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Materials & Chemistry Division

Surface Electrical Conductivity of Single Crystal Spinel in Cesium Vapour

P. Agnew and J.L. Ing

Work undertaken for the European Office of Aerospace Research and Development of the U.S. Air Force under contract number F61708-95-C0002.

2nd April 1995

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1. Introduction

The operation of a thermionic fuel element (TFE) requires the maintenance of good electrical resistance between the anode and cathode, and between the electrodes and the TFE body. A program of research was established as part of the TOPAZ International Program (TIP) with the purpose of investigating the degradation of TFE electrical insulators. The major emphasis of this research has been on the interactions of oxide ceramics with cesium (Cs) vapour, and the resulting decrease of surface resistivity. Previous work has studied the surface electrical conductivity of sapphire exposed to Cs <1>. In this report we describe the results of an experimental investigation of the surface electrical conductivity of single crystal magnesium aluminate spinel at temperatures ranging from 573K to 923K, in the presence of cesium vapour at pressures up to 1Torr. The interest in spinel has arisen in view of its apparent resistance to radiation damage. This is clearly an attractive feature for a material which will be required to operate in the core of a nuclear reactor. In contrast to magnesium oxide and alumina, electron irradiation of spinel produces no dislocation structures. Buckley <2> was unable to produce dislocations under a wide range of irradiation conditions. Clinard et. al. <3> studied neutron irradiated spinel and found it to be resistant to structural damage. In samples of polycrystalline spinel irradiated at 1198K voids were limited to the grain boundary areas and in the single crystal material no voids were found at all.

In a TFE the insulators are exposed to Cs vapour in addition to radiation and so must also show both chemical and electrical resistance to Cs. In this report we describe the effects of Cs on the surface electrical properties of single crystal spinel exposed to Cs under typical TFE operating conditions. Our samples (obtained from 'Commercial Crystal Laboratories Inc.' <4>) were 25.4mm diameter, 0.495mm thick discs of 99.99% pure $MgAl_2O_4$ in the (111) orientation. A standard three terminal (centre, guard and bottom) electrode system was employed. The centre electrode diameter was 10mm and the inner diameter of the guard electrode was 19mm. Further experimental details have been described in a previous paper <1>.

2. Intrinsic Electrical Properties

As a precursor to exposure to Cs we determined the intrinsic bulk and surface electrical conductivity of our samples.

Surface Conductivity

The surface conductivity σ_s was obtained from measured values of the surface conductance G_s . For the guarded electrode geometry the relationship between these parameters is

$$\sigma_s = G_s \frac{\ln(b/a)}{2\pi} \quad (\Omega/\square)^{-1} \quad , \quad (1)$$

where b is the inner radius of the guard electrode and a is the radius of the centre electrode. For our samples the numerical relationship is

$$\sigma_s = 0.102G_s \quad (\Omega/\square)^{-1} \quad (2)$$

Measurements of G_s were taken over the range 455K to 737K. The results are shown in fig. 1 in the form of a plot of $\ln(\sigma_s)$ versus reciprocal temperature.

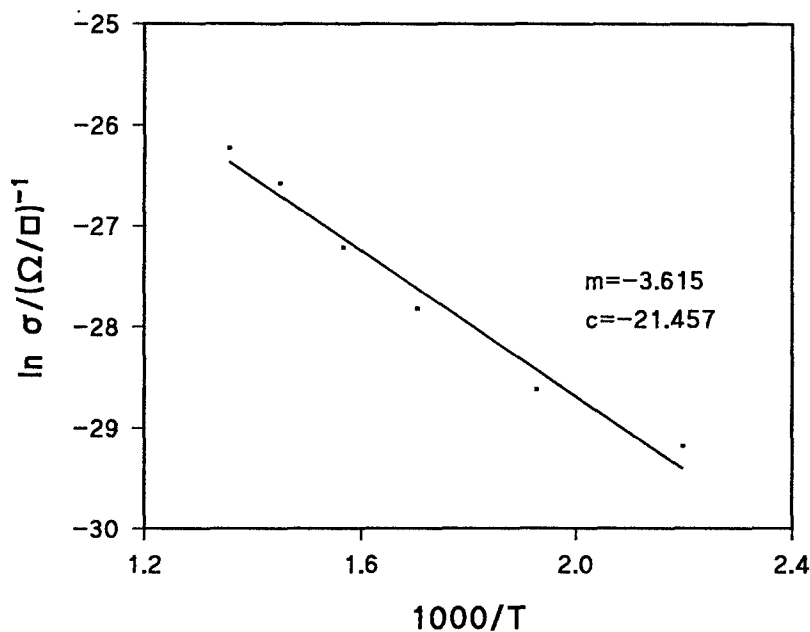


Fig. 1. Temperature variation of the surface conductivity of single crystal spinel.

