High-Pressure Electrical Behavior and Equation of State of Magnesium Oxide from Shock Wave Measurements

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A decrease in resistivity of MgO from $>10^9$ to $<10^4$ cm$^{-1}$ is observed when thin single crystals are shocked in the [010] direction at 500±70 kbar. This effect may be produced by several electronic processes, or by ionic transport in which the effective $O^-$ or $Mg^{++}$ diffusion constants are increased by perhaps a factor of 10$^9$ from those calculated at high pressure (according to Zener's strain energy model). Velocities are observed during passage of varying-strength (50 to 956 kbar) shock fronts through the specimen. These velocities approximate a linear increase in the resistivity material and may arise from electron conduction. Some Hugoniot data to 600 kbar (including measurement of elastic shock amplitudes varying from 35 to 85 kbar) are presented.

INTRODUCTION

EXPERIMENTS were performed on MgO to explore electrical resistivity, voltage generation under high pressure, and high pressure-equation state of MgO when it is shock compressed. Because it is a single crystal of MgO, it is of technological importance, and a study of the mechanics of the transition of MgO at high pressure may possibly be related to studies of the earth's interior since both resistivity and elastic constants have been inferred from geophysical and geological studies, respectively.

Measurements of diffusion$^{4,5}$ of various species and electrical resistivity$^{6}$ in single and polycrystalline MgO at atmospheric or reduced pressures and at high temperatures have been performed in differing gaseous concentrations. Controversy exists$^{7,8}$ as to whether the conductivity at normal pressures above 1350 K in the normal state rise from primarily ionic to electronic carriers.


In this study, the conductivity is not of the extrinsic or intrinsic type usually described in semiconductors. At sufficiently high pressure and temperature, electronic contributions to conductivity are expected when the valence-to-conductance band gap is filled.

Of interest here is a calculation performed by Wada$^1$ which predicts metallic conductivity in MgO when the specific volume is decreased by a factor of $<10^9$. If interest to studies of shock compression is the 10$^9$/cm$^3$ concentration of Fe centers in MgO which has been reported$^2$ to occur in single-crystal MgO after passage of a strong shock-wave disturbance. The result suggests that in the case of the slow deformation$^3$, the shock produces copious numbers of charged defects which may give rise to a substantial (and perhaps temporary) resistivity decrease.

ELECTRICAL MEASUREMENTS

The resistivity experiments summarized in Table I were performed using the longitudinal arrangement (current flow parallel to shock propagation direction) shown in Fig. 1, in which the MgO single crystals were mounted between a metal drive plate and a brass half-cylinder. This arrangement is similar to that employed in measuring resistivity of shocked NaCl and KCl, CaI, and NaCl,$^4$ CaF$^2$,,$^5$ and Al,$^6$ respectively. A flat-topped (near $\approx$ flat-top) shock front which propagates at a velocity $\approx 5$ cm/µsec was obtained.

Table I. Resistivity and shock-induced voltage, MΩ.

<table>
<thead>
<tr>
<th>Shot No.</th>
<th>Explosive</th>
<th>Initial specimen thickness (mm)</th>
<th>Shock pressure (kbar)</th>
<th>Particle velocity (mm/μs)</th>
<th>Shock-induced voltage (MΩ)</th>
<th>Resistivity (Ω·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11 542</td>
<td>A</td>
<td>5.0</td>
<td>70±5</td>
<td>0.744</td>
<td>0.021±0.009</td>
<td>4.21×10¹⁰</td>
</tr>
<tr>
<td>10 582</td>
<td>C</td>
<td>3.4</td>
<td>182±6</td>
<td>0.59</td>
<td>0.04</td>
<td>0.48×10⁻⁹</td>
</tr>
<tr>
<td>10 561</td>
<td>B</td>
<td>2.5</td>
<td>43±2</td>
<td>1.11</td>
<td>6.59×10⁻⁹</td>
<td>8.3×10⁻¹⁰</td>
</tr>
<tr>
<td>10 561</td>
<td>D</td>
<td>4.7</td>
<td>44±2</td>
<td>1.29</td>
<td>6.68×10⁻⁹</td>
<td>8.3×10⁻¹⁰</td>
</tr>
<tr>
<td>10 887</td>
<td>E</td>
<td>3.4</td>
<td>60±3</td>
<td>1.92</td>
<td>6.35</td>
<td>6.25×10⁻⁶</td>
</tr>
<tr>
<td>10 888</td>
<td>F</td>
<td>2.6</td>
<td>78±3</td>
<td>2.23</td>
<td>9.09</td>
<td>8.18×10⁻⁷</td>
</tr>
<tr>
<td>10 464</td>
<td>G</td>
<td>1.9</td>
<td>88±3</td>
<td>2.32</td>
<td>1.2×10⁻⁴</td>
<td>1.0×10⁻⁷</td>
</tr>
<tr>
<td>10 889</td>
<td>H</td>
<td>1.1</td>
<td>96±3</td>
<td>2.60</td>
<td>8.40×10⁻⁵</td>
<td>7.3×10⁻⁸</td>
</tr>
<tr>
<td>10 890</td>
<td>H</td>
<td>1.1</td>
<td>91±3</td>
<td>2.60</td>
<td>8.70×10⁻⁵</td>
<td>9.3×10⁻⁸</td>
</tr>
<tr>
<td>10 891</td>
<td>H</td>
<td>1.2</td>
<td>91±3</td>
<td>2.60</td>
<td>10.2±0.2</td>
<td>9.3×10⁻⁸</td>
</tr>
<tr>
<td>10 891</td>
<td>H</td>
<td>1.5</td>
<td>91±3</td>
<td>2.60</td>
<td>8.04</td>
<td>8.4×10⁻⁸</td>
</tr>
</tbody>
</table>

