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Small-polaron hopping in Mott-insulating UO_2

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Abstract. The DC electrical conductivity in the extrinsic regime of a slightly hyperstoichiometric sample of polycrystalline UO_{2+x} is re-analysed using the general framework of small-polaron theory, taking into account the Mott-insulating nature of the ground state of the stoichiometric material. It is established that above about 150 K the holes move by non-adiabatic hopping, with a mobility activation energy of 0.28 ± 0.02 eV. There is no conflict between electrical and thermodynamic data, contrary to some earlier theories. The implications for existing empirical determinations of the Mott–Hubbard gap, U , and the associated entropy of formation of altered-valency cations in the intrinsic regime is investigated, and new (preferred) values presented. The relatively large carrier densities predicted near melting necessitate some further consideration of the Coulomb interaction and of its influence both on the magnitude of U and on the mobility activation energy. Finally, attention is drawn to some outstanding discrepancies between the semi-empirical values of the small-polaron self-energy and mobility activation energy determined in this work, using Lang–Firsov theory, and those yielded by fully microscopic HADES calculations.

1. Introduction: small-polaron formation in Mott-insulating $\text{UO}_{2\pm x}$

The large disparity in the activation energies associated with the DC electrical conductivity, $\sigma(T)$, and thermoelectric Seebeck coefficient \parallel , $S(T)$, of hyperstoichiometric [1,2] and hypostoichiometric [3] samples of UO_2 empirically indicates that the mobility of the carriers is itself activated—the carriers moving via multiphonon transitions between localized states (i.e. by *hopping*). The first explicit¶ identification of the carriers as *small polarons* was made by Devreese in 1963 [4], and later quantified within the framework of Lang and Firsov's three-dimensional formulation [8] of small polaron theory by Devreese *et al* in 1966 [9].

As is well known, the hopping process can be either adiabatic or non-adiabatic, according to whether or not a carrier is necessarily *always* able to avail itself of an energetically

\parallel The Seebeck coefficient, $S(T)$, of polycrystalline UO_2 is found to be *independent* of temperature [1] in the extrinsic regime (for $700 \text{ K} < T < 1100 \text{ K}$), whilst in the case of *single-crystal* samples it exhibits [2] a small activation energy (equal to the slope of $S(T)$ versus T^{-1}) of magnitude less than one half of the conductivity activation energy.

¶ Although not *explicitly* referred to as such, it *could* be argued that small polarons were in fact subsumed in the earlier analysis (motivated by some even earlier qualitative considerations of Gruen [5] on the nature of the charge transport in UO_2) of the electrical conductivity of grossly hyperstoichiometric UO_{2+x} by Aronson *et al* [6] in terms of *hopping*, following the phenomenological approach of Heikes and Johnston [7], which—it should be noted—actually *predated* the formal development of the (microscopic) theory of small polarons.

equivalent neighbouring site (created through a thermal fluctuation) and move accordingly; this requires that the carrier can tunnel to such a site and stabilize the polarization fluctuation *before* it decays.

Although the associated adiabatic and non-adiabatic mobilities are characterized by different pre-exponential temperature factors— T^{-1} and $T^{-3/2}$, respectively—it is not possible, in practice, to exploit this difference to conclusively establish which mode is actually realized in any given sample of UO_{2+x} , since, even for the best available electrical conductivity data (which are on UO_{2+x}), plots of $\ln(\sigma T)$ and $\ln(\sigma T^{3/2})$ versus T^{-1} fit the data from the extrinsic regime ($T < 1400$ K) almost equally well. Accordingly, it is necessary to return to the details of the underlying theory, and to examine, in particular, the inequalities that demarcate the two types of hopping; such an investigation has never been satisfactorily undertaken for UO_{2+x} . Thus, for example, Devresse *et al* initially [9] simply assumed that the hopping was *non-adiabatic*—only later [2] empirically demonstrating that the associated $\ln(\sigma T^{3/2})$ versus T^{-1} linearity was indeed well satisfied between 140 and 1000 K; on the other hand, whilst Tateno [10] and Ohmichi *et al* [11] did make some attempt to establish which type of hopping is realized, their analyses are inadequate, and in some cases are even based on formulae that are simply not valid for the fluorite structure of UO_2 ! More serious, however, is the almost total absence of any recognition of the *Mott-insulating nature* of the ground state of the stoichiometric material, and any consideration of its repercussions on the specifics of small-polaron formation—an exception being a paper [12] dealing primarily with the electronic properties of the *intrinsic* regime of UO_{2+x} at $T > 1400$ K.

The empirical demonstration [1–3] of hopping in the extrinsic regime of UO_{2+x} indicates that the positive and negative carriers (which are introduced into the material in consequence of its non-stoichiometry) are *not* described by extended states belonging, respectively, to the so-called lower and upper Hubbard ‘bands’ of the Mott-insulating stoichiometric material—as would be the case in the absence of any *further* interactions—but are instead, *re-localized*, in consequence of their strong interaction with the highly polarizable ionic lattice, which, at the temperatures concerned, would (for extended states) entail mean free paths actually *less* than the separation of periodically located cations. This essentially *single-carrier* localization (which can occur *only* at $T > 0$) is to be distinguished from the intrinsically *many-electron* localization (which is strongest at $T = 0$), which characterizes the Mott-insulating ground state—a highly correlated, ‘self-locked’ state in which each U ion has exactly two localized 5f electrons—a configuration that ensures that the total energy of the system is *lower* than it would be were the metallic state predicted by the band model realized; evidently, in consequence of the narrowness of the width, W , of the 5f band, the decrease in electron kinetic energy achieved by delocalizing into an extended Bloch state is insufficient to outweigh the increase in Coulomb potential energy associated with the lowest-energy valence fluctuations about the $(5f)^2$ configuration namely to $(5f)^1$ and $(5f)^3$, which must necessarily occur if a metallic state is to be realized; the empirical Mott-insulating nature of the stoichiometric UO_2 ground state thus signifies that in this material

$$W/2 < U. \quad (1)$$

The many-electron insulating ground state is thus split off to lower energies from the many-electron current-carrying states associated with the above valence fluctuations.

