Stabilization of ferroelectricity in quantum paraelectrics by isotopic substitution

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LETTER TO THE EDITOR

Stabilization of ferroelectricity in quantum paraelectrics by isotopic substitution

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Abstract. $SrTiO_3$ and $KTaO_3$ are incipient ferroelectrics whose phase transition temperature is suppressed by quantum fluctuations. The recent observation of induced ferroelectricity due to exchange of ^{16}O by ^{18}O (1999 *Phys. Rev. Lett.* **82** 3540) is reproduced for the dielectric data by an anharmonic electron–phonon interaction model, and a first order phase transition is predicted. Furthermore it is shown that this isotope effect does not occur in $KTaO_3$ since its local double-well potential is much shallower than that in $SrTiO_3$.

One of the best investigated perovskite oxides is $SrTiO_3$ since it exhibits a variety of interesting physical and chemical properties with a broad range of applications. The high temperature cubic structure is destabilized by a zone boundary mode, which involves the rotation of the oxygen octahedra, at 110 K. Additionally, a zone centre mode instability is anticipated as a precursor over a wide temperature regime which is typical for the occurrence of ferroelectricity. The extrapolation of its frequency to zero would suggest that a ferroelectric transition occurs at a temperature of 37 K. However, analogous to $KTaO_3$, this transition never takes place due to quantum fluctuations which suppress the ordered state. Doping these systems with suitable cations can induce ferroelectricity, with a doping dependent T_c. In addition, ferroelectricity can be induced by an applied electric field or by pressure. While $KTaO_3$ is cubic at all temperatures, $SrTiO_3$ is tetragonal below 110 K and exhibits superconductivity at low temperatures for nonstoichiometric samples. Around 40 K another anomaly has frequently been reported from various experimental techniques [1–4] which gave rise to many speculations and controversies about its origin [5, 6]. In the following the recent experimental work reported in [7], where ferroelectricity is induced by replacing the oxygen ^{16}O with its isotope ^{18}O, is analysed theoretically. While it is well known in other ferroelectric systems, e.g. all hydrogen-bonded ferro- and antiferroelectrics, that isotopic substitution always leads to an increase in T_c, the finding of [7] of isotope-induced ferroelectricity in perovskite systems has not previously been addressed experimentally. Although the isotope effect on T_c in hydrogen-bonded systems is well understood [8, 9], isotopic induction of ferroelectricity has not been discussed previously, even though its occurrence could be anticipated from earlier work [10] in this field.

Theoretically the microscopic understanding of the occurrence of ferroelectricity in perovskite oxides has been substantially improved by lattice dynamical models [11–14] and first principle electronic structure techniques [15, 16] during the last several years. Even though

these systems are nominally ionic, it has been established that a dynamical covalency [17] is inherent to them, which triggers the soft-mode temperature dependence and is the origin of the ferroelectricity. Specifically it has been found that an anisotropic charge density at the oxygen ion lattice site, and a consequent directional transition metal–oxygen p–d hybridization, lower the total energy to stabilize the new phase [18]. The simplest successful approach to model these effects stems from lattice dynamical models which include anharmonicity and p–d hybridization by considering a nonlinear shell model representation [11–14]. The quantitative agreement between experimental data and corresponding model calculations for the relevant temperature dependent quantities justifies the phenomenology inherent to these approaches. In addition first principles calculations [18] fully confirmed the role of the crucial properties of oxygen ion instability common to ferroelectrics. The model calculations not only achieve quantitative agreement with experimental data but also supply a very transparent insight into the microscopic understanding of ferroelectricity. It is therefore worthwhile to test the predictive power of these ideas by investigating the isotopic effects on the ferroelectric properties of $SrTIO_3$ and $KTaO_3$ within the same approach.