*See Table II.
†Derived from happen data generated in shots 10 520, 10 744, and 11 460.
§Derived from shock wave particle velocity and shock pressure.
¶Rate in drive plate from previous determinations with solid explosive.
††Presented by the authors, 1964.
‡Based on shock wave particle velocity different from drive plate.
§§Aluminum-oxide shock wave particle velocity.
¶¶Flash X-ray data from previous determinations with solid explosive.
 discontinued.

topped shock wave, whose duration is at least as great as the shock travel time through the specimen, is pro-
duced in the driver plate by the impact of an explosively
launched planar flyer plate or by a plane-wave-initiated
thick pad of high explosive in contact with the driver
plate (Table II). The resulting shock wave in the driver
plate propagates into the specimen and then into the
brass backing electrode. Because the latter approxi-
mately matches the specimen shock impedance, a
portion of the specimen will remain in the high-pressure
compressed state for a time interval which depends on
both the duration of the shock pulse and the lateral
specimen dimensions. The specimen is thin compared to
the backing electrode or driver plate. The specimen re-
sistivity is measured during the time that a substantial
portion of the specimen is in the high-pressure state
(usually before 0.5 μs has elapsed after the shock front
has left the specimen and is propagating into the back-
ing electrode). The voltage, observed on the oscil-
loscope during this time is related to the specimen

Table II. Explosive and plate accelerating systems.

<table>
<thead>
<tr>
<th>Code</th>
<th>System composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1 in. thick aluminum projectile (speed: 0.64 mm/μs, accelerated by gas gun) + 1 in. aluminum</td>
</tr>
<tr>
<td>B</td>
<td>P-50 + + 2 in. Banzal® + 1 in. 2024 aluminum</td>
</tr>
<tr>
<td>C</td>
<td>P-50 + + 2 in. Banzal® + 1 in. 2024 aluminum</td>
</tr>
<tr>
<td>D</td>
<td>P-50 + + 2 in. 9000 + + 1 in. 2024 aluminum</td>
</tr>
<tr>
<td>E</td>
<td>P-80 + + 4 in. 9000 + + 2 in. Lucite + 1 in. tool steel + 1 in. air (Free-Ram) + 1 in. brass (Anodized 0.025)</td>
</tr>
<tr>
<td>F</td>
<td>P-80 + + 4 in. 9000 + + 2 in. Lucite + 1 in. tool steel + 1 in. air (Free-Ram) + 1 in. brass (Anodized 0.030)</td>
</tr>
<tr>
<td>G</td>
<td>P-80 + + 4 in. 9000 + + 2 in. Lucite + 1 in. stainless steel + 1 in. air (Free-Ram) + 1 in. brass (Anodized 0.030)</td>
</tr>
<tr>
<td>H</td>
<td>P-80 + + 4 in. 9000 + + 2 in. Lucite + 1 in. stainless steel + 1 in. air (Free-Ram) + 1 in. brass (Anodized 0.030)</td>
</tr>
</tbody>
</table>

* P-50 and P-80 done in 6 and 8-in. class explosive plate-wave experiments.
‡ Manufactured by Newes, and Hanger, Inc., Anadale, Texas.

![Mechanical configuration and circuitry, shock resistivity experiments.](image)

The mechanical configuration and circuitry during shock resistivity experiments are recorded on oscilloscope when specimen resistivity approaches zero and infinity, respectively.)
resistivity $\rho$ by

$$\rho = \frac{R_0 A}{L} \left( \frac{V}{I} \right)$$

(1)

Here $R_0$ is the effective resistance in parallel with the specimen (including cable termination), $I$ is the negative of the applied dc voltage, and $L$ and $A$ are the conducton path length and area, respectively. For the results quoted in Table I and Fig. 2, $L$ is taken to be equal to the specimen thickness after shock compression and $A$ equal to either the cross-sectional area of the entire brass electrode or, in the case of the gunning electrodes described below, it is equal to the area of the central brass portion. For the specimen dimensions and viewing system used, the circuit is useful for measuring resistivities in the $10^4$ to $10^8$-$\Omega$-cm range; these correspond to oscilloscope signals $I_i$ of $\sim 0.05$ [uA] to $\sim 0.08$ [uA] volts. As many as six oscilloscopes, two of which had double beams, were used in each shot to record the signals at different writing speeds and sensitivity levels (Figs. 3 and 4). Oscilloscopes were triggered with a pulse originating in the electronic detonating unit which was delayed from the time of the initial explosive detonation using both an electronic and a cable system.

