Observation of Oxygen Frenkel Disorder in Uranium Dioxide above 2000 K by Use of Neutron-Scattering Techniques

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(Received 13 December 1983)

Diffraction and coherent diffuse quasielastic scattering of neutrons have been used to investigate Frenkel disorder of the oxygen sublattice in single crystals of stoichiometric UO_2. Measurements were made up to 2900 K using a special high-temperature furnace. The results provide the first direct evidence for the occurrence of Frenkel disorder in UO_2 and enable estimates of the defect concentration and activation energy to be made.

PACS numbers: 61.70.Bv, 28.40.Gp, 61.12.-q, 65.50.+m

The importance of uranium dioxide, UO_2, as a nuclear reactor fuel has resulted in a great deal of attention being paid over recent years to a thorough understanding of its thermodynamic and transport properties. Crucial to the interpretation of data on the enthalpy and thermal conductivity, and to the extrapolation of these data to the melting temperature, $T_m = 3120$ K, needed in safety calculations, is the possible occurrence of Frenkel disorder in the oxygen sublattice. However, despite much speculation and discussion in the literature there has been no direct experimental evidence for such disorder in UO_2. It is now well established that in other compounds with the fluorite structure, such as the halides PbF_2, $SrCl_2$, and CaF_2, there is a buildup of dynamic anion Frenkel disorder which gives rise to a diffuse specific-heat anomaly at a temperature $T_c \sim 0.8 T_m$, and to a rise of anion electrical conductivity to a value close to that of the ionic melt. Indeed, these halides form a relatively simple example of fast-ion conductors and as such have been extensively studied.[1] In this Letter we report the investigation of oxygen Frenkel disorder in single crystals of stoichiometric UO_2 using techniques of neutron scattering and data analysis which we have previously developed in a comprehensive investigation of the anion disorder in the halide fluorites.[2-4] In that work it was shown that the dynamic disorder can be modeled in terms of short-lived clusters comprising anion Frenkel interstitials, anion vacancies, and relaxed anions, with lifetimes of $\sim 10^{-12}$ sec. With use of such a model the main features of the diffraction data and of the coherent diffuse quasistatic scattering, $S(\vec{Q})$, observed in the fast-ion phase, could be explained consistently. The present work has involved the use of a new high-temperature furnace for neutron-scattering experiments[5] which has enabled data on single crystals of UO_2 to be taken up to ~ 2900 K, the highest temperature yet attained for these types of measurements.

The enthalpy of UO_2 exhibits an exponential increase above ~ 1500 K which cannot be accounted for by contributions from harmonic lattice vibrations and a dilation term alone.[6] Possible contributions from anharmonic lattice vibrations of the oxygen ions[7] and from excitations of crystal-field levels of the U^{4+} ion are estimated to be too small to account for this "anomalous" increase, which early workers[8,11] attributed to the excitation of lattice defects of the Frenkel type. However, MacInnes[12] has pointed out that the nature of the anomaly differs in some detail from that observed in the halide fluorites and has suggested that excitation of electronic transitions of the small-polaron type,[13] represented by $2U^{4+} \leftrightarrows U^{5+} + U^{3+}$, have a lower activation energy and are more likely to be the principal cause of the anomaly. Such electronic activity can also account for the increase in thermal conductivity above 1500 K.[14,15] Very recently Browning, Hyland, and Ralph[16] have shown that by using the best estimate of the contributions of harmonic lattice vibrations, dilation, anharmonic vibrations, crystal-field excitation, and small-polaron excitation, they can account for the enthalpy data up to 2500 K. However, above this temperature they claim that there is an unexplained increase which could possibly be due to Frenkel disorder. In contrast, Fink *et al.*[17,18] suggest that the enthalpy data indicate a "phase transition" in UO_2 at 2670 K, but show no evidence of Frenkel disorder. The enthalpy data may therefore be interpreted to indicate an appreciable contribution from either electronic or Frenkel disorder, or both. Direct evidence for the extent of each type of disorder is badly needed.

