

Lattice Constant Variations in Finely Divided Magnesium Oxide

BY I. F. GUILLIATT AND N. H. BRETT

Department of Ceramics with Refractories Technology
University of Sheffield

Received 22nd May, 1969

The lattice parameter of MgO has been measured as a function of crystallite size at room temperature and at temperatures up to $\sim 1050^\circ\text{C}$. Atmosphere has a pronounced effect on lattice parameter, traces of moisture causing lattice dilation. In the absence of water vapour or adsorbed gases a lattice contraction was observed, the magnitude of which increased with decreasing crystallite size. The data obtained in this work have been compared with those predicted theoretically.

The lattice parameter of finely divided MgO has been the subject of controversy, since various theoretical calculations have given different results. Garvie,¹ using the Born-Landé equation, explained the lattice dilation observed by other workers in MgO of very small crystallite size.² His assumption that the total interionic repulsion was independent of crystallite size was considered by Anderson and Scholz³ to be unjustified. These authors reported preliminary calculations on the size of ionic microcrystals, taking account of the effect of crystallite size on the total repulsion energy, and concluded that a lattice contraction should occur. Curtis⁴ criticized both sets of arguments for being too restrictive. Anderson and Scholz⁵ extended their study using more sophisticated calculations and obtained results which verified their previous predictions. When surface distortion was taken into account in the absence of polarization, the equilibrium ionic separation was little changed. However, after allowing for both polarization and surface distortion the model broke down for crystals containing divalent ions and the authors suggested that a purely ionic model of the surface was inadequate. Benson and Yun⁶ have developed a "shell-core" model for ions in an infinite crystal face. They predicted that the effects of surface distortion in alkali halides are not so drastic as the centro-symmetric force theories would suggest.

Earlier attempts to detect the difference in structure between normal and very small crystals have been reviewed by Rymer,⁷ who considered many previous results to be invalid owing to a breakdown of the diffraction theory when applied to crystals with a size less than 50 Å. This author used electron diffraction techniques to study lithium fluoride films and observed an increase in the lattice dimensions of small crystals in the size range 50-120 Å. Other alkali halides examined⁸ have been found to have normal lattice constants, although the crystal size of these specimens was in no case less than 100 Å. Nicolson⁹ predicted a lattice contraction in small ionic crystals. Using X-ray diffraction methods, only a small change in cell parameter was observed for magnesium carbonate decomposed in air, but a marked decrease was found when the decomposition was carried out under vacuum. Nicolson suggested that this effect was caused by layers of adsorbed gases and that even under vacuum there was incomplete removal of contamination from the surface. Cimino,

Porta and Valigi² obtained similar results with MgO prepared *in vacuo*, but found an expansion of the lattice when the crystals were exposed to air. This phenomenon was explained in terms of a dilatant volume stress imposed by a surface hydroxide layer around the MgO crystallites. The lattice dilation disappeared at crystallite sizes greater than ~ 150 Å, in MgO calcined under vacuum and subsequently exposed to air.

Previous experimental work suffers in that the purity of the powders examined is suspect, particularly with vacuum-decomposed samples; also the effects of contamination of the small crystallites by chemisorbed gases may have been considerable.⁵ Moreover, the methods used for the determination of crystallite size were usually imprecise. In the present work the effect of surface contaminants on very small MgO crystallites has been assessed using very pure materials and particular attention has been given to the precise determination of both the lattice parameter and crystallite size of samples. Thus it is hoped to provide reliable data by which the validity of the different theoretical models may be assessed.

EXPERIMENTAL

Magnesium hydroxide was prepared from Mg metal of 99.997 % stated purity in the following manner. Crystals of magnesium were dissolved in a minimum volume of dilute nitric acid and the solution was boiled until crystallization of magnesium nitrate hydrate commenced. After cooling slowly the crystals were separated from the mother liquor, washed, dried on filter paper and stored in an air-tight container. A solution of these crystals in water was purified by precipitating a head fraction of impurities with ammonia. The filtrate was treated with an excess of ammonia to give a pure $\text{Mg}(\text{OH})_2$ precipitate which was washed, then air-dried at 110°C . All operations were carried out in a nitrogen atmosphere inside a glove box, A.R. materials and high-grade polyethylene apparatus being used throughout. Spectroscopic analysis of the $\text{Mg}(\text{OH})_2$ showed the presence of 50 p.p.m. Al and 10 p.p.m. V, all other elements were below the limits of detection, e.g., Cr, Fe and Mo < 10 p.p.m., Mn < 5 p.p.m.