To exclude the possibility that the observed decrease in resistivity in the very-high-pressure experiments could result from iodine air surrounding the shocked specimens, two of the shots were fired in a chamber containing free-flowing, high-purity helium. This precaution was observed even though a planar shock resulting from impact of a driver plate at 3 mm/sec would give, in air, a shock pressure of $\sim 130$ bar and a temperature of $\sim 6400$ K. This shock state is only in the range in which $N_2$ dissociates (to form $N$), and no ionization is expected.19 It was felt, however, that the effect of shock convergence or even small-scale jetting at the nose edge of the specimen and electrode might

(~108 kbar) silicone oil remains a relatively good insulator (µ ~ 102 G cm).

The shock pressures produced in the MgO specimens were obtained using Hugoniot data and knowledge of the shock state produced in the driver plate by each of the explosive or plate-impact systems. The driver plate state is obtained by: (1) measuring the driver plate free-surface velocity; (2) measuring the flyer plate velocity prior to impaction of the driver plate (shot 11 992); (3) using the Mangunni wire shock pressure transducer; or (4) assuming reproducibility of the pressure produced by a given explosive system. For methods (1) and (2) electrical contact point set 5 and 30 mm apart were used. Using the Hugoniot curves for MgO, the driver and flyer plates, and applying the impedance-matched method, the final shock states in the driver plate and specimen are determined. Method (3), used for the lower pressure shots, gives the shock pressure within a block of C7 epoxy which is in contact with the driver plate. This is obtained from the relative change of the electrical resistance of a Mangunni wire imbedded in the C7 as it becomes compressed by the shock front. From the shock pressure in the C7, the shock states in the driver plate and in the MgO specimen are obtained using the impedance-matched method. No account was taken of the pressure increase which results from shock reflection caused by the slight impedance mismatch at the MgO-ethanol interface or the pressure decrease which results from propagation of rarefaction waves inward from the lateral specimen and electrode surfaces. Both of these effects must occur, even within the 0.5 µsec during which the resistivity measurements are performed. The compression of the specimen in these experiments should be nearly dimensional because the driver assemblies employed generate planar shock waves and the ratio of specimen thickness to diameter is small. Hence the relative change of thickness should equal the specific volume change or

\[ V \times \Delta V = V/V_0 \]  

where \( V \) and \( V_0 \) are the specimen specific volume and thickness, respectively, in the shocked state and the zero subscript indicates the initial or zero-pressure value. For a single shock wave encompassing material initially at rest, with a shock velocity of \( U \) and a particle velocity of \( v \), the specific volume is obtained from the Rankine-Hugoniot mass conservation relation

\[ V = V(U - v)/U \]  

The specimens used were high-purity, single-crystal "Magnesite" supplied by Norton Co., Niagara Falls, N. Y. The crystals chosen for the electrical experiments were transparent and light brown or yellowish in appearance. Specimens approximately 30 mm square were cleaved ([001] plane) to the desired thickness and lapped with alcohol and aluminum oxide powder to ±0.03 mm in flats and parallelism. To assure specimen dryness after mounting the specimen in the shot assembly, the entire assembly was placed in a vacuum chamber (100 µ) and heated to ~100°C for several hours. The vacuum was retained until shortly before the experiment was fired.

Less perfect crystals were used for the Hugoniot experiments, particularly for the greater thickness specimens; the 0.7-mm-thick specimen used in shot 14 461 had several tetrahedron-shaped imperfections which appeared to be internal voids (~0.4 mm in diameter). These were placed so as not to be close to the field of view of the streak camera slit.

RESULTS OF ELECTRICAL MEASUREMENTS

The resistivity obtained for MgO shows a marked and a reproducible decrease (Fig. 2) to values on the order of 30000 Ω cm for shock strengths of 5200-70 kbar. Below that pressure level only a lower limit of the resistivity, ~10³ Ω cm, can be deduced from the noise level of 1 to 2 V recorded on the oscilloscope. (This noise level is also recorded after the shock front leaves the specimen in shots for which a voltage is not impressed on the circuit shown in Fig. 1.)

