High frequency dielectric properties of MgO, Fe/MgO and Cr/MgO

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The study of the dielectric constant and loss in pure single-crystal MgO and in Fe- and Cr-doped crystals, the low frequency results of which have been reported [1], has now been extended to cover frequencies from 500 Hz to 9 GHz. Measurements were made on the same specimens, at room temperature, using bridge, cavity, slotted-line and cavity-resonator techniques. Over the whole frequency range, a good fit is obtained to the Universal Laws of dielectric response: $\sigma_{ac} \propto \omega^n$ and $(\epsilon' - \epsilon_\infty) \propto \omega^{n-1}$ with $n = 0.98 \pm 0.02$ for both pure and doped MgO. At any point in this frequency range the addition of iron or chromium increases σ and decreases ϵ', the changes being more pronounced with iron. These effects are discussed in terms of hopping mechanisms.

1. Introduction

In a recent publication by Thorp and Rad [1] the initial results of a systematic study of the dielectric properties of pure and doped single crystal magnesium oxide were reported. These initial measurements were made at room temperature at relatively low frequencies (500 Hz to 50 kHz). The results showed that, in pure MgO at 1 kHz, the values of ϵ' (9.62) and $\tan \delta$ (2.16×10^{-3}) agreed well with the data of von Hippel and, further, that the conductivity varied with frequency as $\sigma \propto \omega^n$ with $n = 0.98 \pm 0.02$. Doping with either iron or chromium caused significant changes in both ϵ' and σ. In Fe-doped crystals the conductivity increased with iron concentration (at any given frequency) such that, for a crystal doped with 12800 ppm Fe, the value of σ was about four times the value for pure MgO. At all concentrations the variation of $\log \sigma$ with $\log \omega$ was linear, giving $n = 0.98 \pm 0.02$ which was the same n value as for pure MgO. A decrease in ϵ' with increasing Fe concentration was also observed and similar though less pronounced effects were found in chromium-doped crystals. These results were consistent with the observations of Lewis [2] and Shaktin [3].

The study has now been extended to cover a very wide frequency range by adapting Q-meter, slotted-line and resonant-cavity techniques to make them suitable for precision measurements on low loss materials in order to find whether the effects observed at low frequencies also held in the high frequency range; in making these measurements specimens of the same crystals which had been examined previously were used so that valid comparison of behaviour could be made.

2. Experimental procedure

The measurements of dielectric properties and conductivity were carried out using four different techniques, each covering a definite frequency range. At low frequencies (500 Hz–50 kHz) bridge techniques [1] are most appropriate as they can fairly readily be made suitable for precise measurements of the real component of dielectric constant and conductivity. At higher frequencies, i.e. 100 kHz–10 MHz, a standard Q-meter can be utilized and the procedure is similar to the bridge technique; the degree of precision tends to be less particularly at the high frequency end of the range mainly due to lead inductance problems. As the frequency is increased further to the 500 MHz–7.5 GHz range, slotted-line standing-wave methods become more suitable; it is not an easy technique when applied to low-loss materials as high-precision components and instrumentation are required. At very high frequencies all the above methods are inappropriate due to short wavelengths involved and a

cavity-resonator method must be used. These can give very accurate results and have the additional advantage that there is no need to polish the samples.

The principle of the Q-meter is based on the series resonant circuit. The measurements were made in air using a standard Q-meter (Marconi TF 1245) over the frequency range of 100 kHz–30 MHz. The dielectric testing jig (Marconi TJ 155 C/1) was modified using 8 mm diameter circular electrodes and was located inside a metal box to ensure good electrical shielding of the sample.

The effective resistance of the sample at the frequency of the test is given by [4]

$$R = \frac{Q_1 \cdot Q_2}{Q_1 \cdot Q_2} \frac{1}{\omega} \cdot \frac{1}{C_1} \qquad (1)$$

and the real part of the conductivity is given by,

$$\sigma = \frac{d}{A} \cdot \frac{1}{R}, \qquad (2)$$

where Q_1 is the Q-value of the circuit with the sample out of the testing jig, Q_2 is the Q-value of the circuit with the sample in the testing jig, C_1 is the variable capitance of the Q-meter, d is the thickness of the sample and A is the contact area of electrodes with sample.

