SPIRALS ON THE RHOMBOHEDRAL FACES OF GEL GROWN CALCITE

FRANK'S theory[1] of crystal growth has been supported by various workers who have reported growth spirals on a variety of crystals[2-5]. So far, there are no reports of spirals on calcite crystals and these are reported for the first time in this note.

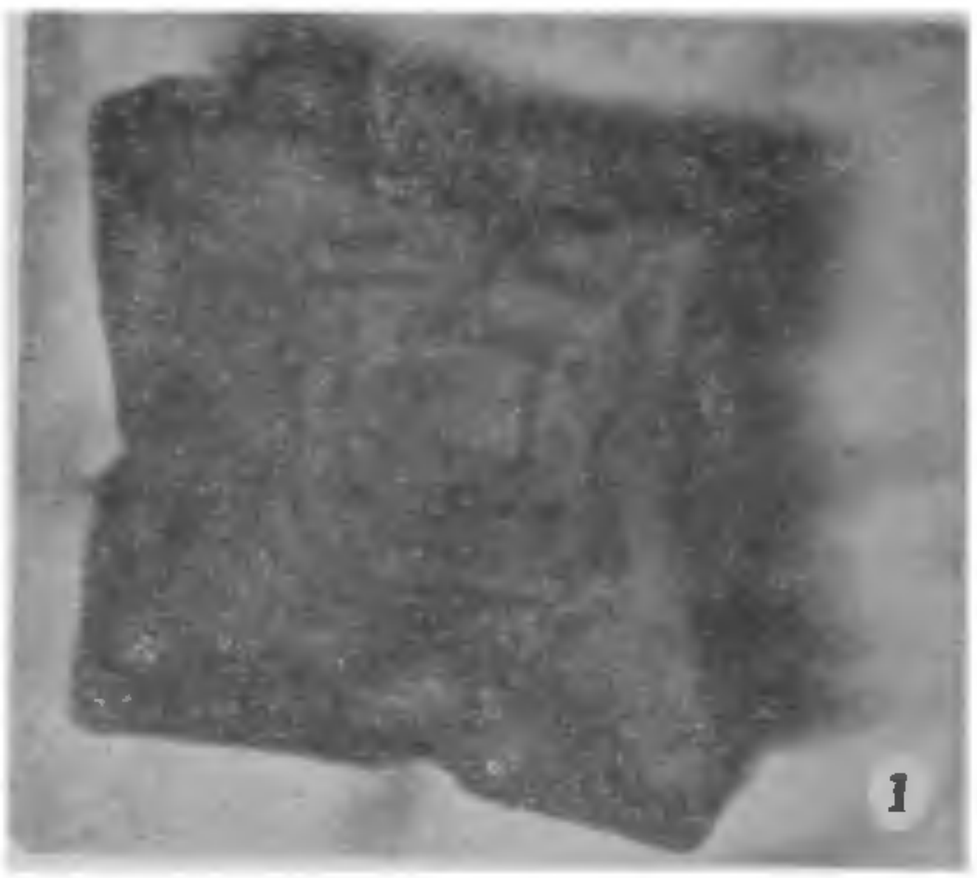
The calcite crystals were grown by the gel method[6]. Sodium silicate solution (density 1·03 gm/cc) was titrated against dilute acetic acid (1 : 10) and the pH was adjusted to 7. The gelling solution was taken in U-tubes (15 × 2 cm) and the length of the diffusion column was 10 cm. After the gel was set, 20 cc of calcium chloride and ammonium carbonate solutions at varying concentrations (0·1 M to 2 M) were poured into the two limbs of the tube. The following reaction takes place in the gel medium

