LETTERS TO THE EDITOR

STUDY OF IMPURITY PRECIPITATES IN DOPED NaCl CRYSTALS BY MEANS OF ULTRASONIC VELOCITY CHANGES

PLINT AND SUBY[1] have found orientation dependence of light scattering and have attributed this to the defect precipitates associated with the dislocations which may form cylinders with axes parallel to the (100) directions. Hyder and Bansigir[2] from light scattering and etching studies have estimated the size of the precipitates to be of 100 Å–200 Å. Later. Hyder, Hari Babu and Bansigir[3] have shown that there were preferential sites in the lattice where the impurities precipitate. Truell[4] has measured the ultrasonic compressional velocities in silicon crystal cubes before and after irradiation with neutrons and from the changes in velocities. calculated the size of the radiation damage regions. The object of this communication is to show that ultrasonic measurements could be used to study the distribution, orientation and size of the impurity precipitates in doped crystals.

Pure and doped sodium chloride crystals grown from the melt by the Kyropoulos technique and cut into cylinders with (001) direction parallel to the cylindrical axis have been used. The cylindrical crystal is then mounted on a special receptacle which could be rotated to any desired orientation with respect to the incident ultrasonic beam. Keeping the crystal at different angles of orientation with respect to the (100) direction, the velocity of longitudinal ultrasonic waves is determined by using the double transducer pulse time of flight method[5] (accuracy 1 in 10^4 and at a frequency of 1·5 MHz) with suitable modifications to suit the present work.

The ultrasonic velocity distribution curves for four samples A, B, C and D are illustrated in Fig. 1. Sample A is pure NaCl grown in a platinum crucible without adding intentionally any impurity. Samples B, C and D were doped with 10 ppm, 10 ppm and 50 ppm of thallium chloride, caesium chloride and cadmium chloride respectively. In Fig. 2 the ratio $\Delta V/V$ (where 'ΔV' represents the relative change in velocity in doped crystal and V the velocity in pure crystal) is plotted for various angles of orientation for all doped crystals.

From Figs. 1 and 2 we can observe, that at any orientation, the velocity in doped samples is always less than that in pure NaCl. The variations in $\Delta V/V$ in doped crystals show that the thallium impurity has precipitated preferentially along (110) direction in NaCl (Tl) whereas there appears to be no such preferential precipitation of the impurities in NaCl (Cs) and NaCl (Cd). These results are in good agreement with those obtained earlier from light scattering studies[2,3].