To ensure good electrical contact, circular gold electrodes of diameter 8 mm were evaporated on the opposite polished faces. This reduced the contact resistances between the electrodes and the specimen [5].

Due to fringing effects, an edge correction is required [6]. The relative permittivity of the sample, ϵ', is given by

$$\epsilon' = \frac{c_1 - c_2}{c_0 + c_e} + 1, \qquad (3)$$

where

$$c_0 = \epsilon_0 \frac{A}{d}$$

and c_e is the edge capacitance. The loss tangent, tan δ, is given by [4]

$$\tan \delta = \frac{Q_1 - Q_2}{Q_1 \cdot Q_2} \cdot \frac{c_1}{c_1 - c_2} = \frac{\epsilon''}{\epsilon'}. \qquad (4)$$

In practice the knowledge of the effective capacitance of c_1 and c_2, C_E, is required

$$C_E = c_{ind} \frac{1}{1 - \omega^2 L \, c_{ind}}, \qquad (5)$$

where c_{ind} is the indicated capacitances c_1 and c_2 and L is the constant inductor used in the resonant circuit.

The error in ϵ' was about 5%, this being set by difficulties in the precise relocation of the specimen; the error in tan δ was somewhat higher.

In the coaxial line technique the dielectric sample whose electrical properties are to be found is placed between the inner and outer conductors at the end of a coaxial slotted-line, as shown in Fig. 1a. The permittivity of the sample can then be calculated from the measured reflection coefficient and phase angle at any desired frequency. The technique is fully described by Roberts and von Hippel [7] and also by Dakin and Work [8]. Other details of this technique can be found in [9] and [10]. Since the absorption of power in the sample is negligible, most of the incident power is reflected and causes a standing-wave pattern on the line. The measured voltage standing-wave ratio (VSWR), and consequently the reflection coefficient and the shift of the first minimum, i.e. phase angle, give the magnitudes of ϵ' and ϵ'', where ϵ' and ϵ'' are the real and imaginary components of the complex relative permittivity, respectively. The idea was originally suggested by Westphal [11] who also attempted to make a suitable sample holder, as shown in Fig. 1c. Initially it is assumed that $\lambda \gg (b - a)$ and $d \ll (b - a)$ [12, 13] where λ = wavelength. The equivalent circuit of the sample impedance is given by $R(\epsilon', \epsilon'')$ and $X(\epsilon', \epsilon'')$, the real and imaginary components of sample impedance, respectively, in series [13], as shown in Fig. 1b. The sample impedance, τ, is given by

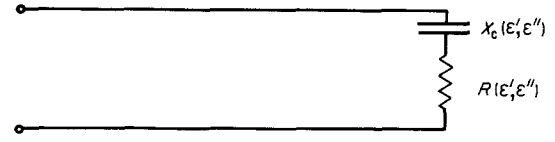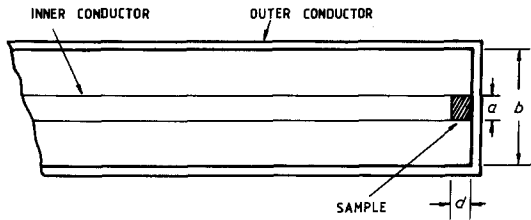$$\tau = -\frac{j}{\omega C}, \qquad (6)$$

where C is the capitance of the sample, i.e. $C = \epsilon_0 \epsilon^* A/d$, where ϵ^* is the complex dielectric constant of the specimen, A is the area of the electrode (m²) and d is the thickness of the specimen (m). Since $\epsilon^* = \epsilon' - j\epsilon''$, the impedance yields real $R(\epsilon', \epsilon'')$ and imaginary $X_c(\epsilon', \epsilon'')$ components

$$R(\epsilon', \epsilon'') = \frac{\epsilon'' d}{\omega \epsilon_0 A(\epsilon'^2 + \epsilon''^2)} \qquad (7)$$

and

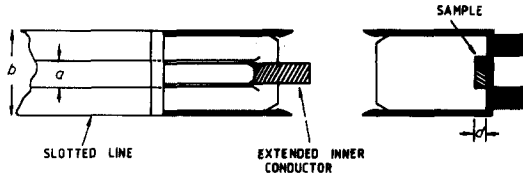$$X_c(\epsilon', \epsilon'') = \frac{\epsilon' d}{\omega \epsilon_0 A(\epsilon'^2 + \epsilon''^2)}. \qquad (8)$$

