An Experimental Determination of the Ionic State of MgO by Single-Crystal Methods

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X-ray diffraction measurements have been made of the intensities of Bragg reflexions from a single crystal of MgO which had been neutron irradiated in order to overcome the effects of extinction. Least-squares refinement of the data in terms of a number of spherical 'prepared' models shows that the best agreement is obtained for the Mg^{2+}, O^{2-} (+2 well) atomic scattering factors combined with the two isotropic temperature factors $B_{Mg} = 0.346$ (0.009) $Å^2$ and $B_O = 0.315$ (0.010) $Å^2$. Three different sets of powder data for MgO have been re-examined and for two of these sets of measurements the best agreement is obtained with a combination of Mg^{2+} and O^{2-} (+2 well) atomic scattering factors, while the Mg^{2+}, O^{2-} (Tokonami) scattering factors gives the best fit to the third set of data. The above sets of X-ray data give various descriptions of the thermal motion in MgO and these results are compared with vibration amplitudes calculated with the use of a simple shell model which yielded the values $B_{Mg} = 0.287$ $Å^2$ and $B_O = 0.350$ $Å^2$ for the isotropic temperature factors.

Introduction

The most recent X-ray intensity data available for magnesium oxide are the powder measurements of To-gawa (1965), Burley (1965) and Raccah & Arnott (1967). Each of these workers carried out intensity measurements with Cu radiation and employed the powder technique to avoid systematic errors introduced by extinction effects when measurements are carried out on single crystals.

Studies of X-ray line broadening in neutron irradiated magnesium oxide by Walker & Hickman (1965) indicated that for doses above 4×10^{20} n.v.t. (at 75–100°C) interaction between dislocation loops leads to the formation of a structure similar to that of a polygonized metal where the cellular structure is apparently equiaxed. This type of structure approximates that of an ideally imperfect crystal and the subsequent neutron diffraction measurements of Sabine (1965) on a MgO crystal irradiated to this dose gave values of the intensity of Bragg reflexions that were extinction free. In this work a small sample of this crystal has been used in an attempt to obtain more accurate and extensive X-ray data.

Theory

Magnesium oxide has the well known NaCl structure with four magnesium ions at $(0, 0, 0) + F.C.T.$ and four oxygen ions at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + F.C.T.$ and the corresponding structure factors are usually expressed in terms of a suitable spherical 'prepared' model given by the relation,

$$F(S) = 4[f_{c,Mg}(S) \exp(-B_{Mg}) \sin^2 \theta) \\ \pm f_{c, O}(S) \exp(-B_O \sin^2 \theta / \lambda^2)] \quad (1)$$

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The terms $f_{c,Mg}(S)$, $f_{c,O}(S)$ are the atomic scattering factors and the terms B_{Mg}, B_O the isotropic temperature factors of magnesium and oxygen respectively. The allowed reflexions for MgO must have h, k, l all odd or all even; the upper sign in (1) applying for h, k, l all even and the lower sign to h, k, l all odd.

Of the various ionic states that can be postulated for MgO, within the framework of the isolated atom approach, only the combination of Mg^{2+} and O^{2-} scattering factors presents any problems. There is no difficulty in obtaining Hartree–Fock (HF) solutions for the Mg^{2+} ion and the HF wave functions of Clementi (1965) for $Mg^{2+}(^1S)$ are used in the calculations to follow (the HF wave functions of Clementi for Mg (^1S), $Mg^+(^2S)$, $O(^3P)$ and $O^-(^2P)$ were used in the calculations for the other combinations of ionic states for MgO). However, the O^{2-} ion does not exist in the free state and it is doubtful that a HF solution would converge to a state with all ten electrons bound for a free O^{2-} ion.

Crystalline O^{2-} ions are stabilized by their environment and Yamashita & Kojima (1952) resolved the above difficulty by assuming that the atomic HF (1s) and (2s) wave functions were the same as those for O^- and then derived the (2p) wave function by a variational principle under exchange interaction with Mg^{2+} in the MgO crystal. The magnesium ion wave functions were also atomic HF solutions. Suzuki (1960) gives the corresponding O^{2-} atomic scattering factor.

Later, Watson (1958) obtained HF wave functions for the (1s), (2s) and (2p) states of O^{2-} by using two different types of stabilizing potential wells in addition to the nuclear potential in the HF calculation. These two stabilizing wells are the +1 and +2 wells of Watson (1958), although he prefers the +1 well solutions. The corresponding atomic scattering factors have also been calculated by Suzuki (1960).

Clementi & McLean (1964) also give HF wave functions for $O^{2-}(^1S)$, but they were not satisfied with the

Table 1. *Atomic scattering factors for various ionic states of oxygen*

The HF wave functions of Clementi (1965) have been used for O(^3P) and O$^-$(^2P). O^{2-} scattering factors have been calculated using the $+1$ and $+2$ well HF wave functions of Watson (1958) and these are compared with the corresponding results of Suzuki (1960) and also with the values tabulated by Tokonami (1965) for the O^{2-} wave functions of Yamashita (1964).