The data are approximated reasonably well by the usual Arrhenius form

$$\sigma_s = \sigma_{s0} \exp(-E_s / kT) \quad (3)$$

A least-squares linear fit to this data give the slope and y-intercept, together with their associated standard errors, as

$$\begin{aligned} \text{gradient} &= -3.615 \pm 0.294 \\ \text{y-intercept} &= -21.457 \pm 0.507 \end{aligned}$$

If the point at 455K is excluded from the analysis a significantly better fit can be achieved, as shown in fig. 2.

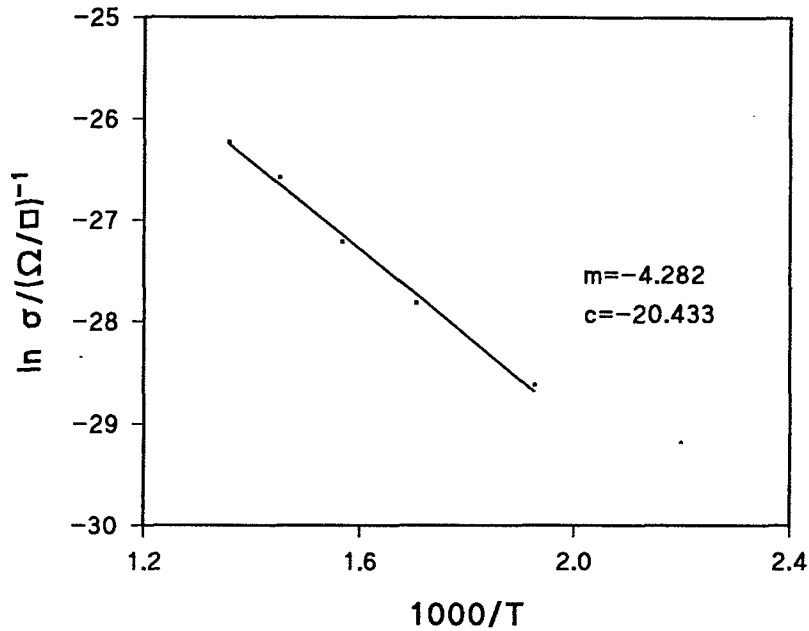


Fig. 2. Temperature variation of the surface conductivity of single crystal spinel. The data point at 455K has been removed from the analysis.

The values of gradient and y-intercept are then

$$\begin{aligned} \text{gradient} &= -4.282 \pm 0.193 \\ \text{y-intercept} &= -20.433 \pm 0.312 \end{aligned}$$

The exclusion of this lowest temperature data point can be justified on the basis that measurements taken at the lowest values of conductivity require long equilibration periods and may give unreliable results if taken too quickly. Using these values we can obtain the following values for the activation energy for surface conduction, E_s , and the pre-exponential factor σ_{s0}

$$\begin{aligned} E_s &= (0.369 \pm 0.017) \text{ eV} \\ \ln(\sigma_{s0}) &= (-20.43 \pm 0.31). \end{aligned}$$

Bulk Conductivity

The bulk conductivity σ_b was computed from measured values of the bulk conductance G_b . The relationship between the two for the guarded electrode configuration is

$$\sigma_b = G_b \left(\frac{t}{\pi(r_0 - \delta)^2} \right) \quad (4)$$

Correction
from P. Agnew

In this equation t is the sample thickness and r_0 is the radius of the centre electrode plus D , where D is one half of the difference between the centre and guard electrode radii. δ is a correction factor which accounts for fringing fields. It is given by the following equation <5>

$$\delta = \frac{2t}{\pi} \ln \left\{ \cosh \left(\frac{\pi D}{2t} \right) \right\} . \quad (5)$$

For our samples the numerical relationship between bulk conductivity and conductance is

$$\sigma_b = 5.782 G_b \quad (\Omega m)^{-1} . \quad (6)$$

Measurements of G_b were taken over the range 626K to 883K. These are presented in fig. 3 in the form of a plot of $\ln(\sigma_b)$ versus reciprocal temperature.

