Investigation of the Negative Thermal Expansion of ZrW_2O_8

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The negative thermal expansion in ZrW_2O_8 was investigated on a microscopic scale by temperature dependent measurements of the electric field gradients at the nuclear probe $^{187}W(\beta^-)^{187}Re$ using time differential perturbed angular correlation spectroscopy. Two distinct nuclear quadrupole interactions $|V_{zz}^{Re1}| = 18.92(4) \cdot 10^{21}$ V/m^2, $\eta^{Re1} = 0.0$ and $|V_{zz}^{Re2}| = 4.55(2) \cdot 10^{21}$ V/m^2, $\eta^{Re2} = 0.053(3)$ were observed at 295 K, which are assigned to the two crystallographically distinct WO_4 tetrahedra of the room temperature structure. Ab initio calculations of electron densities and electric field gradients with 1 : 7 Re-impurities using the full potential linearized augmented plane wave package WIEN97 yield the electric field gradients $V_{zz}^{Re1} = 12.63 \cdot 10^{21}$ V/m^2, $\eta^{Re1} = 0.0$ and $V_{zz}^{Re2} = 4.90 \cdot 10^{21}$ V/m^2, $\eta^{Re2} = 0.0$. The observed temperature dependence of the nuclear quadrupole interactions agrees well with the structural phase transition at 428 K observed by neutron and x-ray diffraction. Our experiments corroborate the suggested mechanism of coupled librations of rigid ZrO_6 octahedra and WO_4 tetrahedra, which is an alternative description of transverse vibrations of oxygen atoms in Zr-O-W bonds, for the negative thermal expansion in ZrW_2O_8.

Key words: ZrW_2O_8; Negative Thermal Expansion; Phase Transition; Time Differential Perturbed Angular Correlation (TDPAC); Hyperfine Spectroscopy.