Hopping and clustering of oxygen vacancies in SrTiO3 by anelastic relaxation

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The complex elastic compliance $s_{11}(\omega, T)$ of $SrTiO_{3-\delta}$ has been measured as a function of the O deficiency $\delta < 0.01$. The two main relaxation peaks in the absorption are identified with hopping of isolated O vacancies over a barrier of 0.60 eV and reorientation of pairs of vacancies involving a barrier of 1 eV. The pair binding energy is $\simeq 0.2$ eV, and indications for additional clustering, possibly into chains, is found already at $\delta \sim 0.004$. The anisotropic component of the elastic dipole of an O vacancy is $\Delta\lambda = 0.026$. The possible role of electrostatic repulsion between vacancies in slowing the kinetics for their aggregation is discussed.

Diffusion and aggregation of oxygen vacancies (V_O) in perovskites are still poorly understood, although they have implications in several types of applications, such as in solid state electrolytes for fuel cells or fatigue in ferroelectrics. One of the most studied perovskites is $SrTiO_{3-\delta}$, which has been heavily doped with V_O since the 1960s, e.g., for inducing superconductivity, but only recent experiments[1,2] raised questions on the assumption that the V_O introduced by high temperature reduction are uniformly distributed over the bulk. In addition, there is a large spread of the estimates of the activation energy for their diffusion,[3] although the prevalent opinion is that in most titanate perovskites the barrier for V_O hopping is $\simeq 1$ eV.[4–6] An O vacancy in a perovskite lattice has tetragonal symmetry and, therefore, an associated tetragonal distortion, or elastic dipole, which reorients by 90° after each jump, causing anelastic relaxation;[7] in addition, being a charged defect, a hopping V_O causes fluctuations of the electric field that, thanks to the quadrupolar interaction with the surrounding nuclei, may be detected by nuclear magnetic relaxation (NMR). Indeed, two relaxation processes are found by NMR in $SrTiO_3$, with activation energies of 0.62 and 1.1 eV, and are attributed to hopping of V_O which are free or trapped by Fe, respectively.[8] On the other hand, $SrTiO_3$ reduced in H_2 presents a rich anelastic relaxation spectrum, including two processes with 0.6 and $\simeq 1$ eV, tentatively attributed to H and V_O hopping.[6] Here, anelastic relaxation measurements on a $SrTiO_3$ crystal reduced in CO are presented, providing evidence that the barrier for hopping of isolated vacancies is indeed 0.60 eV, as also estimated in recent calculations,[9] but aggregation into pairs and possibly chains occurs already at low δ, thus explaining the higher activation energy for diffusion that is generally found.

The sample was cut from a $SrTiO_3$ wafer from M.T.I. Corporation as a bar of $26.15 \times 3.4 \times 0.5$ mm³, with the edges parallel to the $\langle 100 \rangle$ directions. The sample was covered with silver paint on a face, suspended on thin thermocouple wires at the nodal lines, and electrostatically excited on its first and fifth flexural modes at 5.5 and 74 kHz; the electrode-sample capacitance was part of a resonant circuit, whose frequency (~ 10 MHz) was modulated by the sample vibration, thus allowing the vibration to be detected. The real part of the s_{11} compliance could be measured from the fundamental resonance frequency f as $s'_{11} = \rho^{-1}(0.973 fl^2/h)^{-2}$

$= 3.64 \times 10^{-13}$ cm²/dyn at room temperature, where l, h, and ρ are sample length, thickness, and density.[7] The elastic energy loss coefficient $Q^{-1} = s''_{11}/s'_{11}$ was measured from the free decay of the sample vibration or from the width of the resonance curve. The jumps of V_O cause a reorientation by 90° of the direction of the nearest neighbor Ti atoms and, therefore, also of the associated tetragonal elastic dipole λ (actually a quadrupole), having only two independent diagonal elements λ_1 and λ_2; the resulting relaxation $\delta s''_{11}$ of the compliance causes a peak in $Q^{-1}(\omega, T)$,[7]

$$Q^{-1} = \frac{\delta s''_{11}}{s'_{11}} = \frac{2}{9} \frac{c v_0}{s'_{11} k_B T} (\Delta\lambda)^2 \frac{\alpha(\omega\tau)^\alpha}{1 + (\omega\tau)^{2\alpha}}, \quad (1)$$

where $\Delta\lambda = \lambda_1 - \lambda_2$, c is the concentration of the relaxing defect, v_0 is the molecular volume, $\omega = 2\pi f$, $\tau = \tau_0 e^{W/k_B T}$ is the relaxation rate over a barrier W, the parameter $\alpha \lesssim 1$ reproduces a possible broadening, and the maximum occurs near the temperature where $\omega\tau = 1$.