$\frac{\sin\theta}{\lambda}$ (Å^{-1})	O(^3P)	O$^-$(^2P)	O^{2-} ($+1$ well)		O^{2-} ($+2$ well)		O^{2-} (Tok)
			Present	Suzuki	Present	Suzuki	
0·00	8·000	9·000	10·000	10·000	10·000	10·000	10·000
0·05	7·799	8·671	9·523	9·491	9·567	9·551	9·633
0·10	7·249	7·838	8·371	8·357	8·482	8·475	8·671
0·15	6·479	6·795	7·030	7·027	7·162	7·159	7·423
0·20	5·631	5·758	5·801	5·802	5·909	5·908	6·174
0·25	4·815	4·837	4·788	4·789	4·857	4·857	5·081
0·30	4·094	4·068	3·993	3·994	4·028	4·028	4·192
0·35	3·492	3·451	3·383	3·383	3·395	3·394	3·498
0·40	3·008	2·968	2·918	2·918	2·917	2·916	2·968
0·45	2·630	2·597	2·565		2·557		
0·50	2·338	2·313	2·298	2·298	2·288	2·287	2·274
0·60	1·945	1·934	1·938	1·938	1·929	1·929	1·891
0·70	1·713	1·710	1·721	1·721	1·714	1·714	1·676
0·80	1·567	1·566	1·578	1·578	1·574	1·574	1·543
0·90	1·462	1·462	1·472	1·472	1·469	1·469	1·447
1·00	1·376	1·376	1·382	1·382	1·381	1·381	1·367
1·10	1·297	1·296	1·300	1·300	1·299	1·299	1·291
1·20	1·220	1·219	1·221	1·221	1·220	1·220	1·216
1·30	1·144	1·143	1·144	1·144	1·143	1·143	1·142
1·40	1·069	1·068	1·068		1·067		
1·50	0·996	0·994	0·994		0·994		0·995
1·60	0·924	0·923	0·923		0·922		
1·70	0·856	0·854	0·854		0·854		0·856
1·80	0·791	0·789	0·790		0·789		
1·90	0·730	0·728	0·728		0·728		0·729
2·00	9·672	0·670	0·671		0·670		

final parameters that they obtained owing to a combination of non-convergence in the self-consistent field procedure and the fact that wave functions for excited states were also produced. These wave functions were not used in the calculations to be described below.

Recently Yamashita (1964) improved his previous calculations by use of the (1s) and (2s) wave functions for the $+1$ well of Watson (1958). Tokonami (1965) gives the relevant atomic scattering factor.

The atomic scattering factors for the various ionic states of oxygen are given in Table 1. Similar values for the different ionic states of magnesium are given in Table 2. The values given in these tables have been calculated by numerical integration using Simpson's rule over the 441-point mesh of Herman & Skillman (1963). Hanson, Herman, Lea & Skillman (1964) showed that this method is numerically accurate to seven significant figures. Unfortunately the wave functions of Yamashita (1964) have not been published to date, and thus it was not possible to repeat the atomic scattering factor calculation for this version of O^{2-}. Instead the values given by Tokonami (1965) are listed in Table 1. The results for the ($+1$ well) and ($+2$ well) O^{2-} wave functions are compared with those given by Suzuki (1960) and slight differences occur at small values of (sin θ)/λ.

Table 2. *Atomic scattering factors for various ionic states of magnesium using the HF wave functions of Clementi (1965) and the assumption of spherical symmetry*

$\frac{\sin\theta}{\lambda}$ (Å^{-1})	Mg(^1S)	Mg$^+$(^2S)	Mg^{2+}(^1S)
0·00	12·000	11·000	10·000
0·05	11·506	10·754	9·914
0·10	10·470	10·156	9·662
0·15	9·499	9·451	9·265
0·20	8·733	8·766	8·751
0·25	8·075	8·110	8·155
0·30	7·444	7·464	7·512
0·35	6·813	6·821	6·853
0·40	6·190	6·191	6·206
0·45	5·590	5·588	5·591
0·50	5·028	5·025	5·020
0·60	4·052	4·050	4·040
0·70	3·291	3·289	3·281
0·80	2·723	2·722	2·717
0·90	2·312	2·311	2·309
1·00	2·018	2·017	2·018
1·10	1·808	1·807	1·809
1·20	1·656	1·656	1·658
1·30	1·543	1·543	1·545
1·40	1·456	1·456	1·457
1·50	1·384	1·385	1·385
1·60	1·323	1·323	1·324
1·70	1·268	1·268	1·268
1·80	1·216	1·216	1·216
1·90	1·166	1·166	1·165
2·00	1·118	1·118	1·117

Effects of ionicity occur mainly at low values of $(\sin\theta)/\lambda$ and this is expected from Fourier transform theory since contributions from different numbers of outer electrons are involved. Unfortunately the lowest angle reflexion of MgO, 111, occurs at a value of $(\sin\theta)/\lambda$ that is just too large to enable the main differences between the various scattering factors to be detected. However, information can still be obtained from the low angle reflexions of MgO since there are significant differences between the scattering factors over a reasonably wide range of $(\sin\theta)/\lambda$.

