FREQUENCY DEPENDENCE OF ELECTRICAL CONDUCTIVITY AND DIELECTRIC CONSTANT OF UO$_2$

N. HAMPTON, E.A. SAUNDERS, G.A. SAUNDERS, D. VIGAR

School of Physics, University of Bath, Claverton Down, Bath, BA2 7AY, UK

and

A.M. STONEHAM

Theoretical Physics Division, AERE, Harwell, Didcot, Oxon, OX11 0RA, UK

The dielectric constant and electrical conductivity of single crystal and polycrystalline UO$_2$ are found to be frequency dependent. The dielectric constant measured at low frequencies is anomalously large at room temperature but decreases to a limiting value (~ 25) below about 130 K. A knee observed in the temperature dependence of the conductivity of polycrystalline UO$_2$ corresponds to a process having an activation energy of 0.15 eV.

The electrical conductivity and dielectric constant of single crystal and polycrystalline UO$_2$ have been measured between 100 K and 300 K. Preliminary experiments indicated that these properties might be strongly frequency dependent, a feature not previously observed for UO$_2$. Hence a.c. bridge techniques have been adopted, the measurement frequency being variable between 1 kHz and 5 MHz. Stoichiometric samples were prepared in the form of thin discs with opposing faces silver coated to form electrodes. Electrical connections were made with a phosphor bronze spring securing the sample onto a copper base plate. The conductivity and dielectric constant were derived from impedance measurements made using a four-terminal method.

The frequency dependences of the dielectric constant and conductivity obtained at room temperature are given in fig. 1. The dielectric constant ϵ_r as a function of frequency f can be fitted by an equation of the form

$$\epsilon_r = Af^m \tag{1}$$

with $m = -0.98 \pm 0.02$ and $A = (9.8 \pm 2.0) \times 10^7$. The steep increase at low frequencies of the measured value of ϵ_r, approaching a $1/f$ dependence, is a characteristic feature of a number of ionic conductors. This effect is not compatible with any simple circuit element, though it may be attributed to space charge [1,2]. It is unlikely

that these low frequency effects result from diffusion of oxygen ions across the electrode sample interface, as this would result in an $f^{-1/2}$ dependence of the impedance [2] which is not observed: the gradient of the log σ versus log f plot is 0.17 ± 0.02. The large capacitance measured at low frequencies (fig. 2) decreases rapidly with the temperature. Limiting values of the dielectric constant, independent of frequency up to 10 kHz, are reached when the temperature is reduced below about 130 K; these values were measured as 25.5 and 22.8 for single crystal and polycrystalline UO$_2$ respectively at 120 K. These limiting values are consistent with the static dielectric constants ϵ_S ($= 23$ [3], 21.5 [4]) obtained from optical measurements. The rate of decrease of ϵ_r with temperature, and the temperature at which the limiting value of the dielectric constant is achieved are frequency dependent. These effects can be attributed tentatively to a decreasing mobility associated with the carriers responsible.

The temperature dependence of the conductivity of polycrystalline UO$_2$ shows a knee (fig. 3). The shape and temperature (T_p) of this interesting novel observation exhibit a frequency dependence; an activation energy E_p ($= 0.15$ eV) and a characteristic frequency f_0 ($= 1.7 \times 10^{-4}$ Hz) for the process responsible has been obtained using
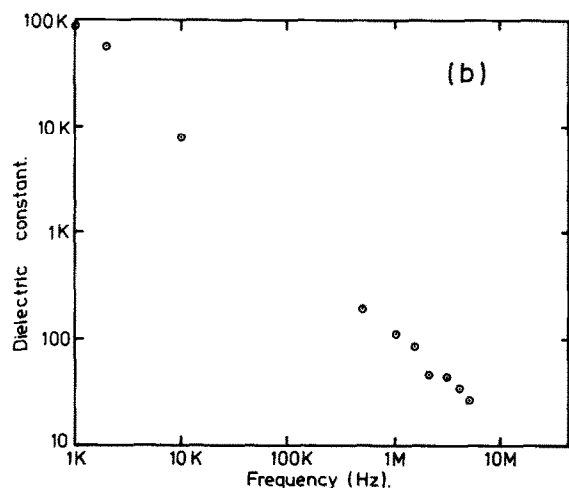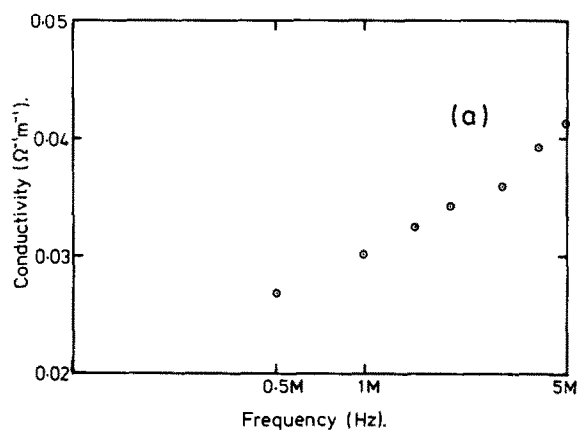
Fig. 1(a) The frequency (f) dependence of the electrical conductivity σ of single crystal $UO_{2.00x}$ measured at 291 K. The gradient of a log σ–log f plot is 0.17 ± 0.02. (b) The frequency dependence of the dielectric constant of single crystal $UO_{2.00x}$, measured at 291 K. The gradient of the log ϵ_r–log f plot is -0.98 ± 0.02.

