A Comparison of Defect Centres formed in Oxides by Explosive Shocking and High-energy Radiation

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E.s.r. and reflectance spectroscopic techniques have been used to compare point defects present in MgO, ZnO, and SiO_2 both after explosive shocking and after irradiation with high-energy γ-rays, electrons, and neutrons. A high correlation of shocking with irradiation exists in MgO, none in SiO_2, and ZnO occupies an intermediate position.

   In MgO, explosive shocking induced ionisation with trapping of electrons at existing defects and produced vacancy defects (F^+ and F_2^+) by displacement of lattice ions. In SiO_2 none of these effects were present but there is evidence of contamination with carbon as a result of the explosion. This significant difference in behaviour to shocking is reflected in the different physical properties of these oxides, but could also be brought about by a suitable choice of explosion conditions.

A RECENT paper [1] concluded that no correlation existed between defects formed in solid materials by explosive shock and those formed as a result of γ- or neutron-irradiation. Some time ago we studied the effects of explosive shocking on MgO, ZnO, and SiO_2 in considerable detail and now report on the comparison of these with γ-, electron-, and neutron-irradiation specimens.

   Whereas high energy ($\geqslant 1$ MeV) electron and fast neutron irradiations produce displacements in these oxides, which lead to vacancy defects such as F^+ and V centres, together with their corresponding interstitial defects, γ-irradiation is inefficient in displacement processes and point defects are only formed if lattice defects capable of trapping the electrons and holes produced by ionisation processes exist before irradiation. It has long

[1] M. C. R. Symons, J. Chem. Soc. (A), 1971, 1648.

been known that mechanical shocking by grinding or shaking oxides leads to the formation of vacancy defects as a result of the movement of dislocations through the lattice. Wertz and his co-workers[2] showed that F^+ centres in oxides, sulphides, and selenides of the alkaline-earth metals could be formed either by grinding or by neutron-irradiation. In MgO, which is shocked *in vacuo*[3] at 20 °C, paramagnetic defects are generated both in the bulk (F^+) and on the surface (F_s^+) of crystallites and these react on subsequent exposure to oxygen or air. Similar defects are observed[4] after neutron-irradiation *in vacuo*.

EXPERIMENTAL

Magnesia was AnalaR grade, zinc oxide Reagent grade, and silica Specpure grade; all oxides were used without further purification. Explosive shocking was carried out at E.R.D.E. in cylindrical bombs of mild steel by the method described elsewhere.[1,5] Powders were extracted from the sealed bombs after shocking by cutting off the screw end. With the exception of the magnesia, gross iron contamination was removed from samples by means of a magnet. Irradiations with ^{60}Co γ-rays at $\leqslant 40$ °C involved a 1000 Ci Co source and a dose rate of *ca.* 4×10^{15} eV g^{-1} s^{-1}. 1.2 MeV electrons at $\leqslant 50$ °C were obtained from a Van de Graaff generator at a dose rate of *ca.* 10^{20} eV g^{-1} s^{-1}, while reactor irradiations were conducted at *ca.* 100 °C in BEPO with a fast neutron (*i.e.*, >1 MeV) flux of *ca.* 3×10^{11} cm^{-2} s^{-1}. All irradiations were carried out in silica ampoules and in the case of electrons the ampoules were equipped with flat silica windows of thickness 250 μm to allow the electron beam to penetrate the powder with minimal loss of energy in the silica. E.s.r. spectra were obtained from the samples in contact with the atmosphere at 25 °C on a Varian 4502 spectrometer operating at *ca.* 9.3 GHz and with 100 kHz field modulation. A Cary 14 recording spectrophotometer fitted in the Type I mode was used to provide the diffuse reflectance spectra of oxides and this technique is discussed in detail elsewhere.[6] The e.s.r. and reflectance measurements were made at A.E.R.E.

RESULTS AND DISCUSSION

Magnesium Oxide.—E.s.r. spectra. Magnesium oxide powder was found to be tightly packed at the screw end of the bomb in which it had been shocked, but became progressively looser with depth and was free-flowing at the base. This difference is a function of the shock intensity.

The cylindrical explosive configuration detonated from one end is an arrangement which gives rise to a conically convergent shock wave passing into the bomb. The downward propagation results in substantial reinforcement of pressure in the lower part of the hollow cylinder by reflection of the shock from the solid base[5]

and strong shock interactions also arise along the axis of the cylinder by virtue of the convergence effect. These regions of high shock intensity are demonstrated as areas of carbonisation in a bomb loaded with a transparent rubber. In addition, four thin vanes of carbonised material radiating from the central axis reflect the four-fold symmetry of initiation of the charge.[1,5]

Similar conclusions regarding the distribution of shock intensity have been made from X-ray line broadening studies.[7] These imply substantial dislocation densities in shocked powders[8] and an associated microstrain which is greatest in axial and basal regions of the bomb.