Although it appears impossible, from only these results, to deduce precisely the nature of the mechanism which produces the observed resistivity decrease, certain limitations—particularly on possible intrinsic transport processes—may be imposed from the results of normal pressure, high-temperature experiments on MgO. At temperatures greater than 1800°C, and at both high (1 to 10⁴ bars) and low (10⁻⁷ to 10⁻¹³ bars) oxygen partial pressure, Mitolo suggests that the electrical conductivity results from electronic carriers (possibly produced by thermally activated point defects). Mitolo concludes that at lower temperatures the Mg²⁺ ion is the predominant charge carrier with impurities determining electrical behavior down to 1800 K (the lower limit of his experimental range). Davies, on the other
hand, concludes that at both high and low temperatures, conductivity results from either Mg²⁺ or O²⁻ transport, depending again upon oxygen pressure and, at lower temperatures, impurity level.

It is interesting to compare the resistivities obtained in ambient-pressure, high-temperature experiments with those obtained in the present shock experiments. At the shock pressure level at which the MgO resistivity decreases to 1000 Ω-cm (specifically 912 kbar, Table III) a shock temperature of 733 K is calculated. In contrast to the shock wave result, this same resistivity (~1000 Ω-cm) is achieved only at ~2000 K at ambient pressure. (This temperature is inferred from the extrapolation of Mitoff’s resistivity data by two orders of magnitude in resistivity.) One may also compare the shock resistivity (at 917 kbar and 733 K) with the resistivity value that might be measured at ambient pressure and 733 K. By extrapolating the ambient-pressure resistivity data to lower temperatures, an upper bound of 100 Ω-cm at ~733 K is obtained. This result is valid only if charge transport processes with the same activation energy as at ~1300 K remain dominant down to 743 K.

From these comparisons it may be concluded that the low resistivity observed at a fairly low temperature under shock compression is not due to the same temperature-dependent ionic or perhaps electronic processes as those observed at essentially zero pressure, but instead involves processes which may be unique to the high pressure and severe deformation encountered by the shocked MgO.

One possible mechanism which may give rise to the observed resistivity decrease is electronic conduction, either extrinsic from impurity-produced energy levels lying between the valence and conduction band (normally separated by ~9 eV), or intrinsic from a pressure-induced reduction in the energy gap between the valence and conduction band. Verification of the dominance of either of these processes requires additional resistivity shock experimentation and perhaps such other types of measurements as determinations of the optical properties of MgO in the shocked state.

A calculation of the effect of compression on the electronic band structure of MgO is reported by Wada. He finds that the conduction and valence band of MgO overlap when the lattice spacing is reduced to 1.87 Å (V̅ₐₕ = 1.415). This compression is greater than that achieved in these shock experiments, and extrapolating the Hugoniot data described below it would be achieved at somewhat greater than 2000 kbar. This may be compared with the 1030 kbar which Wada obtained by evaluating a Born-Mayer type of equation of state. The observed resistivity decrease may also be due to an ionic transport mechanism. For this case it is possible to set a lower limit on the diffusion constant of the dominant charge transport process which gives rise to the resistivity decrease. This is accomplished by demanding that the total number of carriers per unit volume, n, does not exceed the total number of atoms per unit volume, N₀. Using the Nerst-Einstein equation

$$ D = kT/\mu_0 (e^+ e^-) $$

(4)

where D is the self-diffusion constant, $\mu_0$ is the magnitude of the electrical charge of the appropriate carrier, $e$ is the resistivity, and $kT = 4.184 \text{ J/mole}$, the usual meaning, we demand that

$$ D \geq kT/\mu_0 (e^+ e^-) $$

(5)

Taking a value of shock temperature of 733 K at 917 kbar (Table III, Eq. (5) given for $p = 10^9$ Ω-cm,

$$ 2 \times 10^{-15} \text{ cm}^2/\text{sec} $$

(6)

Heat $e$ is nominally taken as two electronic charges. Values of the diffusion constant for Mg²⁺ and O²⁻ of 6×10⁻²⁰ and 5×10⁻²⁰ cm²/sec may be calculated at 733 K from the data of Linder and Yudson and Osbi and Kingery, respectively. These values substituted into Eq. (4) both result in $n \lesssim 2 \times 10^{10}$ cm⁻³ carriers at 733 K. This value far exceeds $n_0$ and the minimum number of vacancies (actually $10^{10}$/cm³ F centers) found to be present in explosively shocked MgO which has been recovered after exposure to high shock pressure. It is expected that the diffusion constant used

