . The investigation was concentrated on the 1/5 mixture.

# Conclusions

All x-ray work was carried out using a Norelco diffractometer with copper radiation. A furnace modified from the design of Mauer and Bolz<sup>(6)</sup> was used for high-temperature x-ray studies. Temperature calibration was accomplished by using the thermal expansion of the platinum specimen holder as a standard<sup>(7)</sup>. Specimen alignment corrections were made by measuring several high-angle peaks and extrapolating the d-spacings to  $2\theta = 180^\circ$ . Diffraction lines from (751), (840), (431), and (844) planes were used for precise parameter measurements. The presence of the stable low temperature phase was determined using peaks at  $25^\circ 2\theta$  (210) and  $27.6^\circ 2\theta$  (211), and rates of transformation were calculated using the change of intensity of these lines as a measure of the change in crystal structure.

Pellets of the various lithia-alumina compositions were quenched in water from  $1400^\circ\text{C}$  to obtain samples that retained the high-temperature crystal structure. These samples were then placed in a furnace held at temperatures between  $700^\circ$  and  $1000^\circ\text{C}$  and soaked for 96 hours. The samples were removed from the furnace periodically and the intensity of the diffraction peaks determined.

Thermal expansion of the 1/5 composition was obtained by use of the x-ray furnace and measurement of the high-angle lines previously mentioned. A precision dilatometer incorporating a specimen two inches long was also employed to further investigate the expansion in the region of the high temperature transition.

Electrical resistivity measurements were made using platinum electrodes, a General Radio 650-A impedance bridge, and a General Radio 1302-A oscillator which produced a 10,000 cycles per second signal. Direct current measurements were attempted but were abandoned because of excessive polarization effects.

### III RESULTS

The x-ray diffraction patterns obtained on the high and low-temperature forms are essentially the same as those given by Datta and Roy. Lattice parameters are given in table one.

A thermal expansion curve for  $\text{LiAl}_5\text{O}_8$  from x-ray data is shown in figure one. Data near the transition temperature were not obtained at sufficiently narrow temperature intervals to justify drawing the curve with inflections in the region around  $1300^\circ\text{C}$ . However, the dilatometer results clearly show a linear expansion amounting to 0.1% between  $1250^\circ$  and  $1290^\circ\text{C}$ . Lejus and Collongues show the expansion to be slightly larger - about 0.2%. Whether the expansion occurs at a given temperature or over a narrow temperature range cannot be deduced from the dilatometer data because the temperature gradient across the sample is not known with sufficient accuracy.

Electrical resistivity changes with temperature for  $\text{LiAl}_5\text{O}_8$  are shown in figure two. Activation energies for ionic diffusion computed from the curves are 38 kcal./mole and 16 kcal./mole.

The transition from the metastable high-temperature form to the low-temperature form as a function of time and temperature for different lithia-alumina composition is shown in figures three and four. The transition data for the 1/5 composition are replotted in figure five in which it is assumed that ionic diffusion is the rate controlling process. If this is true, the amount of new phase formed is proportional to log time ( $C = k \log t + A$ ). The slope of the curve is then equal to the rate constant ( $k$ ). If the rate constant is determined at several temperatures, a plot of log  $k$  versus reciprocal temperature yields the activation energy for the process. Such a plot is shown in figure six. The activation energy computed for the transition from the metastable to the stable phase is 5.3 kcal./mole.



## IV DISCUSSION

As previously stated, the work of Datta and Roy resulted in the conclusion that the phase change occurring in lithium aluminate is a reconstructive transition rather than an order-disorder transition. A reconstructive transition is a first-order reaction in which there is a discontinuity in the internal energy-temperature curve at the transition temperature. An order-disorder transition is second-order in that there is an inflection point in the internal energy-temperature curve but the curve is continuous. Also, the change from order to disorder occurs over a range of temperatures, whereas a reconstructive transition occurs at a specific temperature if sufficient time is allowed. Structure-sensitive properties in a system undergoing a change from the ordered to the disordered state should, therefore, change over a range of temperatures rather than at a specific point.