The model Hamiltonian we consider is given by:

$$H = \frac{1}{2} \sum_n \left[\sum_{i=1,2} m_i \dot{u}_{in}^2 + f'(u_{1n+1} - u_{1n})^2 + f(v_{1n} - u_{2n})^2 + f(v_{1n+1} - u_{2n})^2 \right.$$
$$\left. + g_2 w_{1n}^2 + \frac{1}{2} g_4 w_{1n}^4 \right] \tag{1}$$

where m_1 represents the TiO_3 cluster mass, m_2 refers to the Sr sublattice mass, u_{in} and v_{1n} are core and shell displacement coordinates with the dipole displacement $w_{1n} = v_{1n} - u_{1n}$, f', f are harmonic intersite electron–phonon and phonon–phonon couplings. The terms proportional to g_2 and g_4 induce an onsite double-well potential which is caused by the configurational instability of the oxygen ion O^{2-} [19]. We use the selfconsistent phonon approximation (SPA) to calculate T_c, the isotope effect on it, the temperature dependence of the soft mode ω_f, and the dielectric constant. This corresponds to a cumulant expansion of the cubic term in w in the equation of motions, which is equivalent to a first order correlation correction within a perturbation theory [20]:

$$g_2 w_{1n} + g_4 w_{1n}^3 = [g_2 + 3g_4 \langle w_{1n}^2 \rangle_T] w_{1n} = g_T w_{1n}. \tag{2}$$

The phase transition temperature T_c is defined by $g_T = 0$, with

$$\langle w_{1n}^2 \rangle_T = \frac{1}{N} \sum_{q,j} \frac{\hbar}{\omega_{q,j}} w_{1,q,j}^2 \coth \frac{\hbar \omega_{q,j}}{2kT} \tag{3}$$

and $w_{1,q,j}$ being the momentum q and branch j dependent eigenvector and $\omega_{q,j}$ the corresponding frequency. From the equations of motion, the $q = 0$ transverse optic mode frequency ω_f is given by:

$$\omega_f^2 = \frac{\omega_0^2 g_T}{\mu \omega_0^2 + g_T} \tag{4}$$

where $\omega_0^2 = 2f/\mu$ is the optic rigid ion zone boundary frequency and μ the reduced cell mass.

The temperature dependence of the soft mode is completed governed by equation (3) and various regimes, differing from mean-field behaviour, result from the use of the onsite double-well potential in w. Specifically, at low temperatures a dimensionality crossover from mean-field to a quantum regime is predicted [21] which causes an enhancement of the critical exponents and induces a suppression of long range ordered ferroelectricity. Also at high temperatures substantial deviations from mean-field behaviour occur since ω_f^2 tends to the
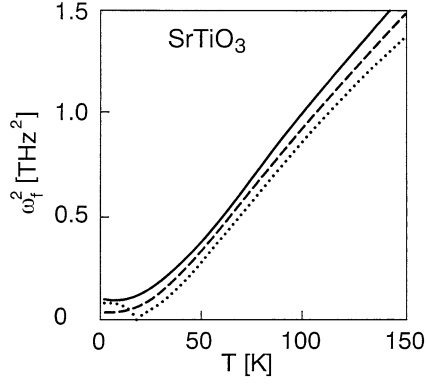
Figure 1. Temperature dependence of the squared soft mode frequency of $SrTiO_3$; the full line corresponds to the ^{16}O system; the dashed line is the partially substituted system (50% ^{16}O and 50% ^{18}O) and the dotted line is the fully substituted system.

Table 1. Model parameters for $SrTiO_3$ and $KTaO_3$ (see text for details on the new parameters g_2 and g_4).

	f $[10^4 \text{ g s}^{-2}]$	f' $[10^4 \text{ g s}^{-2}]$	g_2 $[10^4 \text{ g s}^{-2}]$	g_4 $[10^{22} \text{ erg}]$	$m_1(^{16}O)$ $[10^{-22} \text{ g}]$	m_2 $[10^{-22} \text{ g}]$	Γ [THz]
$SrTiO_3$	14.41	1.27	−1.41	1.57	1.55	1.46	0.38
$KTaO_3$	4.07	0.58	−0.49	0.51	2.88	0.65	0.38

rigid ion value which causes saturation and leads, within the present model, to a critical exponent of $\frac{1}{3}$ due to the adiabatic approximation [12, 13]. Beyond this approximation the exponent becomes $\frac{1}{2}$ [22]. A detailed discussion based on the free energy considerations will be given in another work [23]. Here we concentrate on the explanation of the new experimental findings of isotopic induced ferroelectricity.

