Curvature of gypsum crystals induced by growth in the presence of impurities

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Abstract

Gypsum crystals were grown at 25, 35, and 45 °C from solutions containing different ionic impurities (Mg^{2+}, Na^+, Cd^{2+}). Curved gypsum crystals formed from the solutions enriched in magnesium or cadmium, whereas, in the presence of sodium, gypsum always grew undeformed. The mechanism of the curvature is described and an interpretation based on crystallographic considerations is given. Curvature is the result of impurity incorporation followed by crack formation and mechanical twinning which releases the internal stresses.

KEYWORDS: gypsum, curved crystals, mechanical twins, impurity absorption.

Introduction

IN nature, some rock-forming minerals exhibit important morphological deformations such as crystal curvature. This has been observed, for instance, in chlorites, micas, talc, stibnite, graphite, and native silver (Bétekhtine, 1968; Nicolas and Poirier, 1976). In these cases, curvature seems to be related to mechanical deformation resulting from geological events subsequent to the initial crystal formation, e.g. metamorphism. However, crystals which grow in sedimentary environments may also exhibit such deformations and the question remains open whether they were curved during the crystallization process or later. Natural gypsum crystals (De Michele, 1974; Shearman and Orti Cabo, 1976; Currens, 1981) belong to this class. In a previous study on the influence of impurities on gypsum crystallization (Rinaudo et al., 1988; Franchini-Angela and Rinaudo, 1989) we observed that curvature of the crystals took place during their growth without any external intervention. In this paper, we describe the experimental conditions and give an interpretation based on crystallographic considerations.

Experimental

Precipitation of gypsum, $CaSO_4 \cdot 2H_2O$, occurred from solutions obtained by mixing, in a conical flask, 50 ml of equimolar stock solution of calcium chloride, $CaCl_2 \cdot 2H_2O$, and 50 ml of stock solution of a sulphate salt, the cation being either monovalent (Na^+) or divalent (Mg^{2+}, Cd^{2+}). After mixing, the concentration of the solutions ranged from 0.02–0.05 moles/l. The solutions were stored at 25, 35 or 45 °C and regularly observed using an optical microscope. The precipitated crystals were collected at different time intervals and observed by SEM. In some cases, the crystals were grown in small solution volumes on glass plates and continuously followed by microscopy in order to observe when curvature takes place.

The nature of the crystalline phase and the cell parameters were checked by X-ray methods (powder, precession, and Laue methods; Cu-$K\alpha$ radiation). The Laue method was also used for determining whether the crystal curvature is continuous across the whole crystal or due to juxtaposition of crystal domains displaced with respect to each other.

Results

Under all crystallization conditions, the gypsum crystals exhibit a needle-like habit. Their morphology consists of the classical {010}, {120} and {111} forms. Only the crystal habit is slightly affected by the foreign ions (mainly by Cd^{2+}). The
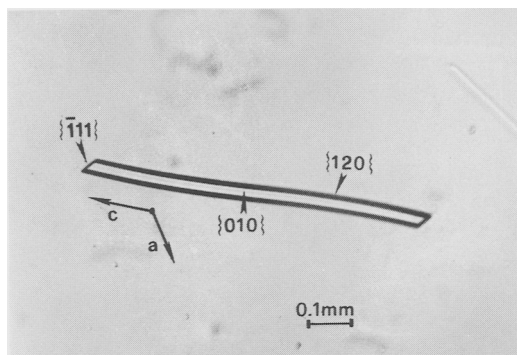
FIG. 1. Curved gypsum crystal grown at 35 °C from a solution at 3×10^{-2} mol/l in cadmium sulphate and calcium chloride.

curved crystals are shorter and more bulky than the crystals grown from pure solutions. The first-precipitated crystals, formed at high initial supersaturation, are elongate, but do not exhibit any apparent defect or curvature. They are often twinned according to the (100) twin law. In contrast, the crystals of the second generation, formed at lower supersaturation, are generally curved with only one exception. This involves solutions containing sodium ions, which favour the crystallization of straight elongate needles.
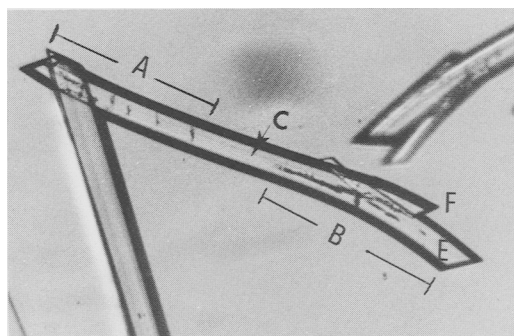

FIG. 2. Gypsum crystal showing a linear undeformed region (C) and cracks along the [100] direction in regions A and B. At one extremity the crystal has split into two, E and F.