$\text{Mg}(\text{OH})_2$ powder was decomposed at 325°C overnight, then raised through a series of temperatures (table 2) in a modified Rigaku-Denki high-temperature attachment to a Philips 1050/25 goniometer, under a vacuum of 10^{-6} mmHg. In all cases, the selected temperature was maintained longer than 16 h before commencing the scan. Temperature measurement was made by a thermocouple placed in a platinum sample holder in which a bed of powder < 0.5 mm thick was held. The diffractometer was calibrated before and after individual experiments with spectroscopically pure Ni sponge ($a = 3.5238$ Å at 26°C) and pure MgO obtained from the hydroxide by calcination at 1550°C for 70 h ($a = 4.2113$ Å at 23°C).

The (200) diffraction peak of samples was step-scanned near the peak maximum at intervals of 0.01 or 0.05° (2θ) depending on the breadth of the profile. The position of the peak maximum was found with a precision better than 0.005° (2θ) by fitting the data to a parabola using the method of least-squares. Other reflections were not employed since none was sufficiently intense in the finest powders to allow reasonable counting times. Lattice parameters were calculated (± 0.0005 Å) from the position of the peak maximum, using the experimentally determined (200) diffraction peak of the MgO standard to compensate for absorption.

The crystallite size of samples was determined from a continuous scan of the (200) diffraction peak in the following manner. The peak half-breadth was measured, corrected for $K\alpha_1\alpha_2$ doublet broadening assuming a profile shape described by the equation $^{10} y = (1 + x^2)^{-2}$, (where y is the profile intensity at x° (2θ)), and converted to integral breadth using Ferguson's relationship,¹¹ $B_1 = 1.225 B_{\frac{1}{2}}$, where B_1 and $B_{\frac{1}{2}}$ are the integral and half breadths respectively.

The profiles were then corrected for instrumental broadening using the relation,¹² $\beta = B_1 - b^2/B_1$, where β is pure diffraction broadening and b_1 is the corrected instrumental broadening. The values of β obtained were inserted in the Scherrer equation with a shape

factor of unity.¹³ In addition, the step-scan data from four samples were analyzed after the method of Stokes,¹⁴ using an I.C.T. 1907 computer and a programme developed by Harrison.¹⁵ This method determines the value of β after correcting for absorption and Lorentz and polarization effects and makes no assumptions regarding peak profile shape.¹⁶ The values of crystallite size obtained using this method agreed to $\pm 1 \text{ \AA}$ ($\sim \pm 1 \%$) with those obtained as outlined above. The close correspondence of these methods of analysis has also been noted by Wagner and Aqua.¹⁷

In a preliminary experiment, $\text{Mg}(\text{OH})_2$ powder was decomposed as above, cooled to room temperature and the lattice parameter and crystallite size were determined. Air, dried by passing through towers of molecular sieve, was then admitted into the system and the measurements repeated. Finally, the powder was exposed to moist (laboratory) air and re-examined. Subsequently, powders were decomposed then raised to a selected calcination temperature and exposed to moist air directly on cooling to room temperature (except in two cases where the lattice parameter was measured under vacuum at room temperature).

RESULTS AND DISCUSSION

The crystallite size of the product MgO remained constant at 49 \AA during the preliminary experiment, but the lattice parameter changed from 4.2204 (vacuum) to 4.2198 (dry air) and 4.2310 \AA (moist air). These results show the effect of atmosphere on lattice parameter, in particular the dilation due to moisture. The results of further experiments are given in table 1 and shown in fig. 1 on curves A

TABLE 1.—LATTICE PARAMETER AND CRYSTALLITE SIZE VALUES OF MgO MICROCRYSTALS MEASURED AT ROOM TEMPERATURE

crystallite size D (\AA)	lattice parameter (\AA)*		Δr° (\AA)	
	vacuum	moist air	vacuum	moist air
43†	—	4.248 1	—	0.018 4
49	4.220 4	4.231 0	0.004 6	0.009 9
55†	—	4.235 5	—	0.012 1
62†	—	4.223 0	—	0.006 0
70	4.205 4	4.219 6	—0.003 0	0.004 2
102†	—	4.213 4	—	0.001 2
188	4.210 2	4.211 5	—0.000 6	0.000 2

* lattice parameter corrected to 23°C .