An understanding of how deviations from stoichiometry act to ‘unlock’ the stoichiometric Mott-insulating ground state is greatly facilitated by the availability of an effective *single-particle* representation [13] of this intrinsically *many-electron* phenomenon,

in which the lower filled half of the (non-interacting) Bloch band can be considered to be separated by a gap of magnitude U from the upper empty half—*provided*, however, that the *one*-electron states in these two bands (which now represent the so-called ‘upper’ and ‘lower’ Hubbard ‘bands’ of the *many*-electron theory) are understood to be *occupation number dependent*—in the sense that the states in the upper band exist only by virtue of the completely filled ones in the lower band.

Consistent with the positive [1] and negative signs [3] of the Seebeck coefficient in the extrinsic regimes of UO_{2+x} and UO_{2-x} , respectively, stoichiometric deviations are considered to introduce holes in the lower ‘band’ (in the case of UO_{2+x}), and electrons in the upper ‘band’ (in the case of UO_{2-x}). *It is with respect to these (occupation number dependent) bands that small-polaron formation in both the extrinsic and intrinsic† regimes of $UO_{2\pm x}$ must be considered*; for U ($\simeq 3$ eV) is, by far, the dominant energy in the system, being one order of magnitude larger than typical small-polaron self-energies, E_p , or mobility activation energies.

The criterion that a single carrier forms a small polaron is that the energy lowering, E_p achieved through the carrier’s interaction with the self-induced lattice polarization in the absence of any translational motion, should outweigh that achieved by delocalization into an extended Bloch state at the bottom of a band of width W , on which the effect of the polarization is neglected—i.e. it is necessary that

$$|E_p| > W/2. \quad (2)$$

Since this condition holds at *all* cation sites if it holds at one, the localized orbitals will superpose to yield extended Bloch-like states; in addition to being shifted by E_p , the width, W_p , of the associated *small-polaron band* will be much *narrower* than W , in consequence of the reduction in the value of the overlap integrals entailed by the tighter binding ($E_p < 0$) that now obtains at any site. The fact, however, that at the temperatures of interest (~ 1000 K) the mobility of the holes in UO_{2+x} is empirically known to be *activated* means that unless an energetically equivalent environment is established (via a thermal fluctuation) at a nearest-neighbour site to the one occupied, the carrier will remain *localized*, and, accordingly, *not* be described by an extended Bloch function; in general, this must be anticipated when $W_p < kT$, the fulfilment of which is easier the higher the temperature since $W_p(T)$ is a strongly decreasing function of T [8]. The Mott-insulating nature of $UO_{2.00}$, however, greatly facilitates the fulfilment of (2) since, in accordance with the above remarks, W must be identified with one of the two Hubbard ‘bands’; thus in the case of UO_{2+x} , for example,

$$W \rightarrow W_h \simeq n_h W/2 \quad (3)$$

where W_h is the (occupation-number-dependent) width of the lower Hubbard *hole* band, in which it is assumed there are n_h holes per U ion ($n_h \leq 2x$). At the stoichiometries concerned ($x \leq 10^{-3}$ —see below) it is clear that

$$W_h \ll W/2. \quad (4)$$

In section 2, the hopping conductivity of the extrinsic regime of polycrystalline UO_{2+x} is analysed—in the light of the above remarks—within the framework of Lang and Firsov’s (three-dimensional) formulation [8] of small-polaron theory. The implications of the deduced non-adiabatic character of the hopping on the energy spectrum of the intrinsic

† See section 3 below.

regime (at $T > 1400$ K) are elaborated in section 3, and new empirical values obtained for the Mott–Hubbard energy gap, U , in UO_2 and for the formation entropy of the associated altered-valency (carrier) states. The paper concludes (section 4) by drawing attention to (i) the desirability of including interaction with lattice modes *other* than solely the longitudinal optic (LO) mode usually considered and (ii) the difficulty in reconciling the results of the present analysis with those of microscopic (HADES) calculations based on inter-atomic potentials.

2. Application of small-polaron theory (Lang–Firsov) to the extrinsic regime of UO_{2+x}

Given the FCC structure of the cation sublattice of UO_{2+x} , the measured conductivity, σ , can be expressed as follows, in terms of the longitudinal components, σ_{kk} ($k = x, y, z$), calculated by Lang and Firsov:

$$\sigma = \frac{1}{3} \sum_k \sigma_{kk} \quad (5)$$

where σ_{kk} is given [8] by

$$\sigma_{kk} = \frac{ne^2}{2kT} \sum_g \Gamma_1(\mathbf{g}) g_k^2 \quad (6)$$

$\Gamma_1(\mathbf{g})$ is the hopping probability to any *one* of the z nearest-neighbour cation sites (all assumed to be unoccupied) located by a vector \mathbf{g} with respect to the occupied cation, where

$$|\mathbf{g}|^2 = \sum_k g_k^2 \quad (7)$$

(= $a_0^2/2$, for the fluorite lattice). a_0 is the standard (anion-based) lattice constant of the fluorite lattice, such that

$$a_0^3 = 4\Omega \quad (8)$$

where Ω is the primitive cell volume (which contains *one* unit of UO_2) in terms of which the number density, n , of carriers in UO_{2+x} is given by

$$n = f(x)/\Omega \quad (9)$$

the simplest possibilities for $f(x)$ being

(i) $f(x) = 2x$, consistent with the supernumerary electron (hole) associated with each of the two charge-compensating $\text{U}^{3+}(\text{U}^{5+})$ ions *both* being free, i.e. *not* bound to the O vacancy (interstitial),