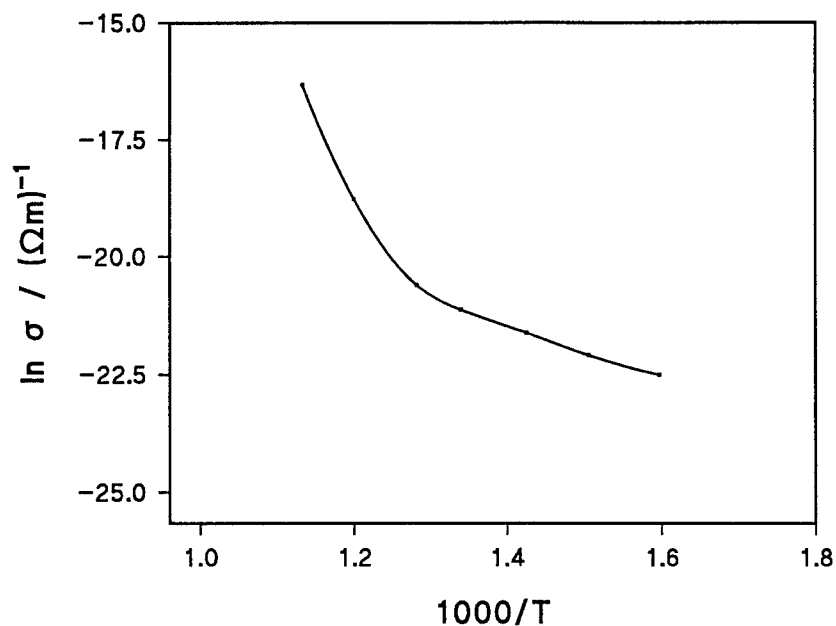


Fig. 3. Temperature variation of the bulk conductivity of single crystal spinel.

The data divide into two quite separate regions having different activation energies, as emphasized in fig. 4.

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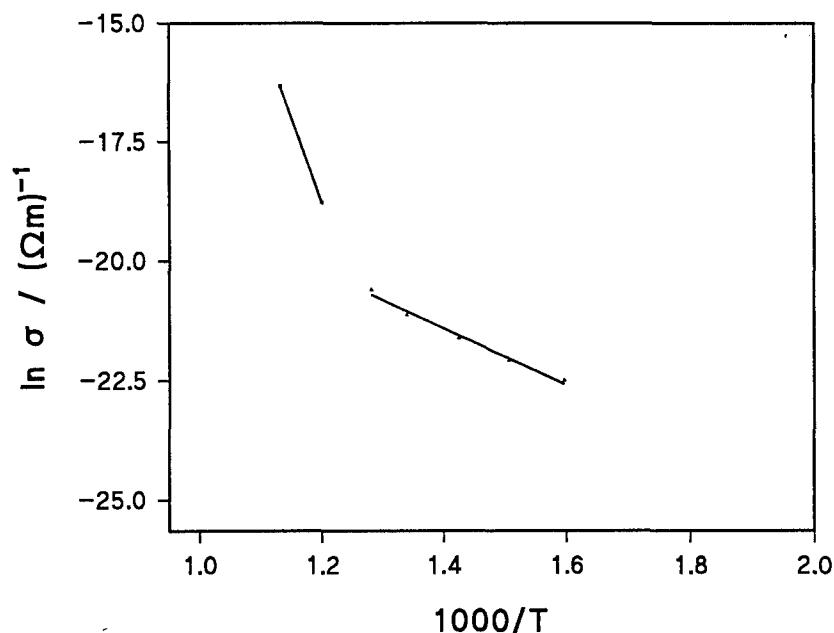


Fig. 4. Temperature variation of the bulk conductivity of single crystal spinel, emphasizing the two different activation energies.

