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## Comment on the physical mechanisms of the 37 K and 65 K anomalies in strontium titanate

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**Abstract.** We show that the relaxation mechanism for ultrasonic and dielectric anomalies at 65 K is due to long-wavelength ( $q = 0$ ) optical phonons that would be described at  $\Gamma'_{25}$  ( $F_{2g}$ ) in the cubic  $O_h$  high-temperature phase whose frequency is known to be 62 meV ( $499 \text{ cm}^{-1}$ ) at the R-point Brillouin zone boundary; for the anomaly at 37 K the interaction is also with a  $q = 0$  phonon, but it is with a different symmetry silent  $F_{2u}$  branch of the  $O_h$  phase at 33 meV ( $268 \text{ cm}^{-1}$ ). Since the eigenvector of this mode at 33 meV is known exactly (it is the only mode having the  $F_{2u}$  irreducible representation) and since it involves only oxygen motion (by symmetry), we can conclude rigorously that only oxygen displacements contribute to the dielectric relaxation at 37 K. The other temperatures at which the dielectric loss exhibits maxima (namely, 8, 18 and 30 K) are all proportional to the known energies of  $q = 0$  transverse optical phonons (at 48, 110 and  $171 \text{ cm}^{-1}$ ), suggesting that the observed sequence of five relaxation peaks involves the same defect (polar clusters of oxygen vacancies?) interacting in turn with each phonon mode as temperature is increased. This provides a single mechanism for all relaxation peaks, which heretofore had received interpretation in terms of qualitatively different mechanisms.

The dielectric and ultrasonic anomalies in  $\text{SrTiO}_3$  at 37 K and 65 K are well known and have been reviewed recently [1–4]. Various models have been proposed to explain them, especially that at 37 K; these include the existence of a macroscopically coherent quantum state [5], the onset of second sound [6–9], the effect of polar clusters [2, 3, 10–13], anharmonic phonon interactions [14] and the effects of domain wall freezing [15–19].

In the present article we point out that the dielectric relaxation mechanisms quantitatively evaluated by Chen Ang *et al* [1–3] clearly show that the dipolar interactions are with very specific, identifiable  $q = 0$  long-wavelength optical phonons.

The most important things established, thus far, about the relaxations at 37 K and 65 K are that they are qualitatively different. That at 65 K is dilatational, as inferred from its specific elastic coefficient anomalies [14], and it exhibits [1] positive temperature dispersion (that is, a shift in the temperature at which the dielectric loss peak is maximum to lower temperatures as frequency is decreased). That at 37 K is a dynamic shear anomaly [14], and its dispersion is [1] negative (lower temperature peak at higher frequencies). The negative dispersion of the 37 K anomaly is similar to that in dipolar glasses and suggests a possible connection with the models of Viehland *et al* [20].

Quantitative evaluation of the frequency dispersion by Ang Chen *et al* [1] showed that the 65 K relaxation is of Arrhenius form

$$t = t_0 \exp(U/kT) \quad (1)$$

**Table 1.** Thermal energies  $kT$ , phonon energies  $E$ , and activation energies  $U$  for dielectric relaxations in SrTiO<sub>3</sub>.

Temperature $T_i$ of dielectric loss peak [1–3] (K)	$kT_i$ (meV)	Arrhenius activation energy $U_i$ (meV)	$q = 0$ phonon energy $E$ [21, 25] (meV)	Ratio $U/kT$ or $E/kT$
65	5.6	$62 \pm 2$	62 (499 cm <sup>-1</sup> ) F <sub>2g</sub>	11.1
37	3.2	$33 \pm 1$	33.5 (268 cm <sup>-1</sup> ) F <sub>2u</sub>	11.5
30	2.6	—	29 (235 cm <sup>-1</sup> ) B <sub>2g</sub>	11.2
23	2.0	$45 \pm 1$ †	22 (178 cm <sup>-1</sup> ) F <sub>1u</sub>	11.0
18	1.5	—	13.6 (110 cm <sup>-1</sup> ) F <sub>1u</sub>	11.0
8	0.7	—	6.0 (48 cm <sup>-1</sup> ) A <sub>1g</sub> (Γ <sub>25</sub> )	11.7