(ii) $f(x) = x$ —corresponding to only *one* electron (hole) being *unbound* at the temperatures concerned ($T > 700$ K).

It should be noted that *both* possibilities are consistent with the T independence of the Seebeck coefficient, S , found [1, 22] in *polycrystalline* samples of UO_{2+x} at $T > 700$ K. On the other hand, the very small carrier activation energy that characterizes the observed [1] increase in S at $T < 500$ K (the value of which is close to that (≤ 0.1 eV) found [2] in *single crystals* of UO_{2+x} at *all* temperatures up to the onset of the intrinsic regime) is, perhaps, more readily understandable in terms of (ii) as a consequence of the reduction in binding energy effected through Coulomb interaction with the hole which *remains* bound.

It should be stressed, however, that the essential results and conclusions of the following analysis do *not* depend critically on which of the two forms for $f(x)$ is actually adopted†; for definitiveness, $f(x) = 2x$ will be assumed—the repercussion of the alternative choice being simply a magnification in the deduced value of J by a factor of $\sqrt{2}$ —a modification which, it should be noted, does *not* entail any violation of the important inequality in (20) below.

According to whether the hopping is adiabatic or non-adiabatic, the form of $\Gamma_1(g)$ is as follows:

$$\Gamma_1(g) = \begin{cases} \nu_0 e^{-\epsilon_a^*(g)/kT} & \text{adiabatic} \\ J^2 \sqrt{\pi/\epsilon_a kT} e^{-\epsilon_a(g)/kT} / 2\hbar & \text{non-adiabatic} \end{cases} \quad (10)$$

$$(11)$$

In the case of UO_{2+x} , the overlap integral J is an effective one pertaining to the lower Hubbard band, the value of which (in accordance with (3) is a factor of n_h smaller than that (J_0) that determines the width, W , of the rigid non-interacting (single-carrier) band via $W = 2zJ_0$, where z is the number of nearest-neighbour cations.

It should be noted that in the non-adiabatic case, Γ_1 is still dependent on the LO frequency, ν_0 (here assumed to be dispersionless), via the activation energy $\epsilon_a(g)$ (see (21) below), whilst the associated $T^{-1/2}$ prefactor modifies the T^{-1} dependence characteristic of classical hopping based on the Einstein relation between mobility and diffusion constant. The corresponding conductivities thus take the form

$$\sigma(T) = (\sigma_0/T) e^{-\epsilon/kT} \quad \text{adiabatic} \quad (12)$$

$$\sigma(T) = (\sigma_1/T^{3/2}) e^{-\epsilon_a/kT} \quad \text{non-adiabatic} \quad (13)$$

where, for the specific case of fluorite $UO_{2\pm x}$ (with $z = 12$), the prefactors σ_0 and σ_1 can be written (using (5)–(9) and noting that $\sum_g \Gamma_1(g) = z\Gamma_1$) as follows:

$$\sigma_0 = 8xe^2\nu_0/ka_0 \quad (14)$$

$$\sigma_1 = (4xe^2/ka_0)(J^2/\hbar)\sqrt{\pi/k\epsilon_a}. \quad (15)$$

Whether, for a given material (specified by the value of x), the hopping is adiabatic or non-adiabatic is determined by the so-called adiabatic parameter, η_2 , defined by

$$\eta_2 \equiv (J^2/h\nu_0)\sqrt{1/\epsilon_a kT} \quad (16)$$

the criteria being

$$\eta_2 = \begin{cases} \gg 1 & \text{for adiabatic hopping} \\ \ll 1 & \text{for non-adiabatic hopping.} \end{cases}$$

† Some empirical guidance as to which is the more realistic choice could be obtained by (i) extending existing (room-temperature) measurements of dielectric loss to much higher temperatures and (ii) appropriate analysis of the observed dependence of the extrinsic electrical conductivity on O_2 partial pressure.

The correlation-reduced rigid lattice overlap integral, J and the conductivity activation energy ϵ_a , can now be determined by fitting (13) to the experimental conductivities, $\sigma(T)$.