Neutron-scattering techniques provide a convenient probe of lattice disorder in UO_2 since uranium and oxygen have similar scattering lengths and very small incoherent cross sections. Diffraction enables a time-averaged distribution of the ions within a unit cell to be obtained, as well as information on the average lattice vibrations. Coherent diffuse scattering is only observed from a system if it is disordered, and the function $S(\vec{Q})$ is directly related to the instantaneous correlations between the disordered ionic positions. If the diffuse scattering is quasielastic (QES) the temporal behavior of these correlations may be probed by measurement of the scattering function $S(\vec{Q},\omega)$. Preliminary neutron-diffraction measurements on UO_2 and a search for diffuse scattering up to $\simeq 2400$ K have been reported previously.[5]

The present measurements were made on single crystals cut in the form of cylinders from boules of UO_2 obtained from Degussa A.G. The five samples (Nos. 1–5) investigated by diffraction were ~ 1.6 mm in diameter and 4 mm long, and the three samples (Nos. 6–8) examined for diffuse scattering were $\simeq 8$ mm in diameter and 15 mm long. All the samples were reduced in an atmosphere of hydrogen at 1773 K for several hours to ensure stoichiometry which was verified by chemical analysis. They were then sealed by electron-beam welding under vacuum in chemical-vapor-deposited tungsten cans which had been coated with TaN. The cans were mounted in the furnace by welding them to tungsten support tubes, which were attached at the low-temperature end. These acted as sight tubes for an infrared pyrometer for the highest-temperature measurements. At temperatures up to ~ 2300 K, W/W-26% Re thermocouples were used. Temperature stability was to $\pm 10°$, and the overall accuracy estimated to be $\pm 40°$ at the highest temperatures. The diffraction measurements up to 1900 K were made at the Institut Laue-Langevin, Grenoble, with use of the D15 diffractometer, and the remainder were made by use of the Mark VI diffractometer in DIDO at Harwell. The incident neutron wavelengths were 1.175 and 1.092 Å, respectively. The diffuse QES measurements were made with the triple-axis spectrometer in PLUTO, Harwell, with constant $k_i = 2.673$ Å^{-1}. Pyrolytic graphite (002) planes were used to monochromate and analyze the neutron energies, and horizontal collimation angles of 96′-40′-30′-60′ before the monochromator, sample, analyzer, and counter, respectively, gave an overall energy resolution full width at half maximum of 1.0 meV.

