

been clearly shown in ion flotation experiments that the use of large amounts of collector serves to reduce the efficiency of the actual flotation mechanism. It is felt that this concentration mechanism in the liquid phase is strongly inhibited in foam separation experiments where, because of the large amounts of collector present, ion concentration must needs take place in the foam phase. Finally, the deleterious effect of micelles upon concentration in the liquid phase is considered of prime importance to the ion flotation process. Accordingly this process was conducted at collector concentrations below the critical micelle concentration (CMC). However, in foam separation experiments this factor does not always seem fully appreciated, where concentrations above CMC are sometimes used.

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References

- ¹ Cardozo, R. L., Euratom (Italy), EUR, 262e, 1963
- ² Davis, B. M., & Sebba, F., *J. appl. Chem., Lond.*, 1966, **16**, 293
- ³ Sebba, F., 'Ion Flotation' 1962 (Elsevier Monographs)
- ⁴ Rubin, A. J., Johnson, J. D., & Lamb, J. C., 'Ion and Precipitate Flotation: A study and comparison of variables', Paper presented to the American Chem. Soc., Sept. 15, 1965
- ⁵ Grieves, R. B., & Wood, R. K., *Nature, Lond.*, 1963, **200**, 332
- ⁶ Rubin, E., Schonfeld, E., & Everett, R., jun., Sub-contract 2024 to Oak Ridge National Laboratory; RAI 104, Oct. 1962
- ⁷ Davis, W., jun., Kibbey, A. H., & Schonfeld, E., ORNL—3811 TID—450, Oct. 1965

THE EFFECT OF GRINDING ON PRECIPITATED MAGNESIUM HYDROXIDE

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Magnesium hydroxide, prepared by precipitation, was ground in a vibratory ball mill for 733 h. Samples were withdrawn at intervals, and examined by thermogravimetric analysis and by X-ray diffraction (the broadening of the lines being analysed using integral breadths), and their specific surfaces were determined by adsorption of nitrogen at -183° .

The results indicate that the particles initially consist of small piles of plate-like crystallites and that they become progressively fractured across their (001) faces, until they are approximately equi-dimensional. By a process of shearing and re-adhesion, the piles become increasingly turbostratic in structure, but distortion of the lattice appears only after 350 h. Water is adsorbed on the surface temporarily exposed during grinding and some, at least, of it becomes buried in the interior of the particles.

Introduction

The most obvious effect of grinding a solid is to reduce its average particle size; but as is well known, the disintegration is opposed by re-aggregation so that after sufficient time a stationary state is set up when the rates of the two processes are equal.^{1,2} Further grinding should then produce no further effect on the average particle size. Grinding might also be expected to distort, or even destroy, the structure of the solid, and some experimental evidence for this is extant.

Thus Bacon³ found that the degree of disorder of the layer planes of graphite relative to their neighbours was greatly increased by ball-milling for long periods; vermiculite⁴ and mica⁵ both show enhanced base-exchange capacity after grinding, and destruction of the structure of montmorillonite⁶ and of wheat starch has been reported;⁷ and several workers have noted the formation of a disturbed layer on quartz particles when ground for long periods.⁸

Thermogravimetric analysis of the ground samples of kaolinite⁹ has demonstrated that after grinding, the structure of the material was strained—for constitutional water was expelled at lower temperatures—but that the kaolinite was

not actually decomposed, since the total content of constitutional water was unchanged.

Precipitated magnesium hydroxide seemed a suitable substance with which to extend this study. Like graphite and kaolinite, magnesium hydroxide has a layer structure, but it differs from graphite in being a chemical compound and from kaolinite in being free of possible complications arising from isomorphous replacement of cations. Moreover, magnesium hydroxide has a definite chemical composition with a clearly defined and relatively simple structure; correspondingly, its thermogravimetric analysis curve is simple in form, so that any structural distortion or decomposition should be detected with relative ease and certainty.

In addition there is considerable information regarding behaviour of magnesium hydroxide as an active solid.¹⁰⁻¹³

Experimental

Materials

The magnesium hydroxide was prepared by the precipitation of 10 litres of N-magnesium chloride solution with an equal volume of N-potassium hydroxide, both chemicals being of Analytical Reagent quality.

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The solutions were run at equal rates through glass jets into an aspirator containing enough water to cover the openings of the jets. This procedure would, it was hoped, ensure that the content of ions adsorbed on the precipitate would be small.