$$f_p = f_0 \exp\left(-E_p/kT_p\right). \tag{2}$$

It is instructive at this stage to assess on the basis of Debye theory the concentration of dipoles which would be necessary to produce the knee. Using this simplistic approach, the data for the knee strength at 2 kHz have been shown to require 8×10^{17} dipoles/cm³, assuming dipole moments of one Debye, with a single relaxation time of 1×10^{-4} s. This corresponds to one centre for each 5×10^4 molecules, a figure which lies well within deviations from stoichiometry in these polycrystalline specimens.
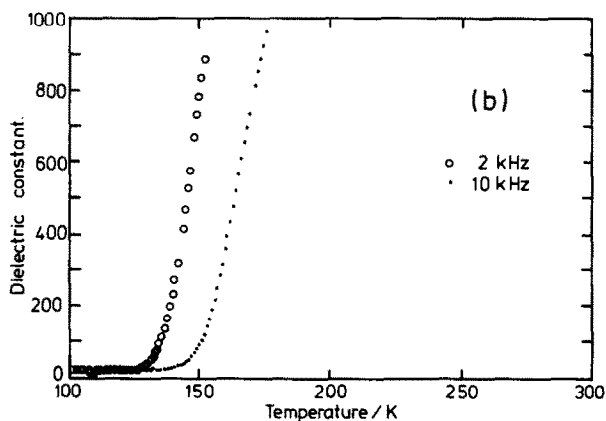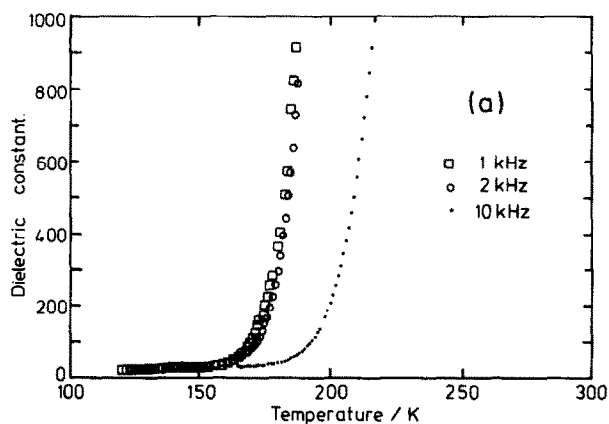

Fig. 2(a) The dielectric constant as a function of temperature at 1 kHz, 2 kHz and 10 kHz for single crystal $UO_{2.00x}$. The low temperature limiting value of ϵ_r is 25.3. (b) The dielectric constant as a function of temperature for polycrystalline uranium dioxide at 2 kHz and 10 kHz. The low temperature limiting value of ϵ_r is 22.8.

