Jahn-Teller phase transitions in icosahedral molecules

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Non-linear molecules undergo distortions when the orbital degeneracy of the highest occupied level is lifted by the JahnTeller effect. If such molecules or clusters of atoms are coupled to one another, the system may experience a cooperative JahnTeller effect (CJTE). In this paper, we describe a model of how the CJTE leads to the crystallization of the disordered phase. The model Hamiltonian is based on a normal mode decomposition of the clusters in order to maintain the symmetry labels. We take account of the electron-strain and the electron-phonon couplings and, by displacing the coordinates of the oscillators, obtain a term that explicitly couples the JahnTeller centers, enabling us to perform a mean-field analysis. The calculations can be done by coupling the clusters via the infinite-range strain fields where the mean-field approximation becomes exact. The calculation of the free energy then becomes straightforward, and obtaining phase diagrams in various regimes follows from the minimization of this free energy. The results show that the character of the phase transition may change from strong to weak first order and even to second-order, depending on the coupling to the vibrational modes. Taken together, these results may serve as a paradigm for crystallization near the transition temperature, where the atoms tend to form clusters of icosahedral symmetry. These results have already been obtained and published in Journal of Physics. Nonetheless, more accurate results are achieved by explicitly coupling the clusters through their normal-modes interactions. Hence the main challenge is the transformation of the spatial-coordinate Hamiltonian into one solely in terms of the normal modes of the clusters. The translation-symmetry of the system enables Fourier transformation of the coordinates, while the point group symmetry gives insight to the general form of the Hamiltonian. The phase diagrams happen to be easily deduced from the Hamiltonian in the phonon coordinates.

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