

## THE DIELECTRIC CONSTANT OF $\text{UO}_2$ BELOW THE NÉEL POINT

N. HAMPTON and G.A. SAUNDERS

*School of Physics, University of Bath, Claverton Down, Bath, BA2 7AY, United Kingdom*

J.H. HARDING and A.M. STONEHAM

*Theoretical Physics Division, AERE Harwell, Didcot, Oxon, OX11 0RA, United Kingdom*

Received 16 December 1986; accepted 7 January 1987

We report measurements of the frequency-dependent dielectric constant of  $\text{UO}_2$  from 4.2 K to above the phase transition at 30 K. The static dielectric constant of 23.6 at 4.2 K is comparable with accepted values at higher temperatures: it is essentially identical in both phases. The effects of undergoing the transition on the dielectric constant are marginal (about 1%) and take place in the temperature range 29 K to 37 K. The displacement of the oxygen sublattice, which occurs at the Néel point, should produce only a 0.05% change on the dielectric constant and of the opposite sense to that measured. Hence the structural changes at the transition are not the primary source of the observed small difference between the dielectric constant in the two phases which probably accrues from the influence of the displacements on a defect-related contribution.

### 1. The phase transition in $\text{UO}_2$

Uranium dioxide  $\text{UO}_2$  undergoes a phase transition at about 30 K first detected by a  $\lambda$ -type feature in the specific heat [1]. Magnetic susceptibility [2–4] and neutron diffraction studies [5] have indicated that the transition is from a high temperature paramagnetic to a low temperature antiferromagnetic state. In the paramagnetic state the crystal structure is fcc (fluorite). Below the transition there is a small shift ( $\sim 0.014 \text{ \AA}$ ) of the oxygen atoms from the fluorite structure positions [6], the magnetic structure comprising ferromagnetic (001) planes stacked in an alternating plus-minus sequence [5]. The magnetisation changes abruptly at the Néel temperature [5,7]: the transition is first order. At the transition there is a rather abrupt change in length of about 20 ppm and the length continues to decrease rapidly as the temperature is further reduced [8]. The volume change at the transition is consistent with its first order character. Little is known about the electrical properties of the low temperature phase. The present objective has been to measure the dielectric constant of  $\text{UO}_2$  (below 77 K) in both phases to ascertain the effect of the phase transition on this property. A theoretical estimate has also been made to establish whether the structural change could produce a significant effect on the dielectric constant.

### 2. Measurements of dielectric constant

The dielectric constant has been obtained from impedance measurements made by an AC bridge technique on a single crystal plate of  $\text{UO}_2$  with evaporated aluminium electrodes. Recent work [9] has identified a boundary layer existing in conjunction with the bulk material for such plate geometry samples. The boundary layer has been found, using impedance plane techniques, to dominate the dielectric properties at moderate temperatures (300 K) but its effects become increasingly less important at lower temperatures. Below 77 K the complex plane profiles show no further evidence of any influence due to the boundary layer. Thus at lower temperatures the standard  $\log Z'$  versus  $\log Z''$  profile is a straight line with a gradient of  $\frac{1}{2}$ , this is expected for the equivalent circuit of a sample whose dielectric properties depend solely on the bulk material [10]. Furthermore the sample impedance is independent of the applied test voltage over the measurement frequency range 1 kHz to 5 MHz; the boundary layer effects should be voltage dependent [11] and have been found to be so in  $\text{UO}_2$  at temperatures in excess of about 150 K [9]. Thus in the temperature range (below 77 K) of this study, the measured dielectric properties are determined solely by the bulk crystal and the equivalent circuit can be represented by a parallel combina-

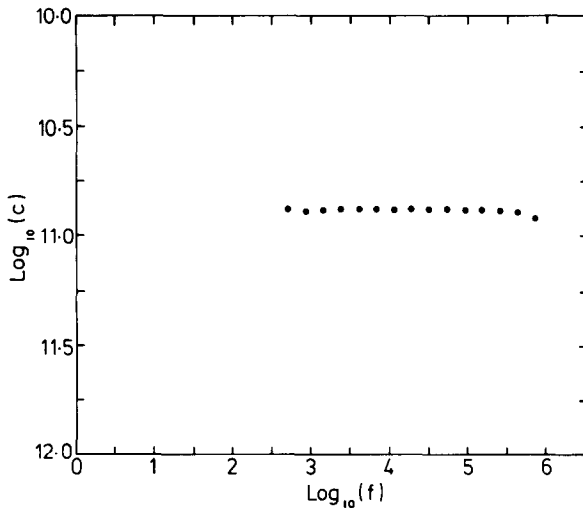


Fig. 1. Capacitance of the bulk material versus measurement frequency at 56 K for test voltage of 0.5 V.