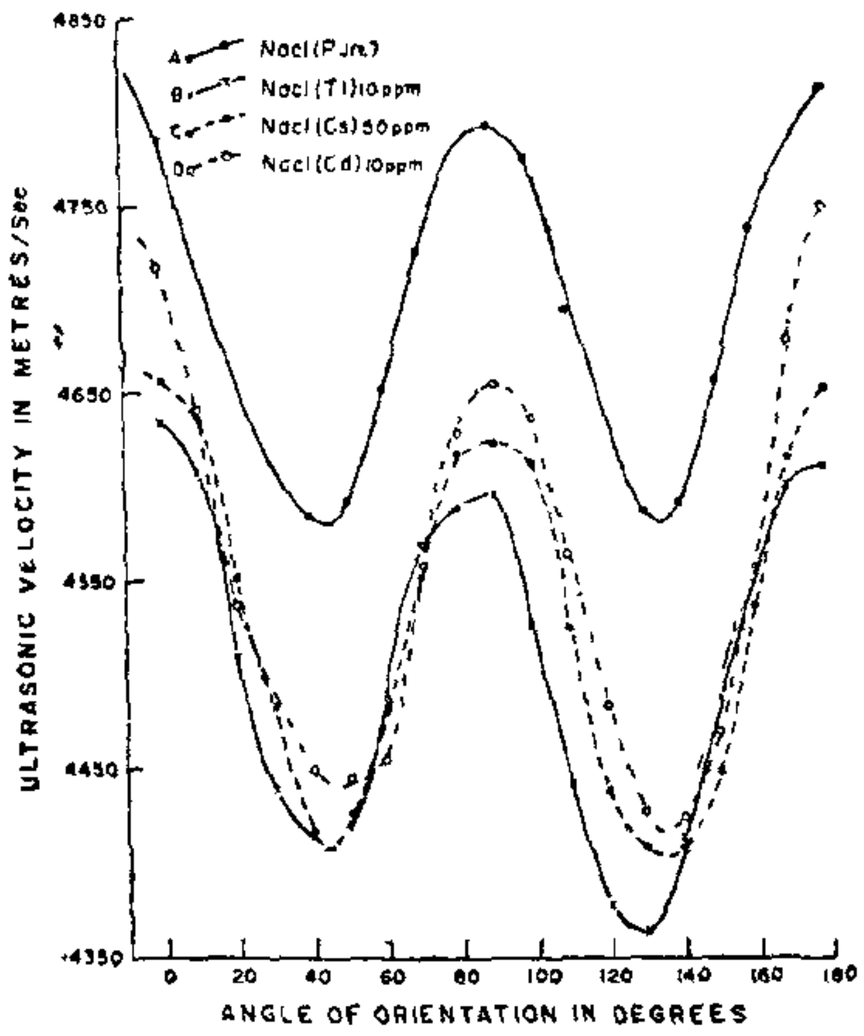

FIG. 1

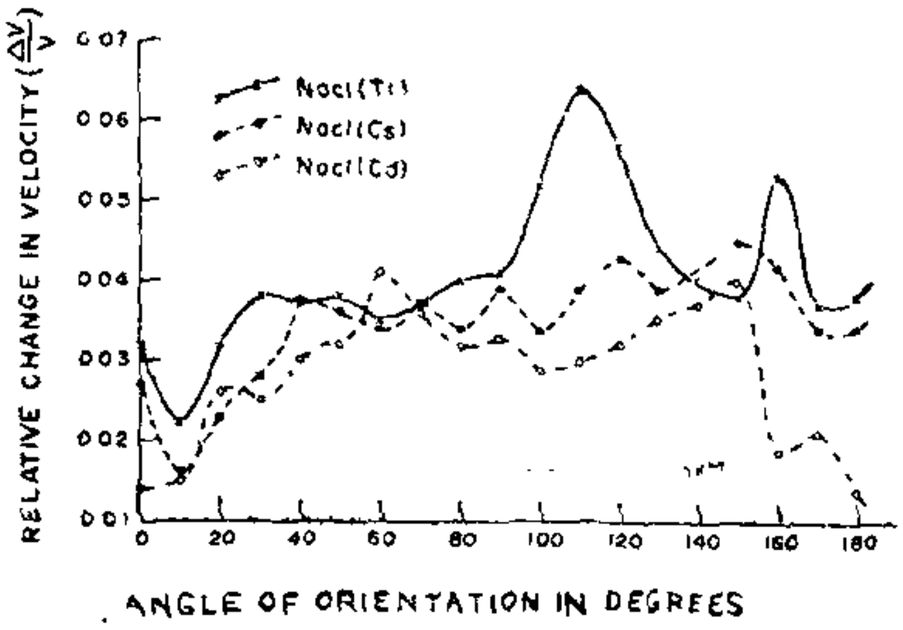

FIG. 2

The size of the impurity precipitates responsible for the velocity change 'ΔV' has been calculated using the method of Truell[4]. According to him, the precipitate or scatterer is assumed to be a spherical cavity and the expression for the velocity change, the size and the number of scatterers is given as,

$$\frac{V' - V}{V} = \frac{\Delta V}{V} = \frac{0{\cdot}47\Delta\tau}{\tau}$$

where V′ is the perturbed compressional wave velocity and V is the compressional velocity in the absence of scatterer. $\Delta\tau/\tau$ is the volume fraction of the scatterers present. In the present work the impurity precipitates act as scatterers.

Taking $(\Delta V/V) = 0{\cdot}068$ at 130° for NaCl (Tl) from Fig. 2, and taking $2{\cdot}23 \times 10^{22}$ atoms/cm³ for NaCl, which means that $3{\cdot}033 \times 10^{21}$ atoms/cm³ are located in regions of distortion, the concentration of thallium chloride in sodium chloride is 10 ppm, meaning thereby that $2{\cdot}23 \times 10^{17}$ atoms/cm³ are in the distorted region. Thus the results show that there should be about $1{\cdot}36 \times 10^{4}$ atoms in a single region of distortion or precipitate and if this is assumed to be spherical, the radius of such a precipitate would be 50 Å. Thus the precipitate size would be approximately 100 Å. Similarly by taking the minimum change in velocity at 10°, *i.e.*, $(\Delta V/V) = 0{\cdot}022$, the size of the precipitate comes out to be 80 Å. The size of the precipitates in NaCl (Cs) and NaCl (Cd) vary from 50 Å–70 Å and 30 Å–40 Å respectively. The results presented above demonstrate the applicability of the ultrasonic measurements to study the distribution, orientation and size of the impurity precipitates.

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APPLICATION OF FIRST ORDER KINETIC EQUATION FOR THE EVALUATION OF KINETIC PARAMETERS BY DTA-URANYL OXALATE TRIHYDRATE SYSTEM

Differential thermal analysis (DTA) and thermogravimetry (TG) have become important tools in the investigation of solid decomposition reactions. A number of methods[1-5] have been proposed for the evaluation of kinetic parameters using a lumped parameter model of the heat transfer process and assuming that the Arrhenius rate equation is applicable. The assumptions of Borchardt and Daniels are valid only for stirred solutions as has been shown by Reed *et al.*[6] and Mellings *et al.*[7] from a detailed mathematical study of DTA curves. It was however shown in our earlier paper[8] that the first order kinetic equation could be applied successfully for the determination of activation energy for the decomposition of sodium bicarbonate. This method has been extended to the study of the initial dehydration of uranyl oxalate trihydrate.