† results obtained from powders not decomposed in the Rigaku-Denki attachment but in a separate vacuum furnace.

(vacuum) and B (moist air).^{*} A progressive lattice dilation occurred with decreasing crystallite size; this has been observed by other workers, notably Cimino *et al.* The hypothesis that this dilation was an effect of disorder has been considered, but profile analysis by the method of Rymer⁷ showed that the strain broadening contribution was negligible. Other workers have reported the absence of strain,^{2, 18} or only very small strains,^{19, 20} in MgO of small crystallite size. Moreover, Montgomery, Stromberg and Jura²¹ have shown that induced strain in MgO is completely removed by annealing at $\sim 500^\circ\text{C}$.

The relatively large increase in lattice parameter of the high-surface-area material on exposure to moist air suggested that some rehydration of the powders may have occurred at room temperature under vacuum. If so, one could expect even lower

^{*} The data have been plotted using the method of Anderson and Scholz⁵ to facilitate comparison with their predicted data. Δr° is the difference in lattice parameter between perfect crystals and microcrystals. The microcrystals were assumed to be cubes containing N^3 ions with (100) surfaces. N is calculated from the formula $N = (D/d) + 1$, where D = crystallite size and d = interplanar spacing of the MgO (200) reflection.

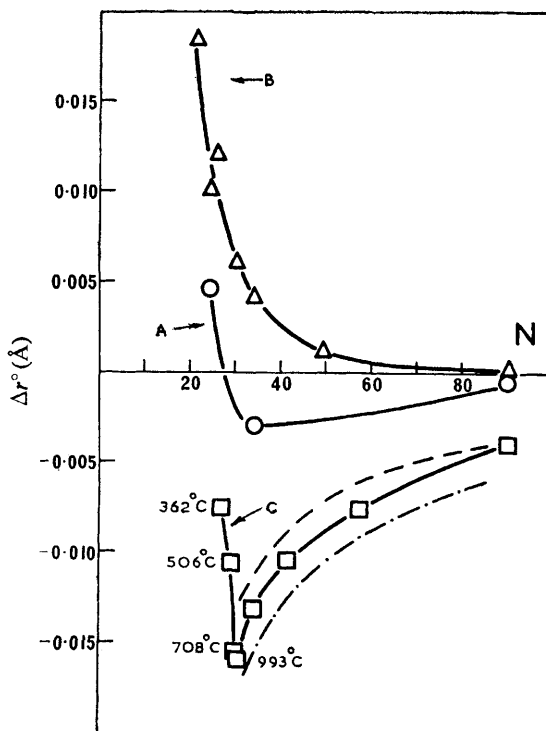


FIG. 1.—Change in the equilibrium separation Δr° of ions with N , for MgO microcrystals in various atmospheres. The microcrystals are assumed to be cubes having N^3 ions. Curve A, \circ , *in vacuo* at 23°C; curve B, \triangle , in moist air at 23°C; curve C, \square , *in vacuo* at various temperatures, corrected to 23°C. The calculated values of Anderson and Scholz⁵ are included for comparison, ---- repulsion parameter = 3 Å⁻¹, — · — · — repulsion parameter = 2.5 Å⁻¹.

