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The temperature dependence of permittivity in MgO and Fe–MgO single crystals

J. S. THORP
Department of Applied Physics and Electronics, University of Durham, Durham, UK
N. E. RAD
Department of Engineering, University of Tabriz, Iran
D. EVANS, C. D. H. WILLIAMS
Department of Physics, University of Durham, Durham, UK

The permittivities (ε') of undoped MgO and iron-doped Fe–MgO single crystals have been measured over the temperature range 20 to 650° C for frequencies between 500 Hz and 50 kHz. From 25 to around 200° C the temperature dependence of ε' fits well with Havinga's formula and the value of $[(\varepsilon' - 1)(\varepsilon' + 2)]^{-1}(\partial\varepsilon'/\partial T) = 1.02 \times 10^{-5}\,\mathrm{K}^{-1}$ found for undoped MgO agrees closely with data published for lower temperature ranges; this increases considerably with the addition of iron, rising to $2.85 \times 10^{-5}\,\mathrm{K}^{-1}$ for MgO single crystals doped with 12 900 p.p.m. iron. Above 200° C the permittivity changes much more rapidly than the Havinga formula predicts, the variation being greater in iron-doped specimens. The frequency dependence of ε' is also temperature-dependent; below 200° C ε' follows $[\varepsilon'(\omega) - \varepsilon'_\infty] \propto \omega^{(n-1)}$ with $n = 0.98 \pm 0.02$ for all samples, but above 200° C the value of ε' falls more rapidly with frequency than would be expected from this law. The effect is more pronounced for MgO with 12 900 p.p.m. iron. The results are discussed in terms of a contribution to the measured permittivity arising from temperature-enhanced conductivity.

1. Introduction

For several years interest has been sustained in the electrical properties of magnesium oxide, partly because of its importance as a refractory insulator. Recently attention has been increasingly directed towards understanding the role of impurities in determining the conductivity of the material. Mitoff [1] was one of the first to confirm that near room temperature the conductivity is electronic rather than ionic, and he pointed out that the conductivity is dominated by impurities. More recently a systematic study of single crystals of magnesium oxide of carefully controlled and characterized compositions was initiated by the present authors. In their examination of the dielectric behaviour of undoped MgO, iron-doped MgO and chromium-doped MgO, initially from 500 Hz to 500 kHz (Thorp and Enayati-Rad [2]) and later for an extended frequency range from 500 kHz to 9 GHz (Thorp *et al.* [3]), it was found that in both the pure and doped crystals a very good fit to the universal law of dielectric response [4–6] was obtained, ε' varying as $[\varepsilon'(\omega) - \varepsilon'_\infty] \propto \omega^{(n-1)}$ with $n = 0.98 \pm 0.02$ in all specimens over the whole frequency range examined. It was also found that for both iron-doped and chromium-doped single crystals the conductivity (at any given frequency) increased quite noticeably with dopant concentration, the effect being rather more pronounced with iron than with chromium. It was suggested that this increase could be attributed to the increase in the number of vacancies introduced to maintain charge compensation when the trivalent dopant ion was substituted for the divalent magnesium. This explanation was substantiated by later observations [7–9] that with divalent dopants such as cobalt, nickel and manganese no increase in conductivity was found even at relatively high dopant concentrations.

The temperature variation of the permittivity of solids which are perfect dielectrics depends on three factors related to the expansion and polarizability of the material. These have been studied by Havinga [9], who considered them in the light of the Clausius–Mosotti equation and expressed the temperature dependence at constant pressure P in the form

$$\frac{1}{(\varepsilon' - 1)(\varepsilon' + 2)}\left(\frac{\partial\varepsilon'}{\partial T}\right)_P = A + B + C$$

Here the three quantities A, B and C have the following significance. Firstly, A represents the decrease in the number of polarizable particles per unit volume as the temperature increases and is a direct effect of the volume expansion; B relates to the increase in the polarizability of a constant number of particles as the available volume increases due to the temperature increase; C reflects the change in polarizability due to temperature changes when the volume remains constant. It may be noted that the volume term A is inversely related to ε' but both B and C are directly proportional to ε'. Methods of measuring A, B and C have been discussed by Havinga [9] and by Bartels and

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Smith [10], their magnitudes usually being calculated from plots of permittivity against temperature. Bosman and Havinga [11] have also found that the sum $(A + B)$ is always positive and hence it contributes to an increase of ε' with increasing temperature; however, the factor C is negative for those types of material with $\varepsilon' > 10$ while being positive for those with $\varepsilon' < 10$. Thus, the temperature dependence of permittivity (given above) is always positive for $\varepsilon' < 20$ and negative for $\varepsilon' > 20$; in the case of magnesium oxide $\varepsilon' = 9.6$ so a positive temperature dependence is expected.

