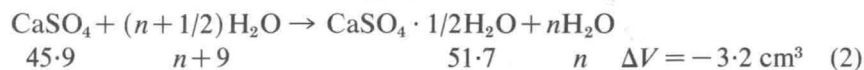Fig. 7. (A) Standard 'well' mount X-ray diffraction pattern of anhydrite taken immediately after heating to $375 \pm 25°C$ for 3 hr. $MoK\alpha$ radiation, 1/4 deg 2θ per min scanning speed. (B) Anhydrite plus water in X-ray vessel cycled and left at 200 bars pressure at room temperature. Same scanning conditions as in (A). (C) Anhydrite plus water in X-ray vessel cycled and left at 50 bars at room temperature. Same scanning conditions as in (A) and (B).

data or in their interpretation, but in any case the changes observed here are more obvious than those reported for the above phases. Inasmuch as they appear not to have been observed before, their existence seems dependent upon the presence of excess water and slight pressure.

In view of the probable effect of water pressures in stabilizing these phases we can examine the $P-V$ relations for the equations
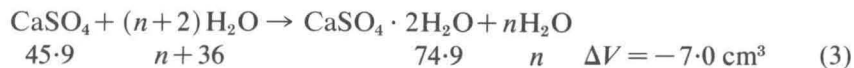
$$CaSO_4 + (n+1/2)H_2O \rightarrow CaSO_4 \cdot 1/2H_2O + nH_2O$$

$$45\cdot9 \qquad n+9 \qquad\qquad 51\cdot7 \qquad n \quad \Delta V = -3\cdot2 \text{ cm}^3 \quad (2)$$

and

$$CaSO_4 + (n+2)H_2O \rightarrow CaSO_4 \cdot 2H_2O + nH_2O$$

$$45\cdot9 \qquad n+36 \qquad\qquad 74\cdot9 \qquad n \quad \Delta V = -7\cdot0 \text{ cm}^3 \quad (3)$$

Table 2. *Interplanare spacings and intensities observed with* $CaSO_4$ *in the presence of water (A) at* 200 *bars pressure* and (B)* 50 *bars pressure**

| (A) | | | | (B) | |
d (Å)	I/I_0	$h\,k\,l$	d_{obs} (Å)	d_{calc} (Å)	I/I_0
3·92[1]	5	1 1 1	3·92	3·92	2
3·61	100	0 0 2	3·57	3·57	100
3·57[1]	50	0 2 0	3·40	3·41	5
3·52[2]	40	2 0 1	2·94	2·95	30
3·40[1]	3	2 2 0	2·340	2·346	70
2·84[2]	15	1 0 3	2·236	2·236	20
2·49[2]	10	0 3 1	2·170	2·165	80
2·351[1]	10	3 0 1	2·063	2·064	5
2·331[2]	20	1 2 3	1·868	1·870	5
2·219	5				
2·103	5	$a = 6·46_9$Å			
2·088[2]	15	$b = 6·81_5$Å			
2·061[1]	5	$c = 7·14_8$Å			
1·877[3]	10				
1·672	10				
1·649	10				
1·527	15				
1·423	5				
1·400	5				
1·280	5				

*Mokα 45 kV, 20 mA, 1/8 deg min. scan speed, 1/4 deg divergence and scatter slits, 0·006 receiving slit.

(1) = observed in Table 2 (B).

(2) = anhydrite.

(3) = spacings smaller than this value may be indexed as anhydrite or distorted anhydrite.

with molar volumes of each phase, where n is added only to indicate an excess but finite quantity of water within the (closed) system. Because pressure within the system acts on all phases, the volume of water entering into the solid phases during the reaction must be taken into account.

The above relations demonstrate that at constant temperature both the hemihydrate and gypsum are stable with respect to anhydrite at moderate pressures. At higher pressures we take into account the compressibility relations for gypsum and anhydrite given by Madelung and Fuchs[9] and the equation of state for water as given by Li[10]. The molar volumes for equation (3) from left

to right at 5000 bars are 45·5, 31·1 and 74·0, indicating only a slight pressure effect upon the solid phases. The volume change, however, is now −2·6 cm³, and in the vicinity of 10,000 bars volumetric equilibrium between the left and right sides of equation (3) is reached. The above relations were obtained from data of somewhat limited accuracy inasmuch as the constants for the second terms of the quadratic compression equations were not determined by Madelung and Fuchs for the two solid phases. However, inasmuch as the volume change contribution by these phases is small compared to that of water, little error will be introduced into the calculations.
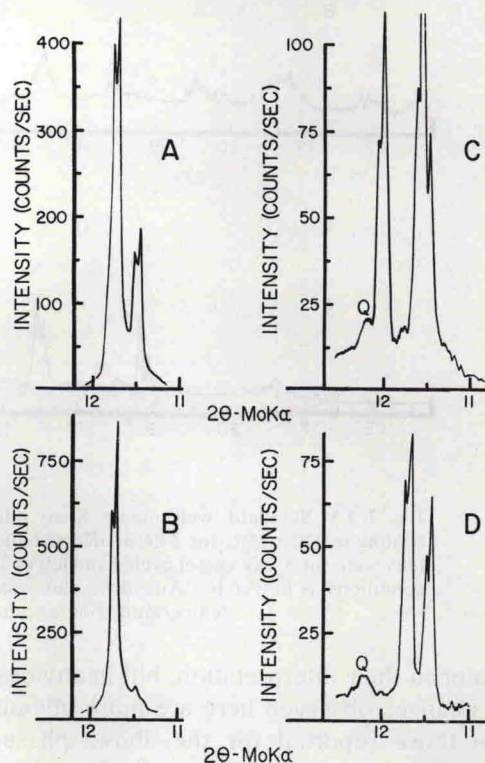

Fig. 8. (A) Peaks observed between 11 and 12 deg 2θ from natural dry anhydrite open to the atmosphere for three months. (B) Same material as in (A) above but heated $375 \pm 25°C$ 3 hr. Standard 'well' mount. (C) Anhydrite in the presence of distilled water in X-ray vessel, showing same region as in (A) and (B). Q is peak from quartz internal standard. Pressure is 25 bars at room temperature. No pressure cycling. (D) As above except pressure raised to 1200 bars and reduced to near 1 atmosphere.