

A novel property of solids: orientational polarizability induced by the Jahn-Teller and pseudo-Jahn-Teller effect

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In 1912 Debye stated that there might be solids with disordered, almost freely rotating local dipoles. He expected them to undergo orientational polarization under applied electric fields, like in polar liquids. Debye predicted their spontaneous polarization at a low temperature, like the Curie temperature in ferromagnets. According to his estimates, orientational polarizabilities should be by orders of magnitude larger than the displacive ones. The discovery of the first in the long list of solids with these properties, known today as ferroelectrics, followed eight years later. However, the orientational nature of their polarizability was not revealed until our works. We show that such almost-freely rotating, local disordered dipoles occur in solids due to the Jahn-Teller effect (JTE) or pseudo-Jahn-Teller effect (PJTE). Owing to the vibronic coupling, the lower sheet of the adiabatic potential energy surface (APES) is unstable at the high-symmetry point $Q = 0$. Absolute minima of the APES correspond to several low-symmetry distortions of the molecular frame or even a potential trough. In non-centrosymmetric clusters, the corresponding distortion creates an electric dipole. Resonating between these minima wells by tunneling or over-the-barrier transitions, the induced dipoles perform hindered rotations in space, like the molecular dipoles in polar liquids. In external electric fields, the dipolar minima are not equivalent. Trapped in the well lowered by the applied field, the same for all sites, the field-oriented local dipole determines the orientational polarization.

Similarly, in centrosymmetric crystals, like BaTiO_3 , the PJTE in each Ti center induces an off-center displacement of the Ti^{4+} cation creating local dipole moments [1]. The disordered local dipolar distortions resonate between the eight equivalent minima. As a result, they become trapped in the lower well along the electric field. According to numeric estimates, the orientational contribution to polarizability is by orders of magnitude more robust than the one due to the displacive shift of the sublattices. Taking the ZnO:Ni^{2+} crystal as an example for revealing the orientational effect, we significantly extended the methodology for solving JTE problems in tetrahedral systems, including spin-orbital interaction and

tunneling splitting [2]. In this case the Ni^{2+} ions in the tetrahedral environment of the oxygens, subjects to the $T \otimes t_2$ JTE problem, undergo dipolar distortions along one of the four equivalent minima of the adiabatic potential energy surface. The detailed calculations for this system yield its much larger polarizability due to the orientational effect in accordance with the experimental data.

[1] I. B. Bersuker; *Phys. Lett.* **20** 589 (1966); I. B. Bersuker; V. Polinger; *Condens. Matter* **5** 68 (2020);

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