The effect of the converging shock is initially to consolidate the powder within the bomb and force it to occupy a reduced volume. This occurs both by grinding and shattering processes.[7] If sufficiently strongly driven, shock reflections and rarefactions arising at free surfaces can be such as to subject the compacted material to tensional forces capable of rupturing it. (This is clearly seen in the severe longitudinal rupture of solid steel rod wrapped with explosive.) Thus the MgO remains consolidated only in the less severely stressed screw end of the bomb. The e.s.r. spectrum of the shocked magnesium oxide indicated the presence of F^+ centres (oxygen ion vacancy with an unpaired electron, also noted by Symons[1]), Cr^{3+} ions, and adsorbed O_2^- species, whereas only Cr^{3+} ions were present in unshocked powder. The hyperfine structure observed for the F^+ centre was identical to that recorded by Wertz *et al.*[9]

In keeping with the above observations, the relative F^+ centre concentrations varied down the bomb and were 0.06 at the screw end, 0.85 in the middle, and 1.00 at the base. At the base the F^+ centre line width was 0.62 gauss, which is comparable with that of neutron-irradiated powders, and the concentration of F^+ centres was 1.2×10^{15} spins g^{-1}. Since the MgO was shocked in the presence of air and its specific surface area was relatively high (71—104 m^2 g^{-1}), this concentration is only 10—20% of that expected had the MgO been shocked *in vacuo* or in an inert atmosphere. Previous work on neutron-irradiated MgO has shown that oxygen reacts at 20 °C with F^+ centres which lie within *ca.* 50 Å of the crystallite surfaces.[10] The high residual temperature of the powder after explosive shocking permits enhanced diffusion, which must significantly reduce the F^+ centre concentration originally generated.

In addition to the nuclear hyperfine ($I = \frac{5}{2}$) lines[9] surrounding the main F^+ centre there exists a weak peak on the high-field side at $g = 2.0008$. Isochronal annealing studies were carried out on the shocked oxide and the intensities of the main F^+ centre and the latter signal are

[2] J. E. Wertz, J. W. Orton, and P. Auzins, *Discuss. Faraday Soc.*, 1961, **31**, 140.

[3] R. L. Nelson, A. J. Tench, and R. W. Wilkinson, *Proc. Brit. Ceram. Soc.*, 1965, **5**, 181.

[4] R. L. Nelson, A. J. Tench, and B. J. Harmsworth, *Trans. Faraday Soc.*, 1967, **63**, 1427.

[5] D. B. Hartley, E.R.D.E. Technical Note, in preparation.

[6] R. L. Nelson and J. W. Hale, *Discuss. Faraday Soc.*, 1971, **52**, 77.

[7] A. C. Greenham and B. P. Richards, *Trans. Brit. Ceram. Soc.*, 1970, **69**, 115.

[8] R. W. Heckel and J. L. Youngblood, *J. Amer. Ceram. Soc.*, 1968, **51**, 398.

[9] J. E. Wertz, P. Auzins, R. A. Weeks, and R. H. Silsbee, *Phys. Rev.*, 1957, **107**, 1535.

[10] R. L. Nelson and A. J. Tench, *Trans. Faraday Soc.*, 1967, **63**, 3039.

presented in Figure 1. The initial increase in F^+ signal amplitude on raising the temperature to 350 °C is due to the $F \rightarrow F^+$ centre transition wherein an electron is excited out of the two-electron trap (F) to leave an unpaired electron centre (F^+). Above 350 °C the F^+ centre concentration decreases monotonically with increasing temperature and this is due partly to annihilation of the anion vacancy and partly to the formation of vacancy aggregates. The F_2^+ centre consists of two adjacent vacancies with a single unpaired electron and this accounts for the signal at $g = 2.0008$ which has
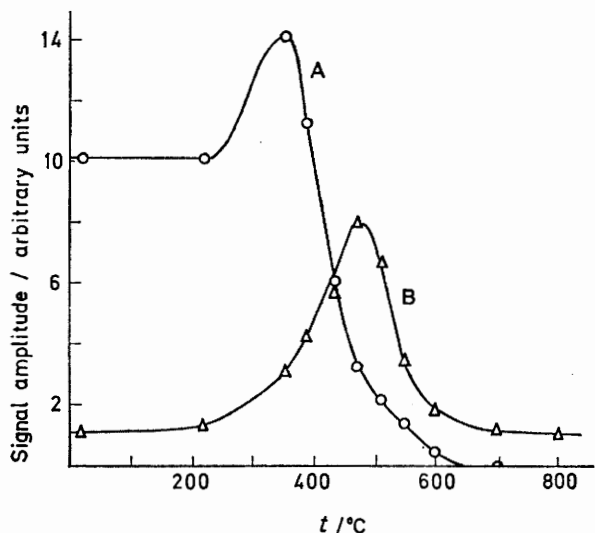