The sludge was washed repeatedly by decantation with CO_2 -free water, the water was then evaporated at 80° under the partial vacuum from a water pump, and the solid was finally dried in a desiccator over phosphorus pentoxide.

Procedure

The grinding was carried out in a vibratory ball mill. The solid (102 g) was placed along with 34 porcelain balls 2 cm in diameter in the (cylindrical) jar which was 10 cm high by 10 cm in diameter. Samples were withdrawn for examination after the following times (h): 1, 4, 8, 16, 76, 124, 211, 350, 503, 650 and 733. (A period of some weeks elapsed between the withdrawals at 503 and 650 h respectively, because of the breakage of the mill. The 503-h sample was stored meanwhile in a desiccator without desiccant.)

Each sample was then submitted to the following tests:

(a) *Determination of specific surface* by sorption of nitrogen at -183° using the standard Brunauer-Emmett-Teller (BET) procedure,¹⁴ with a volumetric apparatus.¹⁵ Outgassing was for 1 h at 15° , one further hour whilst the temperature was being raised to 125° , and two final hours at 125° . The cross-sectional area of the nitrogen molecule was taken as 17.0\AA^2 . The BET plot was a good straight line except with the 650- and 733-h samples.

(b) *Thermogravimetric analysis* in air, the balance being of the ordinary analytical type. The temperature of the furnace was raised at 6 deg c per minute, and the weight was determined at frequent intervals.

(c) *X-ray diffraction*, by means of a Philips Diffractometer of Type PW1051, using CuK radiation.

The diffractometer traces did not permit the resolution of the $\alpha_1\alpha_2$ doublet, particularly for the lines at relatively low angles. Lines corresponding to angles below 24° were obtained when necessary with a $\frac{1}{2}^\circ$ slit and the remainder with a 1° slit. Allowance was made for the instrumental broadening, using a well crystallised sample of silicon.

The indexing of the lines was carried out on the basis of the A.S.T.M. powder data file¹⁶ and of Parrish & Irwin.¹⁷ Certain lines were selected as being suitable for the detailed study of the line broadening viz (001), (101), (102), (110) and (111). These lines have a satisfactory profile, are of comparatively high intensity, show a low influence of the $\alpha_1\alpha_2$ doublet, and provide the necessary information for estimating t_{001} , t_{hko} and t_{hkl} , the thicknesses of the crystallites in the directions normal to the respective sets of planes.

From the charts the following quantities were measured:

- (i) integrated intensities (I_i);
- (ii) the height of the peak at the maximum (I_h);
- (iii) instrumental broadening at suitable angles 2θ ; and
- (iv) the integral breadths β_i and the half-intensity widths $\beta_{1/2}$ using the graphical method of Alexander.¹⁸

A sample of well crystallised natural brucite was also measured for purposes of comparison.

Results

The results for specific surface are plotted as a function of time in Fig. 1. The point for 124 h seems anomalous, and it was not possible to carry out a duplicate run to test its validity; it will be noted that, if this point be ignored, the surface area first decreases with time and then increases again, but that at no time does it exceed the initial value.

The results of the thermogravimetric analysis are summarised in Fig. 2 and 3. As is seen, there are two temperature ranges in which a rapid loss in weight occurs, separated by a

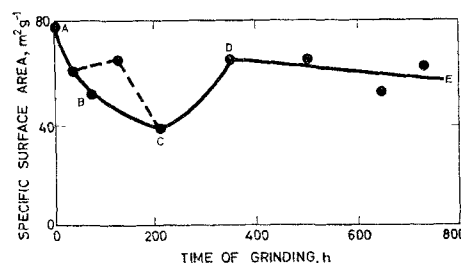


Fig. 1. Specific surface areas of $\text{Mg}(\text{OH})_2$ (determined by sorption of nitrogen) plotted against time of grinding