A closer examination of the atomic scattering factors for O^{2-} in Table 1 shows that the values for the Yamashita (1964) wave functions are different to those calculated from the Watson (1958) HF wave functions. This difference in behaviour is due to the more contracted $(2p)$ state radial charge density for the Yamashita (1964) wave functions.

Table 3. *Structure factors for the various spherical 'prepared' models based on the isotropic temperature factors* $B_{Mg} = 0.346$ Å^2, $B_O = 0.315$ Å^2 *and reduced to an absolute scale by the scale factor* 32·58

| | | | | | | F_{calc} | | |
h	k	l	F_{obs}	$Mg^{2+}O^{2-}$ (+2 well)	$Mg^{2+}O^{2-}$ (+1 well)	Mg^+O^-	MgO	$Mg^{2+}O^{2-}$ (Tok)
1	1	1	11·48	11·62	12·03	12·16	12·46	10·48
2	0	0	54·06	52·86	52·55	52·53	52·22	53·72
2	2	0	40·98	41·03	40·97	41·10	41·21	41·24
3	1	1	12·32	12·72	12·72	12·45	12·29	12·58
2	2	2	32·95	33·81	33·83	33·96	34·10	33·95
4	0	0	29·08	28·81	28·85	28·94	29·06	28·97
3	3	1	9·55	9·69	9·65	9·63	9·56	9·54
4	2	0	24·83	25·12	25·16	25·22	25·30	25·26
2	2	4	22·19	22·28	22·32	22·35	22·40	22·35
1	1	5	7·15	7·16	7·13	7·19	7·16	7·16
3	3	3	7·41	7·16	7·13	7·19	7·16	7·16
4	4	0	17·98	18·21	18·24	18·23	18·25	18·10
5	3	1	5·34	5·34	5·31	5·38	5·37	5·50
6	0	0	16·62	16·71	16·73	16·71	16·73	16·53
4	4	2	16·74	16·71	16·73	16·71	16·73	16·53
6	2	0	15·43	15·45	15·46	15·44	15·45	15·21
5	3	3	4·06	4·04	4·03	4·08	4·08	4·30
2	2	6	14·14	14·37	14·39	14·37	14·37	14·10
4	4	4	13·31	13·45	13·46	13·44	13·44	13·16
7	1	1	3·24	3·13	3·12	3·16	3·16	3·42
5	5	1	3·24	3·13	3·12	3·16	3·16	3·42
6	4	0	12·67	12·64	12·66	12·63	12·63	12·36
6	4	2	11·99	11·94	11·95	11·92	11·92	11·66
7	3	1	2·55	2·48	2·47	2·50	2·50	2·74
5	5	3	2·55	2·48	2·47	2·50	2·50	2·74
8	0	0	10·99	10·75	10·75	10·73	10·73	10·51
7	3	3	2·05	2·01	2·00	2·02	2·03	2·21
8	2	0	10·44	10·24	10·24	10·22	10·22	10·04
6	4	4	10·32	10·24	10·24	10·22	10·22	10·04
2	2	8	9·89	9·78	9·78	9·76	9·76	9·62
6	6	0	9·92	9·78	9·78	9·76	9·76	9·62
7	5	1	1·69	1·67	1·66	1·68	1·68	1·80
5	5	5	1·43	1·67	1·66	1·68	1·68	1·80
6	6	2	9·44	9·36	9·36	9·34	9·34	9·23
8	4	0	9·05	8·97	8·97	8·95	8·96	8·89
9	1	1	1·44	1·42	1·41	1·42	1·42	1·47
7	5	3	1·50	1·42	1·41	1·42	1·42	1·47
8	4	2	8·63	8·61	8·61	8·60	8·60	8·57
6	6	4	8·24	8·28	8·28	8·27	8·27	8·28
9	3	1	1·19	1·23	1·23	1·23	1·23	1·20
8	4	4	7·61	7·68	7·68	7·67	7·67	7·76
9	3	3	0·97	1·10	1·09	1·09	1·09	0·98
7	7	1	1·03	1·10	1·09	1·09	1·09	0·98
7	5	5	0·97	1·10	1·09	1·09	1·09	0·98
10	0	0	7·33	7·40	7·41	7·39	7·40	7·53
8	6	0	7·30	7·40	7·41	7·39	7·40	7·53
10	2	0	7·06	7·15	7·15	7·14	7·14	7·31
8	6	2	6·92	7·15	7·15	7·14	7·14	7·31
9	5	1	1·06	0·99	0·99	0·99	0·99	0·80
7	7	3	1·04	0·99	0·99	0·99	0·99	0·80
10	2	2	6·66	6·90	6·90	6·90	6·90	7·10
6	6	6	6·61	6·90	6·90	6·90	6·90	7·10

Experimental details

The sample of neutron-irradiated MgO could be approximated by a cube with sides equal to 0·12 mm. The lattice parameter, $a = 4·2147 \pm 0·0002$ Å at 20°C, was measured by the method of Bond (1960).