The only available *tabulated* $\sigma(T)$ values are those of Bates [14] on slightly hyperstoichiometric UO_{2+x} , with $x \leq 0.001$. In order that the empirically deduced activation energy, ϵ_a , be *entirely* accreditable to the hole *mobility*, data from a *polycrystalline* sample must be selected, since for such samples the thermoelectric Seebeck coefficient is known [1] to be *independent* of T (at least for $500 \text{ K} < T < 1000 \text{ K}$), indicating a *constant* number of holes (assumed equal to $2x$ per U atom). Covering a particularly large temperature range in both the extrinsic and intrinsic regimes (considered in section 3), the data from the polycrystalline sample B-38-C were selected, and analysed via (13), the results for the *extrinsic* regime being as follows:

$$\sigma_1 = (1.1 \pm 0.3) \times 10^7 (\Omega \text{ m})^{-1} \text{ K}^{3/2} \quad \epsilon_a = (0.28 \pm 0.02) \text{ eV}. \quad (17)$$

With $x \leq 0.001$, and taking $a_0 = 5.5 \times 10^{-10} \text{ m}$ at $T = 1000 \text{ K}$, (15) yields (with $\nu_0 = 1.7 \times 10^{13} \text{ Hz}$ [17, 18])

$$J \geq 0.04 \text{ eV} \quad (18)$$

whence

$$\eta_2 \geq 0.15 \quad (19)$$

indicating† that in this particular sample of UO_{2+x} , the hopping is non-adiabatic, consistent with the inequality

$$J (\geq 0.04 \text{ eV}) < \hbar \nu_0 (= 0.07 \text{ eV}) \quad (20)$$

which reflects the fact that the hole has *less than* unit probability of tunnelling to a nearest-neighbour site *before* the polarization fluctuation—which momentarily renders the site energetically equivalent (to that already occupied by the hole)—decays in a time of order ν_0^{-1} .

It should be noted that for a specified value of x the value of J given by (18) is in the nature of an *upper* limit, deriving as it does from the assumption that the *entire* DC conductivity is due to small polarons. More realistically, a contribution [15] arising from thermal excitation to *large*-polaron states characterized by a *non-activated* mobility should be allowed for—the gap between the large- and small-polaron states being given approximately by the difference $E_p - \alpha \hbar \nu_0$ ($\leq 0.5 \text{ eV}$, using (31) and $\alpha \geq 2$ —see the footnote on page 8).

The definitiveness of the above demonstration of non-adiabaticity is, unfortunately, somewhat undermined by the uncertainty in the value of x —Bates' chemical analysis essentially, establishing only an *upper* limit of 10^{-3} ! Using (15) and (16) it can easily be ascertained that, to ensure $\eta_2 \ll 1$, it is necessary that

$$x \gg 1.4 \times 10^{-4}$$

† It should be noted that to establish whether or not the hopping is adiabatic, for example, it is *not* sufficient simply to establish that the value of ν_0 entailed by (14) agrees with the 'experimental' value (obtained from lattice dynamics studies)—as is done in the work of Dudney *et al* [16]—since it is possible to achieve such agreement in the case of the data from the sample B-38-C simply by assuming $x = 4.6 \times 10^{-4}$ —a value certainly consistent with the cited upper limit of $x \leq 10^{-3}$!

which leaves a rather narrow range for consistency with $x \leq 10^{-3}$; accordingly, it is necessary to seek independent corroboration for *non-adiabatic* hopping. Such is to be found in the remarkably good agreement between the experimental value of the conductivity activation energy ϵ_a (given above in (17)) and that calculated within the framework of Lang and Firsov's formulation of small-polaron hopping, which yields the following high-temperature ($T \gg \hbar\nu_0/4k$) (temperature-independent) expression for ϵ_a , when dispersion of the LO mode of frequency ν_0 is neglected:

$$\epsilon_a = \frac{\hbar\nu_0}{4N} \sum_w |V_w|^2 (1 - \cos \mathbf{g} \cdot \mathbf{w}) \tag{21}$$

where \mathbf{w} denotes an LO wave-vector and \mathbf{g} has the same meaning as in (6); N is the number of primitive cells (of volume Ω) per unit volume of the crystal, and $|V_w|^2$ is a dimensionless coupling constant characterizing the strength of the carrier's interaction with the LO mode, which (following the usual practice) is here treated within a continuum approximation, wherein $|V_w|^2$ takes the following form (familiar from *large-polaron* theory):

$$|V_w|^2 = [4\pi e^2 / \Omega \hbar \nu_0 w^2] (1/\epsilon_\infty - 1/\epsilon_s) \tag{22}$$

where ϵ_∞ and ϵ_s denote the optical and static dielectric constants; $\epsilon_\infty = 5$, $\epsilon_s = 21.5$ [17], whilst $\nu_0 = 1.7 \times 10^{13}$ Hz [17, 18].

The polyhedral structure of the first Brillouin zone of the fluorite structure is well approximated by a sphere of radius w_0 , defined by

$$(2\pi)^3 / \Omega = 4\pi w_0^3 / 3 \rightarrow w_0 \simeq 2\pi/a_0 \tag{23}$$

permitting the RHS of (21) to be evaluated approximately by integration: the result is

$$\epsilon_a = (e^2/a_0)(1/\epsilon_\infty - 1/\epsilon_s)[1 - (a_0/2\pi g)\text{Si}(g w_0)] \tag{24}$$

where $g \equiv |\mathbf{g}| (= a_0/\sqrt{2})$. Evaluation using the above parameter values yields

$$\epsilon_a = 0.25 \text{ eV} \tag{25}$$

—which is gratifyingly close to the experimental value of (0.28 ± 0.02) eV and indicates that the deployed continuum approximation of the carrier–lattice interaction is much more accurate than might have been supposed, given that for *small* polarons the dominant contribution arises from the *short-range* part of this interaction.

