Isotope Effects in Ferroelectricity*

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Motivation—Displacive ferroelectrics (FEs) are characterized by a coordinated displacement of the atoms within a crystal lattice to produce a static internal polarization. At the FE transition there is a cancellation between the short- and long-range forces acting on the atoms, and the frequency of one displacement mode approaches zero. Hence, the lattice is termed "soft" and the dielectric constant becomes large. When the forces are delicately balanced, isotopic substitution for one of the atoms can produce significant changes in the soft mode behavior. This is the case for $SrTiO_3$. We have combined isotopic substitution of oxygen with the application of hydrostatic pressure to probe the detailed physics of this crystal.

Accomplishment—$SrTiO_3$ with naturally occurring ^{16}O (STO-16) is a classic incipient FE: the frequency, ω_s, of one displacement mode decreases and the dielectric constant, ε', rises with decreasing temperature, but the lattice is stabilized at the lowest temperatures by quantum fluctuations of the atoms. This is shown in Fig. 1 where the dashed red line reflects STO-16 data at ambient pressure: ε' (left axis) rises from ~ 300 at room T to a plateau near 20,000 below 10 K, referred to as the quantum paraelectric state. The soft mode frequency $\omega_s(T)$ can be obtained from these data since $\omega_s \sim 1/\sqrt{\varepsilon'}$. Plotting $10^3/\varepsilon'$ (right axis) shows that the displacive mode becomes very soft as T → 0, but the lattice remains stable due to quantum fluctuations. This stability is broken in a crystal where 97% of the ^{16}O is replaced by the isotope ^{18}O (STO-18). $\varepsilon'(T)$ for STO-18 (blue triangles, left axis in Fig. 1) has a pronounced maximum near 24 K, indicating an equilibrium transition to a FE state. The heavier isotope induces a FE state by (a) providing an additional softening in ω_s and (b) reducing the quantum fluctuations. The FE in $SrTiO_3$ (the Slater mode shown by the inset in Fig. 1) is primarily a vibration of the Ti ions against their surrounding oxygen octahedra. Replacing ^{16}O by ^{18}O should reduce ω_s by the ratio of the effective masses in the $Ti\text{-}O_6$ octahedral units or 3%. Our dielectric data accurately confirm this prediction: $10^3/\varepsilon'$ (Fig. 1, right axis) for STO-18 lies 6% below STO-16.

Hydrostatic pressure counteracts the softening from ^{18}O substitution as shown in Fig. 2. Using the maximum in $\varepsilon'(T)$ for different P, the FE transition temperature, T_c, is suppressed at a very rapid −20 K/kbar (inset to Fig. 2). $T_c \rightarrow 0$ near 0.7 kbar and the FE state is replaced by the quantum paraelectric state (shown by the plateau in the 0.7 kbar data at low T). The line through the $T_c(P)$ data shows agreement with the theory for quantum ferroelectrics which predicts that $T_c = A \bullet \sqrt{(1 - P/P_c)}$ where $T_c(P_c) = 0$.

Significance—^{18}O substitution induces a FE state in single crystals of $SrTiO_3$. Our dielectric data $\varepsilon'(P,T)$ demonstrate quantitatively the additional softening of the soft mode frequency that enables a displacive equilibrium FE transition. Because this transition occurs at low T (24 K at ambient P), pressure provides an excellent variable to delicately reverse the mode softening and ultimately suppress the FE state at modest P. These large P effects arise from the fact that T_c is low (in the quantum regime) and the characteristic energies are small. The experiments provide new insight and a better understanding of the physics of ferroelectricity in quantum paraelectrics and perovskite materials in general.

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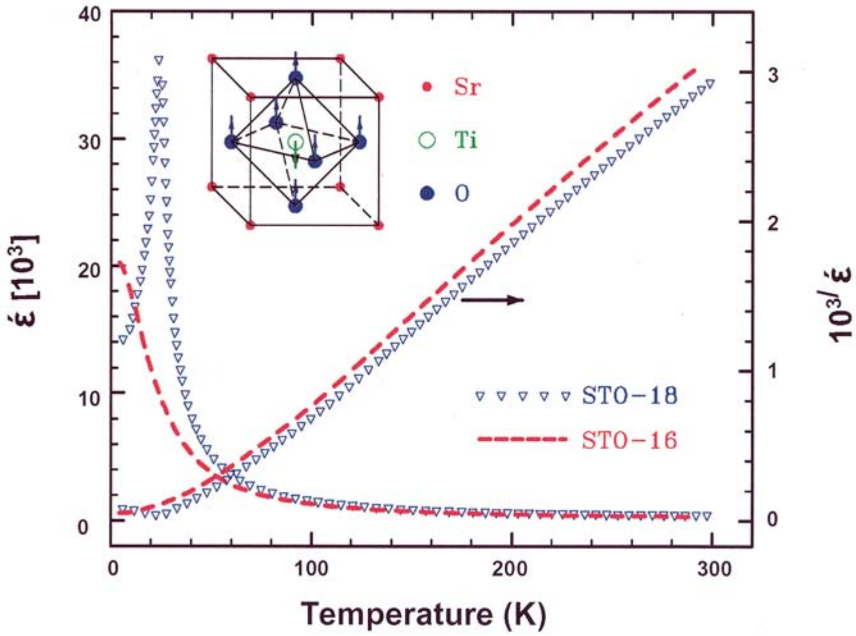

Figure 1. Ferroelectricity in $SrTiO_3$ appears when ^{16}O is replaced by the stable isotope ^{18}O.

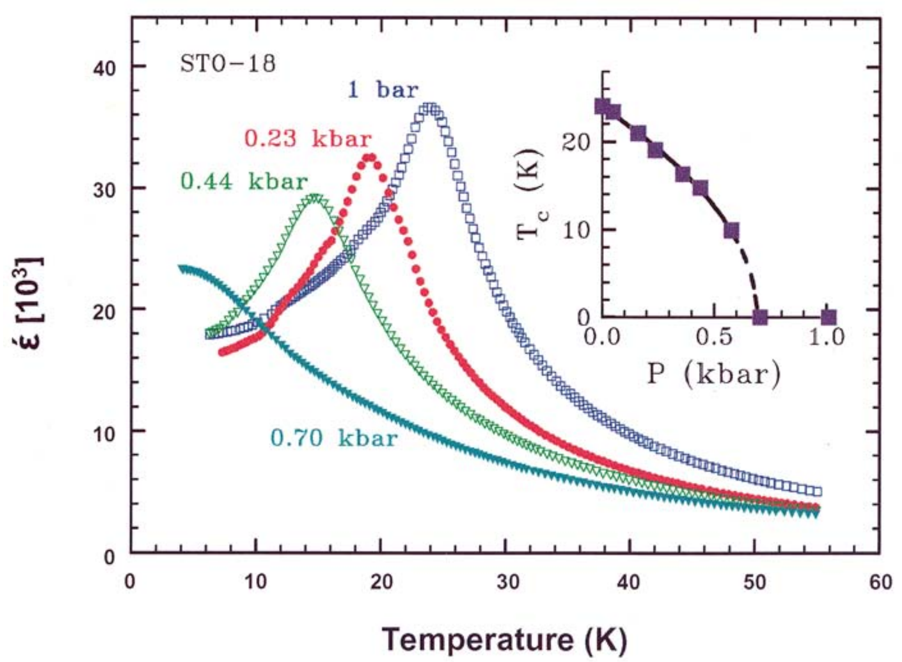

Figure 2. Hydrostatic pressure suppresses the ferroelectric transition in STO-18 near 0.7 kbar.