It has been common practice to interpret conductivity data for UO_2 using a band conduction model [5–8], when an activation energy can be calculated from the gradient of $\log_e \sigma$ against $1/T$ plots. An alternative approach, based upon a small polaron model, has also been employed for UO_2 [5] and also for other fluorite crystals [2]; the activation energy for this process can be derived from the slope of $\log_e \sigma T$ against $1/T$ plots. To examine both models the electrical conductivity as a function of temperature has been measured at a number of frequencies, that obtained at 2 kHz is plotted here in both functional forms for polycrystalline (fig. 3) and single crystal UO_2 (fig. 4). Activation energies obtained from the linear portions of the curves are compared
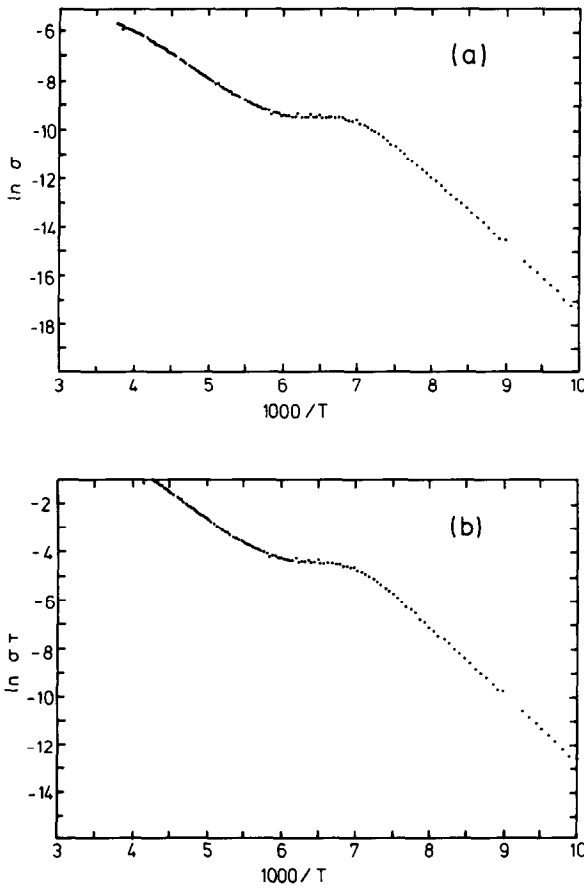
Fig. 3. The temperature dependence of the electrical conductivity of polycrystalline uranium dioxide at 2 kHz, (a) plotted in a form suitable for analysis by a band conduction model, (b) plotted in a form suitable for analysis by a small polaron model.
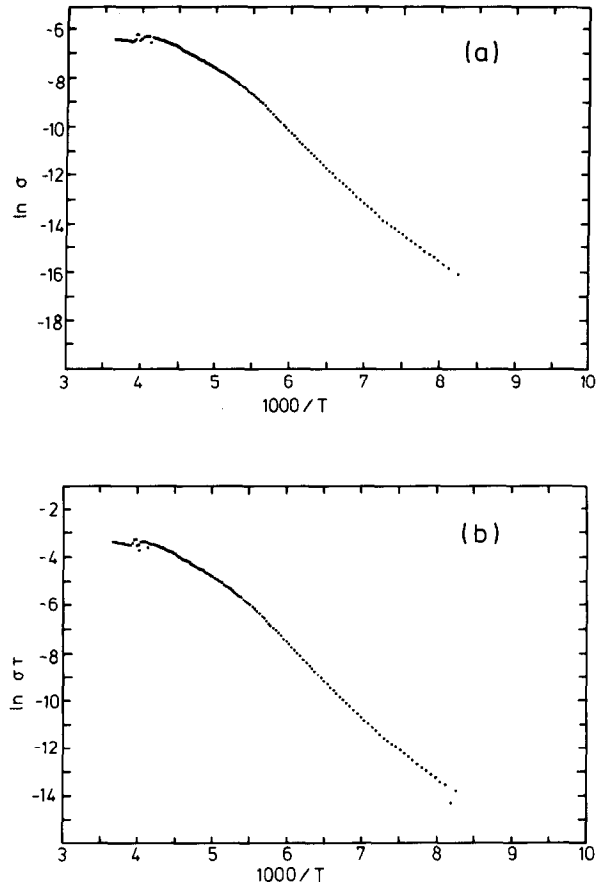

Fig. 4. The temperature dependence of the electrical conductivity of single crystal $UO_{2.00x}$ (a) plotted in a form suitable for analysis by a band conduction mode, (b) plotted in a form suitable for analysis by a small polaron model.

Table 1
Comparison of activation energies obtained from conductivity data as a function of temperature using a band conduction model

Single crystal		Polycrystalline UO_2	
E_A(eV)	Reference	E_A(eV)	Reference
0.13	[5]		
0.14	[6]		
0.17	[7]	0.17	[7]
0.43	[8]	$0.21 \rightarrow 0.12$	[8]
		0.18	This work (above knee)
0.22	This work (below 300 K)	0.22	This work (below knee)

with results of previous workers in table 1. For the polycrystalline samples the activation energies obtained above and below the knee differ somewhat. Differences in the quality of the fits obtained are not sufficiently conclusive to establish the validity of either model. Further experiments are now underway over wider ranges of frequency and temperature with the object of providing data to reassess the mechanism of electrical conductivity of UO_2. At present it can be stated that the conduction mechanisms are frequency dependent and appear to be dominated at room temperature by space charge effects. This would entail a reinterpretation of the electronic transport data. In addition, should the space charges lie in the region of grain boundaries for polycrystalline samples, then the low temperature

ion transport and impurity solubilities would be influenced.

Acknowledgements

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