It is now necessary to check that the basic inequality (2) governing the formation of small polarons is satisfied. Within the Lang–Firsov formulation, the small-polaron self-energy, E_p is given by

$$E_p = -\frac{\hbar\nu_0}{2N} \sum_w |V_w|^2 \tag{26}$$

which, with the same continuum approximation as used for the calculation of ϵ_a , reduces to

$$E_p = -(2e^2/a_0)(1/\epsilon_\infty - 1/\epsilon_s). \tag{27}$$

This invites the introduction of an effective dimensionless coupling constant, γ , defined by

$$\gamma \equiv (2e^2/a_0)(1/\epsilon_\infty - 1/\epsilon_s)/\hbar\nu_0 \tag{28}$$

in terms of which

$$E_p = -\gamma h\nu_0. \quad (29)$$

γ thus replaces the coupling constant, α , of large-polaron theory†. Evaluation of γ using the above UO_2 parameters values yields

$$\gamma \simeq 11 \quad (30)$$

whence, from (29),

$$E_p \simeq -0.8 \text{ eV}. \quad (31)$$

In accordance with the remarks following (2) and (11), this value of E_p must be compared with the half-width of the lower Hubbard hole 'band', W_h , which, in terms of the empirically determined (effective) overlap integral, J , is given by

$$W_h/2 = zJ. \quad (32)$$

Thus for UO_2 with $z = 12$ and $J = 0.04 \text{ eV}$, the basic inequality ((2) with $W \rightarrow W_h$) required for small-polaron formation is indeed satisfied.

Knowing the value of γ , it is now possible to investigate how well the following condition—which ensures that the small polarons move by *multi*phonon transitions (i.e. by hopping)—is satisfied:

$$T \gg T_0 (= h\nu_0/2k \sinh^{-1} \gamma). \quad (33)$$

Evaluation of T_0 indicates‡ that $T_0 \simeq 130 \text{ K}$; thus for $T \gg 130 \text{ K}$, the probability of a nearest-neighbour intersite transition as a *multi*phonon process dominates§ that by tunnelling in a small-polaron band with *no* change in the number of phonons ('diagonal' transitions in Holstein's terminology); the onset on the associated activated behaviour in the drift mobility is clearly evident in figure 4 of [3].

With the establishment of band transport in UO_{2+x} at $T < 130 \text{ K}$, the activation energy for semi-conduction should exhibit a reduction, corresponding to the *loss* of the *mobility* activation energy which characterizes the hopping regime. Any residual conductivity activation energy must then be connected with the energy required to free the holes from their associated interstitial (excess) O ions (or clusters thereof) i.e. the holes are *not* free as they are at higher temperatures. In this circumstance, the thermoelectric Seebeck coefficient should develop a T dependence with an activation energy equal to that of the conductivity; the onset of such a T dependence is already evident in the Seebeck coefficient of UO_{2+x} at $T < 500 \text{ K}$ [1]. Thus, for $130 \text{ K} < T < 500 \text{ K}$ the conductivity activation energy should exhibit an *increase* above the values realized at $T > 500 \text{ K}$ and at $T < 130 \text{ K}$ —precisely the behaviour observed in the data of Ishii *et al* [19], but at somewhat higher temperatures ($500 \text{ K} \leq T \leq 600 \text{ K}$).

To conclude our discussion of the non-adiabatic hopping exhibited by Bates' B-38-C sample of UO_{2+x} with $x \leq 10^{-3}$ at $T \gg 130 \text{ K}$, attention is drawn to some additional inequalities, which Lang and Firsov show are entailed by their analysis.

† $\alpha \equiv \frac{1}{2}(e^2/r_p)(\epsilon_\infty^{-1} - \epsilon_s^{-1})/h\nu_0$, where r_p is the large-polaron radius defined by $r_p \equiv \sqrt{\hbar/2m^*\omega_0}$. For $m^* \geq m$, $\alpha \geq 2$, and $r_p \leq 7.4 \times 10^{-10} \text{ m}$, entailing the *inapplicability* of large-polaron theory to UO_2 for $m^* \geq 4m$, when r_p becomes *less* than the inter-cation separation, $a_0/\sqrt{2} (\simeq 3.9 \times 10^{-10} \text{ m})$.

‡ It may be noted that this value of T_0 is consistent with the rough estimate of $h\nu_0/4k$ as the temperature that demarcates hopping and band motion.

§ i.e. the probability that $\Gamma_1 \gg W_p/\hbar$, where W_p is the width of the small-polaron hole band defined by $W_p = W_h e^{-S(T)}$, where [8] $S(T) = (1/2N \sum_w |V_w|^2 (1 - \cos w \cdot g) \coth(h\nu_0/2kT))$. At $T = 1000 \text{ K}$, $S \simeq 8$, which ensures the required inequality is well satisfied. (N has the same meaning as in (21).)

(i) The restriction to nearest-neighbour hopping subsumed in their formulation is valid provided a second parameter, η_3 , satisfies

$$\eta_3 \ll 1 \quad (34)$$

where η_3 is defined by

$$\eta_3 \equiv J^2/\epsilon_a kT. \quad (35)$$

Evaluation, via (17) and (18), indicates that this inequality is well satisfied at $T = 1000$ K, where

$$\eta_3 = 0.07.$$

(ii) η_2 can be expressed in terms of a hop duration time, t_0 , defined by

$$t_0 \equiv \hbar/\sqrt{\epsilon_a kT} (\simeq 4 \times 10^{-15} \text{ s, at } T = 1000 \text{ K}) \quad (36)$$

which satisfies

$$t_0 \ll \Gamma_1^{-1} (\simeq 2 \times 10^{-12} \text{ s}) \quad (37)$$

where Γ_1 is defined by (11); this inequality indicates that the hopping is Markoffian. In addition, Γ_1 satisfies

$$\Gamma_1 (\simeq 5 \times 10^{11} \text{ s}^{-1}) \ll \nu_0 (1.7 \times 10^{13} \text{ s}^{-1}) \quad (38)$$

which ensures that after the hole has made a multiphonon transition to a neighbouring site it has time to stabilize the polarization fluctuation before hopping to another site.