The permittivity and loss studies referred to above were limited to measurements made at room temperature and below, and are now being extended to higher temperatures. The temperature dependence of the permittivity of MgO single crystals doped with the divalent ions Ni^{2+}, Mn^{2+} and Co^{2+}, respectively, was recently examined by Hossain and Thorp [12] at one frequency (1 kHz) and $[(\varepsilon' - 1)(\varepsilon' + 2)]^{-1}(\partial\varepsilon'/\partial T)$ was found to be positive in agreement with theory [11]. We have now extended this study to the trivalent ion system Fe^{3+}/MgO and in doing so have examined the temperature dependence of permittivity at various frequencies between 500 Hz and 50 kHz.

2. Experimental procedure

The single-crystal specimens on which measurements were made were grown by the electrofusion method using powders and were obtained from W. & C. Spicer Ltd (Cheltenham, UK). They included undoped MgO and MgO doped with iron at concentrations of up to 12 900 p.p.m. Fe as determined by X-ray fluorescent analysis. Before the electrical measurements were made the specimens were examined by electron spin resonance (ESR) techniques in order to ascertain the structural nature of the dopant and the extent to which other paramagnetic impurities might be present; the ESR spectra revealed that, in the as-received single crystals, the detectable iron or chromium was present as the respective trivalent ions Fe^{3+} or Cr^{3+} occupying substitutional magnesium sites [7, 13] and that no other paramagnetic species were observable.

The samples used for the permittivity mesurements were in the form of thin slices (10 mm × 10 mm × 0.3 mm), with surfaces made parallel and flat by conventional lapping and polishing techniques which gave the surface flatness to within 0.25 μm.

The method adopted for capacitance measurements on the samples was very similar to that described earlier by the authors [2]. Circular gold electrodes of 8 mm diameter were evaporated on to the opposite polished surfaces of the samples to provide well-defined electrode areas and to facilitate the connection of leads to the sample. Platinum wires were attached to the gold electrodes with platinum paste. Each specimen assembly was pre-fired in an auxiliary furnace at 300° C to get good mechanical and electrical bonding of the electrodes and leads. The other ends of the platinum wires passed through holes in silica rods and were connected to the bridge.

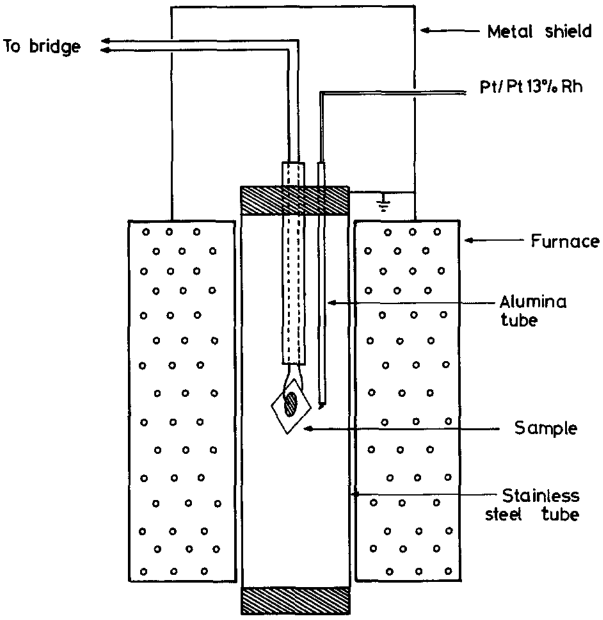

Figure 1 Schematic arrangement for measuring permittivity at high temperatures.