FIGURE 1 Isochronal annealing of shocked magnesia; A, F^+ centre ($g = 2.0023$); B, F_2^+ centre ($g = 2.0008$)

previously been identified during the annealing of F^+ centres in neutron-irradiated magnesia.[2] The F_2^+ centre concentration reaches a maximum close to the point at which the rate of annealing is a maximum, thus confirming the mechanism of vacancy aggregate formation. Since the F_2^+ concentration after annealing at 470 °C is a considerable fraction of the original F^+ concentration, this suggests that vacancy aggregation is the main annealing process up to 470 °C whereas vacancy annihilation by interstitials takes over above this temperature.

The F^+ centre resonance at $g = 2.0023$ possessed weak hyperfine lines [9] resulting from ^{25}Mg interactions ($I = \frac{5}{2}$) in similar relative amplitude to neutron-irradiated powder. The sharp F^+ centre resonance in material from the middle and bottom sections was superimposed on a broader signal probably owing to the adsorbed O_2^- species (Figure 6b of ref. 11). This molecular ion is also formed when MgO is irradiated with γ-rays,[11] u.v.,[12] or subjected to electrical discharge in the presence of oxygen or air. The Cr^{3+} signal at $g = 1.9795$ [13] with four hyperfine lines arising from ^{53}Cr interactions ($I = \frac{3}{2}$) is four times less intense in the shocked MgO obtained from the middle or base of the bomb than in

unshocked MgO or shocked material from the screw end. This decrease in Cr^{3+} concentration is accompanied by an appearance of the Mn^{2+} sextet [13] which is absent from unshocked material. The Cr^{3+} signal is due to chromium ions in substitutional sites of cubic symmetry in the MgO lattice [13] and in unshocked material the concentration of Cr^{3+} is of the order of 10 p.p.m., whereas the concentration of Mn^{2+} ions which are evident after shocking is $\leqslant 1$ p.p.m. These results indicate that ionisation occurs during explosive shocking and that the electrons thus released are subsequently trapped either at the surface as O_2^- ions or at Mn^{3+} and Cr^{3+} impurity sites within the crystallites to form Mn^{2+} and Cr^{2+} species. In the lightly shocked material from the screw end these effects are not observed.

Reflectance spectra. Powder from the middle section of the bomb was withdrawn and the reflectance spectrum of this was compared with that of unshocked material. These spectra are presented in Figure 2 and reveal the following features. The unshocked MgO has a minor absorption at 280 nm (4.4 eV), which may be due to an optical transition of Cr^{3+} since it is not present in material of higher purity (*cf.* Figure 1 of ref. 6), and the main u.v. absorption edge is below 200 nm (6.2 eV). The shocked material does not have the minor absorption at 280 nm but possesses a much more intense absorption with $\lambda_{max.}$ at 240 nm (5.1 eV). There is an increased general absorption at longer wavelengths compared with unshocked material, but this could be due either to the decreased crystallite size of the shocked material or to contamination (see later). The absorption peak at 240 nm could be due to F^+ centres, which have previously [14] been shown to absorb at 4.98 eV, but alternatively could be due to a surface condition of low contamination or high strain similar to that present on MgO material [6] which has been evacuated at high temperature (*ca.* 1000 °C). The specific surface area of the MgO was observed to increase from 71 to 104 m^2 g^{-1} as a result of explosive shocking and, whereas the surfaces of the original MgO are likely to be grossly contaminated with adsorbed water and carbon dioxide, the fresh surfaces induced by the explosion are likely to have much lower contamination. Annealing of the shocked MgO by heating at 500 °C causes the minor peak at 280 nm to appear, owing to the recovery of the Cr^{3+} signal, while the peak at 240 nm has started to decay. After annealing at 950 °C the latter absorption has almost disappeared and the spectrum is similar to that of the unshocked material, apart from the general absorption throughout the 200—800 nm region which is unaffected by annealing.

From the above studies of e.s.r. and reflectance spectra, four features are common to MgO powders subjected to explosive shocking or high-energy irradiation: (i) Increase in specific surface area; neutron

[11] R. L. Nelson, J. W. Hale, and B. J. Harmsworth, *Trans. Faraday Soc.*, 1971, **67**, 1164.

[12] J. H. Lunsford and J. P. Jayne, *J. Chem. Phys.* 1966, **44**, 1487.

