Noncontact Atomic Force Microscope Dissipation Reveals a Central Peak of SrTiO$_3$
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 SrTiO$_3$, 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.

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 SrTiO$_3$. 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 ($V = V_{CPD}$) during the experiment.

Figure 1(a) shows the power $W(T)$ dissipated by the pendulum AFM as a function of temperature at different spots on the SrTiO$_3$ surface and at different tip-sample distances, as measured by the shift of the resonance frequency $\Delta f$. The dissipation is inferred from the standard expression [10] $W = W_0[A_{exc}(z)/A_{exc,0} - f(z)/f_0]$ in terms of the measured distance-dependent excitation amplitude $A_{exc}(z)$ 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 $\Delta f$ 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 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 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 SrTiO$_3$- (2 × 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 $p \approx 4.2$, in excellent agreement with that expectation.

We can now directly relate the observed dissipation to the critical central peak of SrTiO$_3$. The noncontact tip vibrating at $f \approx 11$ kHz and at large distance is a very weak perturbation on the underlying SrTiO$_3$. Thus, we can make use, rarely appropriate in nanofriction, of linear response theory. Moreover, since the AFM perturbation affects a sufficiently large portion of SrTiO$_3$, 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 $\chi$, in the form

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

where $W_0$ is the dissipation of the free cantilever ($T$ independent in the considered temperature range), $\chi$ is an appropriate momentum average of the lattice susceptibility $\chi(q, \omega, T)$, $\alpha$ 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 $\Omega$ 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 $\Pi$ would lead, in the standard textbook description of a displacive transition [25], to a $T$-dependent shift of $\Omega$, resulting in a Lorentzian peak in $\text{Im} \chi(\omega)$ at $\omega_\infty(T) = \sqrt{\Omega^2 + 2\Delta(T)}$, of width $\Gamma_0$, such that $\omega_\infty(T) \to 0$ at $T = T_c$. However, the neutron data of SrTiO$_3$ 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 $\omega_{\text{low}}$, the central peak, phenomenologically captured [5] by an additional contribution to the self-energy $\Pi$

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

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

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

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

$$\chi(0) = \int_0^\infty d\omega \frac{\text{Im} \chi(\omega)}{\pi \omega} = \frac{1}{\omega_{\text{low}}^2(T)} \sim T^{-\gamma}. \quad (4)$$

The divergence of the order-parameter susceptibility $\chi$ with an exponent $\gamma$, 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 SrTiO$_3$ 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 $\omega_{\text{peak}}(T) = \omega_{\text{low}} \omega_\text{low}^2(T) / \omega_\text{low}^2(T)$, which moves towards 0 as $T \to T_c$. We can now consider the temperature dependence of the linear response AFM dissipation at the fixed and very low oscillation frequency.
$\omega_{\exp} = 2\pi f$. As $T \to T_c$ from above the dissipation will increase, roughly as $r^{-2r}$, because $\omega_{\exp} \ll \omega_{\text{peak}}(T) \sim r^{-r}$, to reach a saturation value at $T = \tilde{T}$ such that $\omega_{\text{peak}}(\tilde{T}) \approx \omega_{\exp}$. Essentially, $\tilde{T}$ (here about 1 K above $T_c$) is the temperature below which $CP$ fluctuations average out. Correspondingly, below $T$ the dissipation levels off as we can essentially take $\text{Im}\chi_{CP}(\omega_{\exp}) \approx \omega_{\text{low}} \delta^2(T)/[\omega_{\exp} \omega_{\text{low}}(T)]$, which depends very mildly on $T$ [experimental values for $\delta^2(T)$ and $\omega_{\text{low}}(T)$ are given by Ref. [5]]. We finally obtain an overall predicted critical form for the AFM dissipation:

$$W = W_0 + \frac{U}{1 + V t^{2r}},$$

where $U$ and $V$ are positive constants. [In the notation of Ref. [5], $V t^{2r} = r^2 \omega^4_{\text{low}}(T)/[\omega_{\exp} \omega^3_{\text{low}}(T)]$ and at low $t$ the relevant dependence on temperature is given by the $\omega^3_{\text{low}}(T)$ 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 $r^{-2r}$ provides a good fit well above $T_c$, followed by a saturation when $t < \tilde{t} \sim 10^{-2}$. Taking from Ref. [5] $\omega^3_{\text{low}} \approx 0.3$ meV$^2$ and $\omega^3_{\text{low}}(\tilde{t}) \approx 0.04$ meV$^2$, we finally observe that this saturation of AFM dissipation determines the low-energy width parameter $\omega_{\text{low}}$ as $\omega_{\text{low}} = \omega_{\exp} \omega^3_{\text{low}}(\tilde{t})/\omega^3_{\text{low}}(\tilde{t}) \sim 83$ 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 $\omega_{\text{low}}$ of the central peak in the dynamical structure factor $S(\omega) = \text{Im}\chi(\omega)/\omega$ now obtained as an intrinsic property of SrTiO$_3$ 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 $\omega_{\text{peak}}(T) = \omega_{\text{low}} \omega^3_{\text{low}}(T)/\omega^3_{\text{low}}(T) \approx 3.2 r^r$ 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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