<table>
<thead>
<tr>
<th>Specific heat, $c_p$</th>
<th>Hugoniot pressure, $P_H$ (kbar)</th>
<th>Hugoniot temp, $T_H$ (Κ)</th>
<th>Temperature along Hugoniot, $T_A$ (Κ)</th>
<th>20°C (isotherm), MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0056</td>
<td>424</td>
<td>427</td>
<td>3.174</td>
<td>62.8</td>
</tr>
<tr>
<td>0.0082</td>
<td>489</td>
<td>432</td>
<td>3.393</td>
<td>59.8</td>
</tr>
<tr>
<td>0.0082</td>
<td>516</td>
<td>432</td>
<td>3.486</td>
<td>55.9</td>
</tr>
<tr>
<td>0.0082</td>
<td>538</td>
<td>432</td>
<td>3.505</td>
<td>56.8</td>
</tr>
<tr>
<td>0.0082</td>
<td>550</td>
<td>432</td>
<td>3.595</td>
<td>56.8</td>
</tr>
<tr>
<td>0.0082</td>
<td>561</td>
<td>432</td>
<td>3.605</td>
<td>56.8</td>
</tr>
<tr>
<td>0.0082</td>
<td>572</td>
<td>432</td>
<td>3.615</td>
<td>56.8</td>
</tr>
<tr>
<td>0.0082</td>
<td>583</td>
<td>432</td>
<td>3.625</td>
<td>56.8</td>
</tr>
<tr>
<td>0.0082</td>
<td>594</td>
<td>432</td>
<td>3.635</td>
<td>56.8</td>
</tr>
<tr>
<td>0.0082</td>
<td>602</td>
<td>432</td>
<td>3.645</td>
<td>56.8</td>
</tr>
<tr>
<td>0.0082</td>
<td>610</td>
<td>432</td>
<td>3.655</td>
<td>56.8</td>
</tr>
</tbody>
</table>
in Eq. (4) should be markedly decreased by high pressure.

An estimate of the effect of pressure on the diffusion constant of an isotopic species may be obtained by applying at least one of the theoretical treatments of the effect of pressure on activated processes presented by Keyes. The diffusion constant may be written as

$$D = \frac{1}{2} \left( \frac{\Delta G^s}{RT} \right)^{1/2} \left( \frac{V}{V'} \right)^{1/2},$$

where $f$ is a geometrical factor, $a$ is the lattice spacing, $\tau$ is the vibrational frequency of the carrier, and $\Delta G^s$ is the appropriate Gibbs activation energy for the diffusion process. $\Delta G^s$ may include the energy required to create a vacancy in addition to that required for an ion and vacancy to interchange positions. The pre-exponential factor in Eq. (7) may be written

$$\frac{1}{\sqrt{2\piRT}} \left( \frac{V}{V'} \right)^{1/2},$$

where $a$ is a constant and $\frac{1}{\sqrt{2\piRT}}$ is Götze's factor. Equation (8) results from assuming that the carrier vibration frequency is proportional to the Debye temperature and hence $V^{1/2}$. Differentiating Eq. (7) with respect to pressure at constant temperature gives

$$\frac{dD}{dP} = \frac{1}{2} \left( \frac{\Delta G^s}{RT} \right)^{1/2} \left( \frac{V}{V'} \right)^{1/2} \frac{d\ln V}{dP},$$

where $d$ is assumed not to vary appreciably with $P$ and

$$\frac{d\Delta G^s}{dP} = \frac{1}{2} \left( \frac{\Delta G^s}{RT} \right)^{1/2} \left( \frac{V}{V'} \right),$$

Equation (9) follows from Eqs. (4) and (9) and (21) of Keyes treatment of Zener's transition energy model. Since the value of $\Delta G^s$ is £64 for diffusion of Mg$^{2+}$ or (V') below 90 K in MgO, the first term in the bracket in Eq. (9) is neglected since generally $\gamma f/V'^{1/2}$. Equation (10) may be integrated to give the Gibbs activation energy as a function of compression along an isostatic axis as

$$\Delta G^s = \Delta G^s_0 (V'/V)^{1/2} - \frac{1}{2} \left( \frac{\Delta G^s}{RT} \right) \frac{dV}{dP},$$

or

$$\Delta G^s = \Delta G^s_0 (V'/V)^{1/2} - \frac{1}{2} \left( \frac{\Delta G^s}{RT} \right) \frac{dV}{dP}.$$

Equations (11) and (12) are obtained by assuming either $\gamma$ or $\gamma f/V'^{1/2}$ is constant along an isostatic axis, $\Delta G^s_0$ denotes the Gibbs activation energy at zero (ambient) pressure. Substitution of Eqs. (11) and (12) into Eq. (9) (with the first term in the bracket deleted) and integration yield

$$\Delta G^s = \Delta G^s_0 (V'/V)^{1/2} - \frac{1}{2} \left( \frac{\Delta G^s}{RT} \right) \frac{dV}{dP},$$

or

$$\Delta G^s = \Delta G^s_0 (V'/V)^{1/2} - \frac{1}{2} \left( \frac{\Delta G^s}{RT} \right) \frac{dV}{dP}.$$

where $\gamma$ and $\gamma f/V'^{1/2}$ are again considered constant for Eqs. (13) and (14), and $\Delta G^s$ is the observed-diffusion constant at zero pressure. Equation (13) yields the values of $10^{-4}$ and $10^{-5}$ cm$^2$/sec for $\Omega_2$ and Mg$^{2+}$ diffusion, respectively, at a compression (V'/V) and temperature of 0.727 and 733 K. Equation (14) yields the value of $0$ of $10^{-4}$ and $10^{-5}$ cm$^2$/sec for $\Omega_2$ and Mg$^{2+}$ diffusion, respectively. All these values violate the condition of Eq. (6).