3. Implications for the intrinsic conductivity regime

It is now generally accepted that the onset of intrinsic semiconduction in $UO_{2\pm x}$ near† 1400 K ($= T_i$) is connected [20] with the formation of small polarons by carriers occupying states in both the upper *and* lower Hubbard ‘bands’—the carriers themselves being produced by the following thermally induced disproportionation of the Mott-insulating ground state, first considered by Catlow and Lidiard [21]:



The onset of the intrinsic semiconductivity is reflected in a marked increase in the conductivity activation energy, near T_i , from the value that characterizes the lower-temperature (extrinsic) regime.

As first noted by Hyland and Ralph [12], the T independence of the (negative) *intrinsic* Seebeck coefficient discovered‡ by Bates [22]—and corroborated much later by Killeen [23]—is consistent with equal conductivities of the electrons and holes associated with the

† The precise temperature depends on the degree of non-stoichiometry, x .

‡ The trend of the (positive) extrinsic Seebeck coefficient *towards* zero is clearly evidence in figure 7 of the earlier work of [1].

U^{3+} and U^{5+} ions, and hence with their equal *mobilities*. On the reasonable premise that the hopping character of the U^{5+} holes is *independent* of their mode of formation, it then follows that the intrinsic (thermally produced) carriers in both the lower and upper Hubbard 'bands' are unstable against small-polaron formation, and at the (high) temperatures concerned ($T \gg \hbar\nu_0/4k$) move non-adiabatically between localized states by multiphonon transitions. Consequently, the formation energy of the altered-valency states in (39) is *precisely*† the Mott–Hubbard energy gap U , discussed in section 1—an empirical evaluation of which can thus be obtained from the activation energies (ϵ_a^i and ϵ_a^x , respectively) that characterize the intrinsic and extrinsic regimes—that of the latter being simply the mobility component of the former; thus

$$U = 2(\epsilon_a^i - \epsilon_a^x) \quad (40)$$

whilst the associated formation entropy, ΔS , is given‡ by

$$\Delta S = 2k \ln(x \sigma_1^i / \sigma_1^x) \quad (41)$$

where the σ_1 are the non-adiabatic prefactors introduced in (13). Fitting (13) to the conductivity data of sample B-38-C in both intrinsic and extrinsic regimes yields

$$\epsilon_a^i = (1.62 \pm 0.04) \text{ eV} \quad \epsilon_a^x = (0.28 \pm 0.02) \text{ eV}$$

$$\sigma_1^i = (4.1 \pm 0.8) \times 10^{11} (\Omega \text{ m})^{-1} \text{ K}^{3/2} \quad \sigma_1^x = (1.1 \pm 0.3) \times 10^7 (\Omega \text{ m})^{-1} \text{ K}^{3/2}$$

whence (assuming an x -value of 0.001)

$$U = (2.68 \pm 0.09) \text{ eV} \quad \Delta S/k \simeq (7 \pm 1). \quad (42)$$

These values of U and ΔS are quite different from those deduced in [12] using not tabulated data but Killeen's (Arrhenius) *parametrization* [23] of his own data, which did *not* correctly reflect the non-adiabatic character of the hopping in UO_{2+x} , established above. It is clearly important to now investigate the repercussions of the present re-evaluation of U and ΔS on other conductivity-dependent properties of the material such as the ambipolar contribution to thermal conductivity; this will be done elsewhere.

Applying the law of mass action to the equilibrium represented by (39) yields, in the intrinsic regime—where $[U^{3+}] = [U^{5+}]$ ($\equiv n$, say) —

$$n^2 / (1 - 2n)^2 = e^{-U/kT} e^{\Delta S/k} \quad (43)$$

so that for $2n \ll 1$, n is given approximately by

$$n \simeq n_0 = e^{-U/2kT} e^{\Delta S/2k} \quad (44)$$

Calculation of $n_0(T)$ using the new values of U and ΔS deduced above (42), indicates an increase from a value approximately equal to that of x ($\equiv 0.001$) near 1500 K to 0.23 at

† In the sense that the small-polaron relocalization actually effects the realization of the 'atomic limit' often invoked in the theory of Mott insulators.

‡ It should be stressed that the appearance of x in (41) is an artifact of the adopted mode of analysis— σ_1^x itself being linearly proportional to x ; this ensures that ΔS is *independent* of x (as, of course, it must be, since it refers to the intrinsic regime).

melting (T_m)—a value so large that it invalidates the approximation leading to (44), and necessitates a reversion to the exact equation (43) — the solution of which for $n(T)$ can be expressed in terms of $n_0(T)$ as follows:

$$n(T) = n_0(T)/[1 + 2n_0(T)]. \quad (45)$$

This yields $n(T_m) \simeq 0.15$ —a value some 30% lower than $n_0(T_m)$, and a reduction one might anticipate would be reflected as a *sublinear departure from the $\ln(\sigma T^{3/2})$ versus T^{-1} line* at the highest temperatures—a trend that should be further enhanced by the reduction in mobility activation energy that must occur at high carrier concentrations as more than one carrier starts to compete for the *same* lattice distortion.