The question of whether the system under study is an order-disorder reaction or a reconstructive transition is primarily of academic interest. There is no evidence in the literature that oxide systems possess the ability to undergo order-disorder transitions. Although some solid solutions (for example, the feldspars) show ordered structures, these materials do not have a critical temperature at which disordering takes place. Kingery<sup>(8)</sup> states that the energy required for such a transition in oxide systems is so large that the reaction will not occur. The evidence presented in this report is certainly not conclusive, nor is that of Datta and Roy. The intensities of the (210) and (211) diffraction lines do not decrease appreciably at temperatures close to and below the transition temperature. The volume increase at the transition temperature and the change in electrical resistivity occur at least over a narrow temperature range, if not at a given temperature. The question that remains unanswered is what is the temperature interval within

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which the system is in a partially ordered state between the completely disordered and the maximum ordered state if ordering does take place. Batterman<sup>(9)</sup> has shown that disordering occurs within a 5°C. interval in Cu Au<sub>3</sub>. The property variations previously noted (decrease in line intensity, volume increase, resistivity change) could easily have changed over a five degree range without being detected. The spectroscopic results of Datta and Roy and of Tarte for the two aluminate phases are identical, only the interpretations are different. Tarte states that such spectra differences have been observed in other systems he has studied. The questions raised by Datta and Roy are justified - indeed, these questions arose during the course of this work. However, insufficient data have been presented by all of the investigations to resolve the problem at this time.

The graphs showing the linear relationships between the concentration of the phase being formed and the time allowed for the reaction to take place (figure five) show some apparent anomalies. The reaction constants computed from the line slopes increase, as would be expected, from 800° to 900°C. However, the constants decrease at 950° and 1000°C. This irregularity can be explained by noting the curves in figure two. It can be seen that the formation of the stable phase at 950° and 1000°C is more than 50% completed in the first 15 minutes of reaction time. No data were obtained for a period of less than 15 minutes because of the time required for the cold sample to reach thermal equilibrium when placed in the hot furnace. Van Bueren<sup>(10)</sup> shows that in order-disorder transformations the rates may be represented as dependent upon diffusion in the initial stages of ordering. It would appear that in the lithium aluminate studied, the reaction rate is diffusion controlled up to a given point (which is dependent on temperature) and the reaction kinetics

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may actually be represented by two reaction constants. The reaction constants computed and the data plotted for 950° and 1000°C represent the second stage of the process and the first stage occurred in less than 15 minutes. These data show that the rate of reaction after the reaction has proceeded beyond a certain degree at a given temperature is not controlled solely by diffusion. It appears that reduction of strain energy by partial ordering reduces the driving force for diffusion.

The activation energy for the reaction, as computed from reaction constants, is 5.3 kcal./mole. This figure is lower than the values of activation energy found from electrical resistivity measurements either above or below the transition temperature. The low activation energies are indicative of the large number of vacant lattice sites in a normal spinel and the increased vacancy concentration in the lithium-aluminate spinel (as shown by the chemical formulae of Lejus and Collongues).

In the phase diagram for  $\text{Li}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  presented by Lejus and Collongues, a solid solution region between  $\text{Li Al}_5\text{O}_8$  and  $\text{Al}_2\text{O}_3$  was shown. The solid solutions were not stable at low temperatures. The instability was confirmed in the present investigation, and was evidenced by the precipitation of alpha alumina from the  $\text{Li}_2\text{O}\cdot 6\text{Al}_2\text{O}_3$  composition when it was held at 800°, 850°, and 900° C. However, the phase diagram shows no solid solution for  $\text{LiAl}_5\text{O}_8$  in the lithia-rich direction. The present study showed no second phase formation in either  $\text{Li}_2\text{O}\cdot 4 \text{ Al}_2\text{O}_3$  or  $\text{Li}_2\text{O}\cdot 4.5 \text{ Al}_2\text{O}_3$ . The data for the amount of product formed as a function of temperature (figure three) show that the rate of reaction is a function of composition for the solid solution studied. The 1/5.5 and 1/6 compositions gave equal reaction rates at 900°C. However, the 1/6 composition precipitated alumina resulting in a composition equal to or approximating the 1/5.5 ratio. The presence of a second solid phase should

