

Noncontact Atomic Force Microscope Dissipation Reveals a Central Peak of SrTiO₃ Structural Phase Transition

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The critical fluctuations at second order structural transitions in a bulk crystal may affect the dissipation of mechanical probes even if completely external to the crystal surface. Here, we show that noncontact force microscope dissipation bears clear evidence of the antiferrodistortive phase transition of SrTiO₃, known for a long time to exhibit a unique, extremely narrow neutron scattering “central peak.” The noncontact geometry suggests a central peak linear response coupling connected with strain. The detailed temperature dependence reveals for the first time the intrinsic central peak width of order 80 kHz, 2 orders of magnitude below the established neutron upper bound.

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Second order structural phase transitions leave a clear mark in all thermodynamical, mechanical, equilibrium, and nonequilibrium properties of bulk crystals. It was proposed some time ago that the critical fluctuations should also leave a footprint in the frictional dissipation of external mechanical probes such as an atomic force microscope (AFM) when the temperature crosses the phase transition in the underlying bulk [1]. The recent successful detection of a superconducting transition in the linear response mechanical dissipation of a noncontact, pendulum-type AFM tip hovering more than 1 nm above the sample surface [2] suggests that continuous structural transitions might also be detectable in this manner. Here, we present a first realization of this idea, with direct application to a most classic example, the antiferrodistortive transition of SrTiO₃ just above 100 K. At this phase transition the high temperature ideal cubic perovskite crystal structure becomes unstable against a zone-boundary phononlike displacement of the ions, leading to a cell doubling and a tetragonal *I4/mcm* symmetry at lower temperatures. This exquisitely second order “displacive” transition historically provided a clean realization of nonclassical critical exponents [3]. A very intriguing feature of this system, originally uncovered by neutron scattering, and later confirmed by other techniques, is the so-called “central peak” [4–7]. Very close to the critical transition temperature T_c , inelastic neutron spectra showed, besides ordinary critical fluctuations—which proliferate and soften but never reach zero frequencies, a strikingly narrow peak (less than the 6 MHz width resolution) centered at zero frequency, whence the name.

The central peak (*CP*) intensity appeared to obey the static critical exponents of the transition, but despite considerable efforts the actual nature and width of the central peak were not uncontroversially established [8].

Here, we show that noncontact pendulum AFM dissipation, measured far from actual contact with the surface, reveals for the first time a structural phase transition, and it does so by revealing the *CP* of SrTiO₃. A linear response analysis shows that the *CP*-related mechanical loss peak is as narrow as 80 kHz, a frequency orders of magnitude below the neutron established upper bound. Moreover, even if it cannot strictly determine the intimate nature of the *CP*, the mechanical coupling suggests a connection with critical fluctuations of strain, which are known to be associated with those of the main antiferrodistortive order parameter [9].

The probe consisted of a very soft, highly doped silicon cantilever (ATEC-Cont from Nanosensors) with spring constant $k = 0.1$ N/m, suspended perpendicularly to the surface with an accuracy of 1° and operated in the so-called pendulum geometry where the tip vibration describes an arc parallel to the sample surface. The peculiarity of this technique is to detect phenomena, in this case phase transitions, that happen in the bulk, by means of a noninvasive, ultrasensitive and local surface probe, as opposed to traditional probes such as neutrons and x rays, which invade the bulk in a much more global fashion. Moreover, the pendulum AFM is a kilohertz probe, sensitive to phenomena and to fluctuations that may take place on a much slower time scale than that accessible with neutrons or x rays. The

oscillation amplitude A of the tip was kept constant to approximately 5 nm using a phase-locked loop feedback circuit. The cantilever was annealed in ultrahigh vacuum (UHV) up to 700 °C for 12 h, which results in the removal of water layers and other contaminants from both the cantilever and the tip. After annealing the cantilever quality factor, frequency, and internal damping were equal to $Q = 7 \times 10^5$, $f_0 = 11$ kHz, and $W_0 = 2 \times 10^{-12}$ kg/s, respectively. The annealing is also known to reduce all localized charges on the probing silicon tip [2], which is neutral, since the tip-sample contact potential difference was compensated ($V = V_{\text{CPD}}$) during the experiment.