From the transmission line theory, and assuming that

(a)

(c)

(b)

Figure 1 (a) Coaxial line with sample; (b) Equivalent circuit; (c) Sample holder configuration.

$$\tau = R(\epsilon', \epsilon'') - j X_c(\epsilon', \epsilon''), \qquad (9)$$

the real and imaginary parts of the relative permittivity of the sample can be found in terms of the reflection coefficient, ρ, and its angle, θ, [14, 15],

$$\epsilon' = \frac{2|\rho| \sin \theta}{\omega C_0 \tau_0 (|\rho|^2 + 2|\rho| \cos \theta + 1)} \qquad (10)$$

and

$$\epsilon'' = \frac{1 - |\rho|^2}{\omega C_0 \tau_0 (|\rho|^2 + 2|\rho| \cos \theta + 1)}, \qquad (11)$$

where ω is the angular frequency, τ_0 is the characteristic impedance (50 ohms) and C_0 is the capacitance of the equivalent capacitor with air as the dielectric.

As the above equations show, ϵ' and ϵ'' can now be calculated if $|\rho|$ and θ are known. These can be measured using slotted-line techniques at the desired frequency. Iskander [12] has pointed out that the fringing field affects the permittivity measurements. He has shown that the measured value of ϵ' is usually larger than the true value, while the measured value of ϵ'' is not affected by the fringing. He has also shown that the measured value of ϵ' is larger than the time value by a factor of B/A, where A is the capacitance of the parallel plates and B is the fringing capacitance. In this experiment the fringing effect was shown to be not important since it was found that using two different sizes of sample did not affect appreciably the magnitude of ϵ'.

One of the most successful methods for measuring sample dielectric properties at microwave frequencies is the perturbation technique using a cavity resonator. The technique involves the insertion of a small piece of a dielectric material inside the resonant cavity, placed on the end of a thin silica rod which is then suspended in the position of maximum electric field. The resultant shift of the resonant frequency of the cavity gives the real part of the complex dielectric constant and the change in the quality factor, Q, gives the imaginary part; the theory was first given by Casimir [16] and was further extended and developed by Waldron [17, 18] and others [19, 20]. The results are

$$\frac{\Delta f}{f_0} = -2(\epsilon' - 1) \frac{V_s}{V_0} \qquad (11)$$

and

$$\Delta \left(\frac{1}{Q} \right) = 4 \epsilon'' \frac{V_s}{V_0}, \qquad (13)$$

where V_s is the volume of the sample, V_0 is the volume of the cavity, Δf is the change in the resonant frequency and ΔQ is the change in the Q-factor. By introducing a sample into the cavity the resonant frequency of the cavity is lowered [21] and if change in both the resonant frequency and the Q-factors of the unperturbed and perturbed cavity are measured, ϵ' and ϵ'' can be determined. Limitations of this method are that the frequency shift should be much less than 1% and that the volume of the material introduced should not alter the field inside the cavity appreciably. Advantages of this method are that the sample does not require polishing and its dimensions are smaller compared with those of samples necessary for use in bridge and Q-meter techniques. A critical analysis of the four experimental techniques used has been made by Rad [22].