Although the carrier multiplication mechanism appears to account for the decrease in resistivity observed in the slow deformation experiments on alkali halides performed by Camagni and Mazur, 23 in the present experiments an unconstrained high energy carrier density, which would be in fact far greater than the number of atomic per unit volume, would be required. It may be concluded from this argument that for isotonic activity of the magnitude observed, the effective diffusion constant of the appropriate isotopic species must be greatly enhanced under shock, by perhaps 39 or more orders of magnitude over that predicted under high pressure by the Zener transition-energy model. It may be that such a radical increase in diffusion constant actually occurs and is the same as or closely related to the so-called pipe diffusion observed in deformed LiF. 24, 25 Undoubtedly a large number of discontinuities, which also give rise to vacancies, are produced by the passage of the shock front. In this case the effect is probably meaningful to such a relation was indeed observed in the shock-resistivity experiments performed on CsCl and KI. 23, 26

SPECIMEN-INDUCED VOLTAGES

In addition to signals resulting from the decrease in MgO resistivity, signals with amplitudes varying from 10 to 100 V at shock strengths varying from 70 to 936 kbar appear across the viewing resistor (Fig. 1) during propagation (through) within the specimen. The excitation which produces these voltages is believed to originate within the specimen, since shock waves (e.g., shots 10-581 and 10-563) essentially identical signals are observed when no dc voltage is impressed. As in the case of shock propagation through alkali halides in which a similar effect is observed, 26 the struc-

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tion of these specimen-induced signals corresponds closely (±0.03 μsec) with the estimated transit time of either the elastic or deformational shock through the specimen (at high pressure the time resolution does not permit differentiation between these two). In one lower pressure shot (11 592) in which a thick specimen was used, the difference in velocity between the elastic and the following deformational shock permitted suffi-
cient time resolution of the specimen-induced voltage so that signal features could be correlated with the elastic and deformational shock transit times. It is interesting that changes in signal amplitude are observed at times which correspond closely to exit of both the elastic and deformational shocks from the specimen (Fig. 5).

The specimen-induced voltages from the guarding electrode experiments (only the center electrode results are quoted) and those using solid electrodes are given in Table I. As suggested by Allison and Hauser, the voltage observed when the shock enters the specimen (which, when resolved in these experiments, was the maximum voltage) may be scaled by multiplying by the initial specimen thickness and dividing by the specimen or, in this case, electrode area (Table I and Fig. 6). In the case of the approximately 1-mm-thick specimens, systematic errors in the measurement of the specimen-induced voltage (duration of ~0.1 μsec) were probably present because of the inductance in the cables leading to the oscilloscopes. The specimen-induced voltages appearing across the outer guarding electrode were found to be as much as 90% greater (shot 10 890) than those generated at the center electrode. This latter effect, as well as the general variation with shock strength and the association of different signals with both the elastic and deformational shock front (shot 11 542), suggest that these specimen-induced voltages result from the net displacement of charged defects (produced by the shock deformation) in the specimen material. The scaling law suggested by Allison and Hauser supplies what appears to be an adequate ordering to the data and is consistent with a model for which the voltages observed are produced by net volume polarization of the shocked MgO (dipoles oriented in the direction of shock propagation).

**HUGONIOT DATA, MAGNESIUM OXIDE**

Three plane-wave, inclined mirror (streak camera) shock experiments on magnesium oxide provided Hugoniot pressure-volume data at the 170-, 420-, and 600-kbar pressure levels (Table IV and Fig. 7). These experiments were performed primarily so that the pressures achieved in the magnesium oxide in the shock-resistivity experiments could be estimated from measured shock states in the driver plates. Flat and inclined mirrors were employed to measure (a) the transit

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times of both the elastic (first) and deformational (second) shock fronts through the specimen; (b) the free-surface velocities imparted by the incident shock to the driver plate; and (c) the free-surface velocities of the specimen resulting from internal reflection of the elastic and deformational shocks. The elastic shock was computed assuming that the free-surface velocity equals twice the shock-particle velocity; the second or deformational shock state was computed using the impedance-match method. To obtain the deformational (second) shock velocity \( U_2 \) when two shock fronts are present, the interaction of the elastic waves—which has reflected from the specimen's free surface—on the oncoming deformational shock must be taken into account. The resulting value of \( U_2 \) was found to be insensitive to the details of this interaction; therefore, for simplicity, an elastic interaction was assumed. In this case the apparent velocity

\[
\frac{U_1}{U_1 - U_2} = \frac{\rho_0 v_0}{\rho v} \frac{\rho_0}{\rho - \rho_0} \frac{U_1}{U_1 - U_2}
\]

is related to the deformation shock velocity by

\[
U_2 = \frac{\rho_0 v_0}{\rho v} \frac{\rho_0}{\rho - \rho_0} \frac{U_1}{U_1 - U_2} \left( U_1 - U_2 \right)
\]

Here \( U_0 \) is the specimen free-surface velocity resulting from interaction of the first shock with the free surface. The errors in determining the shock and particle velocities in these shots are believed to be less than 1% and 5%, respectively. The agreement between the (final state) particle velocities obtained from taking one-half the specimen free-surface velocities and those deduced from the driver plate free-surface velocities using the impedance-match method (Table IV) implies that the shock and subsequent reflection are non-reversible.

