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The Mobility of Large Anions in Crystals with the Fluorite Structure

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Abstract

The thesis reports several questions that arise in connection with the thermally induced phenomenon called superionic conduction in the case of halides and oxides with the fluorite structure, principally (i) how can such “large” anions in a tightly packed configuration move amongst their neighbours with no apparent disruption? and (ii) how can the experimentally observed “crowdion” structures that involve more than 25% reduction in separation of anions be stable? A third question is posed by the experimentally observed specific heat anomaly that always accompanies the increase in anionic mobility with increasing temperature. The literature review found no answers to these questions, and the thesis records two lines of theoretical research that were followed by the author. Both lines sought mechanisms that would “break degeneracy” and thus allow the observed mobility and clustering. In part 1 the breathing shell concept (Schröder, 1966) is examined. A model was devised to emulate “breathing” by spatially perturbing the potential constraint used by Watson (1958) to calculate the in-crystal wave function for the O^{--} (which has not been observed as a free ion). The energetics calculated from this model are compatible with the thermal effects being studied and a “scenario” of breathing ions leading to short lived clustering is developed. The energetics are non linear, and the “scenario” is expanded qualitatively to suggest the role of various types of solitons. The author concludes that solitons are largely responsible for the “degeneracy breaking” and the specific heat anomaly. However nothing in Part 1 explains the low temperature stability of the fluorite structure where large anions are clustered. In part 2 a quantum mechanical examination of the cohesive energy of the fluorite structure is undertaken in the specific case of doped Zirconium Dioxide for which there was conveniently available basic data. Watson’s wave functions were fed into simple density functionals following the method of Gordon and Kim (1972). This was a seminal and successful application of the so called local density approximation (to a uniform electron gas for the purposes of calculating kinetic and exchange-correlation energies). An improvement is proposed – partitioning the electron population according to orbitals and calculating separate kinetic energies. Using this improvement a double potential well in the cohesive energy is discovered that would explain the clustering of anions in the fluorite structure at low temperatures.

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