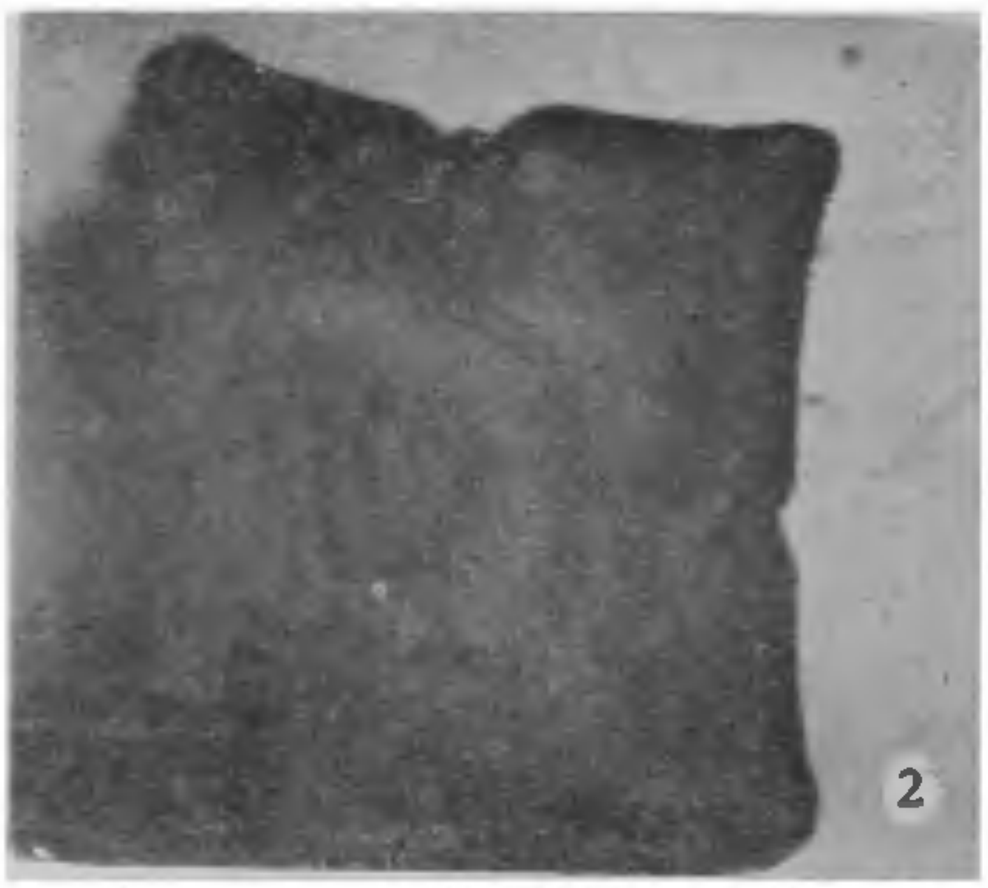
$$CaCl_2 + (NH_4)_2CO_3 \rightarrow CaCO_3 + 2NH_4Cl.$$

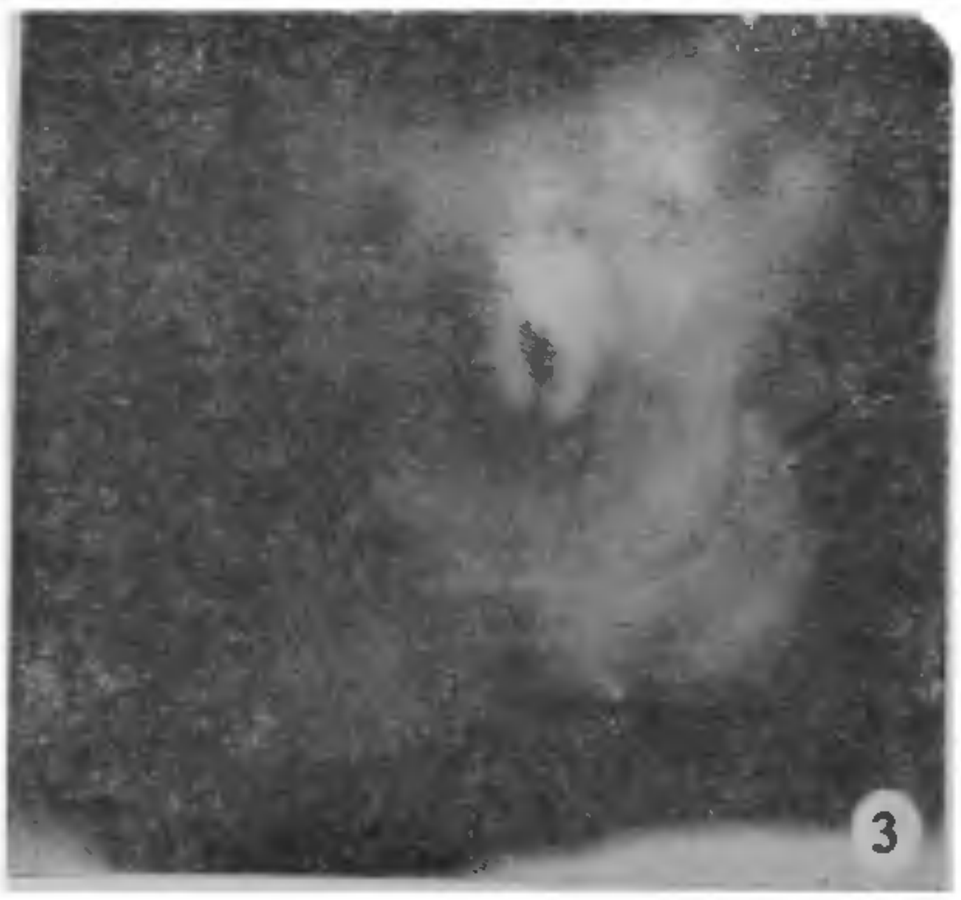
The crystals were harvested after one month and washed well and observed under a metallurgical microscope. Spirals were observed only on crystals formed near the ammonium carbonate region when 1 M to 2M concentrations of ammonium carbonate and 0·1 M to 0·2 M concentrations of calcium chloride were used. These crystals were found to be very small (about 0·5 mm in length). Chemical and optical analysis showed that the crystals consisted of calcium carbonate.