tion of a resistance and a capacitance. Measurement of the capacitance leads directly to the dielectric constants of the bulk material through knowledge of the sample dimensions, only the static constant  $\epsilon_0$  being accessible with the frequencies used here. The capacitance  $C$  as a function of frequency  $f$  at temperatures below 77 K remains almost constant ( $dC/df \approx -3 \times 10^{-19} \text{ F Hz}^{-1}$ ), a typical example of the data (obtained at 56 K) being shown in fig. 1. The gradient of the capacitance versus frequency profiles is a slowly varying linear function of temperature. The static dielectric constant  $\epsilon_0$  has been obtained by extrapolation of the capacitance data towards zero frequency (0.1 Hz). This zero frequency capacitance can be attributed wholly to the bulk property of the crystal. This attribution has been validated in two ways: firstly the calculated characteristic frequency ( $7.9 \times 10^{-2} \text{ Hz}$ ) that would be expected for the boundary region is far below the accessible measurement frequencies; secondly it has been shown experimentally that the capacitance is independent of applied voltage, for voltages up to 35 V: the boundary contributions to the electrical properties of  $\text{UO}_2$  depend markedly upon the voltage [9].

The dependence of  $\epsilon_0$  upon temperature (both on cooling and warming) is shown in fig. 2. Here the effect of the 20 ppm length change at the phase transition upon the physical dimensions has been taken into account when calculating the dielectric constant. The main source of experimental error arises from the determination of the gradient of the profiles. The initial aim of the work was to establish the behaviour of the

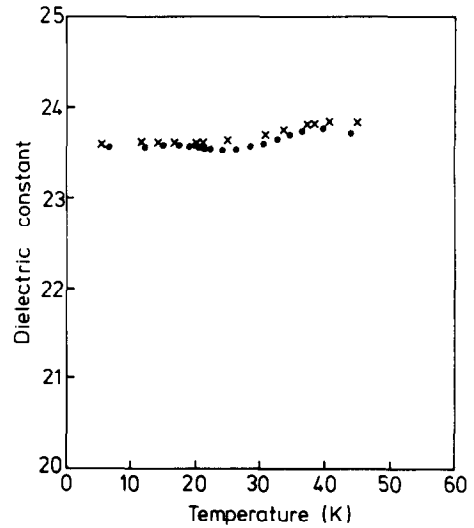


Fig. 2. Dielectric constant of monocrystalline  $\text{UO}_2$  as a function of temperature. The structural transition occurs close to 30 K. (x) cooling, (●) heating.

dielectric constant  $\epsilon_0$  in the vicinity of the phase transition and in the low temperature phase. The effect on  $\epsilon_0$  at the transition is found to be small but identifiable with the experimental methods used. The static dielectric constant is only about 0.8% larger in the high temperature phase than in the low temperature form. The errors in the absolute values of the zero frequency dielectric constant are about 1%. These errors can be attributed, almost wholly, to the extrapolation procedure because plots of the capacitance, at selected frequencies, versus temperature indicated a capacitive, and hence dielectric constant, change of approximately 0.8% across the transition region; the errors involved in determination of the relative change in the capacitance across the transition is substantially less than this ( $< 0.1\%$ ), so we are in no doubt that the value larger by 0.8% in the high temperature phase shows a real effect.

The dielectric constant in the paramagnetic phase has previously been measured by a number of workers both at high frequencies [12–16] and under static conditions [9, 16–19]. In principle the results of measurement of the dielectric constants of  $\text{UO}_2$  at microwave and quasi-DC frequencies might be expected to be the same. However, above 150 K the boundary region contributes to the capacitance of plate geometry specimens measured at low frequencies. A value of  $\epsilon_0$  of 36 measured at 77 K is consistent with data previously reported [9,16]; that this value is rather larger than that ( $\epsilon_0 = 24$ ) measured at microwave frequencies has been ascribed

to dipolar contributions resulting from excess oxygen beyond stoichiometry [9]. The value (23.6) obtained here at 4.2 K for  $\epsilon_0$  in the antiferromagnetic phase is for most purposes identical with that now accepted for the paramagnetic phase and remeasured here as 23.8 (at 45 K).