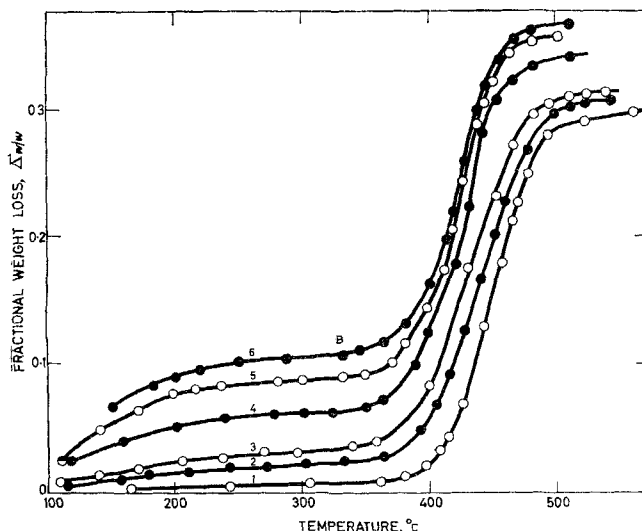


Fig. 2. Thermogravimetric analysis of samples of milled $\text{Mg}(\text{OH})_2$. Temperature rise 6° per minute. The loss in weight per g ($-\Delta w/w$) is plotted against the temperature T . Time of grinding, curve (1) 0 h; (2) 211 h; (3) 350 h; (4) 503 h; (5) 650 h; (6) 733 h

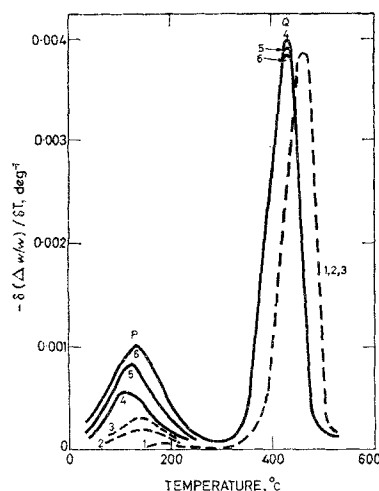


Fig. 3. Thermogravimetric analysis of the samples of $\text{Mg}(\text{OH})_2$ referred to in Fig. 2, plotted as $-\delta(\Delta w/w)/\delta T$ against T

short range in which the weight changes only slowly. Samples were still losing weight at the highest temperatures of the curves, and with three samples (0, 350 and 503 h) the temperature was taken up to 1020° and maintained there for 30 min. to determine the loss in weight between B and 1020° (deemed to correspond to complete decomposition). This loss was 30.9, 31.1 and 31.1% respectively for the three samples and was therefore close to the theoretical figure, viz. 30.88%, for the complete conversion of $\text{Mg}(\text{OH})_2$ into MgO .

The higher temperature peak (Q) of Fig. 3 clearly corresponds to the decomposition of $\text{Mg}(\text{OH})_2$ to MgO , whereas the lower temperature peak (P) is plausibly ascribed to the loss of adsorbed water. The location of the peak is not appreciably altered by grinding for periods up to 350 h, but it is progressively, but slightly, lowered as the time of grinding increases above 350 h; the lowering signifies that the structure has become distorted,¹⁹ a conclusion supported by the X-ray data.

In Fig. 4 the results for β_i for each selected line are plotted against the time of grinding. The typical pattern of brucite was found in all samples. In the sample ground for 733 h some lines at high values of θ were so diffuse that they merged into the background.

Discussion

From Fig. 4 it is seen that the breadths of all the peaks other than 001 increase continuously during grinding. The run as a whole may be divided into three sections as regards the behaviour of these peaks: (I) (0 h to 211 h) during which continuous broadening is observed; (II) (211 h to 350 h) where, except for the 001 line, the line breadths remain constant; and (III) (350 h onwards) where the broadening again increases.

In principle, line broadening may be caused either by a diminution in particle size or by distortion of the structure. Thus (ignoring the 001 line) one may infer that during Period II neither of these processes is occurring; but, since grinding is a continuous process one would expect that if distortion took place during Period I it would be intensified in Period II. Thus the line broadening in Period I is probably caused by reduction in crystallite size rather than by structural distortion. This inference is supported by the fact that the intensity of the lines does not diminish throughout Periods I and II,