The soft mode temperature dependence has to be calculated selfconsistently from equations (3) and (4) and is shown in figure 1 for $SrTiO_3$. The parameters used are given in table 1 and have been obtained from the experimental phonon dispersion curves where the zone boundary optic and acoustic modes define f and f'. The harmonic and anharmonic core shell couplings have to be calculated selfconsistently. They have been optimized as compared to [6] and [13] in order to fit the low temperature behaviour of the soft mode more closely to the experimental values than previously done. The effect of partial (50%) isotopic substitution of ^{16}O and ^{18}O is taken into account by enhancing m_1 correspondingly. The phase transition is still suppressed by quantum fluctuations (see figure 1) but the soft mode frequency is decreased as compared to the ^{16}O data. The full replacement of ^{16}O by ^{18}O (dashed curve in figure 1) induces a further decrease in ω_f^2 and a phase transition takes place at 15 K where $\omega_f^2 = 0$. It is important to note that below 15 K the soft mode is finite again but does not follow a Curie–Weiss law as quantum fluctuations govern this regime.

The corresponding dielectric constant is calculated from:

$$\varepsilon(\omega) = 1 + 4\pi N \alpha(\omega) \tag{5}$$

where N is the number of atoms per unit volume and for a homogeneous dipole w:

$$\alpha(\omega) = \frac{e^2}{\mu} \sum_j \frac{f_j}{\omega_j^2 - \omega^2} \text{ and } f_j \approx \mu \langle w^2 \rangle_T. \tag{6}$$

The calculated dielectric constants are shown in figure 2 for the three cases discussed above, where a small damping Γ (5% of ω_0 in $SrTiO_3$ and 10% of ω_0 in $KTaO_3$) has been included which is of the order of the experimentally observed one [22] (see table 1). This damping
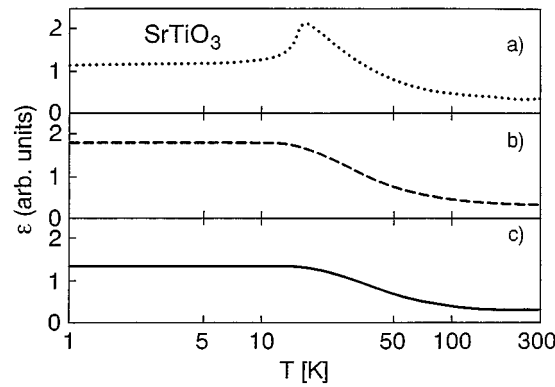
Figure 2. The static dielectric constant ε as a function of temperature for $SrTiO_3$; (a) represents the fully substituted system, (b) represents the partially substituted one, and (c) represents the pure ^{16}O compound.
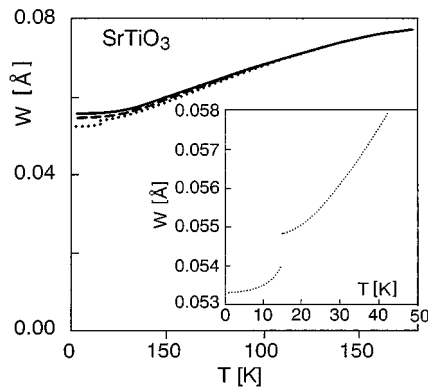