not effect the rate transformation, and, if  $\text{LiAlO}_2$  were present, the 1/4, 1/4.5 and 1/5  $\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$  composition should have shown equal transformation rates. This work thus suggests that solid solution of  $\text{LiAl}_5\text{O}_8$  with both  $\text{Al}_2\text{O}_3$  and  $\text{Li}_2\text{O}$  exists.

## V CONCLUSIONS

The evidence presented in this report, as well as previously published data, could be used to support either an order-disorder reaction or a reconstructive phase transition in the lithia-alumina system. It does not appear that the problem will be solved without thermodynamic data. An order-disorder transition would show a discontinuity in the specific heat versus temperature curve but not in the heat content-temperature curve. Such data would have to be obtained over a closely controlled and narrow temperature range because the properties that have been studied change over a few degrees of temperature change if not at a specific temperature.

The solid solution of alumina in  $\text{LiAl}_5\text{O}_8$  has been confirmed. Solid solution of lithia with  $\text{LiAl}_5\text{O}_8$  is proposed on the basis of reaction rates of the various compositions studied.

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TABLE I

## Lattice Parameters of Lithia-Alumina Compositions

Mol. Li <sub>2</sub> O/	Mol. Al <sub>2</sub> O <sub>3</sub>	a <sub>0</sub> (Å)
	1/4	7.909 ± 0.003
	1/4.5	7.908
	1/5	7.907
	1/5.5	7.908
	1/6	7.909

TABLE II

## Transition Temperatures of Lithia-Alumina Compositions

Mol. Li <sub>2</sub> O/	Mol. Al <sub>2</sub> O <sub>3</sub>	T <sub>c</sub> (°C.)
	1/4	1280° ± 10°C
	1/4.5	1290°
	1/5	1280°
	1/5.5	1290°
	1/6	1290°