For the reduction-oxidation treatments, the sample was inserted in a flattened cylindrical holder of Pt that was exposed to a flux of 1 bar of O_2 or 0.9 Ar+0.1 CO, and heated by induction within a quartz tube cooled with water. Each reduction was preceded by oxygenation for 1.5 h at 950 °C that restored the white translucent aspect. The O deficiency was deduced from the mass change and from the temperature T_0 of the cubic-to-tetragonal transformation appearing as a step in the elastic compliance near 105 K.[6] The highest deficiencies were estimated from the mass loss as 0.0066 ± 0.001 and 0.0070 ± 0.001, and resulted in $T_0 = 92.4$ and 91.7 K, respectively. The assumption of a linear $T_0(\delta)$ combined with $T_0(0) = 105.2$ and 106.9 K before and after the cycle of experiments yield $T_0(\delta) = (106 - 2050\delta)$ K; the reported doping δ is deduced from this relationship. The shift of $T_0(0)$ suggests that the 14 high temperature treatments for reduction, homogenization, and reoxidation, each preceded by mechanical removal of the silver paste, may have introduced some damage in the sample (only part of the results is reported here).

Figure 1 presents the $Q^{-1}(T)$ curves in the as-received state (curve 0) and after various reduction treatments: $\delta = 0.00088$ after 1 h at 950 °C (curve 1), $\delta = 0.0018$ after 1 h at 1000 °C (curve 2), $\delta = 0.0041$ after 3 h at 1085 °C
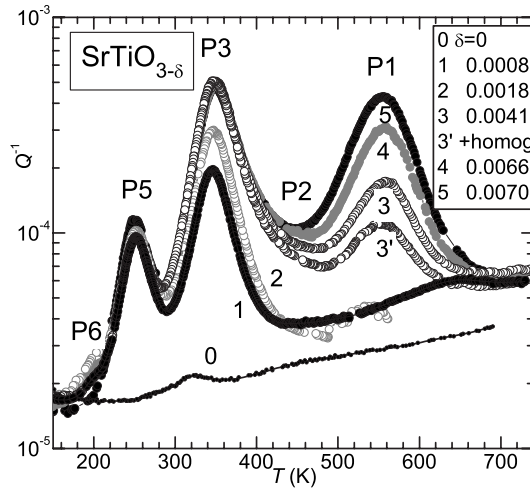
FIG. 1. Elastic energy loss coefficient of $SrTiO_{3-\delta}$ measured at 5.4 kHz at various concentrations of V_O. The sequence is according to δ and not chronological.

FIG. 2. Anelastic spectra corresponding to curves 1, 2, and 5 of Fig. 1, measured on the first (circles) and fifth (lines) modes.

(curve 3), $\delta=0.0066$ after 3 h at 1100 °C (curve 4), and $\delta=0.0070$ after 3 h at 1150 °C (curve 5). After reduction, the sample was cooled to room temperature in 2 min (curves 3, 4, and 5) or homogenized for 1 h in the same reducing atmosphere at 800 °C (curves 1, 2, and 3′); at such low temperature, no further O loss occurs. The $Q^{-1}(T)$ curves confirm our previous measurements on ceramic samples,[6] with six peaks here labeled P1–P6 starting from high temperature.

All of them are shifted to higher temperature when measured at higher frequency, indicating that they are due to thermally activated relaxation processes; this is shown for curves 1, 2, and 5 in Fig. 2. Peak P1 has an activation energy of $\simeq 1$ eV and, therefore, it had been associated with the jumps of V_O (we were not aware of Ref. 8), while peak P3 had been associated with H hopping, since its intensity saturated immediately and the reductions were carried out in H_2 atmosphere.[6] Here, there is no reason for H contamination, and therefore, such an assignment must be excluded. Peak P5 is certainly associated with doping, but with a very weak dependence for $\delta>0.001$; it might be related to polaronic relaxation or off-center Ti and it will not be considered further; a minor peak P6 and indications for another peak between P3 and P5 are hardly detectable.