The empirical *absence* of such behaviour in the data of sample B-38-C does not necessarily negate these considerations, however, in consequence of another effect which becomes important at high carrier densities, and which acts in the *opposite* direction—namely that U becomes a *decreasing* function of n , through screening effects—as first pointed out by Fröhlich [24] (and later elaborated by Yoffa and Adler [25])—a decrease that, under appropriate conditions, can actually result in a phase transition to a metallic state! Whilst (empirically) this does *not* occur in $UO_{2\pm x}$ (at least at $T < T_m$), *some* (subcritical) reduction in the magnitude of U must quite generally be anticipated, entailing a compensating *superlinear* trend *above* the $\ln(\sigma T^{3/2})$ versus T^{-1} line.

4. Discussion

Whilst a reasonably self-consistent treatment of small-polaron hopping in $UO_{2\pm x}$ is afforded by the Lang-Firsov formulation adopted above—which indicates that in the case of the polycrystalline data analysed the hopping is *non-adiabatic*—this formulation (in common with most others) considers the interaction of an electron *only* with the LO mode of the lattice vibrations. In view of the large cation-anion mass difference in UO_2 , however, *acoustic* modes might be anticipated to be active in polaron scattering—as first pointed out by Meijer and Polder [26] in another connection, and actually considered (but not quantified) within the context of small-polaron theory by Sewell [27]. Clearly, it would be desirable to extend the present analysis to include the effect of this additional interaction; this will be done on another occasion.

Finally, attention is drawn to the values of the self-energies (E_p) of the additional electron and hole associated with U^{3+} and U^{5+} (i.e. the so-called small-polaron binding energies), which can be extracted from the microscopic HADES calculation [28] of the Mott-Hubbard energy U (equal to the formation energy associated with the disproportionation equilibrium represented by (39)); here, certain polarization energies (which will shortly be related to E_p) reduce† U below the value ($I + A$), where $I (> 0)$ and $A (< 0)$ are, respectively, the ionization energy and electron affinity of the U^{4+} ion, as defined by the decomposition of (39) into the sum of the following two processes:



† Thus in the case of U^{3+} , for example, the *additional* electron induces a polarization of the local ionic environment with which the other two interact attractively, thereby effectively reducing the overall on-site Coulomb repulsion.

Taking polarization effects into account, U is given by

$$U = I + A + [P(3+) + P(5+)] \quad (47)$$

where $P(3+)$ and $P(5+)$ denote the energy gains arising from the polarization induced by the altered-valency U^{3+} and U^{5+} cations, and includes contributions both from the displacement of the nuclei of the surrounding ions and from the deformation of their electron shells. Using a Madelung potential energy ($= -39.67$ eV), corresponding to the value of the lattice constant ($= 5.5 \times 10^{-10}$ m) assumed in the calculations of section 2, HADES yields the following values for the polarization energies:

$$P(3+) = -5.02 \text{ eV} \quad P(5+) = -6.05 \text{ eV}. \quad (48)$$

It is to be noted that $P(5+)$ is *not* identifiable with the small-polaron self-energy, E_p , since the latter, as defined by (27), involves *only* the effect of *displacement* of the ions surrounding the site of the supernumerary hole, since the ultraviolet polarization associated with the deformation of the ionic electron shells is always fully excited; it is precisely the removal of this latter contribution that the $(\epsilon_{\infty}^{-1} - \epsilon_s^{-1})$ factor in (27) effects. Thus E_p must be compared, not with $P(5+)$, but rather with $[P(5+) - P_{\text{opt}}(5+)]$, where $P_{\text{opt}}(5+)$ is value of the polarization energy calculated holding the nuclei of the ions surrounding the U^{5+} cation *fixed* at their equilibrium lattice sites and allowing only the electron shells to relax.

The HADES results for these 'optical' polarization energies are

$$P_{\text{opt}}(5+) = -3.53 \text{ eV} \quad P_{\text{opt}}(3+) = -3.12 \text{ eV}. \quad (49)$$

Thus

$$[P(5+) - P_{\text{opt}}(5+)] = -2.52 \text{ eV} \quad (50)$$

—a value which is approximately a factor of three *larger* than that of E_p ($= -0.8$ eV) given by (31). The *approximate* equality of $[P(5+) - P_{\text{opt}}(5+)]$ and $[P(3+) - P_{\text{opt}}(3+)]$ entailed by (48) and (49) is, however, gratifying, in view of the *exact* equality of the electron (U^{3+}) and hole (U^{5+}) activation energies, ϵ_a , implied by the T -independent Seebeck coefficient of the intrinsic regime, which underlies the analysis of section 3 based on [12]; for ϵ_a and E_p are closely related, as can be seen by comparing (21) and (26).

Whilst it is tempting to attribute the discrepancy between the value of E_p given by (31) and the one that can be extracted (50) from the HADES calculations to inadequacies in the interatomic potentials used in the latter, it should be noted that the HADES value of U_{opt} —calculated using above values of P_{opt} —is actually *more* discrepant with the corresponding empirical value deduced [30] from optical experiments (in which the nuclei do *not* have time to relax) than is the (thermal) value U_{th} —calculated using the *full* P values—with the empirical value deduced in section 3 (42) from low-frequency (DC) electrical conductivity data!; thus

$$U_{\text{opt}}(\text{HADES}) = 8.1 \text{ eV} \quad \text{cf } U_{\text{opt}}(\text{experiment [30]}) = (4.6 \pm 0.8) \text{ eV}$$

$$U_{\text{th}}(\text{HADES}) = 3.64 \text{ eV} \quad \text{cf } U_{\text{th}}(\text{experiment}) = (2.68 \pm 0.09) \text{ eV}.$$