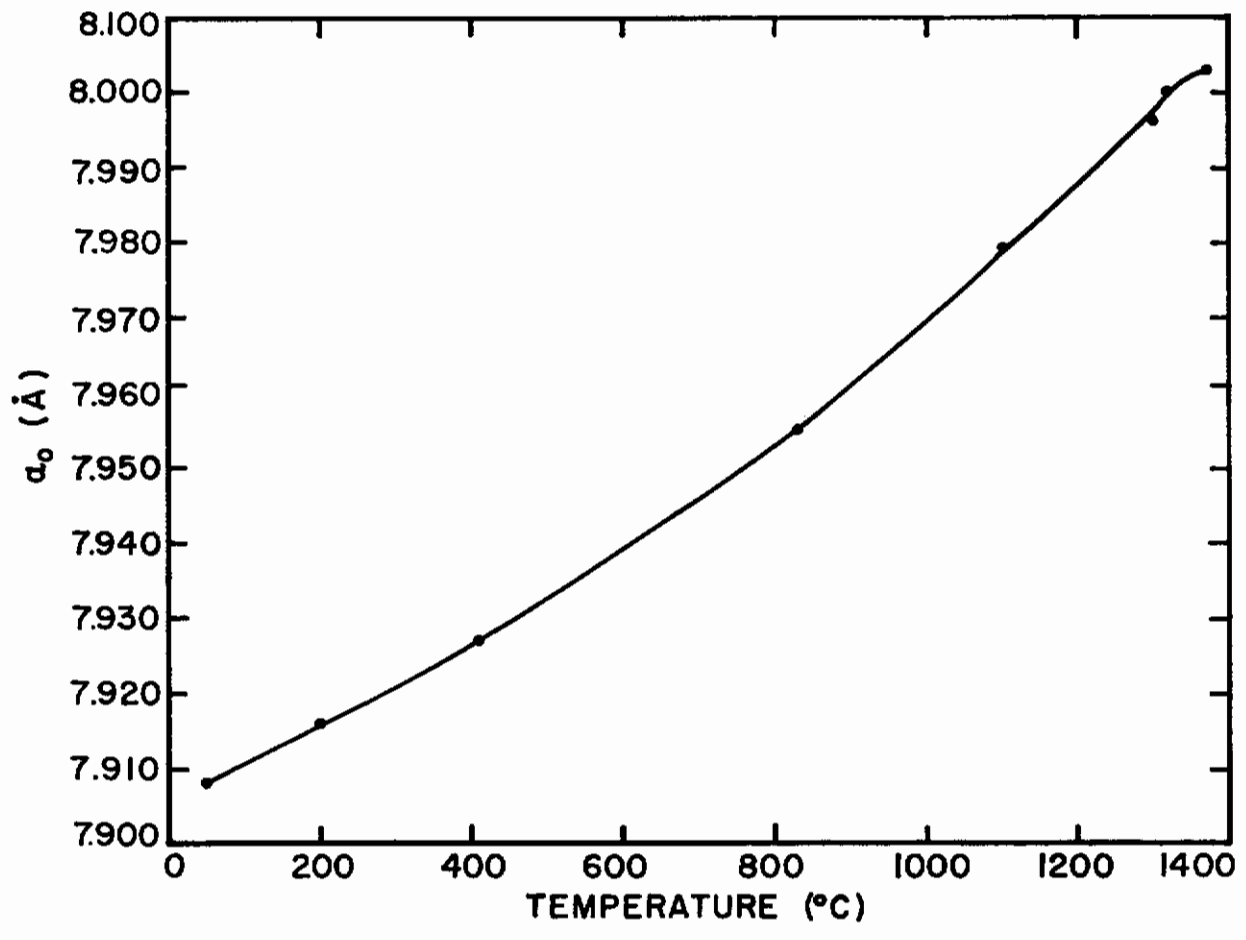


Fig. 1 Thermal Expansion of  $\text{LiAl}_5\text{O}_8$