In both types of measurement some deterioration of the sample occurred at the highest temperatures, most probably due to evaporation. During the diffraction measurements a standard reflection was measured at regular time intervals at each temperature, and the intensities of the other reflections were normalized with use of the smoothed time variation of the standard. This procedure proved quite reproducible and consistent as judged by the intensities of equivalent Bragg peaks. As an additional check on the stoichiometry, data were taken at ambient temperature before and after each cycle of high-temperature diffraction measurements. In each case the best fit was obtained with the regular fluorite structure, $Fm3m$; that is, a face-centered cubic lattice of side a_0 with a basis of a U^{4+} ion at the origin and O^{2+} ions at the $\pm(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ positions. An extensive set of data from one sample measured at 293 K was analyzed in terms of the regular fluorite structure to yield a value of the scattering length of uranium $b_U = 0.8417 \pm 0.0017 \times 10^{-12}$ cm relative to that of oxygen $b_O = 0.5805 \times 10^{-12}$ cm, in excellent agreement with a recent neutron interferometer measurement.[19] In order to determine the presence of any Frenkel disorder, a fraction, n_d, of oxygen ions were allowed to leave their regular sites when fitting to the high-temperature data. These were assumed to occupy either or both of two extra defect sites in the "empty" oxygen cubes: the twelve "I," interstitial, sites at positions $\pm(\frac{1}{4}+y,\frac{1}{4}-y,0)$ and the eight "R," relaxed anion, sites at $\pm(x,x,x)$ relative to the cation sites. The relative population of these sites was assumed to be given by six different models, described by Dickens *et al.*,[3] and these were each fitted to the data at each temperature. The best-fitting model was judged to be that giving the lowest weighted R factor, which was generally in the range 4%–6%, compared with values of $\simeq 25\%$ if the data at the highest temperatures were fitted by the regular fluorite structure. The parameters fitted at each temperature, in addition to n_d, were a scale and extinction parameter, isotropic thermal parameters B_i for the uranium ($i = \mathrm{U}$) and oxygen ($i = \mathrm{O}$) regular sites and the extra defect sites ($i = R$ and I), an anharmonic thermal parameter C_{123}^{0} for the regular oxygen site,[20] and the positional parameters x and y. The data were corrected for thermal diffuse scattering. The regular fluorite structure (Model I) best fitted the data only at 293 K. Above 1800 K some disorder was indicated, with Model II, allowing vacancies on the oxygen sublattice with defective anions spread uniformly over the cell, or Model V, with the defective anions only populating the R sites, giving the better fits in the range to 2403 K. Model VI, with a ratio of population of I to R sites of 1:2, fitted the data best at 2572 K and above. The latter corresponds to 3:1:2 clusters of defective anions [where the ratio denotes vacancies:(true interstitial):(relaxed ions)], each cluster comprising a Frenkel pair with a true interstitial anion near the midoxygen position causing its neighbors to relax into R sites in the adjacent empty cubes.[4] For the 3:1:2 clusters the fraction of oxygen anions forming Frenkel defects is $n_f = n_d/3$. The optimum values of $x = 0.34 \pm 0.01$ and $y = 0.05 \pm 0.03$ were almost independent of temperature, and the values of n_d determined were found to be relatively insensitive to the model fitted. The values of n_d given by the best-fitting models are plotted in Fig. 1(a), where it is clearly seen that oxygen disorder occurs above $\simeq 2000$ K, and that it increases with temperature increase.

A confirmation of the occurrence of oxygen-lattice disorder is given by the observation of coherent diffuse QES above 2000 K in each of the three samples investigated. The intensity observed at zero energy transfers from sample 6 as the scattering vector is scanned along the [100] direction is shown in Fig. 2 where it is compared with that observed from CaF_2.[2] Energy analysis of the scattering from UO_2 shows it to be quasielastic, with energy width increasing with temperature increase. The $\vec{Q}$ and ω dependence is qualitatively similar to that found in the halide fluorites, and since the scattering from CaF_2 can be well accounted for in terms of defect clusters[2,4] similar to the 3:1:2 clusters described above, the presence of the scattering in UO_2 gives strong evidence for the occurrence of oxygen Frenkel disorder. In the case of CaF_2, the peak integrated diffuse QES intensity is found to move away from the (200) point along [100] as the temperature is increased between 1373 and 1513 K.[4] The intensity of the QES from UO_2 is also found to peak along [100], near (2.15,0,0). The intensity from sample 8 at this point, integrated over energy transfer, was normalized by comparison with the integrated intensity of the TA phonon at (1.85,1.15,0) measured at the same temperature, to give the scattering per anion $X(\vec{Q}) = S(\vec{Q}) \times \exp(2B_0 \sin^2\theta/\lambda^2)$. This is shown in Fig. 1(b), where it is seen that above 2000 K the intensity builds up in a similar manner to that of n_d determined from diffraction. The comparison may be carried further by adopting the 3:1:2 cluster model of the disorder, in which case the maximum QES intensity per *defective* anion, $Y(\vec{Q})$, may be calculated.[4] $Y(\vec{Q})$ is found to peak near (2.15,0,0) with a

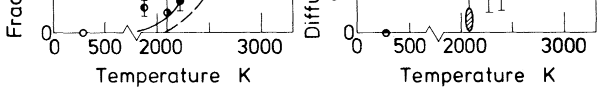

FIG. 1. (a) Temperature variation of $n_d = 3n_f$ deduced from diffraction data on UO_2 under the assumption of a 3:1:2 cluster model. Shading of circles differentiates data from five different samples. Chain line is best fit of activation expression given in text to lower-temperature data. Broken lines denote range of values deduced from diffuse QES. (b) Temperature variation of diffuse QES scattering from UO_2 observed at (2.15,0,0).

