1. Project Title: UKCP WP2

2. Title of Case Study: Ultra-high temperature properties of ZrC: a fully-anharmonic ab-initio approach

3. Summary of Case Study:

Recent advances in finite temperature first-principles methodology have been applied to calculate ultra-high temperature thermodynamic properties of ZrC. These calculations, which represent a first application of such methods within the burgeoning field of ultra-high temperature ceramics (UHTCs), provide fully anharmonic, DFT-level results at temperatures where experimental data is unavailable or inherently unreliable. This data will in future be used within a CALPHAD reassessment of the ZrC phase diagram, leading to an improved understanding of the phase-stability of this material; crucial for understanding its behaviour for applications in, e.g., thermal barriers, also in fission and fusion-reactors.

Calculations are performed within the framework of the UP-TILD approach [Grabowski 2007], but with key improvements in efficiency: Anharmonic vibrations using optimized interatomic potentials are now used in place of quasiharmonic DFT calculations as the reference solution for thermodynamic integration. This advance, developed as a joint collaboration between the present authors and Grabowski et al, has resulted in an order of magnitude improvement in the efficiency of the method, and further significant improvements are expected.

Using the approach, thermal expansion coefficients and heat capacities have been calculated up to the melting-point for ZrC, and compared with available experimental data and calculations performed within the widely used quasi-harmonic approximation. Both quantities are found to be reduced in comparison to the latter, with a ≈ 20% reduction in the thermal expansion coefficient (α_V = 45 x 10^{-6} / K) and a 15 % reduction in the specific heat-capacity (C_P = 74 J/mol/K) at the melting point (T_m = 3805 K). This brings the results more in line with extrapolated trends in the experimental results, and highlights the importance of including fully anharmonic contributions in the calculation of such properties.

4. Key outputs:

DFT-level accuracy thermal properties have been calculated for ZrC (first-of-kind for UHTCs). These are to be used in future CALPHAD re-assessments of the ZrC phase diagram; providing valuable data at temperatures where the experimental data is absent or of low accuracy.

An order of magnitude improvement in efficiency of the (already-competitive) UP-TILD approach has been achieved. The theoretical improvements and algorithm improvements thereof (in collaboration with Blazej Grabowski and Joerg Neugebauer) will be of great value for future calculations using the approach.

5. Names of key academics and any collaborators:

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Blazej Grabowski, Joerg Neugebauer, Dominique Korbmacher, Albert Glensk (Max-Planck-Institut für Eisenforschung, Max-Planck-Strasse 1, 40237 Düsseldorf, Germany)

6. Sources of significant sponsorship (if applicable):

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7. Who should we contact for more information?

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