THE DIELECTRIC CONSTANT OF UO$_2$ BELOW THE NÉEL POINT

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We report measurements of the frequency-dependent dielectric constant of 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 UO$_2$

Uranium dioxide UO$_2$ undergoes a phase transition at about 30 K first detected by a λ-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 (~ 0.014 Å) 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 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 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 5MHz; the boundary layer effects should be voltage dependent [11] and have been found to be so in 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-
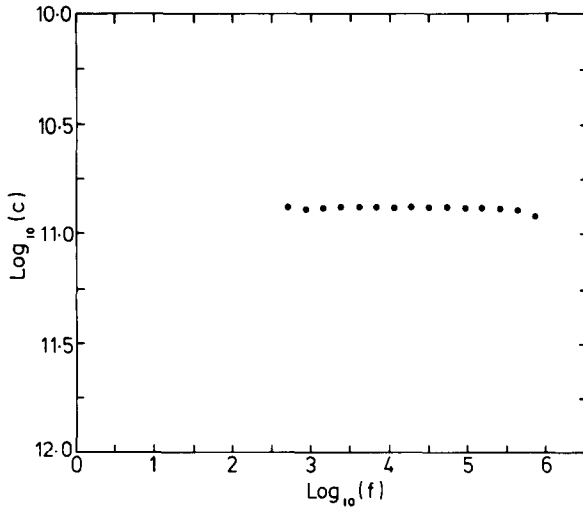
Fig. 1. Capacitance of the bulk material versus measurement
frequency at 56 K for test voltage of 0.5 V.

Fig. 2. Dielectric constant of monocrystalline UO_2 as a func-
tion of temperature. The structural transition occurs close to
30 K. ($\times$) cooling, ($\bullet$) heating.

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 ϵ_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 $(dC/df = -3 \times 10^{-19}$ 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
ϵ_0 has been obtained by extrapolation of the capaci-
tance 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 characteris-
tic frequency $(7.9 \times 10^{-2}$ 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 UO_2 depend
markedly upon the voltage [9].

The dependence of ϵ_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
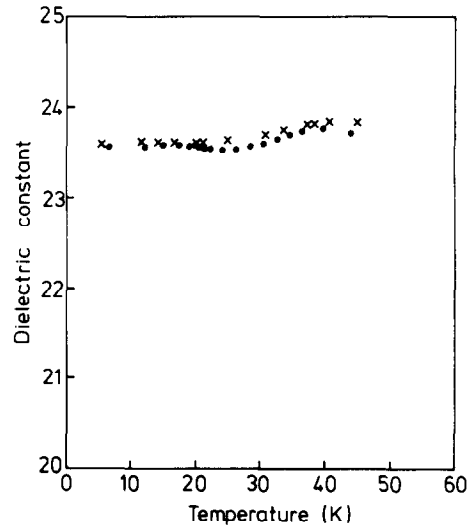aim of the work was to establish the behaviour of the

dielectric constant ϵ_0 in the vicinity of the phase transi-
tion and in the low temperature phase. The effect on ϵ_0
at the transition is found to be small but identifiable
with the experimental methods used. The static dielec-
tric 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 proce-
dure because plots of the capacitance, at selected fre-
quencies, versus temperature indicated a capacitive, and
hence dielectric constant, change of approximately 0.8%
across the transition region; the errors involved in de-
termination 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 condi-
tions [9, 16–19]. In principle the results of measurement
of the dielectric constants of 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 mea-
sured at low frequencies. A value of ϵ_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 ϵ_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 UO_2, and use the Harwell PLUTO code [24]. The three components ϵ_{0x}, ϵ_{0y}, ϵ_{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 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:

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

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 ϵ_0 of UO_2, and that this is not related directly to the atomic displacements at the transition.

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