Spiral patterns were observed on almost all rhombohedral faces. Fig. 1 shows anticlockwise spirals observed on a rhombohedral face. Parts of the arms of the spirals are parallel to the sides of the rhombohedral face. Most of the crystals observed showed double spirals forming closed loops. Fig. 2 shows three such closed loops. It is interesting to note that the closed loops resemble the rhombohedral faces in shape. Etch pits were formed at the centre of the spiral when they were etched with 10% HCl[7] for 20 to 30 secs. The pit formed at the centre of the spiral is shown in Fig. 3.

Frank[1] pointed out that spiral growth might be attributed to the presence of steps associated with dislocations having a screw component to the surface. Burton *et al*[8]. have made a detailed analysis of the growth rate of a crystal by the advancement of growth spirals. Impurities and dust particles can act as the sources of screw dislocations[9]. In order to find the effect of gel density on the growth of these crystals, experiments were conducted in gels of different densities. It is found that the spiral growth does not depend on the gel density. Experiments were also conducted by varying the concentrations of ammonium carbonate and calcium chloride. It was surprising to note that the calcite crystals are







FIGS. 1–3. Fig. 1. Sprial about a single screw dislocation group (× 120), Fig. 2. Closed loops from two screw dislocation of opposite sign (× 120), Fig. 3. Pit formed at the centre of the spiral after etching for 20 to 30 secs in 10% HCl (× 120).

found to grow by spiral mechanism when the concentration of ammonium carbonate is between 1 M and 2 M. However above 2 M solution of ammonium carbonate, these crystals grow in spherulitic and dendritic form.

The growth steps starting from a single screw dislocation group can easily spread on the surface of the crystal as a continuous spiral or successive spirals. This is what we observe in Fig. 1. The formation of double spirals can be explained by assuming that the factors controlling the growth of the crystals might create local slip, with the result that two screw dislocations of opposite sign will be created at the two extremities of the slip. These screw dislocations will give rise to two spirals of opposite sign, which will ultimately form loops as observed in our investigation. Pits formed at the centre of the spirals represent the points of emergence of the dislocations.

Parts of the arms of the spirals are parallel to the respective edges of the rhombohedral face; this leads us to assume that the spiral belongs to calcite and not due to any foreign growth.

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HIGH RESOLUTION NMR STUDIES IN THE SOLUTION OF OXALIC ACID IN DIOXANE

RECENT ultrasonic studies[1-3] on oxalic acid and benzoic acid in dioxane solutions have shown that the adiabatic compressibility of the solution decreases with the increase of concentration, attains a minimum value and then increases with further increase of concentration of the carboxylic acid. The minimum adiabatic compressibility in the solution of oxalic acid in dioxane was observed at the mole fraction of 0·08. This has been interpreted as due to the formation of hydrogen bonds between monomer carboxylic acid and dioxane. The behaviour of the compressibility above the critical concentration has been explained as due to the formation of dimer hydrogen bonds among the carboxylic acid molecules in addition to the hydrogen bonds formed between monomer carboxylic acid and dioxane. High resolution NMR studies would provide a method of verifying the above hypothesis. If dimers are existing below the critical concentration, the chemical shifts should be large since the hydrogen bonds in dimers are stronger than hydrogen bonds between monomer and dioxane. Hence to obtain further confirmation on this aspect, the high resolution NMR chemical shift studies for proton signal in the solution of oxalic acid dihydrate in dioxane are carried out and the results are reported in this paper.