### 3. Estimation of the change in dielectric constant due to oxygen displacements at the phase transition

It is now necessary to estimate the expected change in the dielectric constant which arises directly from the structural distortion [20] which takes place at the transition. This is not an attempt to predict the lattice distortion or its origin (see refs. [21] and [22]) but simply to ascertain whether the observed distortion can produce a significant change in dielectric constant. The calculations are based on a shell model [23] for  $\text{UO}_2$ , and use the Harwell PLUTO code [24]. The three components  $\epsilon_{0x}$ ,  $\epsilon_{0y}$ ,  $\epsilon_{0z}$  of the static dielectric constant and the corresponding components  $\epsilon_{\infty x}$ ,  $\epsilon_{\infty y}$ ,  $\epsilon_{\infty z}$  of the optic dielectric constant have been calculated as a function of the distortion. The distortion moves alternate (010) layers of oxygens in the [100] and  $\bar{1}00$  directions and has the magnitude  $Q$  in units of the anion-anion distance [2.7341 Å at 298 K). Since it is anticipated that the  $\text{UO}_2$  sample will consist of domains with different orientations, the average of the three principal components has been calculated. These averages are fitted quite adequately by:

$$\Delta\epsilon_0/\epsilon_0 = 21Q^2; \quad \Delta\epsilon_\infty/\epsilon_\infty \approx 3.85Q^2.$$

The experimental displacement at the transition is 0.014 Å [20] which would give a relative change  $\Delta\epsilon_0/\epsilon_0$  of 0.05% which is substantially smaller than that measured experimentally (0.8%). It also has the opposite sign, predicting a smaller dielectric constant in the paramagnetic phase than in the low temperature antiferromagnetic phase, although the converse is true. A natural explanation of the small difference between the dielectric constant of the two phases is that the structural distortion suppresses another contribution to the dielectric constant. It is plausible that the inhibited contribution is related to that excess observed at higher temperatures which has been associated [9,12] with small deviations from stoichiometry. We have reported previ-

ously [19] dipolar contributions to the observed dielectric properties and the suppression of a small fraction of these contributions would explain the observed change near the phase transition. Whether freezing out results from making previously-equivalent sites inequivalent (so that reorientation is inhibited) or from changes associated with electronic ordering is not yet clear.

In conclusion the experiments have established that undergoing the first order magnetic and structural phase transition has only a small effect on the dielectric constant  $\epsilon_0$  of  $\text{UO}_2$ , and that this is not related directly to the atomic displacements at the transition.

### References

- [1] W.M. Jones, J. Gordon and E.A. Long, *J. Chem. Phys.* 20 (1952) 695.
- [2] A. Arrott and J.E. Goldman, *Phys. Rev.* 108 (1957) 948.
- [3] W.E. Henry, *Phys. Rev.* 109 (1958) 1976.
- [4] M.J.M. Leask, L.E.J. Roberts, A.J. Walter and W.P. Wolf, *J. Chem. Soc.* (1963) 4788.
- [5] B.C. Frazer, G. Shirane, D.E. Cox and C.E. Olsen, *Phys. Rev.* 140 (1965) A1448.
- [6] J. Faber and G.H. Lander, *Phys. Rev.* 14 (1976) 1151.
- [7] B.T. Willis and R.I. Taylor, *Phys. Lett.* 17 (1965) 188.
- [8] O.G. Brandt and C.T. Walker, *Phys. Rev. Lett.* 18 (1967) 11.
- [9] N. Hampton, G.A. Saunders and A.M. Stoneham, *J. Nucl. Mater.* 139 (1986) 185
- [10] A.K. Jonscher, *Dielectric Relaxation in Solids* (Chelsea Dielectrics Press, London, 1984) p. 62–86.
- [11] I.D. Raistrick, *Ann. Rev. Mater. Sci.* 16 (1986) 342.
- [12] J. Tateno, *J. Chem. Phys.* 81 (1984) 12.
- [13] R.J. Ackerman, R.J. Thorn and G.H. Winslow, *J. Opt. Soc. Am.* 44 (1959) 1107.
- [14] K. Gesi and J. Tateno, *Jpn J. Appl. Phys.* 8 (1969) 1358.
- [15] J. Schones, *Phys. Rep.* 63 (1980) 302.
- [16] J.D. Axe and G.D. Pettit, *Phys. Rev.* 151 (1966) 676.
- [17] A. Briggs, private communication.
- [18] S. Iida, *Jpn J. Phys.* 4 (1965) 833.
- [19] N. Hampton, E.A. Saunders, G.A. Saunders, D. Vigar and A.M. Stoneham, *J. Nucl. Mater.* 132 (1985) 156.
- [20] P. Erdos and J.M. Robinson, in: *The Physics of Actinide Compounds* (Plenum Press, New York, 1983).
- [21] R. Siemann and B.R. Cooper, *Phys. Rev. B* 20 (1979) 2869.
- [22] G. Solt and P. Erdos, *Phys. Rev. B* 22 (1980) 4718.
- [23] C.R.A. Catlow, *Proc. Roy. Soc. A* 353 (1977) 533.
- [24] C.R.A. Catlow and M.J. Norgett, *AERE Report M2936* (1976).