This feature is well known in sapphire (e.g. Pells <6>, Will et. al. <7>). Unfortunately we only have two data points for the high temperature region and so the calculated activation energy in this region may have a large uncertainty. However if we fit the two regions to the Arrhenius form of equation (3), we obtain the following values:

Low temperature region

$$E_b = (0.511 \pm 0.033) \text{ eV}$$
$$\ln(\sigma_{b0}) = (-13.102 \pm 0.546)$$

High temperature region

$$E_b = 3.1 \text{ eV}$$
$$\ln(\sigma_{b0}) = 25.02$$

3. Surface Conduction in Cesium Vapour

Upon exposure to cesium vapour the surface conductivity typically rises by five to six orders of magnitude. The following results describe the pressure and temperature dependences of this effect. Two sets of experiments have been performed (i) Cs pressure held constant, sample temperature varied and (ii) sample temperature held constant, Cs pressure varied.

3.1 Constant Cesium Pressure, Variable Temperature

A constant Cs pressure of 0.1 Torr (corresponding to a reservoir temperature of 481K) was used in these experiments. The sample temperature was varied from 534K to 896K. The variation of surface conductivity with temperature is shown in fig. 5, in the form of a plot of $\ln \sigma_s$ versus $1/T$.

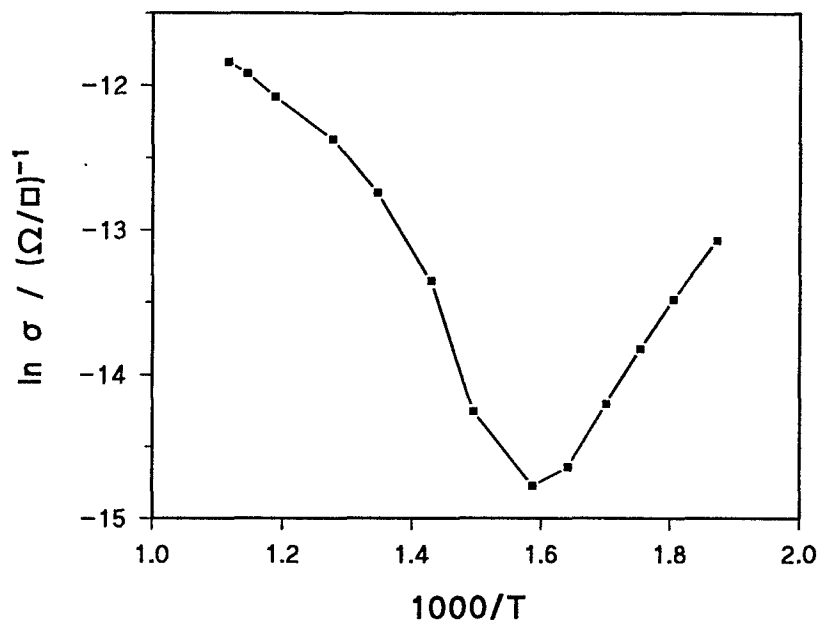


Fig. 5. Temperature variation of the surface conductivity of single crystal spinel exposed to Cs vapour at a pressure of 0.1 Torr

At temperatures below about 625K the trend is for conductivity to decrease with increasing temperature. Above ~ 625 K this trend is reversed.

3.2 Constant Temperature, Variable Cesium Pressure

Two sets of measurements were performed, with the sample temperature held constant at 673K and 873K. The Cs pressure was varied from $\sim 2 \times 10^{-3}$ Torr to ~ 0.8 Torr. The variation of surface conductivity with cesium pressure for a sample temperature of 673K is shown in fig. 6, in the form of a plot of σ_s versus P_{Cs} .