3. Results

In Fig. 2 the data for dielectric constant ϵ' was plotted over the whole frequency range of 500 Hz– 93 Hz for pure MgO, a highly-doped Fe/MgO sample and a Cr/MgO sample. The data lie on parallel straight lines and fit the "Universal Law":
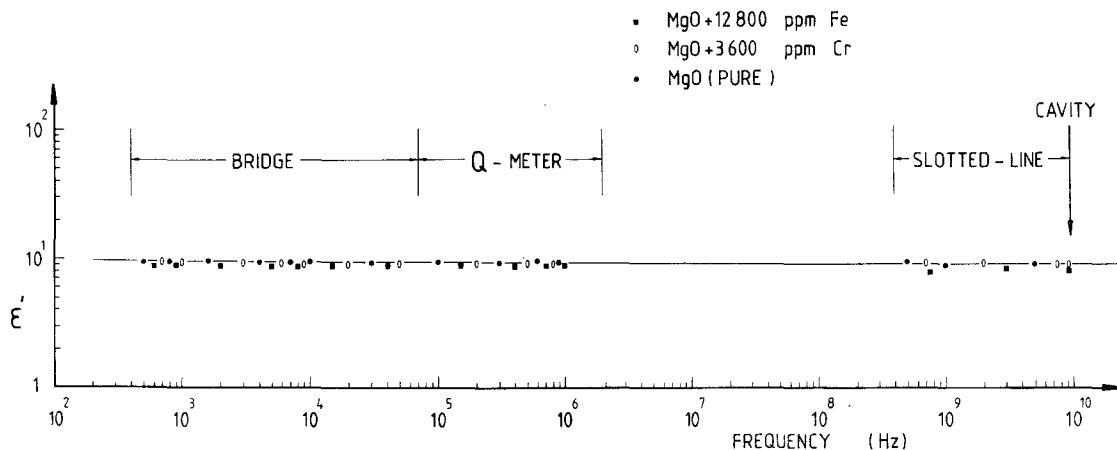
Figure 2 Variation of ϵ' with frequency; MgO (pure), MgO + 12 800 ppm Fe and MgO + 3600 ppm Cr.

$$\epsilon'(\omega) \propto \omega^{n-1}, \qquad (14)$$

with $n = 0.985 \pm 0.02$, supporting the idea that the same hopping mechanism applies over the whole range of frequencies for both pure and doped specimens. Comparison of the variation of ϵ' with frequency for the heavily-doped Fe/MgO sample shows that at all frequencies its dielectric constant is lower than that of the pure MgO; the vaues for the Cr/MgO specimen were indistinguishable from those of the pure MgO.

The variations of loss factors, ϵ'', of pure MgO and heavily-doped Fe/MgO were plotted and are shown in Fig. 3a and both plots exhibit similar characteristics. The microwave data lies on the line extrapolated from low frequencies. The slotted-line results have a considerable error and are displaced from the extrapolation; however, they still keep the same relative differences as are exhibited at low frequency. The variations are linear with slope, n, corresponding to $n = 0.985$ and agree very well with the "Universal Law":
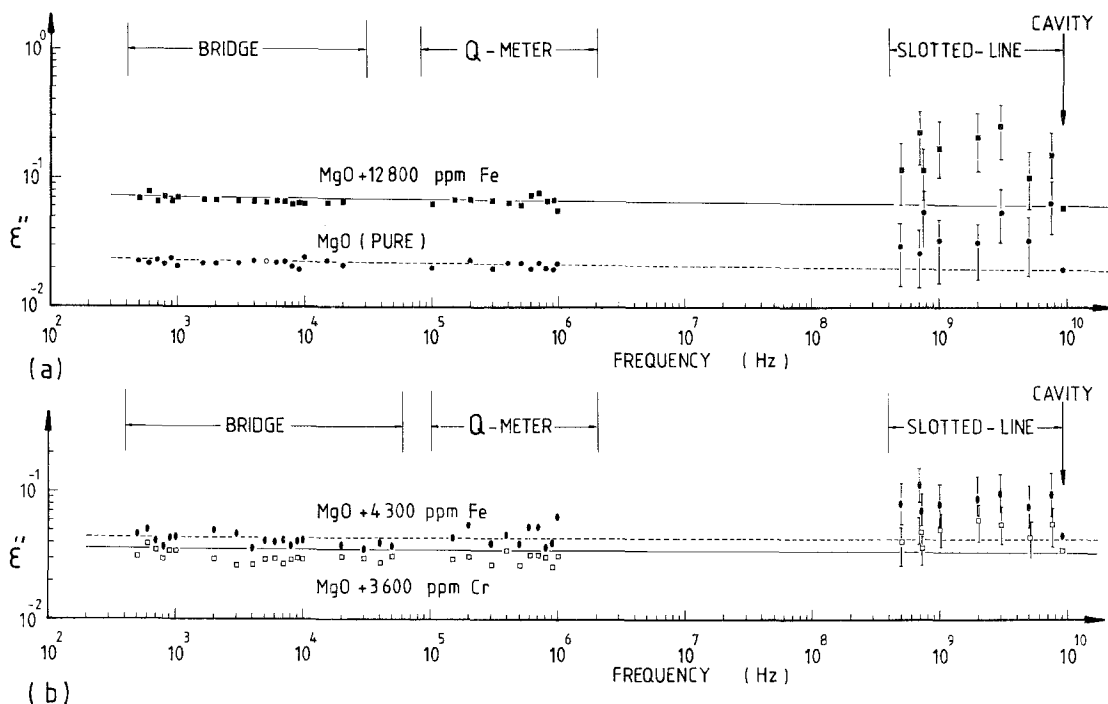