lattice parameter values for finely divided material under ideal conditions, i.e., in the total absence of water vapour or hydroxyl ions. Therefore, measurements were carried out on a $\text{Mg}(\text{OH})_2$ powder at progressively increasing temperatures up to $\sim 1\,000^\circ\text{C}$. The results are given in table 2 and shown in curve C in fig. 1; lattice parameter values were corrected to 23°C assuming a linear expansion coefficient for MgO of $13.63 \times 10^{-6}/^\circ\text{C}$ over the range 25–1 000°C and $12.83 \times 10^{-6}/^\circ\text{C}$ over the range 25–500°C.²² At temperatures around 1 000°C the crystallite size of MgO was initially 62 Å and the growth rate was ~ 3 Å/day. In order to accelerate crystal growth and obtain the last two sets of readings in table 2, the vacuum was reduced to 10^{-2} mmHg pressure, measurements were then carried out under good vacuum after suitable times. The lattice parameter of MgO decreased as the temperature was raised to $\sim 1\,000^\circ\text{C}$ whilst the crystallite size remained almost constant. When crystal growth took place, the lattice parameter increased, but a lattice contraction was still evident at higher crystallite size values. The lowest values of lattice parameter were not reached below 708°C, probably due to the retention of water vapour or hydroxyl ions below this temperature. Anderson, Horlock and Oliver²³ noted the retention of chemisorbed water in vacuum calcines of MgO at temperatures up to 800°C. Further evidence for moisture adsorption was obtained on cooling the 188 Å crystallite size powder to room temperature. The lattice parameter increased from 4.203 5 Å (measured at 1 038°C and corrected to 23°C) to 4.210 2 Å, whilst still under good

vacuum. These results are in contrast to the dilation observed in the presence of moist air but are in accord with those predicted by Nicolson,⁹ and Anderson and Scholz.^{3, 5} The latter workers calculated the change in Δr° with N for MgO crystals at 0 K assuming repulsion parameter terms of $a = 3.0$ and 2.5 \AA^{-1} and that no surface distortion effect is present; their curves are included in fig. 1 for comparison.

TABLE 2.—LATTICE PARAMETER AND CRYSTALLITE SIZE VALUES OF
MgO MICRO-CRYSTALS MEASURED *in vacuo* AT VARIOUS TEMPER-
ATURES

crystallite size D (Å)	temp. (°C)	lattice * parameter (Å)	Δr° (Å)
55	362	4.196 0	−0.007 6
59	506	4.190 0	−0.010 7
61	708	4.180 2	−0.015 6
62	993	4.179 5	−0.015 9
69	1 042	4.184 9	−0.013 2
85	1 042	4.190 3	−0.010 5
119	1 036	4.195 9	−0.007 7
188	1 038	4.203 5	−0.004 0

* lattice parameter corrected to 23°C.

In comparing the results obtained at 1 000°C in this study with those calculated using the Anderson and Scholz model for crystals at 0 K, no attempt has been made to assess the effect of temperature on lattice energy. Curtis⁴ has pointed out the need to include a vibrational energy term in lattice energy calculations for crystals at real temperatures. Secondly, the inclusion of a surface distortion term in their calculations led to positive Δr° values and a breakdown of the model for divalent crystals. The Benson and Yun⁶ treatment gives a smaller change in Δr° (relaxation) for alkali halides after allowing for surface distortion and polarization. However, this model applies to an infinite crystal face, whereas Anderson and Scholz have shown the importance of edge and corner effects. Our results would imply qualitatively that the relaxation effect, if present, is not large.

According to Curtis, the treatments of both Nicolson and Anderson and Scholz agree that $dr^\circ/dN \sim k N^{-2}$, with k positive and of the order of 0.5 \AA . A plot of Δr° against $1/N$ was fitted to a straight line by the least-squares method, viz., $\Delta r^\circ = 0.000 6 - 0.48/N$. This value of k , $0.48 \pm 0.02 \text{ \AA}$, compares with the value of 0.63 \AA calculated by Nicolson from the isothermal compressibility. Taking eqn (4) of Anderson and Scholz³ and inserting values of 2.5, 2.7 and 3.0 \AA^{-1} for the repulsion parameter term A , with $N = 100$, the values of k are 0.50, 0.45 and 0.38 \AA respectively. This is in good agreement with the value of k determined from a plot of the 1 000°C data. The surface tension T of small MgO crystallites can be determined at a given temperature from the relationship,² $\Delta a/a = 4T/3KD$, where K is the bulk modulus, D the crystallite size and a the lattice parameter of the material. The value of T determined for MgO at 1 000°C in this work was 3 900 dyn/cm. A value of 6 573 dyn/cm was calculated for the (100) face of MgO by Nicolson, who stated that his determined values of Δa were between 28 and 60 % of the theoretical value; the discrepancy was assumed to be due to surface contamination or over-estimation in the calculated surface tension value. In the present work, the surface tension of MgO in moist air at room temperature was $-4 830 \text{ dyn/cm}$, calculated for crystallite sizes greater than 62 \AA . Other values in the literature² are $-1 800 \text{ dyn/cm}$, and $-4 000 \text{ dyn/cm}$ calculated from the data of Rosauer and Handy.²⁴ The importance of atmosphere is emphasized by the displacement of the curves in fig. 1, the surface

tension values for samples exposed to air are therefore considered less reliable than those examined under vacuum.