Figure 1(a) shows the power $W(T)$ dissipated by the pendulum AFM as a function of temperature at different

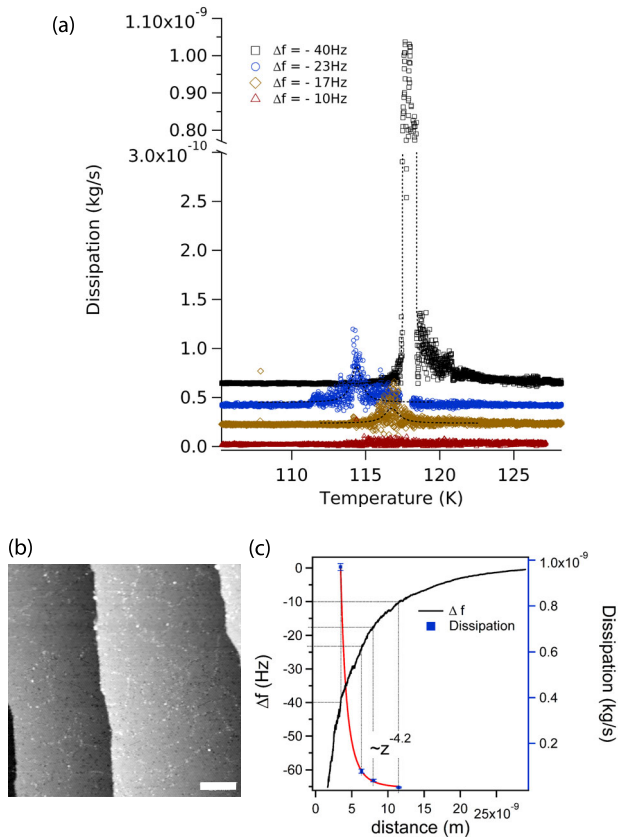


FIG. 1 (color online). (a) Experimental AFM dissipation W as a function of temperature. Raw data, taken at different surface spots and different tip sample distances z . The sharp peak corresponds to the critical temperature of SrTiO_3 in the bulk region under the tip. (b) Low temperature ($T = 5$ K) STM image of $\text{SrTiO}_3(100)$ surface. The image is obtained at constant current $I = 10$ pA and bias voltage $U = 1$ V. The length of the scale bar is equal to 20 nm. More details are given in the Supplemental Material [12]. (c) The distance dependence of the dissipation W , taken as the maximum of the peak shown in (a), at four different spots on the sample. A fit to the experimental data, $W \propto z^{-p}$, is shown in red, with $p \sim 4.2$. This exponent is close to the value $p = 4$ expected for phononic dissipation, as appropriate for coupling to acoustical surface fluctuations of an insulating bulk material.

spots on the SrTiO_3 surface and at different tip-sample distances, as measured by the shift of the resonance frequency Δf . The dissipation is inferred from the standard expression [10] $W = W_0[A_{\text{exc}}(z)/A_{\text{exc},0} - f(z)/f_0]$ in terms of the measured distance-dependent excitation amplitude $A_{\text{exc}}(z)$ and resonance frequency $f(z)$ [where $f(z) = f_0 + \Delta f$] of the cantilever, the subscript for suffix 0 referring to the free cantilever. Since the Young's modulus of the silicon cantilever is temperature dependent also the frequency of the free cantilever changes as a function of temperature, $\Delta f_0(T)$ [11]. In a temperature dependent experiment the total change of the frequency is $\Delta f(T, z) = \Delta f_0(T) + \Delta f(z)$ where $\Delta f(z)$ is the (negative) frequency shift due to the tip-sample interaction. The tip-sample distance z was accurately controlled by means of a feedback loop regulating the z position in such a way that Δf was kept constant [12].

Data at the large distance $z = 12$ nm, corresponding to $\Delta f = -10$ Hz, show a dissipation peak that is barely visible, corresponding to an exceedingly weak van der Waals tip-surface interaction. All other spectra, taken at closer distances, exhibit a narrow dissipation peak at a temperature between 114 and 118 K, depending upon the surface spot investigated, reflecting local changes of T_c determined by inhomogeneous heavy Nb doping, surface oxygen vacancies, and/or stress irregularities. The 105 K transition temperature of stress free pristine SrTiO_3 is notoriously shifted by Nb doping and the formation of oxygen vacancies [17]. At surfaces, moreover, T_c may under suitable conditions show differences of tens of degrees with respect to the bulk, as seen on $\text{SrTiO}_3(110)$ [18]. The dissipation peak in these raw data provides a first qualitative confirmation of the suggested connection between critical structural fluctuations and AFM dissipation [1].