The apparatus was arranged as shown in Fig. 1. It comprised a cylindrical furnace, equipped with a temperature controller such that conditions could be kept constant to within ±5° C. The sample temperature was monitored continuously using a Pt/Pt 13% Rh thermocouple. A stainless steel tube inside the furnace acted as a shield against stray electrical signals. All the measurements were made in air and were restricted to an upper temperature limit of 700° C in order to avoid any risk of gold diffusion into the sample. It should be noted that in making measurements of this kind the relative specimen and electrode sizes are important. Within the restrictions of the available maximum single-crystal sizes (usually less than 1 cm), the diameters of evaporated gold electrodes were so chosen to allow the sample to project beyond them as much as possible; this projection minimized the contribution to the conductance due to surface leakage over the edge of the sample [14]. However, this projecting portion of crystal, whose extent must be at least twice the sample thickness, causes an edge capacitance for which a correction must be made. This correction term has been considered by Scott and Curtis [15].

3. Results

Three groups of measurements were made. In the first the temperature dependences of ε' for undoped MgO and for Fe–MgO were measured at a single frequency, 1 kHz, over a similar temperature range (20 to 200° C) as had been used in most previous measurements on MgO [10, 11] and Ni–MgO [12]. Secondly, the 1 kHz measurements were extended to higher temperatures, up to about 700° C, in order to provide further information on the comparative behaviour of undoped MgO and Fe–MgO. In the third group the frequency dependence of ε', which in previous measurements by the authors [2, 3] had only been studied at room temperature, was examined over a range of different temperatures.

The observed variations of ε' with temperature over the range 20 to 200° C, measured at the fixed frequency of 1 kHz, are shown in Fig. 2. The present data

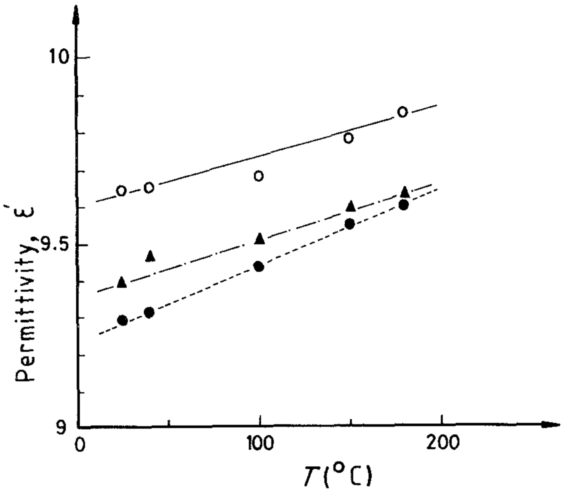

Figure 2 Variation of permittivity against temperature at 1 kHz for (○) pure MgO, (▲) 4300 p.p.m. Fe–MgO, (●) 12 900 p.p.m. Fe–MgO.

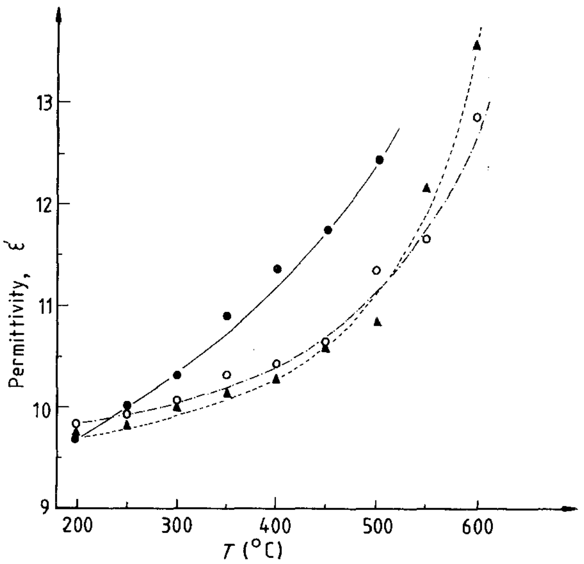

Figure 3 Variation of ε′ against temperature at 1 kHz for (○) pure MgO, (▲) 4300 p.p.m. Fe–MgO, (●) 12 900 p.p.m. Fe–MgO.

refers to 4N undoped MgO and to two iron-doped (Fe^{3+}) MgO specimens containing 4300 p.p.m. Fe and 12 900 p.p.m., respectively. Within this temperature range the variation for each specimen is linear but it is noticeable that, as compared to the plot for undoped MgO, both Fe–MgO plots have greater slopes, the slope increasing with increasing iron concentration; the decrease in room-temperature permittivity with iron addition has been reported previously [2].