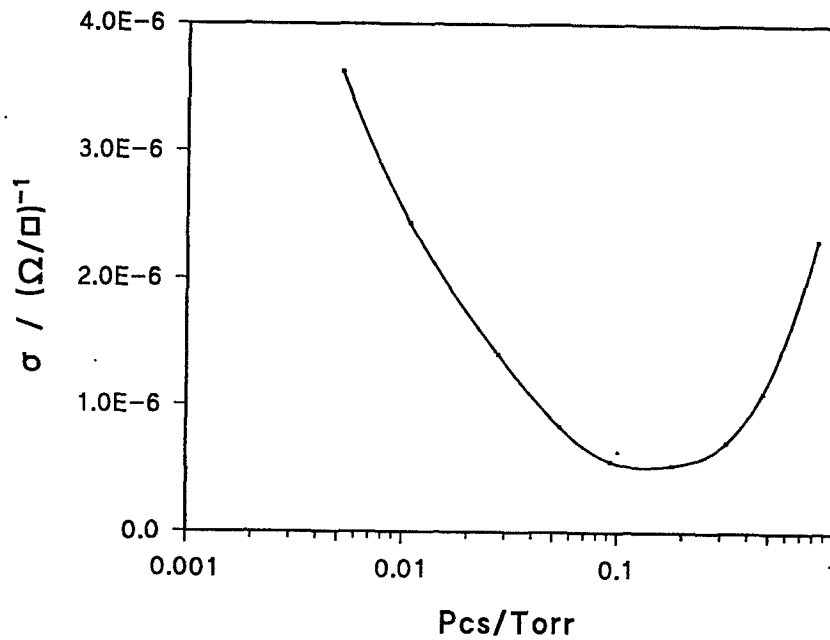


Fig. 6. Pressure variation of the surface conductivity of single crystal spinel at a constant sample temperature of 673K.

The corresponding plot for a sample temperature of 873K is shown in fig. 7.

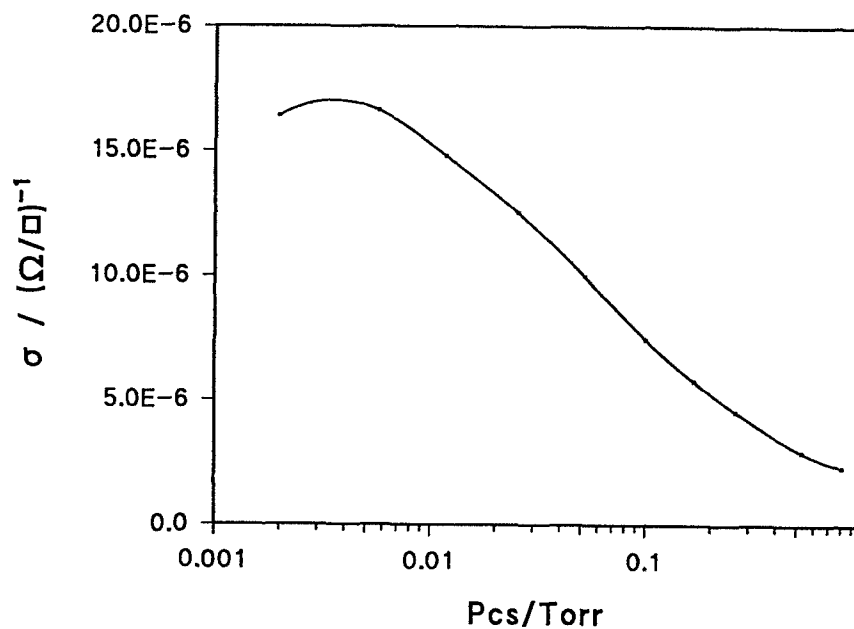


Fig. 7. Pressure variation of the surface conductivity of single crystal spinel at a constant sample temperature of 873K.

The two curves are shown together in fig. 8.