Of special interest is the elastic-shock amplitude (Table IV) which is markedly dependent on both the final shock state and, possibly to a lesser extent, on specimen thickness at a constant final shock state. The elastic shock amplitude increases (33 to 60 kbar) with increasing final shock pressure (450 to 623 kbar); also, the elastic-shock amplitude decreases with increasing shock propagation path length (40 to 55 kbar, 4.7 to 9.7 mm at final shock state of 166 kbar). Both of these effects suggest that the shear stress in MgO under one-dimensional compression, decreases with time. This behavior is similar to the stress-relaxing solid discussed by Duval. In order to facilitate the calculation of temperatures existing within the shocked MgO in the high-pressure state (corresponding to conditions under which the resistivity measurement is performed), the Hugoniot data were fit to the line

\[
U^* = C + S \sigma
\]

where \( S \) and \( C \) are constants. \( U^* \) and \( \alpha \) are either the shock and particle velocity associated with a single shock front or, in the pressure range where two shock fronts are present, the equivalent shock and particle velocity which would correspond to the final (deformational) shock state being achieved by a single shock front. Thus in the case of two shocks

\[
\sigma^* = \frac{U_1 - U_2}{U_2} \left( F_0(V_s - V_p) \right)
\]

where, as usual, the subscripts refer to the first and second shock fronts. From a near square fit of seven data points, reduced according to Eqs. (18) and (19), \( C = 0.65 \) (m/s)/kbar or \( S = 1.85 \). By applying the Rankine-Hugoniot relations for a single shock to Eqs. (18) and (19), the Hugoniot pressure-volume relation may be written

\[
P_a = C(V_a - V_p)/(V_a - S(V_a - V_p))
\]

where \( P_a \) is now used for the pressure along the Hugoniot. In order to calculate shock temperature \( T_{sh} \) the following formula (first derived by Walsh and Christian) giving the temperature along the Hugoniot, is applied:

\[
T_{sh} = T_{sh}^0 [F_{sh}^*(T_{sh})]\n\]

where

\[
F_{sh}^*(T_{sh}) = \int \frac{dT_{sh}}{\left( F_0(V_h - V_p)/(V_h - S(V_h - V_p)) \right) \text{ [1]}}
\]

A small and probably negligible error is introduced because the integration is not performed along the experimental hugoniot curve but along the locus of shock states which would be achieved by a hypothetical single shock transition. \( C_v \) is the specific heat at constant volume and again \( \delta = \gamma / V \) is assumed constant. Because of the high value of the MgO temperature of \( 1013{\text{K}} \) relative to both room and shock temperatures, it is desirable to use a temperature and volume-dependent form for \( C_v \). The temperature dependence of the specific heat was assumed to be given by the Debye formula:

\[
C_v = \frac{3}{\pi^2} \int_0^{\infty} \frac{\omega^3}{e^{\omega T} - 1} d\omega
\]

\[
= \frac{3}{\pi^2} \left[ \frac{12T(\gamma / 3)}{3} \right] \int_0^{\infty} \omega^3 \theta^2 d\theta
\]

The variation of Debye temperature \( \Theta \) with compression is given by:

\[
\Theta = \frac{\Theta_0}{\theta_0^{\gamma - 1} - \theta_0^{\gamma - 1}} = \frac{\Theta_0}{\theta_0^{\gamma - 1} - \theta_0^{\gamma - 1}}
\]

where the \( \gamma \) parameter of the Debye theory is now associated with the thermodynamic Gruneisen's ratio \( V(\partial P/\partial V)^{\gamma - 1} \).