Figure 1(b) shows a scanning tunneling microscope (STM) atomically resolved surface topography of the 1% Nb doped $\text{SrTiO}_3(001)$ surface taken at the low temperature $T = 5$ K. The flat terraces are obtained after a 2h annealing to 1000 °C in UHV [19,20]. Detailed STM images (see also the Supplemental Material [12]) show dark spots (surface defects, perhaps O vacancies [20]) and bright features, decorating what could be edge dislocations [21] or other domain walls.

We now consider the origin of the pendulum AFM loss process. For a start, the tip is sufficiently far from the surface to guarantee that only van der Waals (vdW) (or electrostatic, if charges were present) tip-substrate interactions are relevant. Pure SrTiO_3 is an insulator and the coupling of a neutral tip must be phononic [22]. Resistivity measurements of 1% Nb doped crystals exhibit conducting behavior, however, with a carrier density of about 10^{20} cm^{-3} [23], orders of magnitude below that of a good metal.

Moreover, Auger electron spectroscopy on a $\text{SrTiO}_3-(2 \times 2)$ surface has suggested that the Nb presence is

negligible in the near-surface region [24], so that the low level metallicity due to Nb doping can be considered irrelevant in our experiment. Figure 1(c) shows the maximum dissipation value against tip-sample separation. For a spherical tip oscillating above a solid surface the dissipation is proportional to $F^2(z)$, where $F(z)$ is the static force resulting from the tip-sample interaction. The vdW interaction yields a static force $F(z) \propto z^{-2}$, so that the dissipation due to the creation of phonons in the solid (acoustic phonons in this case, corresponding to the oscillating strain wave under the tip sketched in the inset in Fig. 2), should vary as z^{-4} [2,22]. The experimental distance dependence is indeed best fit by z^{-p} with $p \sim 4.2$, in excellent agreement with that expectation.

We can now directly relate the observed dissipation to the critical central peak of SrTiO₃. The noncontact tip vibrating at $f \approx 11$ kHz and at large distance is a very weak perturbation on the underlying SrTiO₃. Thus, we can make use, rarely appropriate in nanofriction, of linear response theory. Moreover, since the AFM perturbation affects a sufficiently large portion of SrTiO₃, we can approximate its response by means of the bulk response of the material [5,22]. The dissipated tip energy per cycle is, in linear response, proportional to the imaginary part of the bulk lattice susceptibility χ , in the form

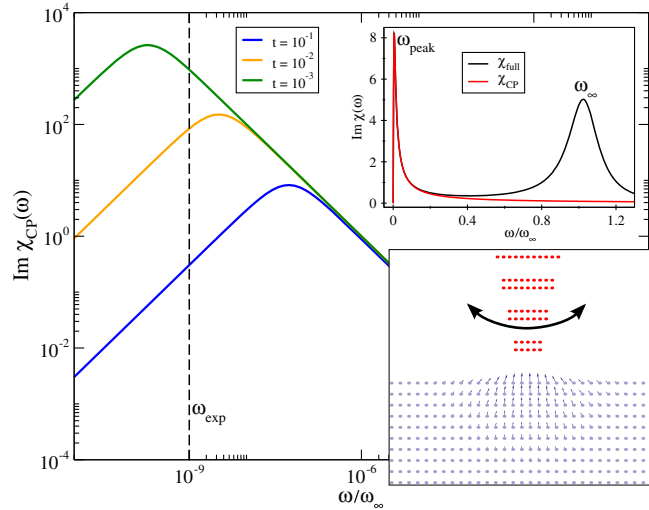


FIG. 2 (color online). $\text{Im}\chi_{\text{CP}}(\omega)$, the low-energy central peak component of $\text{Im}\chi(\omega)$ on a log-log scale for various temperatures, showing a peak at $\omega_{\text{peak}}(T) \sim t^{2\gamma}$ that moves towards 0 as $T \rightarrow T_c$. Upper inset: sketch of the full $\text{Im}\chi(\omega)$ on a linear ω scale, showing the broad soft-phonon Lorentzian at ω_∞ with the sharp low-energy central peak. For clarity we used here a high value of ω_{low} to show both peaks on the same scale. Lower inset: cross section of 3D simulation of a tip perturbing a semi-infinite crystal through a vdW interaction. The tip (red dots) is shown as a truncated pyramid where every atom exerts a $-C/r^6$ vdW potential on the crystal atoms (blue dots), which are held together by a harmonic potential. Arrows (magnified for clarity) represent on a log scale the atom displacements from the relaxed positions.