Intensity data were collected with a General Electric XRD5 X-ray set fitted with a three-circle goniostat using the normal θ–2θ step-scan technique. The scan was carried out for three degrees either side of the peak intensity, in steps of 0·02° with the counting time at each point of the step-scan adjusted to give a constant statistical accuracy of $\sim$0·1% for the integrated intensity.

A NaI (Tl) scintillation counter with pulse height discrimination was used to collect the final set of MgO data. The radiation used was Zr filtered, Mo Kα. The 'base level' and 'gate' of the pulse height analyser were adjusted to avoid the presence of subharmonics of the Mo Kα wavelength. The X-ray tube was operated at 45kV and 15 mA. Preliminary measurements showed that 'dead-time' effects were present in the counting circuits. To measure the 'dead-time' a set of aluminum foils of the same thickness were used. Intensity measurements on a weak reflexion showed that each of the aluminum foils had equivalent transmission factors, the mean 'foil-factor' being $2.748 \pm 0·003$. Subsequent intensity measurements on a strong reflexion as a function of the number of foils used (the multiple-foil method) gave a value of 12μ sec for the 'dead-time' of the counting circuits.

Thirty-three strong reflexions were measured in four equivalent settings and a standard reflexion (the $\overline{6}00$) measured twice per day to check on possible intensity fluctuations.

Aluminum foils were used to attenuate the incident beam in the case of fifteen strong reflexions, so that a peak count rate of 1000 counts per second was not exceeded; the 'dead-time' correction in this case being only $\sim$1%.

Each of the intensity measurements was corrected for 'dead-time' effects by applying the simple correction,

$$I_{\text{true}} = \frac{I_{\text{obs}}}{1 - I_{\text{obs}} \tau} \qquad (2)$$

at each point of the θ–2θ scan; τ being the 'dead-time' of the counting circuits in seconds.

The strong low angle reflexions were corrected for the background structure due to the action of the Zr filter. This background correction required an extrapolation of the background trend at the higher 2θ side of the peak, rather than an average of the background at each side of the peak (Young, 1965). Twenty reflexions were corrected in this way.

Structure factors were now computed from the corrected intensities. Allowance was made for the effects of absorption, the number of aluminum foils and the different counting strategy used for each reflexion before applying the appropriate Lorentz–polarization correction. Transmission factors used in the correction for the effects of absorption were calculated using a Fortran IV program, CDRABS, written by Dr G. Cox of the A.A.E.C. A theoretical value of the transmission factor, μ, equal to 10·7 cm^{-1} was used in these calculations. A list of the final set of structure factors, on an absolute scale, is given in Table 3.

The choice of weights to be used in the least-squares refinement of experimental data is very important. By measuring intensities over symmetry-equivalent reflexions it was hoped that a reasonable weighting scheme could be set up from the sample variance of each reflexion, but with such a small sample (at the most 4) this could lead to an underestimate of the real standard deviation (Arndt & Willis, 1966). Weights were determined by averaging the individual estimated standard deviations (e.s.d's) of each reflexion over ranges of the magnitude of the structure factors, and then allotting this average value of $\sigma_{F_{\text{obs}}}$ to each reflexion in the range concerned.

The main source of errors in the experimental procedure used for the collection of the X-ray intensity data is that introduced by the use of aluminum foils to attenuate the incident beam in the case of strong reflexions. Additional errors are introduced by the need to correct the intensities for 'dead-time' effects and for the action of the Zr filter, and the final set of structure factors obtained are accurate to $\sim$2%.

Least-squares refinement

The experimental structure factors were now refined on the basis of a spherical 'prepared' model, equation (1), by the method of least squares. Allowance was made for the real part of the anomalous dispersion correction for magnesium, $\Delta f' = 0·05$, for Mo Kα radiation (Cromer, 1965); this term is negligible for oxygen. Since the wave functions of Yamashita (1964) were not available at the time of this analysis the analytic forms given by Tokonami (1965) were used in the least-squares program to calculate the value of the atomic scattering factor at the appropriate value of $(\sin \theta)/\lambda$, whereas accurate numerical integration methods were used in all other cases. These analytic forms are;

$$f_{c, \text{O}}(S) = 4·758 \exp(-7·831\ S^2) + 3·637 \exp$$
$$(-30·05\ S^2) + 1·594 \qquad (3)$$

for data in the Cu Kα range

and

$$f_{c, \text{O}}(S) = 2·755 \exp(-3·949\ S^2) + 5·907 \exp$$
$$(-20·64\ S^2) + 1·269 \qquad (4)$$

for data in the Mo Kα range

A comparison af the atomic scattering factors for O^{2-} obtained by using these analytic forms and those listed by Tokonami (1965) is given in Table 4. The fit between these results is not very good but these analytic forms

will be used to give some indication of the results that would be expected from charge densities calculated using the wave functions of Yamashita (1964).