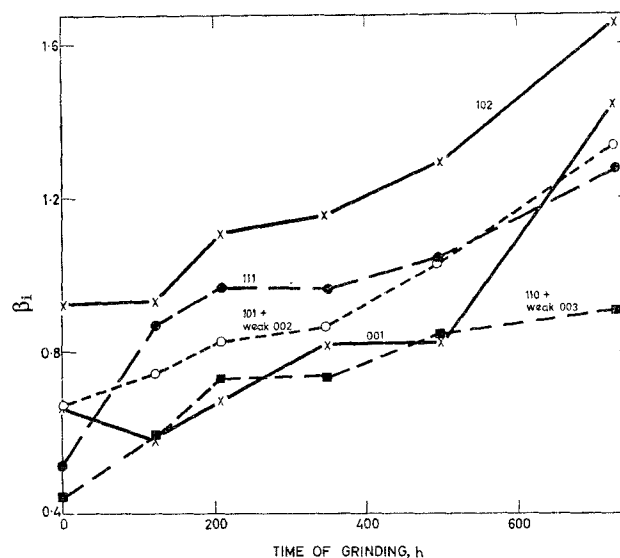


Fig. 4. Integral breadths β_i versus time of grinding, for several lines, of samples of $\text{Mg}(\text{OH})_2$ ground for different periods up to 733 h

and also by the thermogravimetric results: as is seen from Fig. 3, the position of the high-temperature peak Q, which corresponds to the decomposition of $\text{Mg}(\text{OH})_2$ to MgO , is not appreciably shifted by grinding for periods up to 350 h (Periods I and II), but is progressively, though slightly, shifted towards lower temperatures as the time of grinding increases above 350 h (Period III); this suggests that during Period III some distortion of the structure has occurred.³

The increase in line breadth during Periods I and II must, then, be ascribed to reduction in particle size, which will now be discussed. The X-ray results indicate that the original particles of the magnesium hydroxide consist of small piles of plate-like crystallites, each crystallite having a fairly high degree of crystalline perfection; the platelets adhere by their (001) faces but are somewhat twisted about the c-axis relative to one another—a turbostratic structure. This is the well-known Arnfeld phenomenon already observed by several workers (cf. Fricke²⁰).

There are thus three types of dimension to be considered: L , the diameter of the plates (taken, for simplicity, as circular in shape); t , the thickness of the plates; and H , the height of the piles. L , t and H are of course average values. For these calculations the conventional Scherrer formula has been used, viz.

$$t_{hkl} = \frac{K\lambda F}{\beta_i \cos \theta} \quad (1)$$

where t_{hkl} is the distance of separation of the hkl planes, β_i is the integral line breadth, λ is the wavelength of the X-rays (here 1.54\AA , for $\text{Cu-K}\alpha$ radiation), F is a factor to transpose radians to degrees and K is a shape factor. L has been calculated by application of Equation (1) to the (110) interference, taking $^{21}K = 1.18$, i.e. $L = D_{110}$. The values of L for the grinding Periods I and II appear in Table I; and as is seen L diminishes in value by almost one-half in Period I but changes little in Period II.

The quantities H and t require somewhat more detailed discussion. If the arrangement of the platelets in their piles were perfectly ordered, then their (001) reflection would be coherent; H and t would be identical and would be given by $t_{001} = H = t$. If on the other hand the platelets, though still

TABLE I
Results from X-ray line broadening

Time of grinding, h	0	124	211	350
L , Å	326	211	166	165
H , Å	138	160	138	110
t (apparent), Å	82	75	67	65
t , Å	65	65	65	65
n	2.1	2.5	2.1	1.7
π	0.60	0.78	0.95	1.00
S_x (m ² g ⁻¹)	180	208	228	229

(n = number of platelets per pile = H/t)

lying parallel within their piles were completely disordered about the c -axis, then D_{001} would still be equal to H but would give no information about t . Such information would be obtained by a consideration of the reflections from the 101 or 102 planes, since these run from the lower to the upper face of each platelet, but in a disordered pile do not run across from a given platelet to the platelet above or below. The 102 line has been found more suitable for this purpose and the distance t_{102} has been calculated from it. This distance is of course the distance between the 102 planes measured along a normal to them, and can be converted to t by a simple trigonometrical relationship involving cell dimensions, viz.

$$t = 1.25 t_{102} \quad \dots\dots\dots(2)$$

If however a fraction and not the whole of the platelets are twisted about the c -axis, then t_{102} will have a value lying somewhere between t and H .

In Table I, the values of t calculated from Equations (1) and (2), on the assumption that there is complete disorder about the c -axis, are given under the heading t (apparent). As is seen, the value of this quantity diminishes somewhat between 0 and 350 h; and this may arise either from a real diminution in the thickness of the platelets, or from an increase in the disorder within the piles—or of course from both together.