The frequency dependence of the anelastic spectra is shown for curves 1, 2, and 5 in Fig. 2, and the changes in the intensities of the peaks at higher frequency are fully meaningful, since both frequencies were measured during the same run. The main features are (i) the intensity of P3 is $\propto 1/T$ at the lowest δ when P1 is undetectable, and (ii) becomes a strongly increasing function of T at higher δ; (iii) the intensity of P1 decreases faster than $1/T$. All these observations may be explained if P3 is due to hopping of isolated V_O, while P1 is due to the reorientation of pairs of V_O. Indeed, the activation energy of P3, 0.60 eV, is in good agreement with the NMR experiment,[8] while clustering of the V_O in $SrTiO_3$ has been proposed[1,2] and recent calculations suggest that second neighbor pairs of V_O should be stable.[9] The proposed picture is as follows: at very low O
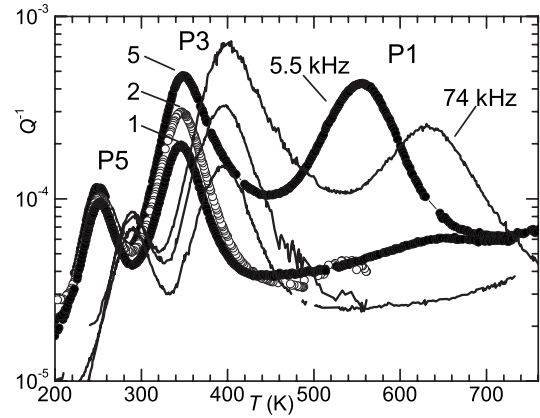
deficiency, practically all V_O are free, with a concentration $c_f \simeq \delta$; the intensity of P3 is $\propto c_f/T$ and, therefore, $\propto 1/T$. Already at $\delta \gtrsim 0.001$, the concentration c_p of pairs of V_O is significant and, due to thermal dissociation, $c_p(T)$ is a decreasing function, while $c_f(T)$ becomes increasing, since $c_f + 2c_p \simeq \delta$. This explains both the pronounced decrease of the height of P1 with T and the fact that the height of P3 reverts to an increasing function of T.

The first attempts to fit all the spectra have been done taking into account only isolated and paired V_O, whose concentrations may be estimated as stationary solutions of rate equations for the formation of pairs with binding energy E_p. In this manner, however, it is impossible to fit all the spectra with the same set of E_p and elastic dipole anisotropies $\Delta\lambda$; in fact, the actual intensity of P1 increases with δ much less than predicted by the model. This suggests further clustering of V_O, e.g., formation of chains along the $\langle 100 \rangle$ directions, which are predicted to be stable;[9] only the V_O at the ends would contribute to P1, since the internal V_O would be bound stronger and require a higher energy for jumping out of the chain, hence contributing to anelastic relaxation at higher temperatures. The quantitative description of the formation of V_O chains cannot be worked out in a simple manner, and it has been chosen to adopt the grand canonical formalism with the approximation of dividing the lattice into small partitions, within which the formation of pairs and chains can be treated exactly.[10] Figure 3(a) shows the configurations of pairs and triplets of V_O that have been considered, besides the isolated V_O with site energy $E_f=0$. A binding energy E_p is attributed to both pairs of the type V_O-Ti-V_O and in adjacent cell faces; E_{nn} to nearest neighbor pairs and E_c to each V_O within a chain, while the ends of a chain contribute with E_p.

The grand partition function[11] $Z=\Sigma_\alpha m_\alpha e^{(n_\alpha\mu-E_\alpha)/k_BT}$ is written for three adjacent cells, so that it is possible to include the formation of chains of up to four V_O. With three cells, it is still easy to count the multiplicities m_α of the possible configurations α with n_α vacancies and with energy E_α by simple inspection, and the calculation of the chemical potential μ and of the concentrations c_α are simple enough to be integrated into the nonlinear least square fitting routine.
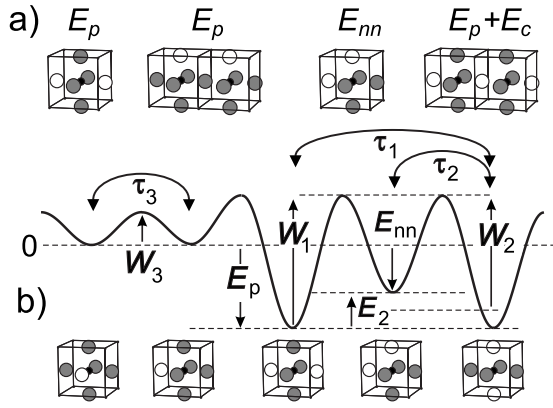
FIG. 3. (a) possible configurations of two or three V_O (empty circles) with the respective energies. The Ti atoms are at the cell centers and Sr at the vertices. (b) Potential energy profile for various jumps of V_O; below each minimum is shown the corresponding configuration.