Table 4. *Atomic scattering factors for O^{2-} based on the wave functions of Yamashita* (1964)

(See Tokonami, 1965)

$\dfrac{\sin \theta}{\lambda}$ (Å^{-1})	$f_{c,O}(S)$, as given by Tokonami	$f_{c,O}(S)$, calc using (3)	$f_{c,O}(S)$, calc using (4)
0·00	10·000	9·989	9·931
0·05	9·633	9·634	9·607
0·10	8·671	8·687	8·723
0·15	7·423	7·433	7·502
0·20	6·174	6·166	6·209
0·25	5·081	5·067	5·048
0·30	4·192	4·189	4·122
0·35	3·498	3·509	3·439
0·40	2·968	2·983	2·951
0·50	2·274	2·268	2·329
0·60	1·891	1·878	1·937
0·70	1·676		1·667
0·80	1·543		1·489
0·90	1·447		1·381
1·00	1·367		1·322
1·10	1·291		1·292
1·20	1·216		1·278
1·30	1·142		1·273

Least-squares refinement of the data was carried out for each model, allowing the scale factor and two independent isotropic temperature factors to vary. The best agreement was obtained with the combination of Mg^{2+} and O^{2-} (+2 well) wave functions. The worst agreement corresponds to the O^{2-} scattering factors calculated by using the analytic form (4). Excluding the results for this case the remaining parameters for each of the four other combinations of scattering factors differed by no more than twice the e.s.d.'s of each of the parameters. An average value of each of the parameters was taken and the agreement calculated on the basis of these parameters. The values of the three parameters averaged in this way are:

$$\text{scale factor,} \quad K = 32\cdot58 \, (0\cdot26)$$
$$B_{Mg} = 0\cdot346 \, (0\cdot009) \, \text{Å}^2 \tag{5}$$
$$B_O = 0\cdot315 \, (0\cdot010) \, \text{Å}^2$$

where the terms in brackets represent the e.s.d. of each parameter as calculated in the least-squares procedure. The agreement factors R, weighted R and $\hat{\sigma}^2$ based on the parameters (5) for the various combinations af wave functions are given in Table 5. The agreement factors are defined by the usual relations

$$R = \frac{\Sigma \, |F_{obs} - F_{calc}|}{\Sigma \, F_{obs}} \tag{6}$$

$$\text{weighted } R = \left[\frac{\Sigma W (F_{obs} - F_{calc})^2}{\Sigma W \, F_{obs}^2} \right]^{\frac{1}{2}} \tag{7}$$

and the estimation of the variance of an observation of unit weight, $\hat{\sigma}^2$, may be calculated using the equation,

$$\hat{\sigma}^2 = \frac{\Sigma \, W (F_{obs} - F_{calc})^2}{(q - n)} \tag{8}$$

where q is the number of structure factors included in the refinement and n is the number of parameters varied in the refinement.

Table 5. *Results for the various combinations of atomic scattering factors for* MgO *based on the averaged parameters*

$K = 32\cdot58$, $B_{Mg} = 0\cdot346 \text{Å}^2$, $B_O = 0\cdot315$ Å^2

Wave functions used	R	Weighted R	$\hat{\sigma}^2$
Mg^{2+} O^{2-} (+2 well)	0·0145	0·0244	3·422
Mg^{2+} O^{2-} (+1 well)	0·0161	0·0269	3·765
Mg^+ O^-	0·0159	0·0266	3·727
Mg O	0·0173	0·0298	4·175
Mg^{2+} O^{2-} [Tok, equation (4)]	0·0223	0·0487	6·824

The value of $\hat{\sigma}^2$ should be unity for an absolute weighting scheme and the values given for $\hat{\sigma}^2$ in Table 5 indicate that the weighting scheme *or* the model used to analyse the data could be improved. There was a large correlation between each of the three parameters refined, approximately 85%, and this must influence the final parameter values obtained. This large correlation is usually observed in least-squares refinement where a scale factor and temperature factors are refined together, and if it had been possible to measure the present data on an absolute scale better values would have been obtained for the B factors of MgO.

If the isotropic temperature factors are assumed to be identical and least-squares refinement is carried out allowing a scale factor and a common isotropic temperature factor to vary, the best agreement again occurs when the O^{2-} (+2 well) wave functions are used; the worst agreement occurring for the O^{2-} (Tok) functions. The two parameters for the four cases, omitting the O^{2-} (Tok) results, differed by no more than twice their e.s.d.'s and an average value was taken giving the parameters

$$\left. \begin{array}{l} B_{ave} = 0\cdot343 \, (0\cdot014) \, \text{Å}^2 \\ K = 32.30 \, (0\cdot38) \end{array} \right\} \tag{9}$$

The agreement factors based on these parameters are given in Table 6. Correlation between the scale factor and the common isotropic temperature factor was 88% and the value of $\hat{\sigma}^2$ was again greater than unity.