Continuous observation during growth shows that curvature began at an early stage in the crystallization. It followed the $2/m$ point group symmetry and affected the whole crystal (Fig. 1). No cracks were visible at this stage. About two days after the start of crystallization, cracks became visible on {010} and propagated along the [100] direction (Fig. 2). They were concentrated in regions where the curvature was more pronounced (A and B on Fig. 2), whereas they were absent in the middle of the crystal (C on Fig. 2). At this stage, the crystal fractures along [001] and the extremities of the needles split in two, each growing independently (E and F on Fig. 2). In most cases the phenomenon is symmetrical with respect to the central part of the crystal (Fig. 3).

Note that crack formation and curvature are not dependent on temperature, at least in the range we have investigated.

The analysis of the crystals by X-ray methods showed that the curved crystals have lattice parameters of $a = 5.68$, $b = 15.15$, $c = 6.29$ Å, $\beta = 113.83°$ (Wooster, 1936; De Jong and Bouman, 1939), the same as those of crystals grown from pure solutions.

Discussion

It is now clear that curvature can be syngenetic with the crystal growth. It occurs at low supersaturation due to the progressive poisoning of the crystal faces by the impurities. At high supersaturation, the absorption kinetics of the foreign molecules are too slow in comparison to those of the main molecules of the crystals. This curvature is accommodated by the crystal elasticity as long as the crystals are very small. Precession patterns on the (010) faces show large bent spots, indicating a continuous deformation of the crystal lattice. During the later stages the stresses are released by crack formation. When observed at higher magnification, the cracks visible on Fig. 2 (A) are underlined by a series of large voids (Fig. 4).
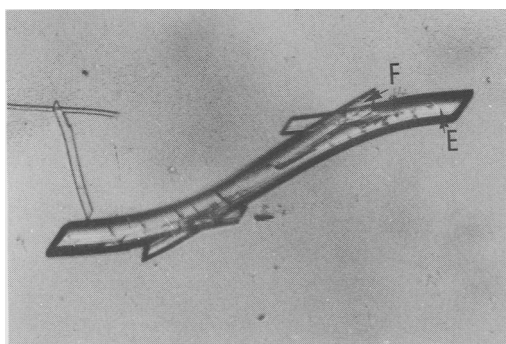

FIG. 3. Typical aspect of a symmetrical curvature resulting in a mechanical twin on a gypsum crystal.

With further growth, the deformation becomes more pronounced and the crystal is highly disturbed. Precession patterns now reveal enlargement of the spots. The Laue patterns, obtained at the crystal extremities (E and F on Fig. 2), reveal two lattices rotated with respect to each other by 18 ± 1° and, less frequently, by 23 ± 1°. In addition, these angles may be directly determined on the optical photographs of the crystals.

The fact that only two angles are observed suggests that there is, at the crystal extremities, either an autoepitaxy of one crystal on the other or a mechanical twin resulting from the torsion of the initial crystal lattice. In the former case, the misorientated crystal should nucleate and grow from a macroscopic defect of the parent crystal but there is no special reason that this should occur symmetrically at both crystal extremities. Indeed, this is rather unlikely to occur. In the latter case, the lattice stresses generate dislocations which gather in sub-boundaries, resulting in fracture of the crystal and the formation of large exposed ledges. In this area a new crystallite can easily develop, growing in the opposite direction with respect to the parent crystal (Fig. 3).
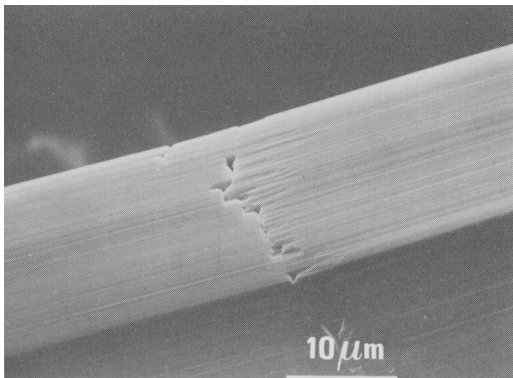

FIG. 4. SEM photograph showing a series of voids emphasizing the cracks occurring on the deformed gypsum crystals.

If this hypothesis is valid, there should exist at 18° and 23° a common coincidence cell which is compatible with point group symmetry of gypsum. In fact two (010) planes, rotated with respect to each other by 18° 58' and by 23° 53', respectively, exhibit superimposition of some reticular points which define the common coincidence cell (Fig. 5). This is delimited by the directions indicated in Table 1. The misfit between the cell parameters is small, especially in the case of the

mechanical twin at 18° 58'. This is in agreement with the fact that the occurrence frequency of this twin is much greater than that of the twin at 23° 53'.

TABLE 1. Geometrical features of the common cell between two (010) gypsum planes rotated by 18° 58' and 23° 53'.