Defining $b=e^{-E_p/k_BT}$, $b_c=e^{-E_c/k_BT}$, and $x=e^{\mu/k_BT}$ results in $Z=1+16x+(17b+67)x^2+(6bb_c+88b)x^3+(bb_c^2+24b^2)x^4$, where $16x$ is the statistical weight of a single V_O in one of the 16 O sites of three cells, $17bx^2$ is the weight of the possible 17 pairs with energy E_p, and so on. The nearest neighbor configuration nn, with energy E_{nn} is the intermediate step for the reorientation of a pair, but its statistical weight is negligible and is omitted. The chemical potential μ must satisfy the implicit equation

$$\delta = \frac{3}{16}c = \frac{3k_BT}{16}\frac{\partial \ln Z}{\partial \mu} = c_f + 2c_p + c_c, \qquad (2)$$

where it is recognized that the maximum possible concentration $c=16$ over three cells corresponds to $\delta=3$. This implicit equation for x has to be solved numerically for each T. The decomposition of c into the various c_α is obtained by keeping track of the contributions of the various terms in Z: $c_f=\frac{3}{16Z}(16x+134x^2+88bx^3)$, $c_p=\frac{3bx^2}{16Z}[17+(6b_c+88)x+(b_c^2+48b)x^2]$, and $c_c=\frac{3bb_cx^3}{8Z}(3+b_cx)$.

Figure 3(b) shows the potential profile of the relaxation processes corresponding to P1, P2, and P3, where W_i are the barrier heights and E_i the site energies taking as zero the isolated V_O. Peak P3 is fitted with Eq. (1) with $c=c_f$, and P1 with $c=c_p$; the intermediate relaxation involving the nn pair should have an intensity proportional to $c_p/[T\cosh^2(E_2/2k_BT)]$, valid for the low concentration limit,[10] and rate $\tau_2^{-1}=\tau_{02}^{-1}e^{-W_2/k_BT}\cosh(E_2/2k_BT)$, where $E_2=2(W_1-W_2)$ is the asymmetry between the two states.

The fit to the case $\delta=0.007$ is shown in Fig. 4, and similar fits are obtained for the other concentrations $\delta>0.001$ assuming binding energies $E_p=0.184$ eV and $E_c=0.26$ eV. The parameters for the isolated V_O deduced from P3 are as follows: anisotropic component of the elastic quadrupole $(\Delta\lambda)_3=0.026$, hopping rate with $W_3=0.60\pm0.007$ eV and $\tau_{03}=(5\pm1)\times10^{-14}$ s; for the pair reorientation (peak P1), $(\Delta\lambda)_1=1.87\times(\Delta\lambda)_3$, slightly less than for two independent V_O, and the reorientation rate has $W_1=0.97\pm0.04$ eV and

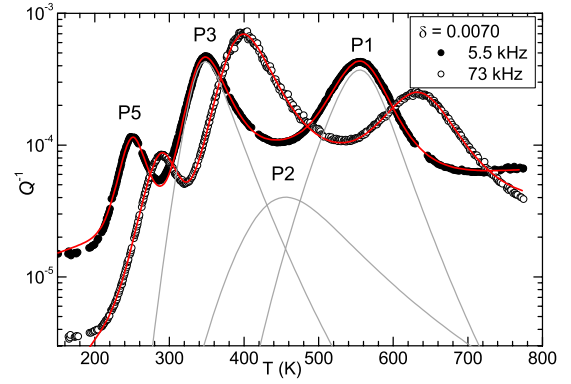

FIG. 4. (Color online) Fit of the experimental curves for $\delta=0.007$ measured at 5.5 and 73 kHz with $E_p=0.183$ eV and $E_c=0.267$ eV; also shown are the components P1, P2, and P3 at 5.5 kHz.

$\tau_{01}=(7\pm4)\times10^{-14}$ s; no broadening is found ($\alpha\gtrsim0.95$) for P1 and P3. The intermediate relaxation P2 has $W_2\sim0.86$ eV and $E_2\sim0.17$ eV, but is much broader and more intense than expected from the intermediate configuration of reorienting pairs, since $\alpha_2\sim0.35$ and $(\Delta\lambda)_2\sim5(\Delta\lambda)_3$. It is, therefore, possible that also other configurations, e.g., third neighbor V_O, contribute to P2; recent calculations, indeed, indicate that the interaction energy of V_O may be quite large also at higher distances.[9] With $\Delta\lambda$ as small as 0.026, the distortion around a V_O is almost isotropic (for interstitial O in bcc metals,[7] $\Delta\lambda\sim1$), as predicted.[12] The small anisotropy makes the long range elastic interaction among the dipoles negligible, especially at these low concentrations, and, in fact, there are no indications of critical slowing down and ordering of the V_O dipoles; these phenomena are instead observed, for example, in the perovskitelike $RuO_{2-\delta}$ layers of $RuSr_2GdCu_2O_{8-\delta}$.[13] Finally, peak P5 has $W_5=0.43$ eV, $\tau_{05}=(1\pm0.5)\times10^{-13}$ s, and $\alpha_5=1$.