Table 6. *Results for the various combinations of atomic scattering factors for* MgO *based on the averaged parameters* $K = 32.30$, $B_{ave} = 0.343$ Å^2

Wave functions used	R	Weighted R	$\hat{\sigma}^2$
Mg^{2+} O^{2-}(+2 well)	0.0188	0.0372	5.206
Mg^{2+} O^{2-}(+1 well)	0.0199	0.0377	5.281
Mg$^+$ O$^-$	0.0203	0.0398	5.579
Mg O	0.0212	0.0419	5.870
Mg^{2+} O^{2-} [Tok, equation (4)]	0.0273	0.0607	8.498

Comparison of the results in Tables 5 and 6 shows that the models including two independent isotropic temperature factors give a better fit to the experimental data, and this can easily be verified by applying the significance tests of Hamilton (1964, 1965). This means that the Mg^{2+}, O^{2-} (+2 well) atomic scattering factors combined with the parameters given in equation (5) give the best fit to the present single-crystal X-ray data for MgO. Structure factors for the various spherical 'prepared' models based on the above thermal parameters and reduced to an absolute scale are shown in Table 3.

Bonding effects

As reported in the author's Ph.D. thesis, an attempt was made to refine the experimental data in terms of a model that allowed for cubic distortion of the oxygen atom, using the formalism of Dawson (1967a). Such a refinement depends on the spherical 'prepared' basis chosen and this was the aim of the above analysis. However, no success was obtained when the Mg^{2+} and O^{2-} (+2 well) combination of wave functions were used since it was not possible to interpret the differences between observed and calculated results in terms of radial distortion functions as it was in the case of diamond and silicon (Dawson, 1967b, c).

Re-analysis of published X-ray powder measurements on MgO

The powder measurements of Togawa (1965), Burley (1965) and Raccah & Arnott (1967) have been re-analysed using the same wave functions and least-squares procedures that were used to refine the single-crystal data.

For the powder data of Togawa (1965) the best agreement was obtained for the combination of Mg^{2+} and O^{2-} (+2 well) scattering factors together with a common isotropic temperature factor $B_{ave} = 0.212$ (0.024) Å^2, since introduction of two independent isotropic temperature factors in the least-squares refinement produced no significant improvement in the fit to the data. On the other hand, in the graphical procedure used by Togawa, the combination of Mg^{2+} and O^{2-} (Tok)

scattering factors was found to give the best fit to the experimental data; the corresponding values for the B factors being $B_{Mg} = 0.24$ Å^2 and $B_O = 0.19$ Å^2 with no estimates of the standard deviations of these parameters. The results based on least-squares refinement and subsequent application of the significance tests of Hamilton are felt to be preferable.

The powder intensity measurements of Burley (1965) were measured on a relative scale using Cu $K\alpha$ radiation, and reduced to an absolute scale by comparison with measurements on rocksalt and by use of a scale factor determined by a graphical procedure. The value of a common isotropic temperature factor determined by the graphical procedure of Burley was $B_{ave} = 0.326$ Å^2 and the experimental data listed in Table 1 of Burley (1965) on an absolute scale have been corrected for the effects of thermal vibration using this overall temperature factor. Thus to obtain a set experimental data corresponding to the measurements of Burley (1965) it was necessary to multiply the values of his Table 1 by the factor $4 \exp(-0.326 \sin^2 \theta/\lambda^2)$. Subsequent least-squares refinement of these data showed that the Mg^{2+}, O^{2-} (+2 well) scattering factors combined with a common isotropic temperature factor $B_{ave} = 0.382$ (0.033) Å^2 gave the best fit to the experimental data.

Raccah & Arnott (1967) carried out relative intensity measurements on powder samples of MgO using nickel-filtered Cu $K\alpha$ radiation. They refined their data by the method of least-squares allowing a scale factor and two isotropic B factors to vary, and obtained the best agreement for the Mg^{2+}, O^{2-} (Tok) scattering factors combined with $B_{Mg} = 0.448$ Å^2 and $B_O = 0.347$ Å^2. No e.s.d.'s are given for their parameters. Re-examination of their data (Table 1 of their paper) showed that the Mg^{2+}, O^{2-} (Tok) scattering factors combined with a scale factor $K = 1.00$ (0.005), and two isotropic temperature factors, $B_{Mg} = 0.460$ (0.028) Å^2 and $B_O = 0.334$ (0.045) Å^2 gave the best fit to their experimental data, and this agrees with their own calculations. However, the present analyses do not confirm their conclusion that the Mg^{2+}, O^{2-} (Tok) scattering factors also gives the best fit to the MgO powder data of both Togawa (1965) and Burley (1965).

Lattice dynamical calculation of the vibration amplitudes of MgO

To gain more information about the thermal motion of the two atoms in magnesium oxide, the vibration amplitudes of each atom have been calculated by means of the Born–von Karman theory of lattice dynamics in the harmonic approximation. These calculations have been based on a simple 'shell' model – shell model I of Cowley, Cochran, Brockhouse & Woods (1963) – with force constants computed from the physical constants given by Peckham (1967).

Peckham (1967) found that this simple 'shell' model gave a fairly good fit to his phonon measurements, the

deviations between calculated and measured frequencies being nowhere greater than 8%. He attempted to adjust the parameters of the model by a least-squares method to fit the six macroscopic constants and the experimentally determined dispersion curves in the symmetry directions. However, he found that an improved fit to the dispersion relation was offset by deviations of the calculated macroscopic constants from their experimental values.