Figure 3. w as function of temperature for $SrTiO_3$; the full line corresponds to the ^{16}O system; the dashed line is the partially isotope substituted system (50% ^{16}O and 50% ^{18}O) and the dotted line is the fully substituted system. The insert shows the temperature dependence of w for the fully substituted system on an enlarged scale.

parameters accounts for multiphonon scattering as well as experimental resolution limits. Both systems, the partially isotopically substituted one and the pure ^{16}O system, exhibit a broad plateau below 25 K, while a peak in the dielectric constants appears for the fully isotopically substituted system coinciding with the soft mode instability. Even though the detailed asymmetry of the peak is different here from that in the experiment, the qualitative agreement with those data is clear. Including an external electric field, which will mainly couple to the local dipole moment proportional to w, will lead to an enhancement of the damping and induce a vanishing of ferroelectricity, as will be shown in a forthcoming paper [23].

Since in our model the relative core–shell displacement coordinate w can be attributed to a fluctuating dipole moment which is analogous to an order parameter [24], it is interesting to investigate its temperature dependence. The results are shown in figure 3 for the three cases discussed above. For temperatures larger than 150 K the three curves are indistinguishable and only small effects of the isotope substitution appear below 150 K. In all three cases w decreases slightly and monotonically to saturate in the quantum regime. Yet, in contrast to the pure system and the partially isotope substituted system, a small discontinuity in w is observed in the fully substituted compound at 15 K. The inset in figure 3 shows this discontinuity on an enlarged scale. Even though the discontinuity in w is only of the order of 10^{-3} Å, it is evidence that the phase transition in fully isotopically substituted $SrTiO_3$ is first order. This finding is not due to spurious effects arising within the SPA [25], since our effective potential is substantially
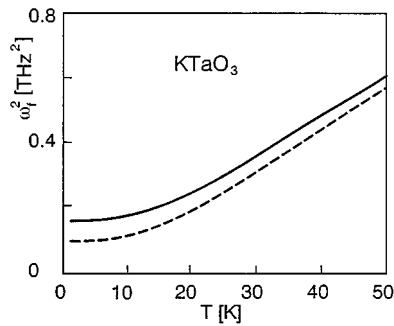
Figure 4. Temperature dependence of the squared soft mode frequency of $KTaO_3$; the full line corresponds to the ^{16}O system; the dashed line is the fully substituted system.

different from a simple Φ_4 potential [26] which therefore, in general, admits for a displacive second-order transition [23].

Finally we have investigated the possibility of having isotope induced ferroelectricity also in the other quantum paraelectric $KTaO_3$. Using the parameters as given in table 1, the calculated squared soft mode frequency is shown in figure 4 as a function of temperatures of the nonsubstituted and the fully substituted systems. The transition to the ferroelectric phase is in both cases suppressed by quantum fluctuations. Even though the frequency is reduced in the fully substituted sample as compared to the ^{16}O system, there is no indication of isotopically induced reentrant ferroelectricity. This finding can be explained by the fact that the oxygen ion related polarizability effects are less pronounced in $KTaO_3$, as compared to $SrTiO_3$, which is evidenced by a much shallower double-well potential. This prediction should be amenable to experimental confirmation.

In conclusion, we have shown that within a nonlinear electron–phonon interaction model, which is based on the configurational instability of the oxygen ion and consequently on dynamical p–d-hybridization effects, the experimentally observed induction of ferroelectricity in $SrTiO_3$ due to oxygen ion isotope substitution can be explained consistently and in substantial qualitative agreement with experimental data. In addition it is predicted that this phase transition is of first order and that small deviations from a Curie–Weiss law exist for the soft mode above T_c, while strong deviations are predicted to appear below T_c in the fully substituted system. The first-order transition is likely to be accompanied by precursor structure such as twinning and tweed textures. For the analogous compound $KTaO_3$ the model calculations give no evidence that a phase transition takes place if ^{16}O is replaced by ^{18}O which we attribute to the shallower local double-well potential of $KTaO_3$ as compared to $SrTiO_3$.

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