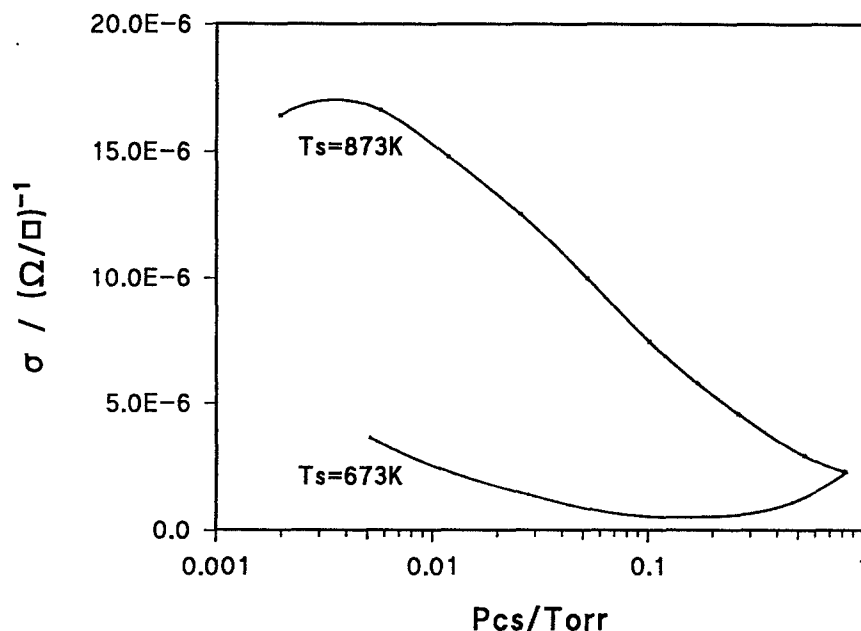


Fig. 8. Pressure variation of the surface conductivity of single crystal spinel at constant sample temperatures of 673K and 873K.

Note that the ordinate axes are linear, not logarithmic. For a sample temperature of 673K the trend is for σ_s to increase with decreasing P_{Cs} for pressures below around 0.15 Torr. For higher pressures the trend is reversed. At the higher sample temperature the minimum moves to higher pressures, probably around 1.5 Torr.

4. Discussion

In figs. 9 and 10 the data for both spinel and sapphire are compared. The conductivity minima in fig. 9 (data at a constant P_{Cs} of 0.1 Torr) both occur at around 625K, with spinel having about a factor of six lower conductivity than sapphire at this point. Under actual TFE operating conditions for metal-ceramic seals (around 870K and 0.5 Torr) the difference is less pronounced, although spinel consistently exhibits a lower surface conductivity. The electrical characteristics of single crystal spinel in Cs vapour therefore appear to be quite satisfactory for use in a TFE.

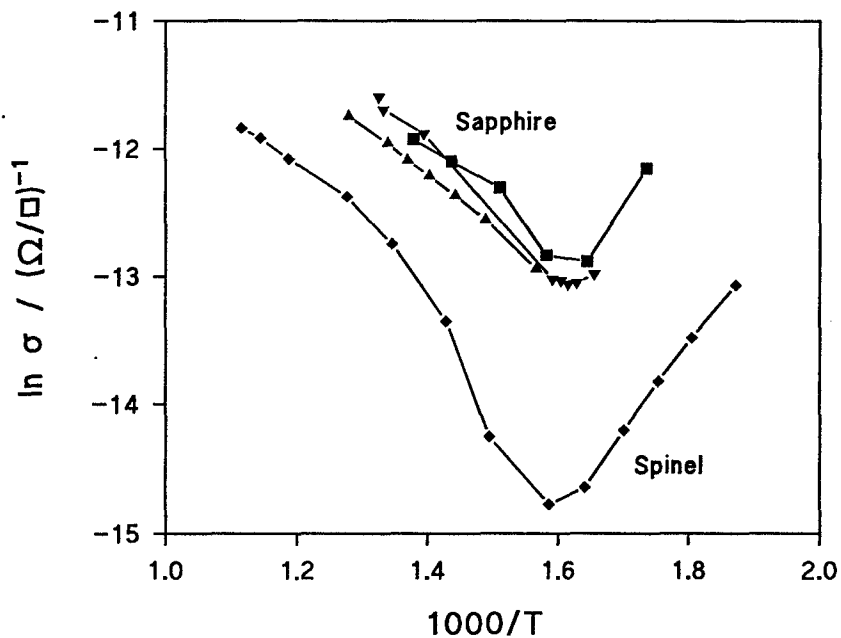


Fig. 9. Comparison of the temperature dependence of single crystal spinel and sapphire exposed to Cs vapour at a pressure of 0.1 Torr.

The surface conductivity of spinel shows a marked insensitivity to cesium pressure, as is also the case for sapphire (fig. 10). Changes in P_{Cs} over three orders of magnitude only result in changes in σ_s by a factor of four or five.