[13] J. E. Wertz, P. Auzins, J. H. E. Griffiths, and J. W. Orton, *Discuss. Faraday Soc.*, 1959, **26**, 66.

[14] J. E. Wertz, G. S. Saville, L. Hall, and P. Auzins, *Proc. Brit. Ceram. Soc.*, 1964, **1**, 59.

irradiation also induces increases of up to 60%. (ii) Generation of point defects by displacement processes; F^+ centres are produced by neutron irradiation. (iii) Trapping of charge carriers at defects as a result of ionisation processes; O_2^- adsorbed species and changes in Mn^{2+} and Cr^{3+} concentrations are induced by γ-irradiation. (iv) Explosive shocking induces increased dislocation densities with associated microstrain,[7,8]
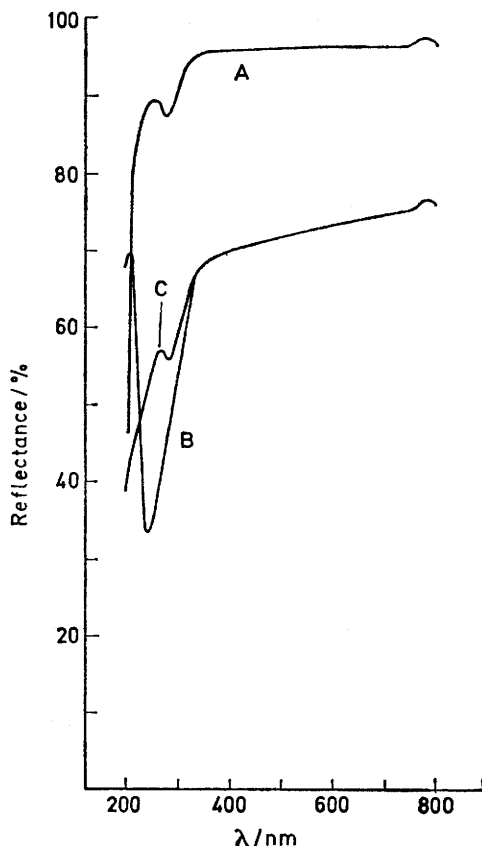

FIGURE 2 Diffuse reflectance spectra of magnesia; A, unshocked; B, shocked; C, shocked and annealed at 950 °C

which is released at sintering temperatures. This effect has also been observed after neutron irradiation.[15]

Zinc Oxide.—E.s.r. spectra. The e.s.r. spectrum of unshocked zinc oxide contained no detectable feature and this, together with the lack of any coloration, suggests a highly stoicheiometric material. After explosive shocking the zinc oxide is brown and the e.s.r. spectrum contains four features. A low intensity signal at $g = 1 \cdot 966$ is probably due to Zn^{1+} donor centres present as interstitials in the lattice and these have previously been observed both as a result of evacuation at *ca.* 500 °C [16] or by irradiation with high energy protons.[17] The main justification in assigning the signal at $g = 1 \cdot 966$ to Zn^{1+} is that the intensity of the e.s.r. signal is directly

linked with the semiconductivity of ZnO and the ability of ZnO to absorb oxygen (*i.e.*, donate electrons). It is generally accepted that ZnO is an n-type semiconductor and that the donor sites are interstitial Zn^{1+} ions lying a fraction of an eV below the conduction band. The second feature is more intense with principal g values at $2 \cdot 002$, $2 \cdot 008$, and a broader structure at lower fields. This is consistent with an adsorbed O_2^- species [11,18] observed after the adsorption of oxygen on zinc oxide which had been outgassed at 500 °C. This adsorption of oxygen on shocked zinc oxide may be due to the trapping of electrons, which have been released either by direct ionisation of lattice ions or as a secondary result of Zn^{1+} donor formation. Symons [1] also observed a paramagnetic resonance in the spectrum of ZnO but assigned it tentatively to NO_3^{2-}.

Adsorption as O_2^- occurs also in shocked nickel oxide, where conductivity and desorption studies [19] show it to be associated with the production of Ni^{3+} positive holes.

A third feature in the e.s.r. spectrum of ZnO at $g = 2 \cdot 018$ has not been identified but is probably due to a V-type centre. Subsequent γ-irradiation of explosively shocked ZnO has no appreciable effect on the Zn^{1+} and O_2^- signals, but the intensity of the signal at $2 \cdot 018$ is increased by a factor of *ca.* 5. Finally, a resonance of low intensity appeared only during exposure of the sample to white light. This resonance at 20 °C had $g_{av} = 1 \cdot 995$ and its behaviour is consistent with that of the F^+ centre in ZnO reported [20] in single-crystal material with $g_{\parallel} = 1 \cdot 9948$ and $g_{\perp} = 1 \cdot 9963$.