$$W(\omega, T) = W_0 + \alpha k_B T \text{Im}\chi(\omega, T), \quad (1)$$

where W_0 is the dissipation of the free cantilever (T independent in the considered temperature range), χ is an appropriate momentum average of the lattice susceptibility $\chi(q, \omega, T)$, α is a positive, distance-dependent constant, and the temperature factor originates from the term $\hbar\omega n_B(\omega, T)$, with n_B the Bose function, in the experimentally relevant regime $\hbar\omega \ll k_B T$. Using the form by Shapiro *et al.* [5], which accurately describes neutron scattering, the order parameter (zone boundary) susceptibility can be written as $\chi(q, \omega, T) = [\Omega^2(q) - \omega^2 + \Pi(q, \omega, T)]^{-1}$, where Ω is a bare soft phonon frequency far from the transition and $\Pi \sim \Delta(T) - i\omega\Gamma_0(T)$ is a self-energy renormalization from anharmonic effects (we shall from now on drop the wave vector q dependence of these quantities). This simple form of Π would lead, in the standard textbook description of a displacive transition [25], to a T -dependent shift of Ω , resulting in a Lorentzian peak in $\text{Im}\chi(\omega)$ at $\omega_\infty(T) = \sqrt{\Omega^2 + \Delta(T)}$, of width Γ_0 , such that $\omega_\infty(T) \rightarrow 0$ at $T = T_c$. However, the neutron data of SrTiO₃ showed that phonon softening is incomplete, $\omega_\infty(T_c) \approx 0.5$ meV, but accompanied by an extra feature centered at some very-low-energy ω_{low} , the central peak, phenomenologically captured [5] by an additional contribution to the self-energy Π

$$\Pi(\omega, T) = \Delta(T) - i\omega\Gamma_0(T) - \frac{\delta^2(T)}{1 - i\omega/\omega_{\text{low}}}. \quad (2)$$

For $\omega \sim \omega_\infty \gg \omega_{\text{low}}$ one recovers the usual soft-phonon Lorentzian peak at ω_∞ , but for $\omega \lesssim \omega_{\text{low}}$ a second peak appears, well approximated by (see the upper inset of Fig. 2)

$$\text{Im}\chi_{\text{CP}}(\omega) = \frac{\omega_{\text{low}}\delta^2(T)}{\omega_\infty^4(T)} \frac{\omega}{\omega^2 + [\omega_{\text{low}}\omega_0^2(T)/\omega_\infty^2(T)]^2}, \quad (3)$$

where $\omega_0^2(T) = \omega_\infty^2(T) - \delta^2(T)$ is the quantity that actually vanishes as $T \rightarrow T_c$. Indeed, the static susceptibility can be shown to be simply related to ω_0^2

$$\chi(0) = \int \frac{d\omega}{\pi} \frac{\text{Im}\chi(\omega)}{\omega} = \frac{1}{\omega_0^2(T)} \sim t^{-\gamma}. \quad (4)$$

The divergence of the order-parameter susceptibility χ with an exponent γ , as the reduced temperature $t = |T - T_c|/T_c$ goes to 0, is a standard result of the theory of critical phenomena. The critical behavior of SrTiO₃ is in the 3D-Ising universality class, for which $\gamma \sim 1.24$ [26]. The low-energy susceptibility $\text{Im}\chi_{\text{CP}}(\omega)$ of Eq. (3) displays a sharp peak at a frequency $\omega_{\text{peak}}(T) = \omega_{\text{low}}\omega_0^2(T)/\omega_\infty^2(T)$, which moves towards 0 as $T \rightarrow T_c$. We can now consider the temperature dependence of the linear response AFM dissipation at the fixed and very low oscillation frequency

$\omega_{\text{exp}} = 2\pi f$. As $T \rightarrow T_c$ from above the dissipation will increase, roughly as $t^{-2\gamma}$, because $\omega_{\text{exp}} \ll \omega_{\text{peak}}(T) \sim t^{-\gamma}$, to reach a saturation value at $T = \bar{T}$ such that $\omega_{\text{peak}}(\bar{T}) \approx \omega_{\text{exp}}$. Essentially, \bar{T} (here about 1 K above T_c) is the temperature below which CP fluctuations average out. Correspondingly, below \bar{T} the dissipation levels off as we can essentially take $\text{Im}\chi_{CP}(\omega_{\text{exp}}) \approx \omega_{\text{low}} \delta^2(T) / [\omega_{\text{exp}} \omega_{\infty}^4(T)]$, which depends very mildly on T [experimental values for $\delta^2(T)$ and $\omega_{\infty}(T)$ are given by Ref. [5]]. We finally obtain an overall predicted critical form for the AFM dissipation:

$$W = W_0 + \frac{U}{1 + Vt^{2\gamma}}, \quad (5)$$

where U and V are positive constants. [In the notation of Ref. [5], $Vt^{2\gamma} = \gamma^2 \omega_0^4(T) / [\omega_{\infty}^4(T) \omega_{\text{exp}}^2]$ and at low t the relevant dependence on temperature is given by the $\omega_0^4(T)$ term.]

