

Tuning the structural instability of SrTiO₃ by Eu doping: the phase diagram of Sr_{1-x}Eu_xTiO₃

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Recently we have shown that the almost multiferroic system EuTiO₃ undergoes a structural phase transition at $T_S=282\text{K}$ from cubic to tetragonal [1]. This transition is analogous to the one of SrTiO₃ at $T_S=105\text{K}$, where the oxygen octahedral rotations freeze out due to the softening of a transverse acoustic zone boundary mode. Besides of this similarity between SrTiO₃ and EuTiO₃, also others exist, namely a strong zone-center optic mode softening reminiscent of a ferroelectric instability, however, suppressed by quantum fluctuations [2, 3]. Both compounds have almost the same lattice constants since the ionic radii of Sr and Eu are the same. As such it is rather amazing that T_S in the Eu compound is more than doubled as compared to the transition temperature of SrTiO₃.

In order to explore the origin of this distinction, we have characterized the phase diagram of Sr_{1-x}Eu_xTiO₃ as a function of x experimentally by electron paramagnetic resonance (EPR) techniques and resistivity measurements. Theoretically a lattice dynamical study of the phase transitions has been performed and complemented by density functional calculations for the end members of the system. From these studies we come to the conclusion that the dynamics of both systems are very different: While STO is in the displacive limit with a shallow broad double potential, ETO obeys order-disorder dynamics characterized by a deep and narrow double well potential, see Figure 1.

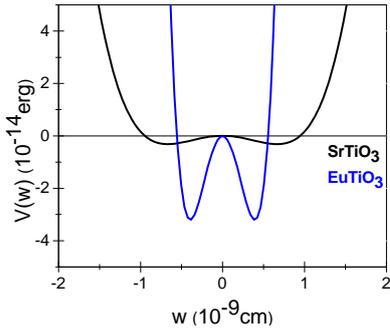


Figure 1: The local double-well potential of STO (black line) and the one of ETO (blue line). The model parameters of ETO are the same as those of STO with a mass enhancement factor of 1.73 applied to m_2 to account for the heavier Eu sublattice and new self-consistently derived double-well defining parameters.

Both EPR and resistivity data show distinct anomalies in their temperature dependencies, which are related to the structural phase transition (Figure 2). From these anomalies the phase diagram has been constructed which is shown in Figure 3.

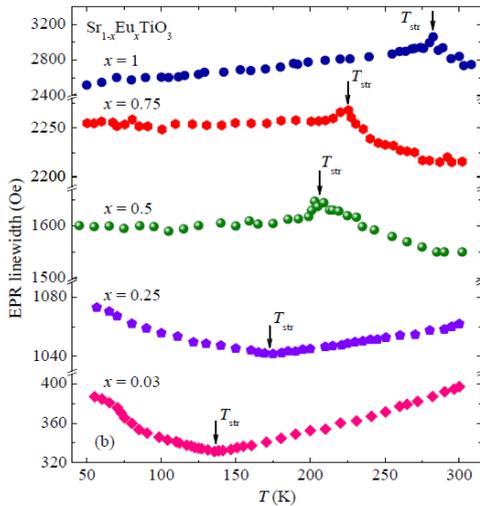


Figure 2: Temperature dependence of the EPR line width for Sr_{1-x}Eu_xTiO₃ samples with $x = 0.03 \leq x \leq 1$. The arrows indicate the structural phase transition temperature, T_S .

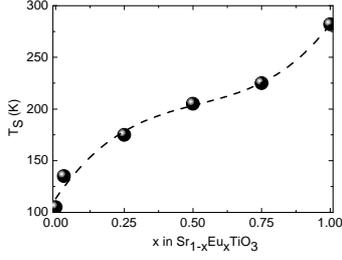


Figure 3: The phase diagram of $\text{Sr}_{1-x}\text{Eu}_x\text{TiO}_3$ as determined from the line width broadening (Fig. 2) and calculated theoretically (dashed line).

Obviously a nonlinear dependence of T_S on x is realized, appearing as a kink in the EPR line width for $x \geq 0.5$, whereas a minimum in the line width at T_S is seen for $x \leq 0.25$. These differences in the temperature dependencies of the line widths are due to a crossover from metallic to semiconducting behavior between $x=0.25$ and $x=0.5$ as evidenced by the resistivity measurements (Figure 4).

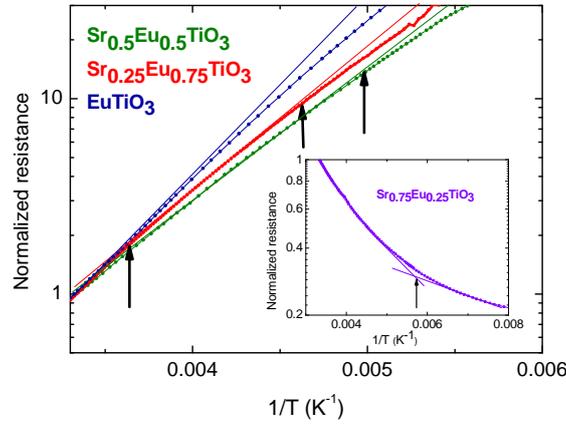


Figure 3: Normalized resistance r/r_0 as a function of inverse temperature with $r_0 = r(T = 300 \text{ K})$ for $x \geq 0.5$. The inset shows the same for the sample with $x=0.25$.

The results from lattice dynamical calculations and density functional theory explain the x -dependent structural phase transitions in terms of a crossover of the dynamics from displacive to order-disorder, since the double-well potentials change from broad and shallow to deep and narrow with increasing x (Figure 1). Simultaneously, the elastic constants are altered from very soft to hard due to optic-acoustic mode-mode coupling for small x and absence of this coupling for $x \geq 0.25$. Both theoretical results are mapped onto each other and almost perfect agreement for the double-well potentials is obtained, thus confirming the conclusions about substantial changes in the dynamics. Further implications are strong paramagnon-phonon coupling for the Eu rich compounds which enables the tuning of the dielectric response by a magnetic field.

References:

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