Reflectance spectra. Both shocked and unshocked samples of ZnO possess the normal absorption edge at 380 nm ($3 \cdot 25$ eV) but, whereas the unshocked ZnO does not absorb in the range 450—800 nm (thus confirming the near-stoicheiometry of the material), the shocked ZnO possesses a considerable absorption at wavelengths longer than the absorption edge and this accounts for the brown colour (Figure 3). A similar general absorption and colouration [21] is produced by evacuation at 500 °C and this is due to the formation of Zn^{1+} donor sites as a result of the loss of oxygen from the lattice. The zinc donor levels lie just below the conduction band and the electrons either in the donor levels or in the band account for the optical absorption. This absorption in the shocked oxide was not significantly affected by annealing at temperatures up to 400 °C, but a considerable reduction in intensity occurred at 500 °C. Even after annealing at 700 °C in air, a temperature at which almost all Zn^{1+} donors are removed by oxidation, the absorption was not identical to that of the unshocked ZnO and the difference may be due to impurities introduced during the explosion. An optical absorption which has been ascribed [22] to F^+ centres in ZnO is

[15] D. G. Walker and B. S. Hickman, *Phil. Mag.*, 1965, **12**, 445.
[16] R. J. Kokes, *J. Phys. Chem.*, 1962, **66**, 99.
[17] R. L. Nelson and M. J. Duck, 'Uses of Cyclotrons in Chemistry, Metallurgy and Biology,' ed. C. B. Amphlett, Butterworths, London, 1970, p. 88.

[18] A. J. Tench and T. Lawson, *Chem. Phys. Letters*, 1971, **8**, 177.
[19] I. M. Hoodless and D. A. Yorath, personal communication.
[20] J. M. Smith and W. E. Vehse, *Phys. Letters*, 1970, **31**, *A*, 147.
[21] R. L. Nelson, unpublished results.
[22] W. E. Vehse, W. A. Sibley, F. J. Keller, and Y. Chen, *Phys. Rev.*, 1968, **167**, 828.

confined to the 380—550 nm wavelength region in neutron-irradiated material, but this anneals completely at 500 °C in air [21] and cannot account for all of the optical absorption in shocked material.
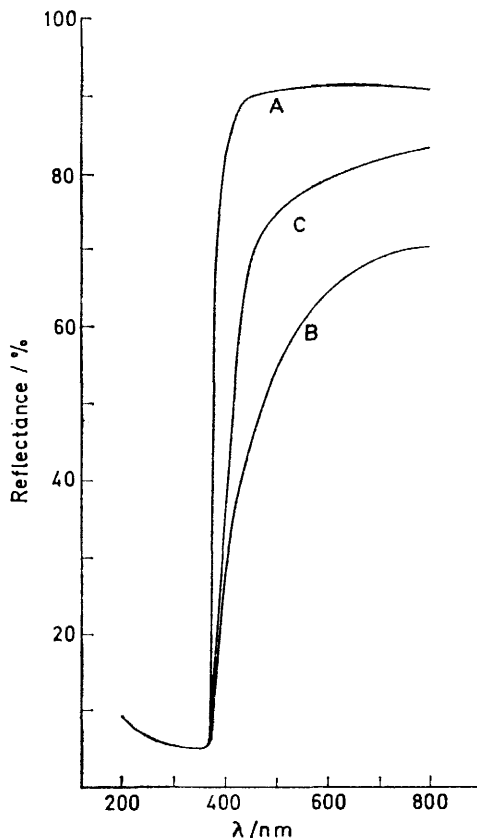

FIGURE 3   Diffuse reflectance spectra of zinc oxide;
A, unshocked; B, shocked; C, shocked and annealed at 700 °C

Although the results of explosive shocking in ZnO are apparently of similar type to those in MgO (*i.e.*, point defects and adsorbed O_2^- species), the mechanism could be explained largely by thermal effects rather than displacement and ionisation processes. Rapid heating during the explosion in a limited oxygen atmosphere probably led to a relatively high concentration of Zn^{1+} donors which subsequently reacted with oxygen to form adsorbed O_2^- ions as oxygen became available. Some evidence of the high temperatures and pressures during shocking comes from the decrease in specific surface area from 5·1 to 2·2 m^2 g^{-1} owing to sintering of adjacent particles.