Only the spectrum with $\delta\simeq8.8\times10^{-4}$ (curve 1 of Fig. 1) cannot be reproduced with the same parameters, but requires $\delta=6.4\times10^{-4}$, slightly smaller than estimated from the transition temperature T_0 but within the error, and $E_p\simeq0.1$ eV; otherwise, it is impossible to obtain the $1/T$ dependence of the intensity of P3. A possible explanation is that there is a fraction of V_O that is strongly trapped at lattice defects; the influence of such defects would be particularly evident in curve 1, since it has the smallest δ and was also the last measurement of the series. Indications of lattice damage accumulated during the treatments are the presence in curve 1 of a broad peak at temperature higher than that of P1 and the shift of T_0 mentioned above.

Let us comment on the time for reaching true thermodynamic equilibrium. In fact, after the sample was reduced at the highest values of δ and cooled to room temperature within a couple of minutes, the distribution of V_O was not in equilibrium. This is demonstrated by the effect of a homogenization treatment of 1 h at 800 °C, here shown in curves 3 and 3′ of Fig. 1: all the peaks remain unaffected except for P1, which decreases. This certainly cannot be explained by O uptake during homogenization, due to the absence of O_2 in the reducing atmosphere, nor can it be explained in terms of

further loss of O, which occurs at higher temperatures and results in an increment of the height of P1. It must be concluded that the concentration of V_O pairs decreases during homogenization due to the formation of more stable O clusters. Within the proposed picture, the suppression of P1 is explainable in terms of lengthening of the chains of V_O which reduces the fraction of pairs and chain ends.

A seeming inconsistency exists between the fact that peaks P1, P2, and P3 imply hopping rates of isolated and aggregated V_O exceeding 10^4 s^{-1} already at 600 K, while the aggregation into longer chains near 1100 K requires hours. The situation is quite similar to that of the ordering of the O atoms in the CuO_x planes of semiconducting $YBa_2Cu_3O_{6+x}$,[14] which also are perovskitelike layers. In that case, the isolated O atoms in the almost empty CuO_x planes ($x < 0.3$) hop over a barrier as low as 0.11 eV and promptly form stable pairs or short chains whose dissociation energy is ~1 eV, but reaching equilibrium with longer O-Cu-O chains requires very long times. The explanation proposed for such a behavior is that the saddle point for an O^{2-} ion to join another O^{2-} ion or chain fragment is higher than that for hopping away from it, due to the electrostatic repulsion. The analogous effect is shown for the V_O in Fig. 3(b), where the saddle points involving pairs are higher than those between free V_O. If we assume that all the saddle points involving pairs are similar, as depicted in Fig. 3(b), then they are higher than in the empty lattice by $W_1 - E_p - W_3 \sim 0.19$ eV.

Notice that the rate for forming and dissociating a pair is not probed by any of the observed peaks (possibly by P2), and it is possible that the enhancement of the corresponding saddle point is even more than 0.19 eV. In this manner, it would be explainable why the rate for constructing and rearranging the chains is much slower than that for the pair reorientation. The fact that it is difficult to assess when the sample is in real thermodynamic equilibrium, together with the approximate treatment of the lattice as an ensemble of triplets of cells, puts some limitation on the confidence of the binding energies E_p and E_c derived from the fits of the anelastic spectra.

In conclusion, the anelastic spectrum of $SrTiO_{3-\delta}$ exhibits relaxation peaks that are assigned to (i) hopping of isolated O vacancies over a barrier of 0.60 eV, (ii) reorientation of pairs of vacancies over a barrier of 0.97 eV, and (iii) jumps involving the intermediate step for the pair reorientation and other configurations. Sizable formation of pairs starts at δ as low as 0.002, and there is evidence of further aggregation, possibly into chains. The pair binding energy is estimated as 0.18 eV, while the binding energy of additional vacancies in a chain is ~0.26 eV.

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