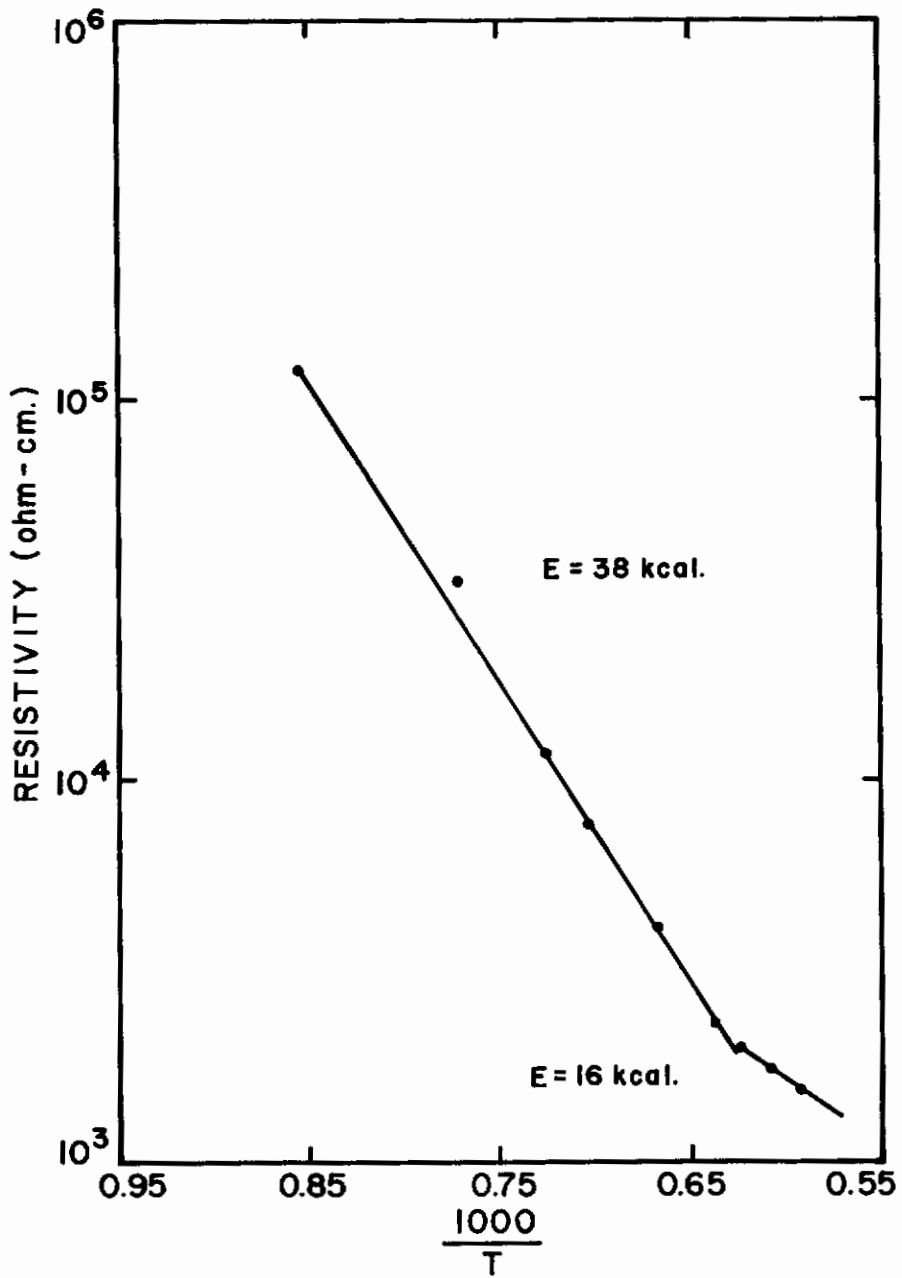


Fig. 2 Change in electrical resistivity of  $\text{LiAl}_5\text{O}_8$  with temperature