The apparatus for DTA has been described earlier[9]. Uranyl oxalate trihydrate was prepared by the method of Buttress and Hughes[10] and the composition was confirmed by analysis. Experiments were carried out in large platinum sample holders with the weight of the sample ranging from 80–130 mg.

Padmanabhan *et al.*[11] and Buttress and Hughes (*loc. cit.*) have studied both by DTA and TG the decomposition of this system. Some typical DTA peaks of uranyl oxalate trihydrate obtained at heating rates of 6, 12 and 18° C/min. are given in Fig. 1. The DTA peaks consist of two endotherms representing the loss of two moles and one mole of water respectively and an exotherm consisting of three close-lying kinks corresponding to the decarboxylation of uranium oxalate.

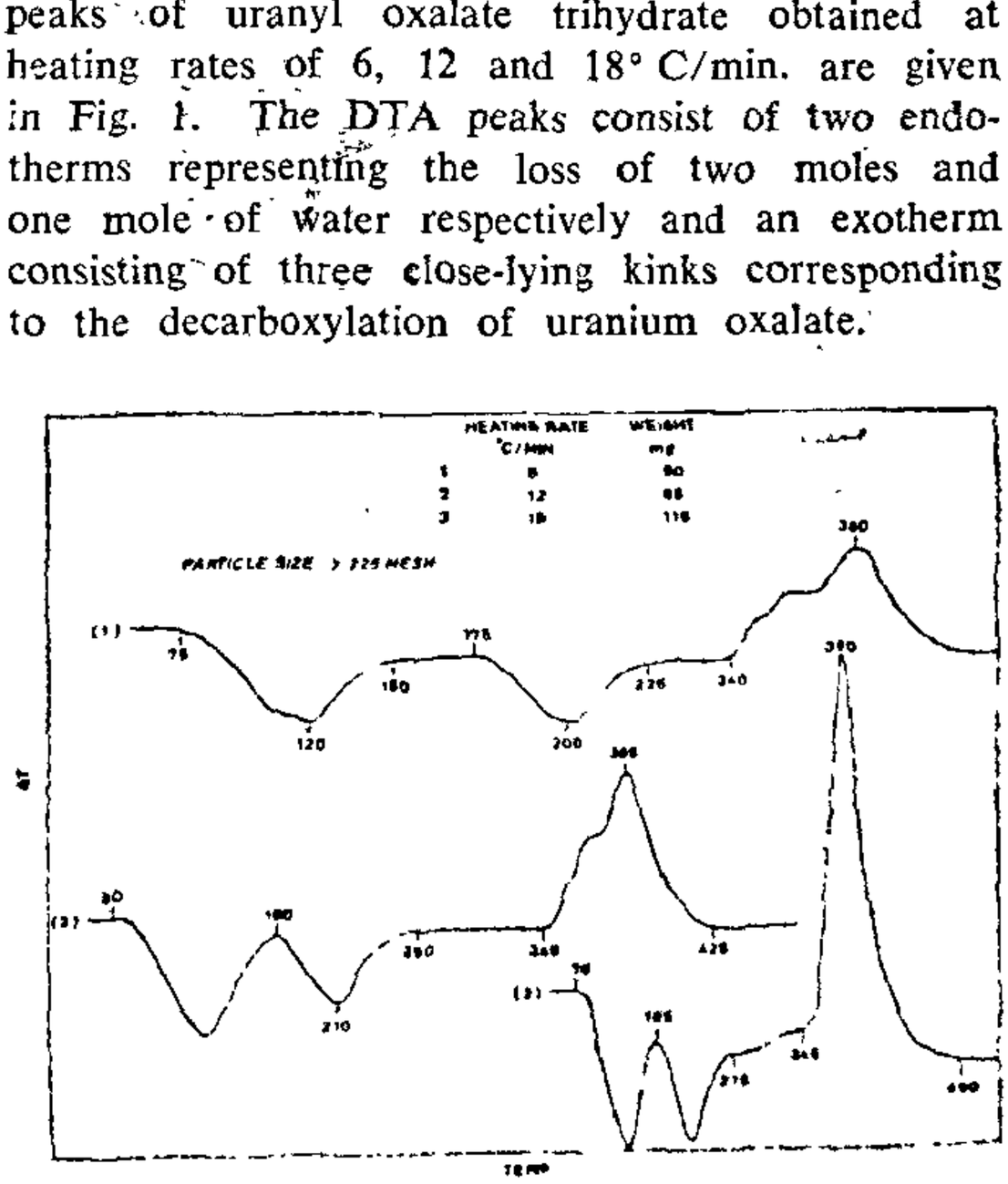

Fig. 1. Some typical DTA peaks of $UO_2C_2O_4 \cdot 3\,H_2O$ *at different heating rates.*

The energy of activation was calculated for the initial dehydration step by the use of the first order kinetic equation on the basis of the proportionality of the peak area, A, to the initial amount of the sample and the area, *a*, swept at time, *t*, to the