The results of the higher-temperature 1 kHz measurements are shown in Fig. 3. These show several features of interest. In the first place the variations are no longer linear, but show increasingly large rates of change as the temperature increases. A marked difference in behaviour between the three specimens is also evident; thus whereas the curves for the undoped MgO and the more lightly doped (4300 p.p.m.) Fe–MgO specimens are fairly comparable up to about 450° C (though diverging thereafter), the temperature variation for the heavily doped (12 900 p.p.m.) Fe–MgO specimen is very much more pronounced and starts to depart from linearity at just over 200° C.

Some results from the third group of experiments are given in Fig. 4, which illustrates the changes in the frequency dependence of permittivity induced by successively increasing temperatures. They refer to measurements made by the low-frequency bridge and Q-meter technique at frequencies up to 50 kHz. The trend of the data is displayed by the lines drawn on the figure. These lines are not intended to define the functional dependence of ε′ on frequency. The upper figure (Fig. 4a) refers to a pure MgO single crystal. It can be seen that there was no significant difference between the results for room temperature and 100° C, both of which showed virtually frequency-independent behaviour. However, as the temperature is increased, the plots show successively stronger frequency dependence. It may also be noted that, at any given frequency, the increase in ε′ caused by a given temperature increment is greater the higher the temperature. With Fe–MgO single-crystal material (Fig. 4b) the same type of general behaviour is observed. Thus, for both the pure and iron-doped crystals the results show that the difference between corresponding high-temperature and low-temperature values of ε′ is greater at a low frequency than at a higher frequency. Preliminary results of one chromium-doped MgO single crystal containing 4300 p.p.m. Cr gave similar results.

4. Discussion

We consider first the 1 kHz data obtained in the temperature range 17 to 200° C. The values of the temperature dependence $[(\varepsilon' - 1)\ (\varepsilon' + 2)]^{-1}(\delta\varepsilon'/\delta T)_P$ were calculated from the experimental observations and are given in Table I which, for convenience, also reproduces other published data on nominally pure

TABLE I Measured and reported values of the temperature dependence for MgO, Fe–MgO and Cr–MgO

Nominal composition	Temperature range (° C)	ε′ at room temperature	Frequency (kHz)	$\frac{10^5}{(\varepsilon' - 1)\ (\varepsilon' + 2)}\left(\frac{\partial\varepsilon'}{\partial T}\right)_P$	References
4N undoped MgO	R.T.* to 200	9.64 ± 0.03	1	1.02 ± 0.02	Present work
MgO	–	9.65	1	–	von Hippel [16]
MgO	R.T. to 150	9.8	250	1.05	Bosman and Havinga [11]
MgO	−223 to R.T.	9.458	(low)	0.998	Bartels and Smith [10]
MgO	−268 to 180	9.83	1	0.969	Wintersgill and Fontanella [17]
MgO + 4300 p.p.m. Fe	R.T. to 200	9.46	1	1.54 ± 0.2	Present work
MgO + 12 900 p.p.m. Fe	R.T. to 200	9.27	1	2.85 ± 0.3	Present work
MgO + 3600 p.p.m. Cr	R.T. to 200	9.55	1	1.22 ± 0.2	Rad [18]

*Room temperature.