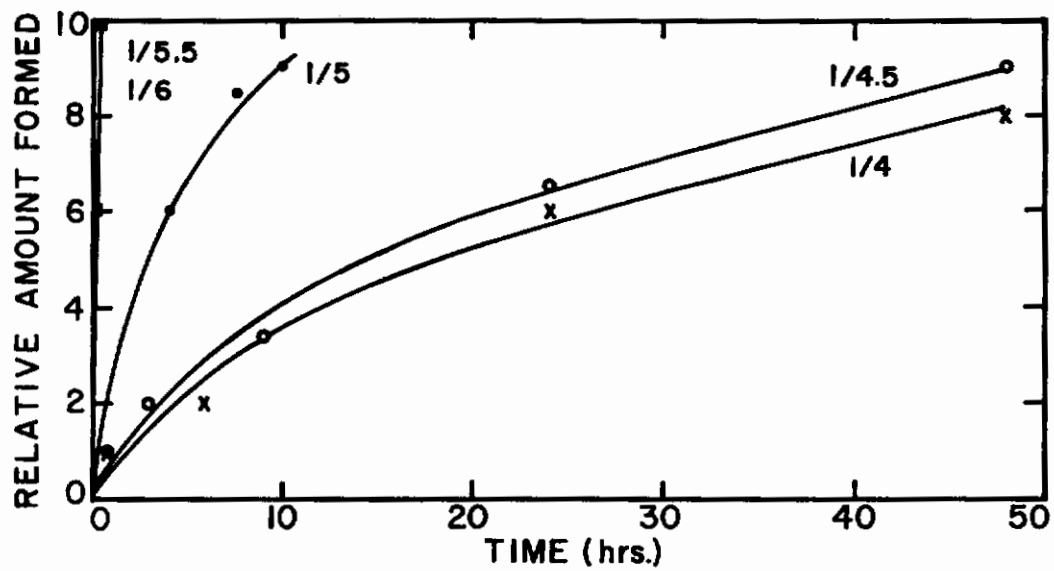


Fig. 3 Relative amounts of stable phase formed in lithium aluminates at 900° C. as a function of time (numbers on curves refer to Li<sub>2</sub>O / Al<sub>2</sub>O<sub>3</sub> Molar ratios)

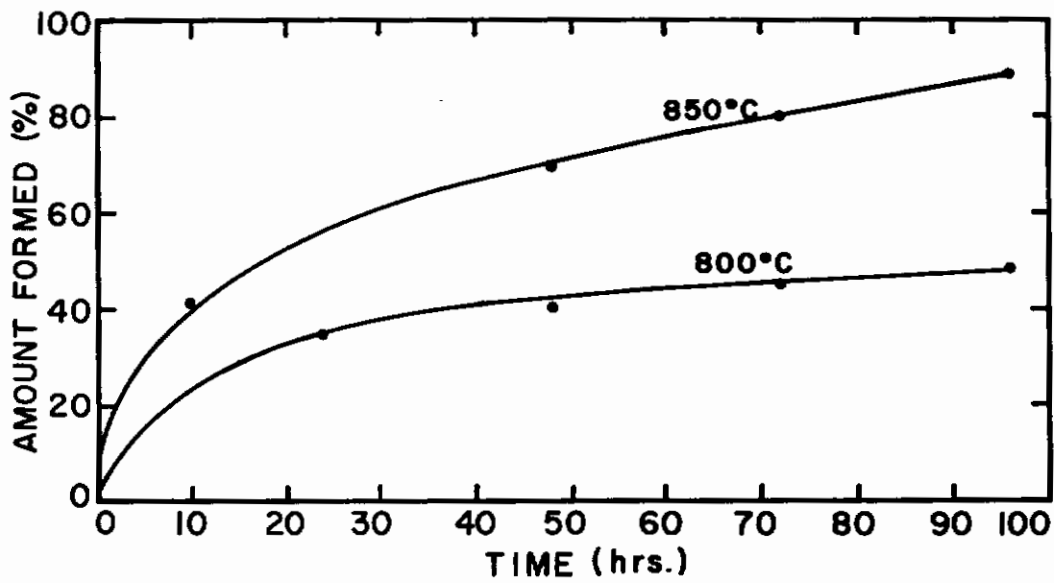
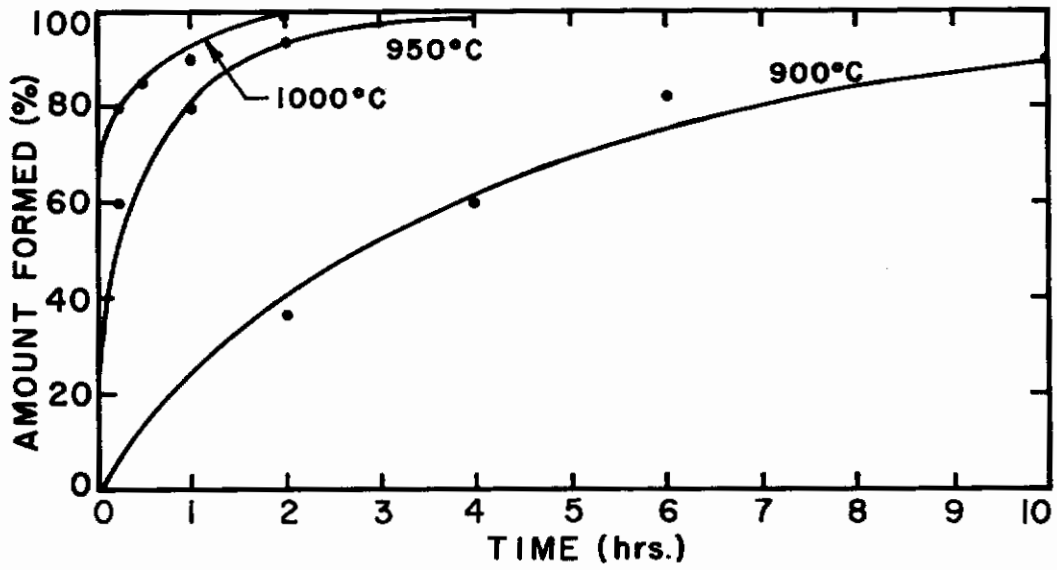