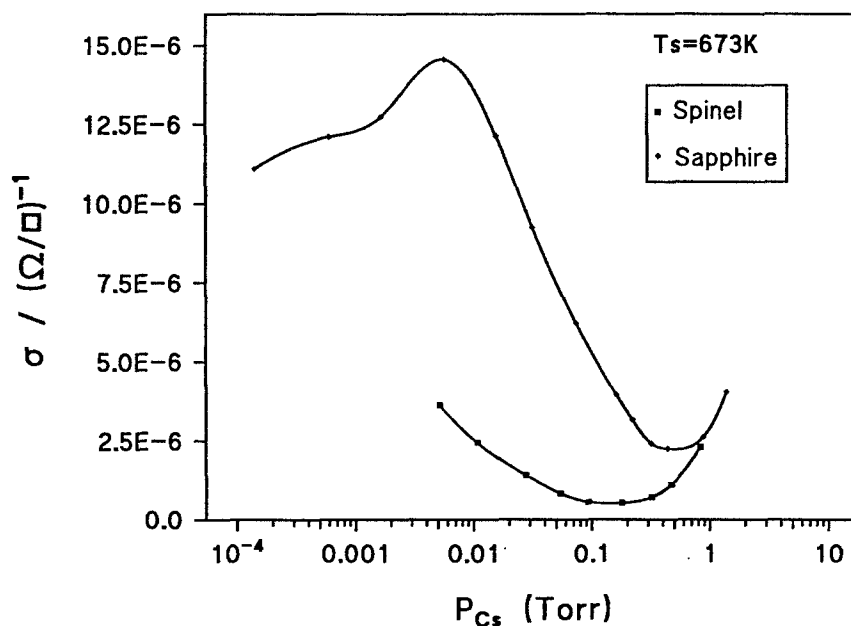


Fig. 10. Comparison of the cesium pressure dependence of single crystal spinel and sapphire at a temperature of 673K.

The curves of $\ln \sigma_s$ versus $1/T$ (figs. 5 and 9) are interesting. In ref. <1> we suggested a qualitative explanation for this curve. On the basis of the observed weak pressure dependence we postulated that the initial large increase in σ_s upon exposure to Cs occurs very rapidly, corresponding to low surface coverage of Cs. This initial Cs coverage increases the 'intrinsic' surface conductivity to a large degree, whilst still maintaining the character of insulator/semi-conductor behaviour. Further deposition of Cs results in relatively small increases in σ_s . Measurements by Zavadil and Ing <8> of the thermal desorption of Cs from sapphire surfaces have shown that this initial layer of Cs is rather tightly bound to the surface and does not desorb significantly at temperatures below 800K. Additional deposits of Cs are somewhat less tightly bound to the surface and desorb significantly in the range 500K to 700K. The observed decrease of σ_s with increasing temperatures, at low temperatures, is then explained as a result of the loss of this less tightly bound Cs from the surface. However as the temperature is increased further, the drop in conductivity due to loss of Cs is more than offset by the increase in the intrinsic conductivity of the surface modified by the initial Cs coverage.

We can make this argument more quantitative in the following manner. Let us regard the surface conductivity as having two components. The first is due to the 'intrinsic' conductivity of the surface, modified by the initial Cs coverage. We have said that this retains the character of conventional insulator/ semi-conductor behaviour and thus will have a temperature dependence of the form

$$\sigma_1 = \sigma_{10} \exp(-E_1 / kT) . \quad (7)$$

The second component is due to the additional, less tightly bonded Cs coverage. The character of this second component should be more akin to conventional metallic behaviour and thus for a constant level of Cs the temperature dependence would only be linear. However under constant Cs pressure the Cs coverage does not remain constant as the temperature is varied. It can be shown from statistical thermodynamic arguments that the equilibrium coverage of a non-interacting ensemble of atoms on a surface has the form

$$n_a = \frac{p}{kT} \left(\frac{h^2}{2\pi mkT} \right)^{1/2} e^{E/kT} , \quad (8)$$

where n_a is the number of adsorbed atoms per unit area, p is the vapour pressure and E is the surface binding energy. The coverage levels in our experiments may not be sufficiently low to justify the numerical accuracy of this expression but the functional dependence on temperature is probably still valid. The temperature dependence in this expression is dominated by the exponential term, thus we can write