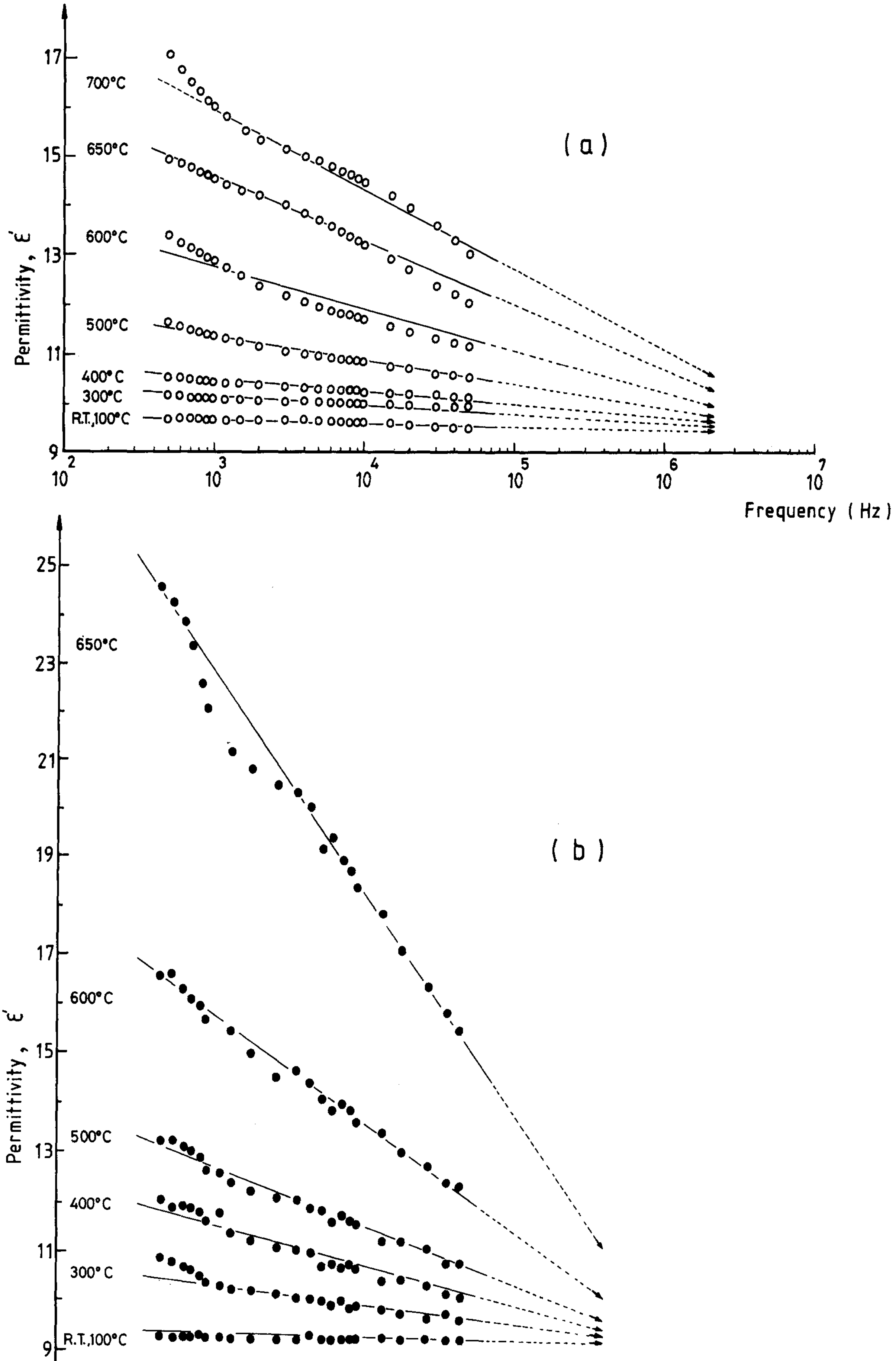

Figure 4 Variation of permittivity against frequency at different temperatures: (a) MgO (pure) and (b) 12900 p.p.m. Fe–MgO (lines show data trend not a function).

MgO. As regards the pure material the room temperature permittivity was found to be 9.64 ± 0.03, in very close agreement with Von Hippel's estimate [16] of 9.65; the value of the temperature dependence obtained was $(1.02 \pm 0.02) \times 10^{-5}\,K^{-1}$, which agrees to within experimental error with the values given by Bosman and Havinga [11] Bartels and Smith [10] and Wintersgill and Fontenella [17]. Table I shows also that the effect of doping with either of the trivalent ions Fe^{3+} or Cr^{3+} is to produce quite a marked increases in the temperature dependence. The increases are more marked with iron than with chromium, and (although crystals of only two dopant levels were available for examination) it seems that the value is concentration-dependent, rising to $2.85 \times 10^{-5}\,K^{-1}$ for 12900 p.p.m. Fe–MgO compared with $1.02 \times 10^{-5}\,K^{-1}$ for undoped MgO.