Fig. 4 Relative amount of stable phase formed in  $\text{Li Al}_5\text{O}_8$  as a function of time at different temperatures

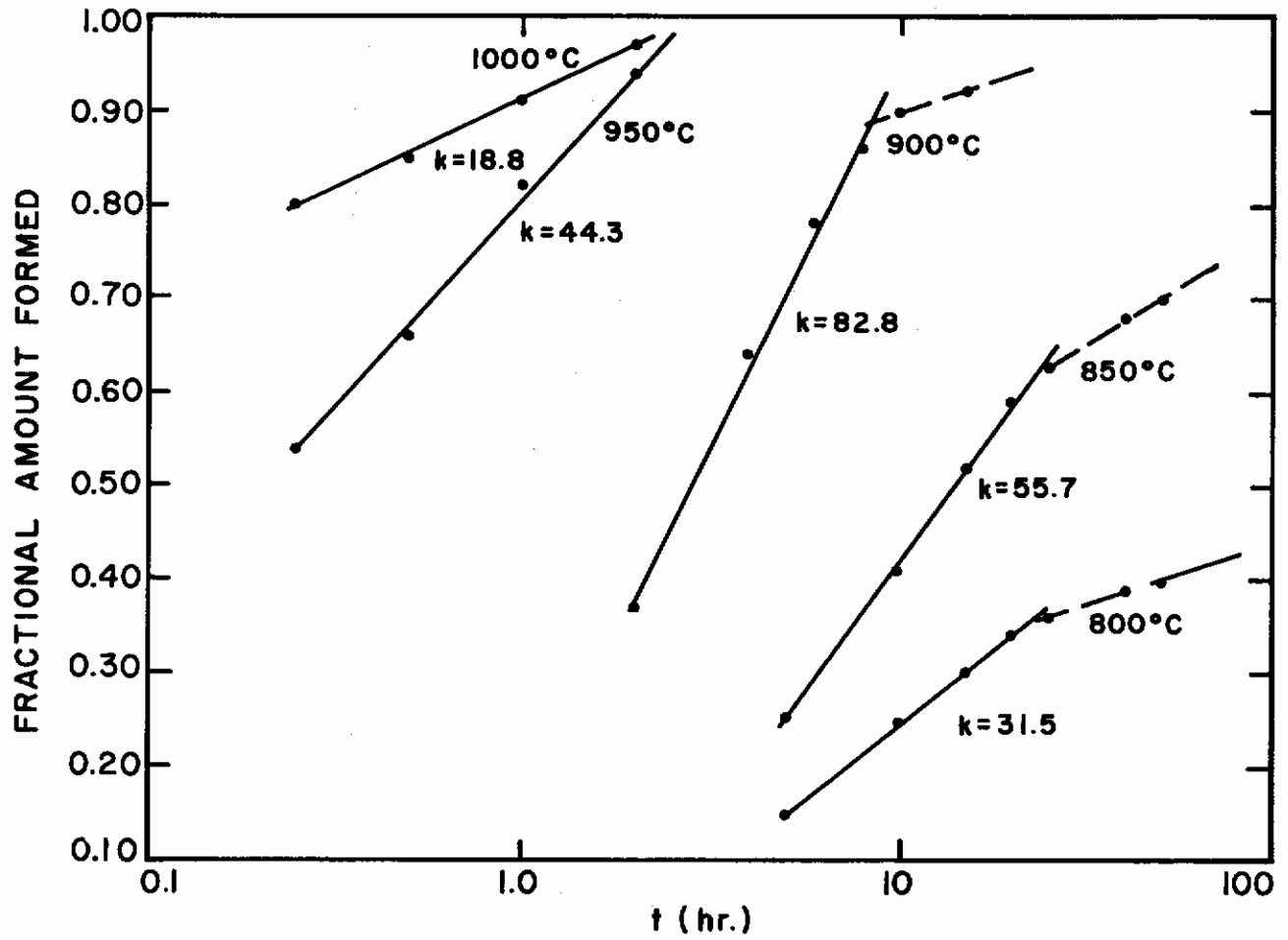