Angles	Directions	Misfit (%)	Deviation (°)
18° 58'	[401]≡[4̄02̄]	0	
	5[001]≡[2̄04]	0	2° 3'
23° 53'	[302]≡[3̄01̄]	6.4	
	4[001]≡[2̄03]	1.9	1° 38'

To explain the origin of the crystal deformation some chemical influences can be considered. The crystal curvature is due to the presence of foreign ions or complexes in solution, especially those of cadmium and magnesium. On the other hand, sodium does not induce any curvature. Atomic absorption analysis (Kushnir, 1980; Rinaudo et al., 1988; Franchini-Angela and Rinaudo, 1989) shows that the crystals incorporate small amounts of these impurities. However, there are important differences in the absorption levels. The concentration of incorporated cadmium (0.2–0.9 ppm) is always 10 times greater than that of the other species. The problem remains open whether the impurities are incorporated as ions or complexes. The only comment we can make here is that the sodium ions are small (1.24 Å, Whittaker and Muntus, 1970) and do not form soluble complexes. If they are absorbed, they do not substantially disturb the gypsum lattice. On the other hand, cadmium and magnesium give rise to large soluble complexes (Rinaudo et al., 1988; Smith and Martell, 1976). If they are incorporated they introduce important lattice defects. In a previous study (Rinaudo et al., 1988) we concluded that absorption of the impurities mainly takes place on the {120} faces. The surface morphology of these faces exhibit many oxygen atoms from the SO_4 groups and the water molecules. The same is valid for the terminal {1̄11} faces. Since absorption of the impurities is equal on symmetrical faces, it is understandable that the crystal takes an S-shape after curvature.

Conclusion

Unlike kinking, which is a secondary deformation of crystals stressed in tension (Nicolas and Poirier, 1976; Baronnet and Olives, 1983), the
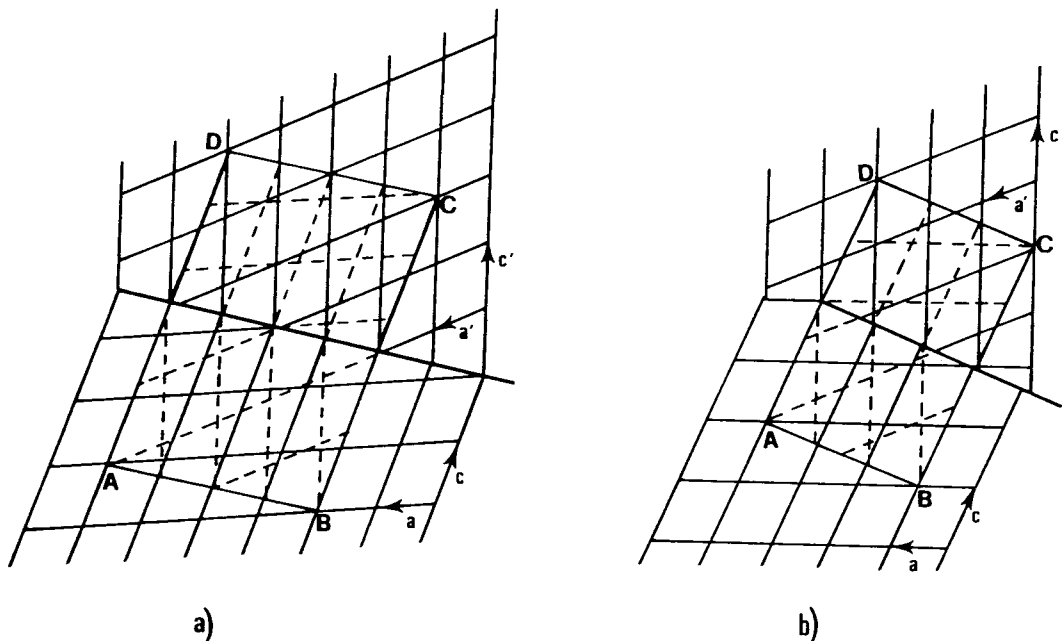
a)   b)

FIG. 5. Two (010) gypsum planes rotated with respect to each other by (*a*) 18°58′ and (*b*) 23°53′. ABCD are the common coincidence cells; the dashed lines represent the continuation of each lattice into the other.

curvature of our gypsum crystals takes place during their growth and is the result of stresses generated by absorption of impurities. There is initially a continuous curvature of the lattice as long as the crystals are small. When the size increases the crystals can no longer accommodate the internal stresses, which are released by a mechanical twin. The angles between the straight central part of the crystal and the distorted extremities are about 18° and 23°. A crystallographic analysis shows the existence of coincidence cells of low parametric and angular misfit between two (010) planes rotated with respect to each other by the angles quoted above.

The present study provides a good example of growth deformation during crystal formation.

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