These discrepancies cannot be due to errors in the employed *calculated* [31] values of the Uranium ionization potentials, since correcting the calculated value of U_{th} to agree with

experiment *still* leaves an unacceptably large error in U_{opt} ; in any case, since only *differences* in ionization energies are involved, any systematic errors arising from inadequacies in the treatment of (atomic) electron correlations within the methodology used to calculate the required ionization energies might reasonably be anticipated to intercancel. Thus, if the experimental values of U_{opt} and U_{th} (42) are accepted, it must be concluded that the source of the discrepancies with the corresponding *calculated* values is the way in which the relaxation of the electron shells is treated within the context HADES, which requires values of both the U and O ionic polarizabilities—both of which continue to be plagued with uncertainties—notwithstanding the agreement of the calculated ϵ_{∞} value with experiment.

It should be noted, however, that *without* such large values $P(3+)$ and $P(5+)$ as reported in (48), it is impossible to reduce U (HADES) to the cited value of 3.64 eV—which is, in any case, still 1 eV higher than the empirical value! On the other hand, given the good agreement between the value of the mobility activation energy, ϵ_a , calculated using small-polaron theory and the experimental value (0.28 eV) deduced by fitting $\ln(\sigma T^{3/2})$ versus T^{-1} to σ data from the extrinsic regime, it is difficult to accept that the corresponding small-polaron calculation of $E_p(5+)$ via (27) could be in error to the extent implied by HADES—especially when HADES predicts [32] a value of ϵ_a (≈ 1 eV) which is so far in excess of the empirical value.

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References

- [1] Wolfe R A 1963 *AEC Research and Development Report (April)* WAPD-270
- [2] De Coninck R and Devreese J 1969 *Phys. Status Solidi* **32** 823–9
- [3] Iida S 1965 *Japan. J. Appl. Phys.* **4** 833–8
- [4] Devreese J 1963 *Bull. Soc. Belge Physique Sér. III* 259–62; see also Nagels P, Devreese J and Denayer M 1964 *J. Appl. Phys.* **35** 1175–80
- [5] Gruen D M 1954 *J. Am. Chem. Soc.* **76** 2117–20
- [6] Aronson S, Rulli J E and Schaner B E 1961 *J. Chem. Phys.* **35** 1382–8
- [7] Heikes R R and Johnston W D 1957 *J. Chem. Phys.* **26** 582–7
- [8] Lang J G and Firsov Y A 1963 *Sov. Phys. —JETP* **16** 1301–12
- [9] Devreese J, De Coninck R and Pollak H 1966 *Phys. Status Solidi* **17** 825–9
- [10] Tateno J 1984 *J. Chem. Phys.* **81** 6130–5
- [11] Ohmichi T, Takeshita H, Fukushima S and Maeda A 1987 *J. Nucl. Mater.* **151** 90–4
- [12] Hyland G J and Ralph J 1983 *High Temp.—High Pressures* **15** 179–90
- [13] Yoffa E, Rodrigues W A Jr and Adler D 1979 *Phys. Rev. B* **19** 1203–12
- [14] Bates J L 1967 Battelle Northwest Laboratory-296 Pt 2
- [15] Sumi H 1972 *J. Phys. Soc. Japan* **33** 327–42
- [16] Dudley N J, Coble R L and Tuller H L 1981 *J. Am. Ceram. Soc.* **64** 627–31
- [17] Schoenes J 1980 *Phys. Rep.* **63** 301–36
- [18] Dolling G, Cowley R A and Woods A D B 1965 *Can. J. Phys.* **43** 1397–413
- [19] Ishii T, Naito K and Oshima K 1970 *J. Nucl. Mat.* **36** 288–96
- [20] MacInnes D A 1980 *Proc. Int. Symp. on the Thermodynamics of Nuclear Fuels (Jülich, 1979)* vol 2 (Vienna: IAEA) pp 129–39

- [21] Catlow C R A and Lidiard A B 1974 *Thermodynamics of Nuclear Fuels* vol 2 (Vienna: IAEA) pp 27–43
- [22] Bates J L 1966 *Symp. on Thermodynamics with Emphasis on Nuclear Materials and Atomic Transport in Solids (Vienna, 1965)* vol 2 (Vienna: IAEA) pp 73–88
- [23] Killeen J C 1980 *J. Nucl. Mater.* **88** 185–92
- [24] Fröhlich H 1966 *Quantum Theory of Atoms, Molecules and the Solid State* ed P O Löwdin (New York: Academic) pp 465–8
- [25] Yoffa E and Adler D 1979 *Phys. Rev. B* **20** 4044–61
- [26] Meijer H J G and Polder D 1953 *Physica* **19** 255–64
- [27] Sewell G L 1958 *Phil. Mag.* **3** 1361–80
- [28] Catlow C R A 1978 *J. Chem. Soc. Faraday Trans. II* **74** 1901–8; for later refinements see [29]
- [29] Jackson R A, Murray A D, Harding J H and Catlow C R A 1986 *Phil. Mag. A* **53** 27–50; 1987 *J. Chem. Soc. Faraday Trans. II* **83** 1171–6
- [30] Baer Y and Schoenes J 1980 *Solid State Commun.* **33** 885–8
- [31] Grant I P and Pyper N C 1978 *J. Chem. Soc. Faraday Trans. II* **74** 1885–900
- [32] Harding J H 1994 personal communication