Cooperative Jahn-Teller Effect in Transition Metal Complexes

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Introduction

Jahn and Teller in 1937 proved that a nonlinear polyatomic molecule in a nuclear configuration with a degenerate electronic ground state is unstable. As a result of the electronic degeneracy there is a strong vibronic coupling and the molecule distorts.

The cooperative Jahn-Teller effect (CJTE) arises as a consequence of high concentration of Jahn-Teller centers in a solid matrix. The CJTE occurs when the energetically most advantageous crystal state is composed of a correlated static distortion. Intermolecular interactions which give rise to a cooperative distortion lead to a phase transition which is driven by the interaction between localized orbital electronic states and the crystal lattice vibrations. The CJTE has played an important role in understanding the nature of vibronic interactions, which are of general importance in solid state chemistry and physics.

$[Cu(C_5H_5NO)_6]X_2$ Complexes

The structural and magnetic properties of $[CuL_6](BF_4)_2$ and $[CuL_6](ClO_4)_2$ (L = C_5H_5NO) have been investigated as two complexes which exhibit the CJTE. These systems were found to be comprised of antiferromagnetically coupled chains $[CuL_6](ClO_4)_2$ and layers $[CuL_6](BF_4)_2$ at low temperature [1,2]. Furthermore, the low temperature phases were characterized by powder and single crystal EPR studies as undergoing CJT ordering of tetragonally elongated CuL_6 octahedra. The ordering was found to be ferrodistortive in the case of $[CuL_6](BF_4)_2$ and antiferrodistortive in the case of $[CuL_6](ClO_4)_2$ [3,4,5]. The relative stability of the ferro- versus antiferrodistortive phase in the mixed anion system $[CuL_6](ClO_4/BF_4)_2$ showed that antiferrodistortive ordering is energetically favored. In order to elucidate the nature of the coupling between two neighboring CuL_6^{2+} ions, EPR studies have been carried out on semidilute (10 percent) $^{63}Cu/ZnL_6X_2$ complexes. The results show that an antiferrodistortive ordering is dominant [6,7].

1-dimensionally connected octahedral complexes

Another characteristic of the CJTE is multistage phase transitions which arise as a consequence of the dynamic and static Jahn-Teller effects. X-ray diffraction and magnetic susceptibility studies have shown that the hexagonal perovskite $RbCrCl_3$ undergoes multistage phase transitions from the ordered to the partially disordered and finally to the completely disordered phase [8,9,10]. However, interestingly, a heat capacity study shows the presence of an intermediate phase between the ordered and the partially disordered phase. The transition was described as occurring in two steps: second order from the partially disordered to the intermediate phase and possible first order from the intermediate to the ordered phase [11].

2-dimensionally connected octahedral complexes

The perovskite-type compound K_2CuF_4 behaves a two-dimensional Heisenberg-like ferromagnet as a result of cooperative distortion of each F^- octahedron around Cu^{2+} [12]. The magnetic percolation problem of F^- ion square lattice has been investigated for the dilute system $K_2Cu_xZn_{1-x}F_4$ ($1 \geq x \geq 0$) [13]. The results showed that the thermodynamic behavior just at the percolation threshold (x = 0.60) is characterized as having a pronounced one-dimensional ferromagnetic character. On the other hand, the percolation threshold for the 1st and 2nd nearest neighbor coupling was calculated to be 0.59 and 0.41, respectively [13]. On the basis of data from phonon-Raman scattering experiments on the diluted system with various x, Yamada and Natsume [14] suggested that the cooperative network is linked by means of the 2nd nearest neighbor interactions in the region of $0.59 \geq x \geq 0.4$.

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