Silica.—E.s.r. spectra. Unshocked silica was white, amorphous to X-rays, and the e.s.r. spectrum contained no detectable resonance. A number of samples from three different bombs of explosively shocked silica were examined. Material in the most intensely shocked lower regions of the bombs was dark, quite black in bomb no. 83, and as with magnesium oxide was relatively free-

[23] A. A. Deribas, N. L. Dobretsov, V. M. Kudinov, and N. I. Zyuzin, *Doklady Akad. Nauk S.S.S.R.*, 1966, **168**, 127.

flowing at the base. A longitudinal cut through bomb 83 showed a sharp transition from apparently uniformly black material in the lower part of the bomb to less severely affected light-coloured silica in the upper half. Elsewhere, a ' smoky glass ' of abnormally high density has been described [23] as the result of explosively shocking powdered amorphous silica but no attempt was made to identify the cause of the colour. Our dark material was somewhat less dense than off-white shocked silica and it is doubtful if the smoky glass is directly comparable.

The shocked samples were again amorphous and possessed a highly symmetrical resonance at $g = 2·0027$. The intensity of this signal increased in parallel with the degree of blackening in the samples, as shown in Table 1. This resonance (Figure 4,B) is Lorentzian in shape with a line width of 0·95 G and has not previously been observed in γ- or neutron-irradiated silica. There is no evidence of hyperfine interactions and this, together with the difference in g-value and saturation behaviour, indicates that the species responsible is different from that ($g = 2·0001$) observed by Symons [1] in black silica similarly obtained by explosive shocking. It is difficult to understand how different g-values for the intense signal in silica have been obtained, since the material studied in this and the previous investigation [1] originated from the same bomb.

Symons concludes that the latter signal results from unpaired electrons trapped at vacancies produced in the silica lattice by explosive shocking. Similar centres
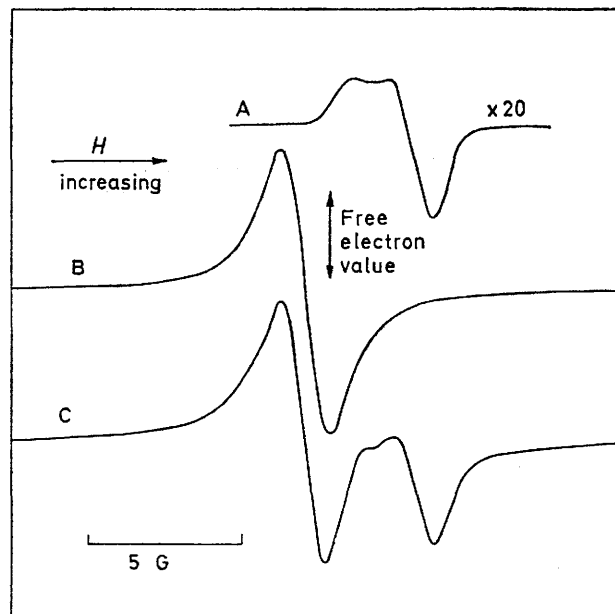

FIGURE 4   E.s.r. spectra of silica after explosive shocking and/or electron irradiation; A, irradiation alone; B, shocking alone; C, shocking followed by irradiation. The field increases from left to right and the arrows indicate the free electron value ($g = 2·0023$)

should be produced by neutron-irradiation although he sees no evidence for this. Accordingly we have studied the effects of γ-, electron-, and neutron-irradiation on the

unshocked material. γ-Irradiation to a dose of 3×10^{19} eV g^{-1} produced only a trace signal at $g_{av} = 2\cdot0008$ and this is likely to be due to electron trapping at pre-existing vacancies or impurities. Irradiation with

TABLE 1

Colour and e.s.r. signal in shocked silica

Sample	Source (Bomb no.)	Specific surface area/$m^2 g^{-1}$	Colour	E.s.r. signal (Relative intensity)
a	Unshocked	211	White	0
b	No. 85	16·9	Off-white	0
c	No. 86, fraction 1	21·1	Pale grey	0·005
d	No. 86, fraction 2	20·8	Dark grey	0·061
e	No. 83, middle	2·4	Dark grey	0·098
f	No. 83, base	5·75	Black	0·862

electrons of energy $>0\cdot5$ MeV is capable of displacing lattice ions to produce isolated point defects and the irradiation of unshocked silica produced the characteristic purple colour and a small signal at $g_{av} = 2\cdot0008$, which increased linearly with dose until the spectrum of Figure 4,A was obtained at a dose of 3×10^{22} eV g^{-1}. This asymmetric resonance with $g_{||} = 2\cdot0017$ and $g_{\perp} = 2\cdot0005$ is probably due to an electron trapped at an oxygen vacancy and has previously been observed after irradiation of fused silica,[24] single-crystal quartz,[24] and a porous glass.[25] Neutron-irradiation might be expected to produce some aggregated defects in addition to isolated point defects, but the spectrum obtained after neutron-irradiation of the present unshocked silica was identical to that in Figure 4,A.

