87e Free Energy of the Solid C60 Orientational Order-Disorder Transition

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Here we show that by using the expanded ensemble Monte Carlo simulation method described, the solid-state free energies and solid-solid phase transitions can be computed accurately. In particular, the free energies of the orientationally ordered crystal phase of C60 at low temperatures and the disordered crystal phase at high temperatures are calculated to an accuracy of ±0.05 kJ/mol. Using the potential model of Sprik et al. [J. Phys. Chem. 96, 2027 (1992)], the order-disorder transition temperature at zero pressure is determined directly from these free energies, and is found to be 218 K. This value is in good agreement with the abrupt changes in configurational energy and unit cell size also found in simulation, although it is somewhat lower than the experimental value of ~260 K due to the inadequacy of the potential. The orientational distinguishability in the ordered phase and the indistinguishability in the disordered phase result in a contribution to the entropy difference of k ln 60, with 60 being the symmetry number of C60. This quantum-mechanical correction for Maxwell-Boltzmann statistics must be taken into account for the accurate prediction of the properties and the phase transition of the C60 crystal.