Figure 3 shows on a log-log scale the data for $W - W_0$ at $\Delta f = -40$ Hz ($z \sim 3.5$ nm) for $T > T_c \approx 117.58$ K. Considering the experimental uncertainty mainly due to noise in the dissipation signal, a slope $t^{-2\gamma}$ provides a good fit well above T_c , followed by a saturation when $t < \bar{t} \sim 10^{-2}$. Taking from Ref. [5] $\omega_{\infty}^2 \approx 0.3$ meV² and $\omega_0^2(\bar{t}) \approx 0.04$ meV², we finally observe that this saturation

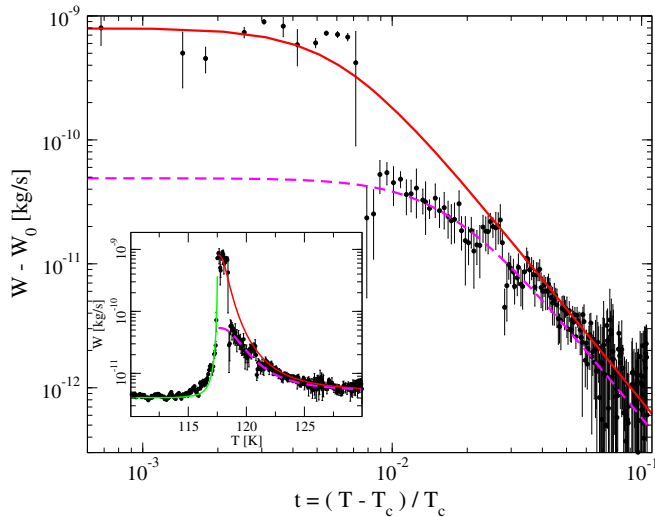


FIG. 3 (color online). Experimental dissipation W above T_c as a function of temperature (black dots). Inset: the same data on a linear temperature scale, showing data both below and above T_c . Red and green lines, fit above and below T_c according to Eq. (5); pink dashed line, fit above T_c excluding the high plateau data. The value of ω_{low} is 156 kHz (solid curve) and 44 kHz (dashed curve), both within a factor 2 of 83 kHz, the value obtained from a simple fit of the saturation temperature (see text). \bar{t} is roughly the temperature where, upon cooling from above T_c , the dissipation levels off to a plateau. Horizontal error bars corresponding to $\delta t \sim 10^{-4}$ are small and are omitted.

of AFM dissipation determines the low-energy width parameter ω_{low} as $\omega_{\text{low}} = \omega_{\text{exp}} \omega_{\infty}^2(\bar{t}) / \omega_0^2(\bar{t}) \sim 83$ kHz.

We draw, in summary, four conclusions. First, bulk structural phase transitions are indeed revealed by AFM dissipation, as was predicted [1]. Strikingly, in the present noncontact realization, this is realized without literally touching the crystal. Second, the pendulum AFM dissipation picks up precisely the long debated central peak fluctuations, here responsible for the dissipation at the extremely low AFM pendulum frequency of 11 kHz. Third, the unknown breadth ω_{low} of the central peak in the dynamical structure factor $S(\omega) = \text{Im}\chi(\omega)/\omega$ now obtained as an intrinsic property of SrTiO₃ is about 80 kHz, well below the upper bound set by the neutron resolution limit of 6 MHz. This CP width is manifested in AFM dissipation as a peak at $\omega_{\text{peak}}(T) = \omega_{\text{low}} \omega_0^2(T) / \omega_{\infty}^2(T) \approx 3.2t^\gamma$ MHz. Fourth, the noncontact, large distance tip-surface coupling elicits a phononic dissipation attributable in turn to a slowly varying tip-induced strain, and not to the primary antiferrodistortive order parameter, to which the far away tip and its motion cannot directly couple. While this realization does not reveal by itself the intimate nature of the CP , which remains open to discussion [8], it does show that the exceedingly slow critical CP fluctuations must involve a large component of strain, which is the secondary and not the primary order parameter of the structural transition.

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