γ-Irradiation of the black, shocked silica also produced a small resonance at $g_{av} = 2\cdot0008$ and in addition a weak doublet at $g = 2\cdot0027$ with splitting $a = 22\cdot9$ G. Electron-irradiation led to the spectrum of Figure 4,C in which both the symmetric signal at $g = 2\cdot0027$ and the asymmetric signal with $g_{||} = 2\cdot0017$ and $g_{\perp} = 2\cdot0005$ are present. The former signal only showed signs of saturation at the highest power, whereas the latter signal saturated readily with the signal amplitude passing through a maximum with increasing power in a

TABLE 2

Annealing of electron-irradiated shocked silica

Relative amplitudes of e.s.r. signals

Annealing temp./°C	Symmetric $g = 2\cdot0027$	Asymmetric $g_{||} = 2\cdot0017$, $g_{\perp} = 2\cdot005$	Doublet $a = 22\cdot9\ g$
20	8·6	3·6	0·6
210	10·6	2·0	0·2
425	14·6	0	0
820	13·9	0	0

manner similar to that of F^+-type centres in other oxides (c.g., MgO). The shocked material after electron-irradiation was then annealed at different temperatures for 30 min and Table 2 presents the results of these isochronal anneals. The asymmetric signal had completely disappeared after annealing at 425 °C for 30 min

and this is in agreement with its assignment to an isolated point defect of the F^+-centre type. The narrow symmetric line shows no sign of annealing at 820 °C and clearly cannot be due to a vacancy defect since diffusion in silica at this temperature is adequate to effect complete recombination of interstitial–vacancy pairs. A more probable explanation of this resonance would be the presence of impurities either in the silica bulk or on the silica surface as a result of their relatively high vapour pressure inside the bomb during the explosion. Surface-area measurements (Table 1) indicate that a 10- to 100-fold reduction in area occurs as a result of the explosion and if the sintering, which this considerable decrease suggests, has taken place while impurities were present in the gas phase, it is likely that these are distributed along grain boundaries of the silica in addition to direct contamination of the subsequent external surfaces.

Analysis for metal traces showed that Fe, Na, Ca, Mg, and Al were all introduced during shocking. Iron at ca. 100 p.p.m. was the major impurity. However, contamination was not significantly different in the black and off-white materials, and no correlation of colour with impurity could be made. The black material found at the base of bomb 83 is undoubtedly associated with the conditions of strongest shock obtaining there and not with a higher level of metallic impurity. The uniform blackness across the radius of this bomb also argues against an explanation in terms of metallic impurities, since silica nearest the walls should be most contaminated.

Further examination of the shocked silica identified the presence of 1% free carbon in the darkest material (sample f) which is clearly responsible for the colour and intense e.s.r. signal. The presence of carbon at this high level is surprising, but whatever the source of this impurity it must be produced in the bulk of the silica before the sintering which takes place immediately after shocking. The sintering process traps the carbon at grain boundaries where it is protected against oxidation in air at high temperatures (>820 °C).

Although carbon monoxide will dissociate to a limited extent in sufficiently strong shock waves,[26] the possibility of adsorbed CO or CO_2 being responsible for carbon formation is ruled out. I.r. spectra and desorption experiments up to 650 °C carried out on unshocked silica identified only adsorbed water. Moreover, silica shocked in a CO_2 atmosphere was no darker than when shocked in air.

The possibility of carbon being driven by the explosive shock out of the bomb of mild steel into the silica bulk is one which receives support from a report that the reverse process (viz., the shocking of carbon into steel) can take place, apparently to considerable depths under conditions of powerful impact.[27] However, the irreproducibility

[24] R. A. Weeks and C. M. Nelson, J. Amer. Ceram. Soc., 1960, 43, 399.
[25] G. M. Muha, J. Phys. Chem., 1966, 70, 1390.

[26] J. P. Toennies and E. F. Greene, J. Chem. Phys., 1957, 26, 655.
[27] I. M. Gryaznov, K. I. Kozorezov, L. I. Mirkin, and N. F. Skugorova, Soviet Physics—Doklady, 1971, 15, 868.

of the silica shots (subsequent samples were recovered white or off-white with little sign of blackening) seems to argue against this explanation.

The sudden transition from light to dark colour noted in material recovered from shot no. 83 suggests that a threshold of shock intensity is required for generation of the carbon impurity, and this would be consistent with the cracking of organic impurities. If hydrocarbon cutting oils used in manufacture contaminate the inner walls of the bomb, we have shown that they can give rise to blackened silica, particularly in the lower regions where the carbon penetrates more deeply into the cavity. Although bombs are normally cleaned with solvent before being filled and fired, trace hydrocarbon impurities left perhaps in the surface layers of steel could account for the variability in carbon content of shocked silica and explain the difficulty of reproducing the early shots showing marked blackening. *Ca.* 2 mg of oil per cm^2 of steel surface would account for the carbon in sample f, and levels of contamination probably well below 100 times less than this for the colour in samples originating from bombs known to have been carefully freed from oil.