The theoretical treatments of lattice parameter changes in ionic microcrystals are based on the assumption of perfect cubes at 0 K. Our data are for real powders which are microporous agglomerates of particles of unspecified shape, containing lattice defects at high temperatures. Nevertheless, the magnitude and direction of the phenomena measured are in good agreement with the predictions of Nicolson and Anderson and Scholz and are contrary to those of Garvie.¹ The lattice dilation effect, which was observed by Cimino *et al.*² in MgO microcrystals exposed to moisture, has been confirmed.

The authors thank the U.K.A.E.A. for the bursary awarded to one of them (I. F. G.).

- ¹ R. C. Garvie, *Mat. Res. Bull.*, 1966, **1**, 161.
- ² A. Cimino, P. Porta and M. Valigi, *J. Amer. Ceram. Soc.*, 1966, **49**, 152.
- ³ P. J. Anderson and A. Scholz, *Mat. Res. Bull.*, 1967, **2**, 895.
- ⁴ R. M. Curtis, *Mat. Res. Bull.*, 1968, **3**, 533.
- ⁵ P. J. Anderson and A. Scholz, *Trans. Faraday Soc.*, 1968, **64**, 2973.
- ⁶ G. C. Benson and K. S. Yun, *The Solid-Gas Interface*, ed. E. A. Flood (Arnold, 1967), vol. 1, chap. 8, p. 203.
- ⁷ T. B. Rymer, *Nuovo Cimento*, 1957, **6**, (suppl. 10), 294.
- ⁸ T. B. Rymer and K. H. R. Wright, *Proc. Roy. Soc. A.*, 1952, **215**, 550.
- ⁹ M. M. Nicolson, *Proc. Roy. Soc. A*, 1955, **228**, 490.
- ¹⁰ L. Alexander, *J. Appl. Phys.*, 1954, **25**, 155.
- ¹¹ I. F. Ferguson, A.E.R.E. Report 3495, 1961.
- ¹² T. R. Anantharaman and J. W. Christian, *Acta Cryst.*, 1956, **9**, 479.
- ¹³ A. J. C. Wilson, *Mathematical Theory of X-ray Powder Diffractometry*, (Centrex, Eindhoven, 1963).
- ¹⁴ A. R. Stokes, *Proc. Phys. Soc. B.*, 1948, **61**, 382.
- ¹⁵ J. W. Harrison, *A.E.R.E. Report* 4918, 1965.
- ¹⁶ I. F. Guillatt and N. H. Brett, *J. Brit. Ceram. Soc.*, 1969, **6**, 56.
- ¹⁷ C. N. J. Wagner and H. N. Aqua, *Adv. X-ray Analysis*, 1964, **7**, 46.
- ¹⁸ P. J. Anderson and D. T. Livey, *Powder Metallurgy*, 1961, **7**, 189.
- ¹⁹ D. K. Thomas and T. W. Baker, *Proc. Phys. Soc.*, 1959, **74**, 673.
- ²⁰ Z. Librant and R. Pampuch, *J. Amer. Ceram. Soc.*, 1968, **51**, 109.
- ²¹ P. W. Montgomery, H. Stromberg and G. Jura, *Solid Surfaces and the Gas-Solid Interface*, ed. R. F. Gould, (Adv. Chem. Series no. 33, Amer. Chem. Soc., Washington, D.C.).
- ²² P. T. B. Schaffer, *High-Temperature Materials, Materials Index*, (Plenum Press, New York, 1964).
- ²³ P. J. Anderson, R. F. Horlock and J. F. Oliver, *Trans. Faraday Soc.*, 1965, **61**, 2754.
- ²⁴ E. A. Rosauer and R. L. Handy, *Proc. Iowa Acad. Sci.*, 1961, **68**, 357.