In remembrance of Ortwin Schirmer: the polaron professor. Research in $BaTiO_3$.

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Abstract

This review article is a personal account of my meetings with Ortwin Schirmer and the common research we had in $BaTiO_3$.

Meetings

After my PhD in 1991 I contacted Ortwin who was an expert in Electron Spin Resonance (ESR) and optical measurements. He invited me in Osnabrück and we decided to do research together in Amsterdam and Osnabrück. This was a fruitful cooperation. The topics were small and large polarons in $BaTiO_3$ (BT) and also the ESR of impurity centers. Ortwin had a phenomenal knowledge of polarons [1] and worked together with Noble laureate Alex Müller at the IBM research center in Rüschlikon Switzerland. Besides the research, Ortwin and I had also a personal relationship and he and his wife Gisela visited several times Amsterdam where I showed them the city and we also visited the famous Rijksmuseum. His wife Gisela is an expert in arts [2].

Unfortunately Ortwin died in January 2020 and as an honor to him I will write about the research we did together. A special remark I want to make: Alex Müller told me that Ortwin almost succeeded in discovery of high temperature superconductivity in WO_3 [3].

Electron Spin Resonance research in $BaTiO_3$

Some research performed with Ortwin is also published in a book I wrote together with Alex Müller [4]. Other parts of the research were done together with Suzanne Lenjer resulting in her PhD degree [5].

At our first meeting we discussed the results of my ESR study of the Fe^{2+}-O^- center in $SrTiO_3$ (ST) under static electric field and uniaxial stress [6]. It's a typical small polaron center. My experience with ESR and uniaxial stress experiments [7] resulted in discrimination between two types of Ti^{3+} centers in BT. The stress equipment was such that it did not affect The Q value of the cavity. The Q value is influenced by the high dielectric constant of ST and BT. Depending on the acceptor content of single crystals BT, two types of Ti^{3+} ESR signals are observed. Acceptor-poor samples, which thus also have low concentrations of compensating oxygen vacancies, V_o, contain isolated Ti^{3+} free small polarons. Acceptor-rich crystals show signals to be attributed to Ti^{3+} next to V_o alkali-acceptor complexes. This model is also supported by a comparison of the optical absorptions and light induced charge transfer transitions of both types of specimens [8].

In BT the alkali ions Na and K, replacing Ba, lead to acceptor levels about 50 meV above the valence band edge. The structure of these defects can be studied by ESR, after light induced valence-band holes have been captured at neighboring O^{2-} ions. Hyperfine interaction with Na, Ba, and Sr impurities, adjacent to the paramagnetic O^-, is identified. The holes are trapped stably below ∼50 K. Their level position is determined by the temperature dependence of the relaxation rate of the light-induced nonequilibrium excess hole population. Photostimulated

small polaron transfer between O^{2-} sites equivalent with respect to Na or K leads to a strong optical-absorption band with peak at 1.3 eV, corresponding to a stabilization energy of the bound hole polaron of about 0.65 eV. The Na^{+}-O^{-} dipoles can be reoriented under uniaxial stress at 4.2 K; a differential stress coupling coefficient of 1.23×10^{-4} m^3 is derived. Several O^- centers associated with partly unassigned acceptors on Ti sites are identified. Their properties are compared to those of the Ba site acceptors. Vibronic *g* shifts are accounted for by a dynamic Jahn-Teller effect involving the twofold degenerate O^- π orbitals [9-10].
The following investigations were special, resulting in the thesis of Suzanne Lenjer. A comprehensive study of conduction polarons in purified BT crystals, containing about 100-ppm Nb as extrinsic ions, is presented. Nb^{5+} is compensated by Ti^{3+} ($3d^1$) ions, many of them isolated. Small Ti^{3+} polarons, stabilized by crystal strains, and polarons of intermediate size in less strained crystal regions are identified. Both species break the point symmetry, indicating stabilization by a tetragonal T2×e Jahn-Teller distortion. There is indirect evidence for the presence of bipolarons in the crystal ground state. They have a rather small dissociation energy, 0.01 eV. The investigations are based on ESR performed at T<20K under application of uniaxial stress. This allows to obtain local information on the intrinsic Jahn-Teller properties of the conduction states of an oxide perovskite. For the small polarons stress has the following effects: (i) aligns the tetragonal Jahn-Teller axes along the stress direction, and (ii) enlarges the radius of the aligned orbitals, transforming them into intermediate ones. The stress alignment of the intermediate polarons is different: The Jahn-Teller axes orient perpendicular to the stress axis. Several of the polaron features are elucidated by comparison with the stress-dependent Jahn-Teller properties of the impurity ion Mo^{5+} ($4d^1$), where the *d* electron is prevented from tunneling to its Ti^{4+} neighbors. The ESR of Ti^{3+} in reduced BT is attributed to polarons bound to doubly filled oxygen vacancies [11-12, 14-15]. Uniaxial stress plays a crucial role in these experiments.
Another stress experiment revealed the following center. An off-center ion near a Ba site in BT as studied by ESR under uniaxial stress [13]. It is a similar center studied before by Ortwin in ST [17].
The last research we did together was the study of Jahn-Teller and off-center defects in $BaTiO_3$: Ni^{+}, Rh^{2+}, Pt^{3+} and Fe^{5+} as studied by EPR under uniaxial stress [18]. By applying uniaxial stress a difference could be made between off-center and Jahn-Teller ions.

Last remark

It was an honor and pleasure to work with Ortwin Schirmer.

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