The second of these causes seems much the more probable: the grinding would tend to bring about a separation of the platelets from one another by a shearing action, and the platelets would then tend to re-adhere through their (001) faces, but in a random manner; the disorder about the c -axis should therefore increase, as it does do. It therefore seems reasonable to suppose that the thickness of the platelets remains virtually constant at 65 Å throughout Periods I and II and that the degree of disorder increases with time of grinding. On this hypothesis it is possible by an extension of established methods (see Appendix) to calculate π , the probability of the stacking disorder of the crystallites within the piles. The values of π so obtained are given in Table I, along with S_x , i.e. the specific surface area of the crystallites calculated by simple geometry on the assumption that the crystallites are circular platelets.

In Period III the lines broaden from 350 h onwards except for the (001) reflection which remains constant between 350 and 503 h. Since the thermogravimetric analysis results indicate that some structural distortion is present at 503 h, the line-broadening during Period III is probably caused by structural distortion. Indeed, since in Periods I and II both t and L reached a constant value, and the piles became completely disordered, structural distortion would seem to be the only remaining explanation for further broadening.

The constancy in width of the (001) line between 350 and 503 h signifies that the value of H is not changing throughout

this period; this behaviour, which is to be contrasted with the increase in width of all the other lines, can be understood in terms of the layer structure of magnesium hydroxide. During this period, some sliding of the plates parallel to the (001) direction can occur, and this would leave the (001) reflections unaffected whilst disturbing all the remaining reflections. The marked increase in width which takes place between 503 and 730 h may then be plausibly ascribed to a diminution in the value of H ; and on this assumption one can calculate the value of H at 730 h, and it comes to $H = 62$ Å, almost the same as the thickness of a single crystallite, suggesting that each crystallite is reflecting independently. In other words, the reinforcement of the (001) reflections by neighbouring crystallites in a pile is being prevented; this interference could be due to the presence, on the surface of the crystallites, of a layer of adsorbed water or of adsorbed carbon dioxide; some evidence in favour of the first of these possibilities is presented below.

The surface area S_N measured by adsorption of nitrogen is, of course, the area accessible to nitrogen molecules, and so will constitute at most the area of the *outside* of the crystallites; moreover, such external faces of the piles as are separated (within the grains of the solid) by distances less than the diameter of a single nitrogen molecule, will not be reached by nitrogen and so will not contribute to the specific surface as measured by the nitrogen method. The diminution in surface area along ABC of Fig. 1 is presumably due to sterilisation of the surface in this way, and the subsequent increase along CD to the opening up of narrow pores of this kind.

Now if it be assumed that the area capable of physically adsorbing water is the same as that measured by the nitrogen method, the average number (m) of monolayers in the (line 2) m at 733 h is found to be nearly 6, which would seem improbably high, particularly as the relative humidity of the atmosphere in the mill would be expected to be much below saturation. On the other hand, if the calculation of m is based on the area of the outside of the crystallites as determined by X-rays (S_x of Table II) the values of m are rarely in excess of a monolayer (Table II, line 3). It is unlikely however that the *whole* of the surface area S_x would be covered with adsorbed water for the time of exposure between shearing and re-adhesion would often be quite short. Thus the real thickness of the adsorbed film at the end of the run must be somewhere between 1.7 and 5.7 monolayers, and very probably lies nearer to the lower figure.

Grinding equilibrium

According to Hüttig,²² a state of equilibrium should ultimately be attained during grinding, when the processes of disintegration and of re-aggregation proceed at the same rates, the one process being the exact reverse of the other so that there is no further observable change. *This equilibrium* refers to geometrical features, i.e. to the size of the grains. In the present study however we are concerned with three levels of aggregation: crystallites, piles and grains. A state of equilibrium for the grains appears to have been reached,

TABLE II
Thickness of layer of adsorbed water

Time of grinding, h	0	211	350	503	650	733
m (calc. from S_N)	0.3	1.9	1.6	3.3	4.5	5.7
m (calc. from S_x)	0.2	0.3	0.5	0.9	1.4	1.7

(m = number of monolayers of adsorbed water)

for after 350 h, S_N did not change greatly; and taken alone this would indicate that grinding equilibrium had been reached; but as we have seen there is evidence that between 350 and 733 h considerable structural distortion was occurring and that water was being progressively adsorbed. Thus both the bulk and the surface properties were changing at the close of the run; consequently, the structure of the grains formed by the adhesion of the piles to one another and the adhesion of crystallites to one another within the piles, will continue to change, for this structure will be a function of the surface energy of the solid. To attain a true grinding equilibrium under the conditions in question it would seem that times longer even than 733 h would be necessary.