Lack of intensity in the energy region above 100 meV prevented Peckham (1967) from completing his measurements of the phonon dispersion relations in MgO. However, Buckland & Saunderson (1967) have now supplemented his results by carrying out measurements of the high frequency longitudinal optical phonons. Comparison of these experimental results with those calculated on the basis of the simple 'shell' model showed; (a) that the agreement was good for phonons in the [110] direction and (b) that at the zone boundary the observed frequencies in the [111] direction were 5% higher and in the [100] direction over 10% higher than the calculated values. Buckland & Saunderson (1967) sent their additional measurements to Peckham so that he could re-run the least-squares fitting program to the complete set of data, but according to Peckham (1968) there has been no significant improvement in any of the fitted models so far obtained over the simple 'shell' model.

The vibration amplitudes of MgO were calculated, on the basis of the simple 'shell' model, by the root sampling technique described by Pryor (1966). A selection of 215,489 points throughout the first Brillouin zone gave the Debye–Waller factors

$$B_{Mg} = 0.287 \text{ Å}^2$$
$$B_O = 0.350 \text{ Å}^2 \qquad (10)$$

showing that the temperature factors, at room temperature, are appreciably different. However, the nature of the fit of the simple 'shell' model to the measured phonon dispersion curves in MgO makes it difficult to estimate the accuracy of these Debye–Waller factors.

Pryor (1966) has mentioned that it is conceivable that the apparent B factors for X-rays and neutrons may not be the same. The ions are known to be deformable and therefore the X-rays, being scattered from the electrons, may be affected by an apparent vibration amplitude different from that of the nucleus. Pryor (1966) examined this possibility by direct calculation taking the 'shell' model at its face value. He carried out calculations for the chloride ion in sodium chloride and concluded that, in spite of the difference in the core and the shell vibration amplitudes, there will never be a detectable difference in the apparent B factors for X-rays and neutrons for sodium chloride.

It is possible that this type of calculation could be more important for ions like O^{2-}, where a larger fraction of the electrons are in the 'shell', but the magnitude of this effect for sodium chloride and the nature of the fit of the simple 'shell' model to the measured phonon dispersion curves in MgO convinced the author that such a calculation was not warranted here.

Discussion

Best agreement for the present single-crystal data and the powder measurements of both Togawa (1965) and Burley (1965) was obtained by use of a combination of Mg^{2+} and O^{2-} ($+2$ well) atomic scattering factors. For the Raccah & Arnott (1967) data, the combination of Mg^{2+} and O^{2-} (Tok) atomic scattering factors gave the best agreement. In each case, however, the best agreement was obtained with an O^{2-} atomic scattering factor based on a contracted charge density. Recalling that the O^{2-} (Tok) atomic scattering factors were calculated using the analytic approximations, (3) and (4), the above results seem to indicate that scattering factors calculated from charge densities based on the actual wave functions of Yamashita (1964) or calculated from a charge density that peaks somewhere between the ($+2$ well) and the Yamashita (1964) charge densities could possibly give the best fit to all sets of experimental data for MgO.

Table 7. *Debye–Waller factors and Debye temperatures of* MgO *at* 300°K

Estimated standard deviations are shown in brackets.

B_{Mg} (Å²)	B_O (Å²)	θ_M (°K)	θ_D (°K)	Comments
0.287	0.350	807	764	Calculated from 300°K physical constants of Peckham (1967).
0.346 (0.009)	0.315 (0.010)	768		X-ray single-crystal results (Mo $K\alpha$ radiation)
0.460 (0.028)	0.334 (0.045)	683		X-ray powder data of Raccah & Arnott (1967) (Cu $K\alpha$ radiation)

B_{ave} (Å²)	θ_M (°K)	Comments
0.212 (0.024)	1009	X-ray powder data of Togawa (1965) (Cu $K\alpha$ radiation)
0.382 (0.033)	711	X-ray powder data of Burley (1965) (Cu $K\alpha$ radiation)
0.396 (0.044)	697	Neutron single-crystal data of Sabine (1965) ($\lambda = 1.1$ Å).

The neutron diffraction measurements of Sabine (1965) on the large neutron irradiated crystal of MgO gave an average temperature factor $B_{ave} = 0.396$ (0.044) $Å^2$. No correction has been applied for the effects of thermal diffuse scattering, in either case, and this would make the observed B factors slightly larger.

Huang (1947) and Kanzaki (1957) have shown that the effects of random centres of dilatation in an elastically isotropic crystal are:

(i)   an isotropic expansion of the lattice,
(ii) an artificial temperature factor and
(iii) diffuse scattering around the reciprocal lattice points.

Since the measured value of the lattice parameter of the neutron irradiated MgO crystal represented a lattice expansion of 0.08%, an artificial temperature factor would be expected to be present in the experimental B factors.