Equations (21), (22), and (23) were simultaneously solved numerically for \( T_s \) (Table III) with the aid of a digital computer, using the experimentally determined values of \( C \) and \( S \) in Eq. (20). It should be noted that the first term in Eq. (21) gives the temperature \( T_o \) at a specific volume \( V \) on the hysteresis passing through the foot of the Hugoniot \( (P = 0, V = V_o) \). The 200°C isotherm points are calculated from the relation

\[
P_s = P_o\left[ \frac{V_o}{V} \right]^{\gamma - 1} - \frac{T_o}{C_v dT_s}
\]

where \( C_v \) is obtained from Eq. (22) and the value for \( \Theta \) is obtained at each specific volume using Eq. (23). The calculations presented in Table III indicate that over the pressure range of the experimental data the difference between the calculated 200°C isotherm and the Hugoniot is negligible. Although the Hugoniot calculated from the values of \( C \) and \( S \) obtained from handbook data tabulated by McQueen et al.13 agrees fairly closely with the experimental Hugoniot to at least 500 kbar, extensive shock-wave measurements recently performed at Los Alamos Scientific Laboratory give values of \( C \) and \( S \) more consistent with the lower pressure values of 65 mm/sec and 1.3, respectively.16,17

The agreement of the experimental isotherm of Peres-Albuine and Drickamer with the Hugoniot curve at high pressures (about 300 kbar) is satisfactory. It is not clear whether the apparent divergence of the Hugoniot data at low pressure14 from the experimental isotherm is of particular significance except that, as in the case of quartz, a positive pressure offset of the deformational Hugoniot from the hydrostatic isotherm expected for an elastic-plastic material appears to be absent. This result implies a fluid-like behavior of MgO in the deformational shock state.

**SUMMARY AND CONCLUSIONS**

A decrease in the resistivity of Norton "Magniite" MgO (shocked along [001]) from \( \rho > 10^{10} \Omega \cdot \text{cm} \) is observed at a shock pressure of 9.2 ± 0.2 kbar. The specimens (thicknesses 1 to 5 mm) were mounted between a metal driver plate and a brass backing electrode (the latter approximately matches the MgO shock impedance). A plate shock wave is driven into the driver plate; this wave propagates through the specimen and then into a brass backing electrode. While the shock is propagating in the backing electrode, the specimen (which is thin compared with the thicknesses of both the driver plate and backing electrode) is assumed to remain at a nearly steady pressure value. The resistivity is obtained by measuring, with fast-oscilloscopes, the current discharged from a capacitor through the specimen within the first 0.5 sec after the shock enters the backing electrode.

Most of the experiments were performed in air, but several shots performed in helium atmosphere gave similar results. The results were likewise unchanged by substituting guarding backing electrodes in place of the solid ones.

The observed resistivity decrease may be due to electrons arising from: (a) impurities producing donor and acceptor energy levels; (b) a compression-induced reduction in band gap; or (c) electron production by an unknown mechanism. On the other hand, the decrease may occur because of enhanced conductivity by ions. Although an increase in ionic carrier density probably results from passage of the shock, the estimates of Mg++ and O++ diffusion constants obtained from the Zener strain-rate model (assuming either \( \gamma \) or \( \gamma / V \) is constant) imply that it is impossible to account for the decreased resistivity solely on this basis. Pipe transport along dislocations4 or perhaps another process is required to increase by a factor of 109 the effective diffusion constants if the observed conductivity is to be attributed to ion motion. Pipe transport along dislocations might result in a lower resistivity parallel to the shock front than perpendicular to it. (Such an effect may actually be observed in KI and CsI.)18,19

Signals (presumably specimen-induced) whose durations correspond closely to the time that the shock fronts are propagating through the specimen and whose amplitudes are independent of the impressed d c voltage

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13 R. G. McQueen, Los Alamos Scientific Laboratory (private communication).

14 F. E. Bichel, Harvard University (private communication).


18 R. G. McQueen, Los Alamos Scientific Laboratory (private communication).

19 F. E. Bichel, Harvard University (private communication).
were recorded in all the electrical experiments. The maximum observed voltages varied from +1.2 to +105 V as the shock strength was increased from 70 to 936 kbar. An important parameter of these data occurs if the observed voltages are multiplied by specimen thicknesses and divided by electrode areas. This results in a scaled voltage of \( \approx 0.2 \) to \( \approx 8.5 \) V/cm over the experimental range. Such a scaling law would apply if a net volume polarization, perhaps arising from net displacement of charged defects, were present in the shocked MgO.

Hugoniot data to 660 kbar were measured and used to obtain shock pressures in the electrical experiments. Shock temperatures and the 20°C isotherm for MgO were calculated by using the Walsh and Christian formula. A constant value of \( \gamma \) and a temperature and volume dependence for \( C_v \) given by the Debye theory were incorporated into the Walsh and Christian treatment. The calculated shock temperature at the pressure level of the observed resistivity decrease is 353 K (at 917 kbar). The calculated pressure offset between the 20°C isotherm (which agrees closely with that measured by Perez-Alberne and Brickman at 300 kbar) and the Hugoniot is negligible over the experimental range (e.g., 14 kbar at 674 kbar). At lower pressure (788 kbar), the lack of a pressure offset of the deformed Hugoniot curve from the hydrostatic indicates a fluid-like behavior for MgO shocked above the Hugoniot elastic limit. The value Hugoniot elastic limit (elastic shock amplitude) is markedly dependent (values from 85 to 898±20 kbar are observed) on the value of the final shock state (106 to 473 kbar) and to a lesser extent on shock propagation path length.

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