Chemically pure AR/BDH samples of dioxane and oxalic acid dihydrate were used in the study. The NMR spectra were recorded in Varian XL 100 NMR spectrometer in the concentration ranges 0·06 to 0·10 mole fraction of the acid. The RF field was kept sufficiently low to avoid saturation effects. The chemical shift for protons in these solutions is calculated with reference to CH_2 signal of dioxane[4] which occurs at 3·7 ppm. The chemical shift in the solution of oxalic acid dihydrate and dioxane has been plotted as function of concentration in Fig. 1. from which it can be seen that the downfield chemical shift initially increases with the increase of concentration and attains the maximum value at the mole fraction of 0·09 and then remains at the same value for higher concentrations.

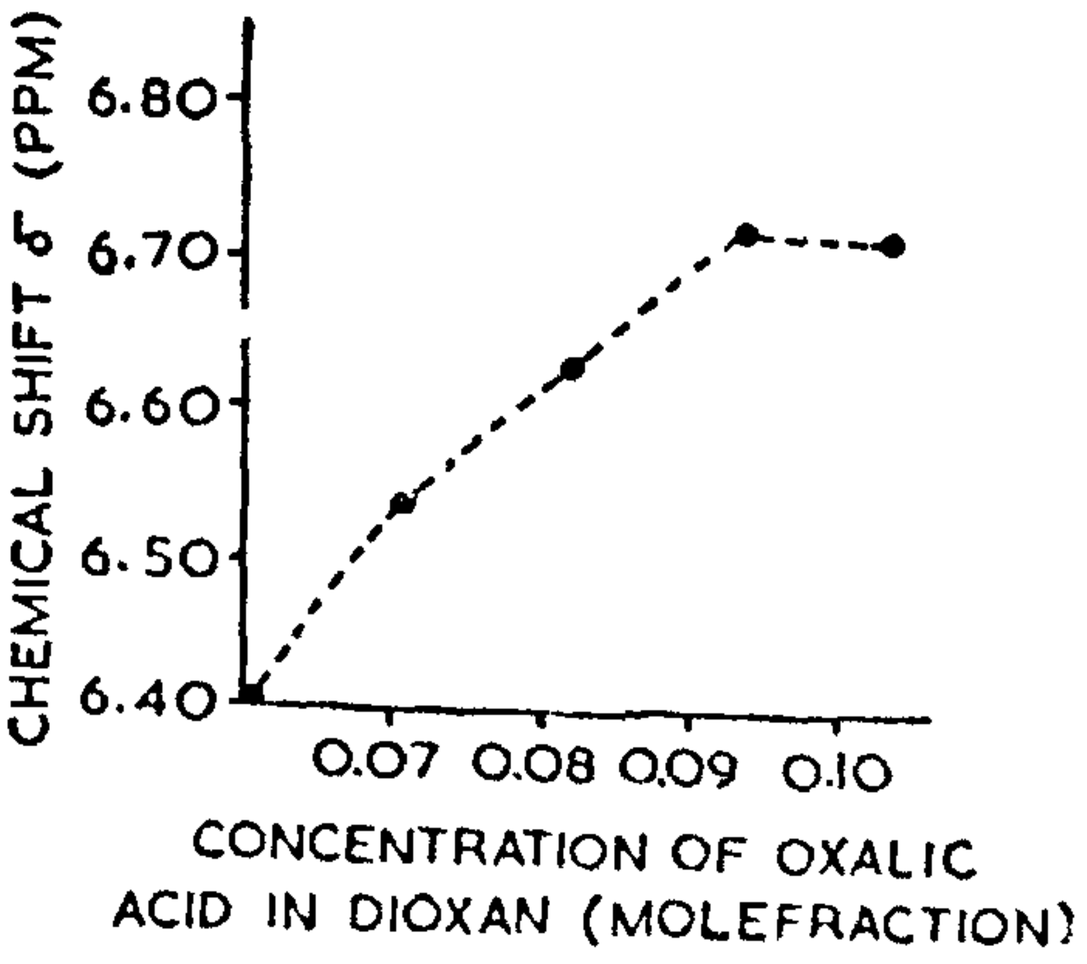

FIG. 1. Graph showing the variation of chemical shift as a function of concentration of oxalic acid in dioxane.