Figure 3 Variation of ϵ'' with frequency; (a) MgO (pure) and MgO + 12 800 ppm Fe, (b) MgO + 4300 ppm Fe and MgO + 3600 ppm Cr.

Nominal composition	$\dfrac{\epsilon''(\omega)}{\epsilon'(\omega) - \epsilon_\infty}$									
	Frequency									
	500 (Hz)	1 (kHz)	5 (kHz)	10 (kHz)	100 (kHz)	200 (kHz)	500 (kHz)	1 (MHz)	500 (MHz)	1 (GHz)
MgO (pure)	0.07	0.07	0.065	0.065	0.077	0.082	0.077	0.077	0.618	0.618
MgO + 12 800 ppm Fe	0.064	0.064	0.064	0.07	0.067	0.067	0.066	0.066	0.106	0.105

$$\epsilon''(\omega) \propto \omega^{n-1}. \qquad (15)$$

Further comparison of Cr- and Fe-doped samples is given by their loss-factor behaviour, plotted in Fig. 3, which shows characteristics similar to their conductivity plots. The important information to be obtained from Fig. 3a and b is the dependence of the dielectric loss on the composition of the samples; it is clear that the dependence is much stronger in the Fe-doped series of crystals than in the Cr-doped ones.

The real and imaginary parts of the complex dielectric constant are related to each other through the Kramers–Krönig relation

$$\frac{\epsilon''(\omega)}{\epsilon'(\omega) - \epsilon_\infty} = \cot\left(\frac{n\pi}{2}\right). \qquad (16)$$

This ratio has been calculated from the experimental data at a number of points in the frequency range from 500 Hz to 9.3 GHz and some data for two samples is tabulated at particular frequencies in Table I. According to Jonscher and Deori [23], this ratio is smaller than unity for $n > 0.5$ and becomes larger than unity for $n < 0.5$.

It may be noted here that, in deriving ratio values, the directly-measured microwave estimate was used for the ϵ_∞ value. For both specimens the ratio is about 0.07 and is constant up to a frequency of 1 MHz; inserting the value of n as $n = 0.98$ gives $\cot(n\pi/2) = 0.03$. Thus, there appears to be fair agreement with Equation 16 (up to 1 MHz) and further, the ratio is smaller than unity, as expected.

At high frequencies (in the 500 MHz to 1 GHz range) the ratio values are much larger than $\cot(n\pi/2)$; this may be due to the growing invalidity of taking the microwave value for ϵ_∞ at frequencies approaching a few GHz and it is probable that the limiting (optical) value for ϵ_∞ should be used instead.

4. Discussion

One of the most important results demonstrated by the present study is that the dielectric features, reported previously at low frequencies [1], appear to hold over the whole frequency range up to 9 GHz. Throughout this range the fit to the Universal Law is good for both pure MgO and iron- or chromium-doped MgO; it was found that $\sigma_{ac} \propto \omega^n$ and that $(\epsilon' - \epsilon_\infty) \propto \omega^{n-1}$ with the value of $n = 0.98 \pm 0.02$. This suggests that, at room temperature, all the evidence is consistent with an interpretation on the basis of single hops between randomly-distributed sites [24, 25]. The fact that the microwave data fit the extrapolations of the low and medium frequency variations well indicates, as might be expected, that the hopping frequency is considerably greater than 9 GHz.