It is interesting to note that the recent measurements at 1 kHz by Hossain and Thorp [12] on Co–MgO and Mn–MgO also showed that the temperature dependence increased with increasing concentration of either cobalt or manganese, respectively, though not by such a large factor (for corresponding concentrations) as was observed here for iron. As mentioned earlier Bosman and Havinga [11] postulated that the temperature dependence of permittivity should be positive if $\varepsilon' < 20$, and the present results confirm that this is so for both pure MgO and for Fe–MgO and also for Cr–MgO. The strong temperature dependence of ε' at low frequencies has been discussed by Rao and Smakula [19]. These authors reported that in CoO and NiO, for example, ε' increased exponentially with temperature above 120 and 150° C, respectively, with corresponding exponential variations of the dielectric loss ε''; they explained these variations in terms of space charge polarization caused by impurities or defects. In the present work on magnesia the 1 kHz data show clearly that at temperatures above about 200° C (Fig. 3) the onset of a regime of much more rapidly increasing temperature dependence is very marked both for undoped and iron-doped crystals. Compared with the undoped crystals, the effect of increasing the iron concentration in Fe–MgO is to reduce the temperature at which non-linear temperature dependence commences.

When analysing the high-temperature data the possibility of the formation of some magnesio-ferrite precipitates in the iron-doped crystals should be considered. This phenomenon has been discussed by several authors [13, 20, 21]. Here, independent measurements were made on commercially available magnesioferrite ($MgFe_2O_4$) powder and these showed that, in the low-frequency region, $\varepsilon' \simeq 24$; consequently even if all the iron present in the doped crystals had been converted, in the time during which the permittivity measurements were made, to magnesio-ferrite so as to form a two-phase dielectric the effect on the measured value of ε' would be small since the highest iron levels were only about 1%. Thus, taken as a whole, a possible explanation for the temperature dependences of ε' would be that at higher temperatures a significant part of the measured ε' comes from a contribution due to quasi-conductivity [22, 23]. This conductivity contribution will be present even in the undoped MgO single crystal, which will have a significant vacancy concentration coupled with impurities at the 5 p.p.m. level [24] or less, but will be greatly enhanced in the doped crystals where, using the trivalent dopant Fe^{3+}, one extra vacancy is required per two dopant atoms in order to achieve charge compensation. It is likely that this conductivity contribution will itself be strongly temperature dependent, and under conditions where this sort of conductivity is important the Bosman–Havinga relationship would not be expected to apply.

We next turn to the effects of temperature on the freuency dependence of ε'. As discussed in our previous papers [2, 3] it has been found that at room temperature ε' for both pure MgO and Fe–MgO is consistent with the universal law of dielectric response [4–6] in that $[\varepsilon'(\omega) - \varepsilon'_{\infty}] \propto \omega^{(n-1)}$ where ω is the angular frequency and $n = 0.98 \pm 0.02$. This held over the whole range of iron concentration examined, i.e. 310 to 12900 p.p.m. Fe, and corresponds to the limiting form of lattice loss [4] in which most dipolar processes have been eliminated, a situation also found in several rigid ceramics and oxynitride glass systems by Thorp *et al.* [25]. Fig. 4 shows that for both pure and iron-doped material ε' falls progressively faster with frequency from a higher starting value as the temperature is increased, the presence of iron producing a larger effect. This behaviour leads to an interesting point illustrated by the dashed extrapolations in Figs 4a and b. Assuming the increase of ε' with temperature to be due to a quasi-conductive process, the extrapolations suggest that the contributions due to the conductivity become negligible at some frequency greater than the upper value used in the present experiment, perhaps in the region 10 to 100 MHz. It appears that the determination of the terms in Havinga's treatment of temperature behaviour should be made at relatively low temperatures and high frequencies. Further work is in progress in an attempt to provide a quantitative discussion of the effect of impurities on the complex dielectric constant as a function of temperature and frequency.

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