

EPR SPECTROSCOPY OF STRUCTURAL PHASE TRANSITION IN CH₃NH₃PbCl₃ HYBRID PEROVSKITE

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Recently, hybrid organic-inorganic compounds have attracted immense attention of the scientific community due to their diverse physical and chemical properties. One of the most interesting and researched subgroups of hybrid perovskites is methylammonium (MA) lead halides MAPbX₃ (where X = I, Br, Cl), due to their potential applications in efficient and low-cost solar cells, LEDs, and photodetectors [1].

Here, we use electron paramagnetic resonance (EPR) spectroscopy to study the dynamics of methylammonium cations and structural phase transitions in methylammonium lead chloride CH₃NH₃PbCl₃. In this work, we employ temperature dependent multifrequency continuous-wave (CW) and pulsed EPR spectroscopy to characterize paramagnetic Mn²⁺ probe ions in MAPbX₃. The temperature dependent CW spectra reveal a sudden increase in the zero-field splitting of the Mn²⁺ ions at about 175 K (Fig. 1). This indicates a first-order phase transition related to the deformation of the inorganic framework due to the tetragonal-orthorhombic symmetry lowering.

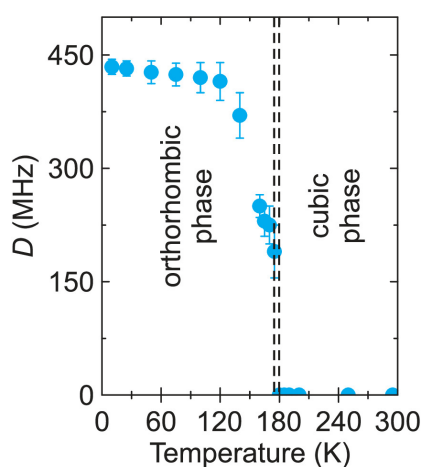


Fig. 1. Temperature dependence of the axial zero-field splitting parameter of MAPbX₃:Mn.

Using pulsed EPR spectroscopy, studying the temperature dependence of the T_1 relaxation time and the decoherence time T_2 of the Mn²⁺ centers in MAPbCl₃, we found that T_1 is governed by the direct process and the Raman process due to optical phonons. We relate the obtained phonon energy of 59(4) cm⁻¹ to the dynamics of the inorganic framework.

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