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Note

Premelting Transition in Uranium Dioxide[1]

J. P. Hiernaut,[2] G. J. Hyland,[3] and C. Ronchi[2]

Thermal analysis of the cooling curves of small samples of uranium dioxide, laser heated in a high-pressure autoclave on a subsecond time scale to a temperature just below the melting point, reveals, in the case of nominally stoichiometric $UO_{2.00}$, a significant λ-like heat capacity peak, indicating a premelting transition in this material. The results are discussed and a simple model is presented in terms of which the observed behavior can be described.

KEY WORDS: heat capacity; laser heating; solid–solid transition; uranium dioxide.

Thermal analysis of the cooling curves of small samples of uranium dioxide, laser heated (in a high-pressure autoclave to inhibit evaporation) on a subsecond time scale to a temperature just below the melting point (T_m), reveals, in the case of nominally stoichiometric $UO_{2.00}$, a significant λ-like heat capacity [$C_p(T)$] preak, indicating a premelting transition in this materiai, in common with that found in other fluorite-type crystals near 0.85 T_m.

The contribution presents some interesting new results obtained from the thermal analysis of UO_2 heated under different Redox conditions. The essential new feature is the discovery of a weak inflexion point in the cooling curve of a stroichiometric UO_2 sample initially heated just below the melting temperature. Most interestingly, it is found that the occurrence

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[2] European Institute for Transuranium Elements, Karlsruhe, Germany.

[3] Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom.

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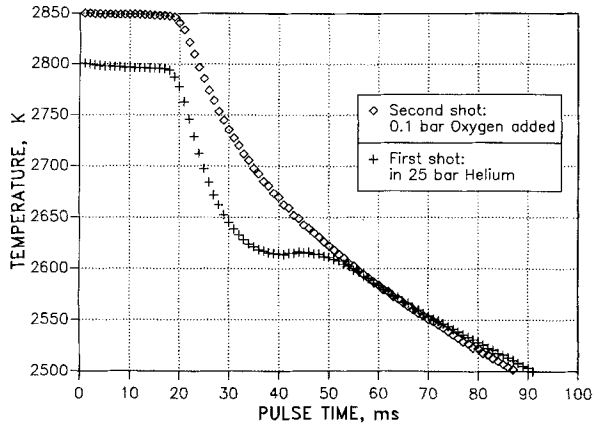

Fig. 1. Cooling curve of a laser-heated sphere (1-mm size) of UO_2, revealing a phase transition around 2630 K (crosses). The same sample heated in an oxidising atmosphere (squares) does not display any localized transition.

of the plateau is sensitively dependent on the oxygen partial pressure in the buffer gas, no plateau being found under *oxidizing* conditions (Fig. 1), while in a reducing environment the plateau typically exhibits *undercooling*, characteristic of a first-order phase transition, the temperature of which is found to increase with increasing reduction of the sample (Fig. 2).

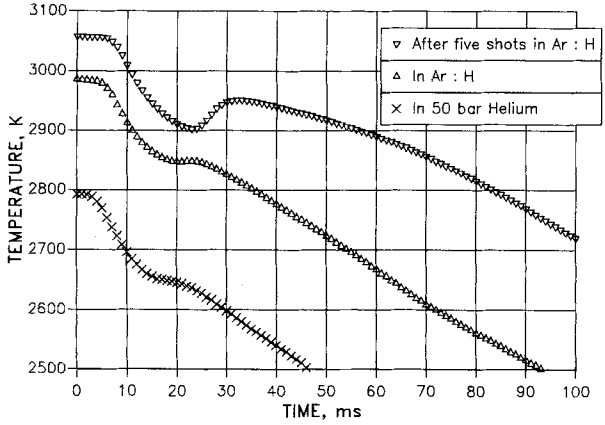

Fig. 2. Same as Fig. 1, but in this case, after an initial shot in helium (crosses), the sample was repeatedly heated in a reducing atmosphere (triangles). The increasingly reduced samples exhibit higher transition temperatures, and in the upper curve "undercooling" is observed, indicating the occurrence of a first-order transition.

Thermal analysis of the cooling curve with respect time yields the heat capacity $C_p(T)$, the inflexion point of the nominally stoichiomatric sample entailing a sharp heat capacity peak (Fig. 3), the existence of which was first *qualitatively* inferred by Dworkin and Breding [1] in (1969, from consideration of the best available enthalpy data [2] on approximately stoichiometric urania. Although our peak is much more λ-like than that obtained from the consequent differentiation of the enthalpy data [3], it is, nevertheless, located at a temperature close to where recent high-temperature neutron scattering experiments [4] indicate a significant increase in the concentration of anion Frenkel defects to a value which appears to saturate between 15 and 20%—a behavior similar to that found in other fluorite structured materials near $0.8T_m$, as the so-called "fast-ion" phase is rapidly, but *continuously*, established.

A simple model is presented in terms of which the observed behavior can be described. The model is based on the hypothesis that the premelting transition is connected with anion Frenkel disorder, whose formation is rendered *cooperative* by attractive interactions between complementary defects (i.e., interstitials and vacancies), which are treated by a mean-field approximation.

The quantitative degree of maximum disorder—realized just above the transition—is, on the other hand, controlled by repulsive interactions between *like* defects, the inclusion of which is adequately accounted by their effect on the configurational entropy.

In stoichiometric urania the phase transition is found to be of *second*

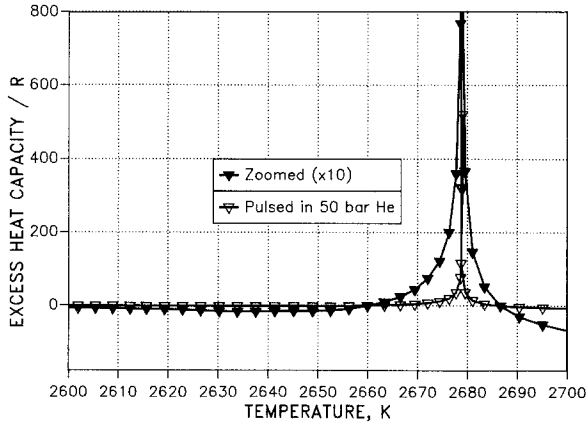

Fig. 3. Measured extracontribution to C_p due to the localized transition in stoichiometric urania. The baseline for $C_p(T)$ was taken from the data of Hein and Flagella [2].

order and characterized by a divergent $C_p(T)$, of the kind reminiscent of a fluid near its *critical point.*

Crucial to reproducing the observed behavior in nonstoichiometric urania is the introduction of a (linear) dependence of the nonconfigurational partial entropy on the prevailing concentration of *intrinsic* Frenkel defects in $UO_{2\pm x}$.

Finally, it was found that the line of the calculated (but unrealized) second-order transition in UO_{2+x} intersects the U_4O_9 phase boundary near where a high-temperature *diffuse* order–disorder transition has been observed in the oxygen superlattice, suggesting that the second-order, λ-like, transition in UO_2 is the fluorite sublattice counterpart of this transition.

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Hubert Van Maele
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