Fig. 5 Data from figure four replotted to fit diffusion equation -  
 $C = k (\log t)$

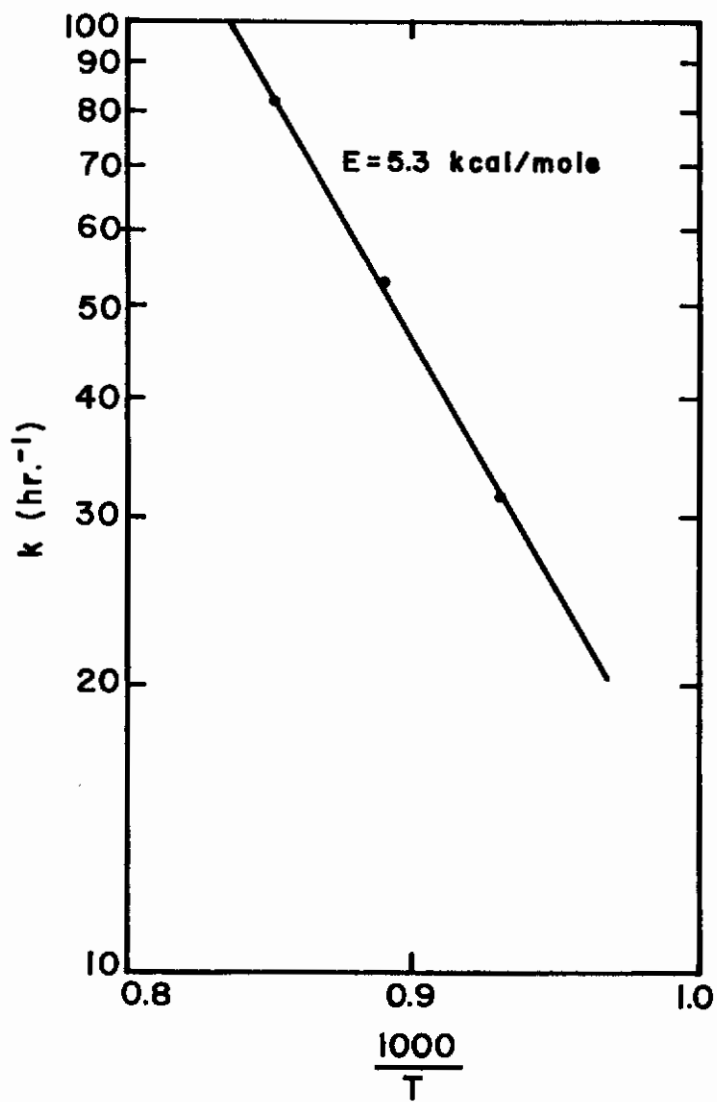


Fig. 6 Variation of rate constants with temperature -  $k = A \exp. (-E/RT)$