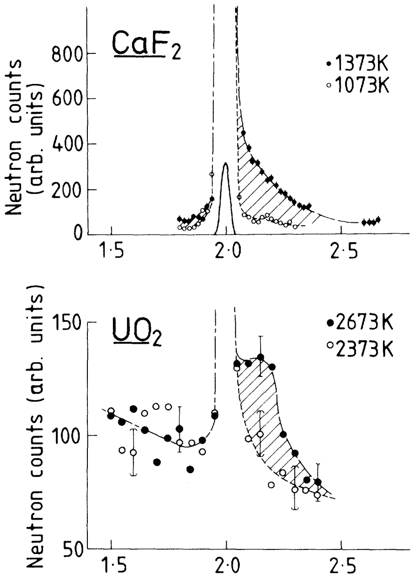

FIG. 2. Elastic diffuse scattering along [ζ00] at two temperatures, from CaF_2 and UO_2. The broken lines are guides to the eye and the shaded region emphasizes the increase in diffuse scattering as the temperature is raised. The solid line indicates the position and width of the (200) Bragg peak. Typical errors are shown.

magnitude dependent on the positional parameters x and y. If two extremes are taken for these parameters, (a) values found from diffraction and (b) values deduced from a hard ionic sphere model, the range of $n_d = X(\vec{Q})/Y(Q)$ shown in Fig. 1(a) is obtained. The overall agreement between the two independent determinations of n_d strongly supports the picture of oxygen Frenkel disorder in the form of clusters of defective anions. From the measured energy width of the scattering we can estimate the cluster lifetime at the highest temperature investigated to be about 3 psec.

The two sets of data described above lead to the firm conclusion that oxygen Frenkel disorder occurs in UO_2 above 2000 K. The variation of the lower-temperature data may be fitted by an expression of the form

$$n_d = 3n_f = (5400 \pm 4000) \times \exp[-(54\,000 \pm 6000)/2kT],$$

suggesting a Frenkel-pair formation energy of $\sim 4.6 \pm 0.5$ eV. However, it must be stressed that at the concentrations of defects measured the presence of interactions may affect the value deduced; indeed, the possibility of saturation at the higher temperatures is suggested by the data. In parallel with the work on UO_2, diffraction measurements have also been made on ThO_2 in which no polaron formation is expected on account of the stable valency of Th^{4+}. Analysis of the data to 2900 K in the manner described above indicates a buildup of oxygen (Frenkel) disorder above ~ 2300 K in this case. It should be noted that just above 2673 K the overall scattering from the larger UO_2 samples examined appeared to decrease more rapidly, and inspection on cooling to 293 K suggested that the crystals had deformed in shape and that a kind of "plastic phase" had been reached. Measurement of elastic constants, to be reported elsewhere, showed a change in the rate of decrease at 2450 K but no highly anomalous softening. This possible "plasticity" is being investigated further, but it is interesting to note that the temperature at which it occurs is close to that originally proposed by Ackerman, Gilles, and Thorn[21] to be the melting temperature of UO_2.

We wish to thank P. Bowen and G. Lander for experimental assistance and advice, and D. Hukin, G. Hyland, J. K. Kjems, D. MacInnes, and M. Rand for helpful discussions. This work has been supported by the Science and Engineering Research Council (U.K.), Atomic Energy Research Establishment, Harwell, and NATO. We acknowledge the use of facilities at the Institut Laue-Langevin, Grenoble.

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