A Genuine Jahn-Teller System with Compressed Geometry and Quantum Effects Originating from Zero-Point Motion

First-principle calculations together with analysis of the experimental data found for 3d⁹ and 3d⁷ ions in cubic oxides proved that the center found in irradiated CaO:Ni²⁺ corresponds to Ni⁺ under a static Jahn–Teller effect displaying a compressed equilibrium geometry. It was also shown that the anomalous positive g∥ shift (g∥−g₀=0.065) measured at T ≈20 K obeys the superposition of the |3z²−r²> and |x²−y²> states driven by quantum effects associated with the zero-point motion, a mechanism first put forward by O'Brien for static Jahn–Teller systems and later extended by Ham to the dynamic Jahn–Teller case. To our knowledge, this is the first genuine Jahn–Teller system (i.e. in which exact degeneracy exists at the high-symmetry configuration) exhibiting a compressed equilibrium geometry for which large quantum effects allow experimental observation of the effect predicted by O'Brien. Analysis of the calculated energy barriers for different Jahn–Teller systems allowed us to explain the origin of the compressed geometry observed for CaO:Ni⁺.