However, the recent work of Sabine & Keating (1968) has shown that the models of Huang and Kanzaki do not apply in the case of MgO irradiated to 4.9×10^{20} n.v.t. (at 75–100 °C), since the defects are not isolated, and that the effect of the artificial temperature factor should not be observed in the neutron and X-ray diffraction experiments on this crystal.

The B-factors for MgO, based on the above analyses, are summarized in Table 7. Only the present single-crystal data and the data of Raccah & Arnott (1967) show that two individual isotropic temperature factors are required to describe the thermal motion in MgO in accordance with the lattice dynamical calculations given here. However, the actual values obtained for the B factors in these two cases are quite different from those given by these lattice dynamical calculations and these differences could be caused by undetected experimental errors in this (and all previous) X-ray work or by inadequacies in the present force constant model for MgO and in the actual calculation of the Debye–Waller factors.

Values of the Debye temperature, given in Table 8, for the various sets of data can also be compared with the value $\theta_M = 802 °K$ given by Baldwin & Thompson (1964), who measured the variation in intensity of selected powder lines with temperature, and with the value $\theta_D = 750 °K$ given by Barron, Berg & Morrison (1959), who carried out heat capacity measurements on MgO at room temperature.

Conclusions

Least-squares refinement of the present X-ray single-crystal measurements on MgO shows that the best agreement is obtained by using a spherical 'prepared' model based on the Mg^{2+}, O^{2-} (+2 well) atomic scattering factors combined with the two isotropic temperature factors $B_{Mg} = 0.346$ (0.009) $Å^2$ and $B_O = 0.315$ (0.010) $Å^2$. Re-examination of the previous powder measurement of Togawa (1965), Burley (1965) and Raccah & Arnott (1967) also shows that an O^{2-} atomic scattering factor based on a contracted charge density gives the best fit to the experimental data. One of the most curious discrepancies in the above analyses is the different B values obtained for the various sets of data and the fact that the present lattice dynamical calculations give $B_O > B_{Mg}$ whereas the X-ray data all give $B_{Mg} \geq B_O$.

The present set of single-crystal measurements represent the most complete set of X-ray data for MgO at present available and together with the neutron diffraction measurements of Sabine (1965) show that extinction free results can be obtained for MgO by using a crystal irradiated to a dose of 4.9×10^{20} n.v.t. (at 75–100 °C).

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One and Two-Phonon X-ray Cross-Section Calculations for the Molecular Crystal Hexamethylenetetramine

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The two-phonon X-ray scattering from hexamethylenetetramine is calculated, and this is compared with the one-phonon result, here independently recalculated. The details of the calculation procedure are fully described, and possible savings in computation discussed. In a few regions of reciprocal space within the Cu *K*α reflecting sphere the two-phonon scattering is larger than the one-phonon scattering. It is therefore essential when making quantitative comparisons with experiment that the two-phonon scattering be considered.

Introduction

Cochran & Pawley (1964) have calculated the one-phonon X-ray scattering cross-section of hexamine (hexamethylenetetramine). Since that time there have been improved measurements of the thermal diffuse scattering (TDS) by Powell (1963) and McMullan (1967). Until the calculation here reported the only comparisons of experiment with theory involved either the one-phonon calculation mentioned above or the Difference Fourier Transform of Amorós, Canut & De Acha (1960). The latter is simply the difference in the squared Fourier transform calculated with and without thermal motion, where the atomic thermal motion is introduced through anisotropic mean-square amplitudes as found by crystallographic structure refinement. The present calculation shows that the effect of the two-phonon process should not be neglected when comparisons with accurate measurements are attempted.

The crystal structure of hexamine is fully described by Becka & Cruickshank (1963). Nearly spherical molecules of symmetry $\bar{4}3m$, are placed on a body centred cubic lattice with only one molecule in the primitive unit cell. The planes (0*kl*), (1*kl*) *etc.* in reciprocal space contain reciprocal lattice points, and it is

customary to make measurements of the diffuse X-ray scattering in the interlayers ($\frac{1}{2}kl$), ($\frac{3}{2}kl$) *etc.* where there is no Bragg scattering. The present calculations are for the ($\frac{1}{2}kl$) interlayer. The one-phonon scattering calculation is here repeated in order to establish a scale.

The model used here is exactly the same as that of Cochran & Pawley (1964), the equations for the calculations coming from Cochran (1963). However, before discussing this in detail mention should be made of a method of calculating in one procedure the effect of all the phonon processes. This has been done for NaCl by Eldridge & Lomer (1967) and Lomer (1966). A model for a small crystal is set up in the computer, and the displacements for all the atoms are calculated for a typical but random set of vibrations. The phonon eigenvectors and eigenvalues are obtained by the use of the model, and therefore the energies in all the possible modes of vibration are known for a given temperature. The displacement configuration is obtained by assigning random phases to all the modes. The total scattering from this small crystal is then found. This must of necessity include all the phonon processes. The calculation is then repeated a number of times, each time taking new random phases, until the averaged calculated intensity becomes stable. The conclusion for NaCl was that most of the TDS is due to one and two phonon processes – calculated separately – but that in some regions the scattering from higher order processes was appreciable. This emphasizes the

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