$$\sigma_2 \propto n_a \propto e^{E/kT} , \quad (9)$$

$$\sigma_2 = \sigma_{20} e^{E_2/kT} , \quad (10)$$

to a fair approximation. The overall surface conductivity is then given by the expression

$$\sigma = \sigma_{10} e^{-E_1/kT} + \sigma_{20} e^{E_2/kT} \quad , \quad (11)$$

At higher temperatures the first term will dominate and at lower temperatures the second term will control the overall conductivity. Thus we can determine the values of (σ_{10}, E_1) and (σ_{20}, E_2) from Arrhenius plots of the high and low temperature portions of the conductivity curve in fig. 5. We have performed this calculation for spinel and obtained the following values:

$$\begin{aligned} \sigma_{10} &= 3.10 \times 10^{-4} \quad (\Omega/\square)^{-1} \quad , \quad E_1 = 0.290 \text{ eV} \quad ; \\ \sigma_{20} &= 9.83 \times 10^{-12} \quad (\Omega/\square)^{-1} \quad , \quad E_2 = 0.565 \text{ eV} \quad . \end{aligned}$$

Using these values we have calculated the overall conductivity according to equation (11). The result is shown in fig. 11, together with the actual data.

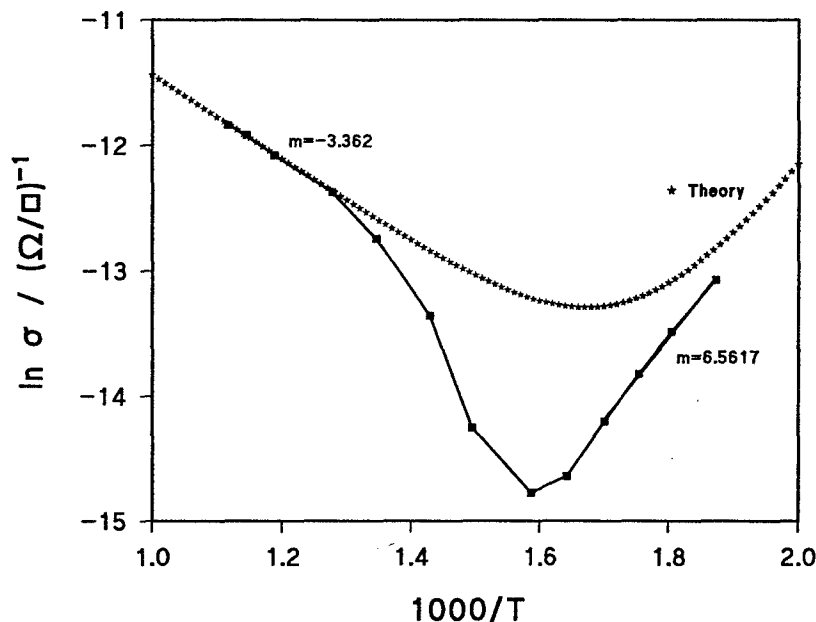


Fig. 11. Comparison of the predicted conductivity curve with experimental data for spinel.

The shape of the curve is approximately correct, exhibiting a minimum in roughly the correct position. However the minimum is too shallow compared to the experimental data. We are currently working on a more detailed explanation of the conductivity in this intermediate region.

5. Summary

We have presented data on the intrinsic bulk and surface conductivity of single crystal spinel. We have then shown how the surface conductivity is increased by five to six orders of magnitude when it is immersed in Cs vapour. Experimental data show that the pressure dependence in the

region 10^{-3} to 1 Torr is weak and that the major part of the resistivity degradation occurs at low Cs pressures, below 10^{-3} Torr. The experimental data for conductivity versus temperature shows a minimum at around 625K. Below this temperature the trend is for conductivity to decrease with increasing temperature. Above ~ 625 K this trend is reversed. We have presented a preliminary explanation which accounts for the qualitative features of this curve. On the basis of the fact that spinel consistently exhibits a lower surface conductivity than sapphire in the presence of Cs vapour we have suggested that this material would perform satisfactorily in a TFE.

Acknowledgments

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