Several comments may be made as regards the effects of doping (Fig. 4). An increase in conductivity occurs due to the addition of iron or chromium at any frequency in the whole range examined; this is in agreement with observations reported by Shakhtin et al. [3], Mitoff [26] and Budnikov and Vanovskii [27] that addition of iron increases the conductivity of MgO. In the discussion of our previous low-frequency results [1] it was suggested that this increase in conductivity might be due to the creation of vacancies by the substitution of a tri-valent ion for di-valent magnesium which would cause an increase in hopping probability. This argument would be expected to hold equally well at high frequencies since it only concerns the total number of hopping sites in the crystal. It is noteworthy that the n values for pure MgO, and all concentrations of either Fe/MgO or Cr/MgO are, within experimental error, identical, which confirms that similar conduction mechanisms are operative. The vacancy model would suggest that, if the dopant were a di-valent ion, no increase in conductivity should be observed and experiments are being conducted on Co/MgO and Ni/MgO to check this.

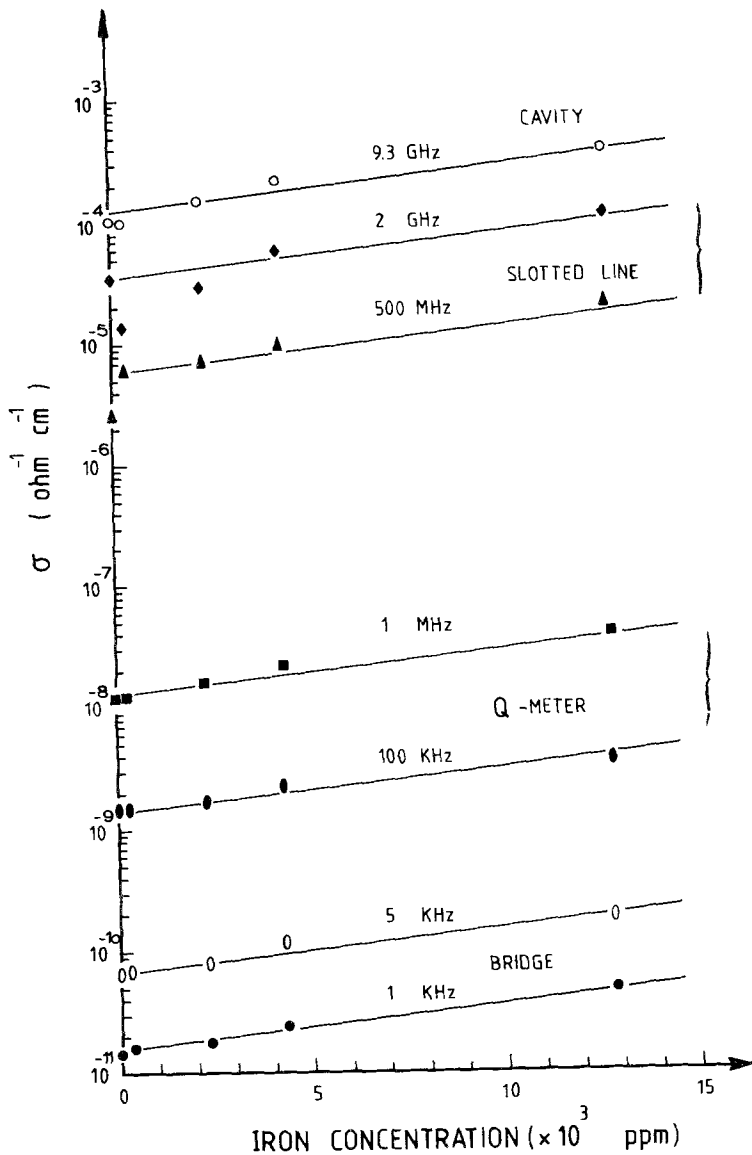We return, finally, to reconsider the fact, now verified over the whole frequency range to 9 GHz,

Figure 4 Dependence of conductivity on iron concentration at various frequencies.