Consistent with the concept of a variable hydrocarbon impurity level in the early shots are the surface areas recorded for the samples of Table 1. Light and dark silicas can be associated with surface-area reductions of 10- to 12-fold (samples b, c, and d) and though sintering is essential to the trapping of any carbon which may be present and generation of the narrow spin signal, the darkest silica (sample f) is not the most heavily sintered (e).

The intense symmetrical resonance at $g = 2\cdot0027$ is consistent with the presence of carbon at surfaces which are not in contact with oxygen. Ingram and others [28] have shown that carbon free radicals which have been formed by pyrolysis of organic materials have g-values close to the free-spin value, are difficult to saturate if the carbon content is high, and can have linewidths of under 1 G with no resolvable hyperfine structure. The presence of oxygen leads to a reversible broadening of this resonance, but this effect is unlikely to be important in the present case if most of the carbon is located at internal grain boundaries. This point is supported by the stability of the signal in silica which is in contact with air at 820 °C. The annealing data of Table 2 indicate that the hyperfine doublet at $g = 2\cdot0027$ anneals at low temperatures and represents a feature such as an interaction with a proton induced by γ- or electron-irradiation but which is relatively mobile and may not be related to the intense symmetric resonance at $g = 2\cdot0027$.

The possibility of carbon production during explosive shocking of magnesia and zinc oxide must also be considered, since these oxides may also be contaminated with adsorbed hydrocarbons. Although carbon may be formed at an intermediate stage in the explosion process,

[28] D. J. E. Ingram, ' Free Radicals,' Butterworths, London, 1958, pp. 207—212.

the massive sintering observed with silica does not occur and the likelihood of re-oxidation of carbon on the external surfaces exists. Some carbon remaining on the surfaces in contact with oxygen may account for some of the optical absorption observed in the present reflectance spectra.

Conclusions.—The three oxides form an interesting series when the results of explosive shocking are compared with those after bombardment with high-energy electrons or neutrons. The results of explosive shocking are summarised in Table 3 and from this, together with

TABLE 3

Summary of the effects of explosive shocking

Property	MgO	ZnO	SiO$_2$
M.p./°C	2800	1975	1600
Colour	Off-white	Brown	Black
Surface area change	Increase	Decrease	Decrease
Evidence for displacements	F$^+$, F$_2^+$	Zn^{1+}, small F$^+$ and possibly V	—
Evidence for ionisation	+	+	—
Evidence for novel e.s.r. features	—	—	+

the previous discussion on the results of high-energy irradiation, it can be seen that for a ceramic oxide of high m.p., MgO, the results of shocking are directly parallel to those of particle bombardment in the presence of air, whereas for SiO$_2$ with a much lower m.p. no such correlation is evident. Symons [1] attempted to apply the latter conclusion generally but we believe that this is not supported by our results. The behaviour of zinc oxide occupies an intermediate position between those of magnesia and silica.

As the shock wave from the explosion moves through the oxide material, lattice dislocations will be generated [7,8] and these will lead to the formation of point defects [2] and possibly defect aggregates, which may or may not be identical to those induced by irradiation. The energy released in the explosion may also result in ionisation processes and in rapid heating. There may therefore be present in any explosive shocking the conflicting effects of defect-formation–ionisation and annealing–sintering and the predominant effect is dependent on the physical properties of the oxide (*e.g.*, m.p.) and on the conditions of explosion (*i.e.*, total energy release). Under the present conditions of explosive shocking, defect-formation–ionisation processes are predominant in the MgO from the strongly shocked middle and lower regions of a bomb. In the shocking of silica, however, the annealing process removes any point defects initially formed in the shock wave and a massive sintering results with the possibility of considerable contamination by impurity vapours. In zinc oxide the thermal effects probably remove many point defects of the F$^+$-type centre, but the high temperatures result in non-stoicheiometry of the oxide with Zn^{1+} donor formation and a subsequent adsorption of oxygen.

It may prove possible by suitable control of the intensity of the explosion to vary the effects on any

selected material over wide limits.[29]   Although explosive shocking appears to be relatively inefficient in producing point defects in oxides it has one advantage over neutron-irradiation in that radioactivation is absent.

[29] A. N. Dremin and O. N. Breusov, *Russ. Chem. Rev.*, 1968, **37**, 392.