

Fig. 5. Oscillation record taken at  $1/4$  deg  $2\theta$  per min in X-ray vessel of anhydrite in the presence of distilled water open to the atmosphere. Large peak at  $11.5$  deg  $2\theta$  is unresolved anhydrite 020-002 doublet.

variation in Bragg-angle and time with peak intensity. This figure shows both the extreme change in intensity of the 020-002 doublet of anhydrite and the momentary appearance of two other peaks whose interplanar spacings are smaller than those of the doublet.

Well over a dozen separate records of this type have been obtained, and in general the peaks that appear about the 020-002 doublet vary in position, although two peaks make an exception of this rule. These pertain to interplanar spacings of  $3.57$  and  $3.61$  Å and

they usually are not resolved. The significance of these spacings will be discussed further below.

A meaningful demonstration of the intensity variability of the  $3.50$  Å spacing (020-002 doublet) of anhydrite is given by fixing the X-ray goniometer at the proper Bragg-angle and allowing the strip-chart recorder to run for several minutes. A 64 min record of this variation using the beryllium cylinder open to the atmosphere is presented as Fig. 6. One observes here that the changes persist over periods as long as 8 min (with minor variations); the longest period of increased intensity observed in 400 mins of recording time was 20 min.

In order for coherent diffraction to result from powder samples, in addition to complying with Bragg geometry, two other conditions must be met; (1) the sample must be sufficiently fine-grained to ensure large numbers of crystals of appropriate orientation for each spectral position, and (2) the grains must not be preferentially oriented. If either, or both, of these conditions are not met, the resulting diffraction pattern will show some or nearly all peaks absent. It appears that in the case of the 020-002 doublet one or both of these conditions are being met only part of the time. That is, there is continuous change in grain size and/or change in grain orientation. Such a phenomenon is best explained by the slight solubility of  $\text{CaSO}_4$  in pure  $\text{H}_2\text{O}$  approximately  $0.2$  gm/100 ml at  $30^\circ\text{C}$ . It appears that we are here observing directly a chemical reorientation resulting from solution and precipitation that is continually going on in a solution at equilibrium. Since the vessel is not agitated, nor the temperature changed, there should be no cause for physical reorientation of the grains, or for chemical disequilibrium to develop.

The phenomenon of appearance of additional peaks in the region of the 020-002 doublet cannot be explained as a function of solubility. Such peaks point to the temporary formation of additional interplanar spacings

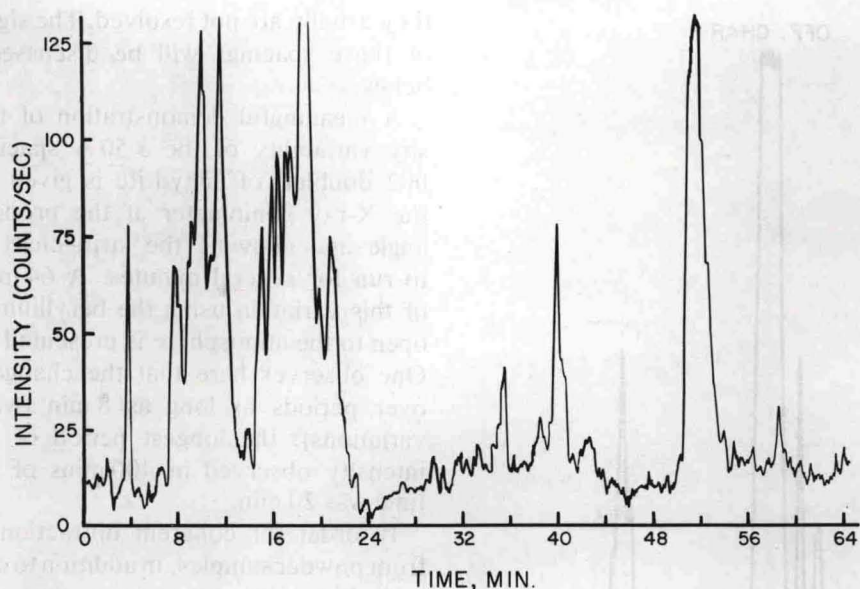


Fig. 6. Continuous time record of intensity variation of anhydrite 020-002 doublet in the presence of distilled water open to the atmosphere.

in the structure, whether it be by expansion of anhydrite spacings or by change in type or quantity of atoms comprising, or lying between a given spacing.

Additional experiments with anhydrite in the presence of water combined with pressures to 1000 bars revealed additional peaks in the pattern as well as elimination of certain anhydrite peaks. In particular the 3.57 and 3.61 Å spacings become stronger with the addition of slight pressures. There is apparently some conditioning of the sample necessary to produce certain of the observed peaks; it was found, for example, that raising the pressure to 300-500 bars and then reducing the pressure to near atmospheric produced the greatest changes in the anhydrite pattern. Figure 7 shows three diffractometer tracings of the changes observed. The standard pattern for anhydrite, but with weak development of the 3.57 and 3.61 Å spacings at about 11.4 deg.  $2\theta$ , is shown in Fig. 7(A). The pattern shown in Fig. 7(B) was produced from anhydrite having undergone the cycle mentioned above

with the exception that the pressure was again raised to 200 bars (with no change in pattern). Figure 7(C) is a pattern from the same sample taken at a pressure of 50 bars. The greatest differences in comparison to the anhydrite pattern are indicated in this run and it is apparent that a completely different phase of  $\text{CaSO}_4$  (undoubtedly partially hydrated) is present.

Table 2 presents the observed spacing and intensity data measured from the patterns of Fig. 7(B) and (C). Some of the spacings from Fig. 7(C) believed to be also present in that of Fig. 7(B) are marked with an asterisk.

### C. Discussion

Comparison of the spacing data of Table 2 with those of Posnjak[6], Flörke[5], Jung[7], and Weiser *et al.*[8] indicates that the new phases observed are not those of hemihydrate, dehydrated hemihydrate (or  $\gamma\text{-CaSO}_4$ ), or of gypsum. There is in general little agreement between these or most other authors either in their own experimental