that the addition of a given concentration of iron increases the conductivity more than the addition of the same concentration of chromium. Two parameters may affect the conductivity, namely the hopping probability and the hopping frequency. At a given concentration the former, being determined by the total number of vacancies, will be constant. The hopping frequency, however, may be regarded as equivalent to an exchange frequency and hence might be expected to depend on the nature of the dopant ions. Recent electron spin resonance experiments, made on the same group of crystals as were examined here, have shown that both in Fe/MgO and Cr/MgO [28] exchange interactions are very important even at low concentrations. In particular, estimates of the exchange frequencies J_{ex} showed that, at any dopant concentration, $(J_{ex})_{Fe} > (J_{ex})_{Cr}$; (in view of the inter-ionic distances involved it seems more likely that superexchange, rather than direct exchange between adjacent dopant ions, is responsible). It is interesting to note that this difference in exchange frequencies is in the same sense as the conductivity difference found in the present dielectric measurements and this suggests that both vacancy and exchange effects may need to be taken into account.

Acknowledgements

References

1. J. S. THORP and N. ENAYATI-RAD, *J. Mater. Sci.* **16** (1981) 255.
2. T. J. LEWIS and A. J. WRIGHT, *J. Phys. D* **1** (1968) 441.
3. D. M. SHAKHTIN, E. V. LEVINTOVICH, T. L. PIVOVAR and G. G. ELISEEVA, *Teplofizika Vysokich Temp.* **5** (1967) 454.
4. "The Q-meter (in theory and practice)" (Marconi Instruments Ltd, St. Albans, UK, 1961).
5. R. MANSFIELD, *Proc. Phys. Soc. London,* **B66** (1953) 612.
6. A. H. SCOTT and H. L. CURTIS, *J. Res. Nat. Bur. Stand.* **22** (1939) 747.
7. S. ROBERTS and R. VON HIPPEL, *J. Appl. Phys.* **17** (1946) 610.
8. T. W. DAKIN and C. N. WORKS, *ibid.* **18** (1947) 789.
9. R. VON HIPPEL, "Dielectrics and Waves" (John Wiley and Sons, New York, 1954).
10. *Idem*, in "Dielectric Materials and Applications" edited by W. B. Westphal (John Wiley and Sons, New York, 1954).
11. W. B. WESTPHAL (ed.), "Dielectric Materials and Applications" (John Wiley and Sons, New York, 1954).
12. M. ISKANDER and S. STUCHLY, *IEEE Trans. Instr. Meas.* **IM-27** (1978) 1.
13. H. E. GREEN, *IEEE Trans. Micro. Theo. Tech.* **MTT-13** (1965) 676.
14. M. F. ISKANDER and S. STUCKLY, *IEEE Trans. Instr. Meas.* **IM-21** (1972) 425.
15. S. S. STUCHLY, M. A. RZEPECKA and M. F. ISKANDER, *ibid.* **IM-23** (1974) 56.
16. H. B. G. CASIMIR, *Phil. Res. Rep.* **6** (1951) 162.
17. R. A. WALDRON, *Inst. Elect. Eng.* **373E** (1960) 272.
18. *Idem.,* "The Theory of the Waveguides and Cavities" (Gorden and Breach Science Publishers, New York, 1969).
19. M. SUCHER and J. FOX, "Microwave Measurements" Vol. II (Polytechnic Press, New York, 1963).
20. E. G. SPENCER, R. C. LE CREW and L. A. AULT, *J. Appl. Phys.* **28** (1957) 130.
21. S. KABASHIMA and T. KAWAKUBO, *J. Phys. Soc. Jap.* **24** (1968) 493.
22. N. ENAYATI-RAD, Ph.D. Thesis, University of Durham, 1980.
23. A. K. JONSCHER and K. L. DEORI, *J. Mater. Sci.* **14** (1979) 1308.
24. M. POLLAK and T. H. GEBALLE, *Phys. Rev.* **122** (1961) 1742.
25. *Idem, ibid.* **138** (1965) A.1822.
26. S. P. MITOFF, *J. Chem. Phys.* **31** (1959) 1261.
27. P. P. BUDNIKOV and V. K. VANOVSKII, *J. Appl. Chem. USSR* **37** (1964) 1249.
28. J. S. THORP and M. D. HOSSAIN, *J. Mater. Sci.* **15** (1980) 1866.