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Appendix

Calculation of π

Suppose we have a sample consisting of N piles. If the probability of disorder is π , then we shall have πN disordered piles and $(1-\pi)N$ ordered ones. From the point of view of X-ray interference, we have in effect $n\pi N$ crystallites of thickness t and $(1-\pi)N$ crystallites of thickness nt (n = number of crystallites per pile). The average value of the apparent thickness, viz. t (apparent), is then

$$t \text{ (apparent)} = \frac{n\pi N.t + (1-\pi)nN.t}{n\pi N + (1-\pi)N}$$

$$\text{This reduces to } \frac{t \text{ (apparent)}}{t} = \frac{n}{(n-1)\pi + 1}$$

By inserting the values of t (apparent), $t (= 65 \text{ \AA})$ and n from Table I, one can immediately calculate the corresponding values of π . These are also given in the Table.

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References

- ¹ Bradshaw, B. C., *J. chem. Phys.*, 1951, **19**, 1057
- ² Hüttig, G. F., e.g. *Z. Metallk.*, 1957, **48**, 352; *Proc. Int. Symposium on Reactivity of Solids*, (Gothenburg), 1952, p. 979
- ³ Bacon, G. E., *Acta crystallogr.*, 1951, **4**, 558; 1952, **5**, 392
- ⁴ Mackenzie, R. C., & Milne, A. A., *Mineralog. Mag.*, 1953, **30**, 178
- ⁵ Mackenzie, R. C., & Meldau, R., *Ber. dt. keram. Ges.*, 1956, **33**, 222
- ⁶ Bloch, J., *Bull. Soc. chim. Fr.*, 1950, p. 774
- ⁷ Lampitt, L. H., Fuller, C. H. F., & Goldenberg, N., *J. Soc. chem. Ind.*, 1941, **60**, 69
- ⁸ e.g., Nagelschmidt, G., Gordon, R. L., & Griffin, O. G., *Nature, Lond.*, 1952, **169**, 539; Gordon, R. L., & Harris, G. W., *ibid.*, 1955, **175**, 1135; Brindley, G. W., & Udagawa, S., *J. Am. Ceram. Soc.*, 1959, **42**, 643
- ⁹ Gregg, S. J., Parker, T. W., & Stephens, M. J., *J. appl. Chem., Lond.*, 1954, **4**, 666
- ¹⁰ Gregg, S. J., Packer, R. K., & Wheatley, K. H., *J. chem. Soc.*, 1955, p.46
- ¹¹ Gregg, S. J., & Packer, R. K., *J. chem. Soc.*, 1955, p. 55
- ¹² Razouk, R. I., & Mikhail, R. S., *J. phys. Chem., Ithaca*, 1959 **63**, 1050
- ¹³ Livey, D. T., Wanklyn, B. M., Hewitt, M., & Murray, P., *Trans. Br. Ceram. Soc.*, 1957, **56**, 217
- ¹⁴ Brunauer, S., Emmett, P. H., & Teller, E., *J. Am. chem. Soc.*, 1938, **60**, 309
- ¹⁵ Gregg, S. J., & Stephens, M. J., *J. chem. Soc.*, 1953, p. 3951
- ¹⁶ X-Ray Powder Data File, A.S.T.M. 1957 (Card no. 7-239)
- ¹⁷ Parrish, W., & Irwin, B. M., 'Data for X-Ray analysis', 1953, Vol. I. (Phillip's Technical Library)
- ¹⁸ Alexander, L., *J. appl. Phys.*, 1954, **25**, 155
- ¹⁹ cf. Gregg, S. J., Parker, T. W., & Stephens, M. J., *J. appl. Chem., Lond.*, 1954, **4**, 666
- ²⁰ Fricke, R., Schnabel, R., & Beek, K., *Z. Electrochem.*, 1936, **42**, 881
- ²¹ Saenz, J. P., & Valverde, R., to be published
- ²² Hüttig, G. F., *Z. Metallk.*, 1957, **48**, 352; *Proc. Int. Symposium on Reactivity of Solids*, (Gothenburg), 1952, **1**, 979; cf. Bradshaw, B. C., *J. chem. Phys.*, 1951, **19**, 1057