† This value from Sotnikov *et al* [19], though phonon-like in energy, does not fit the general pattern.

with  $U_1 = 62 \pm 2$  meV. Here we point out that this is the exact frequency of an optical phonon, which in the cubic high-temperature O<sub>h</sub><sup>1</sup> ( $Pm3m$ ) phase is at the R-point of the Brillouin zone. Similarly, the 37 K relaxation anomaly also satisfies (1), but with  $U_2 = 33 \pm 1$  meV, which is exactly equal [21] to the known ‘silent mode’ transverse optical (TO) and longitudinal optical (LO) F<sub>1u</sub> doublet at 268 cm<sup>-1</sup>.

For optical modes in SrTiO<sub>3</sub> in the cubic phase, the long-wavelength ( $q = 0$ ) optical phonons are divided [22–24] into three triply degenerate, infrared-active F<sub>1u</sub> (Γ<sub>15</sub>) modes (TO at 40, 171 and 560 cm<sup>-1</sup>; LO at 175, 473 and 815 cm<sup>-1</sup>) and one ‘silent’ F<sub>2u</sub> (Γ<sub>25</sub>) mode at 268 cm<sup>-1</sup> (33 meV) that is neither infrared nor Raman allowed [21]. We compare the transverse phonon energies in table 1, expressed in meV rather than cm<sup>-1</sup>, with the temperatures  $kT_i$  at which the dielectric loss peaks (maxima) occur at 8 MHz.

In addition to these cubic-phase modes, which persist into the tetragonal phase with small splittings, there are a number of optical phonons at the R-point (body-diagonal corner) of the Brillouin zone [25]. These are as follows: A<sub>2g</sub> (Γ<sub>2</sub><sup>′</sup>) near 800 cm<sup>-1</sup>; F<sub>2g</sub> (Γ<sub>25</sub><sup>′</sup>) near 500 cm<sup>-1</sup>; F<sub>1u</sub> (Γ<sub>15</sub>) near 400 cm<sup>-1</sup>; E<sub>u</sub> (Γ<sub>12</sub><sup>′</sup>) at 235 cm<sup>-1</sup>; F<sub>1u</sub> (Γ<sub>15</sub>) near 110 cm<sup>-1</sup>; and the F<sub>2u</sub> (Γ<sub>25</sub>) soft mode near 30 cm<sup>-1</sup>. These modes also become describable as  $q = 0$  in the cell-doubled tetragonal 14/ $mcm$ (D<sub>4h</sub><sup>18</sup>) superlattice and can therefore produce strong one-phonon dielectric relaxation processes.

It is important to note that the mode at 268 cm<sup>-1</sup> has no oscillator strength. Therefore the interaction of this LO mode with electronic charges in strontium titanate cannot be of the usual Frohlich interaction form. Moreover, only the oxygen ions move in this mode. The strontium and titanium ions are motionless. Therefore dielectric relaxation involving this optical phonon mode probably involves oxygen vacancies; this differs from the suggestion of Chen Ang *et al* [26].

Similarly, the F<sub>2g</sub> (Γ<sub>25</sub><sup>′</sup>) mode near 500 cm<sup>-1</sup> (originally inferred at 499 cm<sup>-1</sup>) by Nilsen and Skinner [27] has a small oscillator strength, since its polarity arises only below 105 K and in proportion to the order parameter [28–30]; so it also cannot couple efficiently with electronic charge via long-range, coulombic, Frohlich interactions. Hence, it is short-range deformation interactions that must be examined.

To examine deformation potential interactions it is useful to examine actual eigenvectors for the modes in question. The eigenvectors of these modes are shown in illustrations by Herzberg [31] and are not reproduced here. The 33 meV mode is known exactly by symmetry, since it is the only mode having irreducible representation F<sub>2u</sub>. It consists of diagonal displacements of the four planar oxygen ions about the central titanium ion; that is, for oxygen ions initially centred on the ABO<sub>3</sub> cube faces along [100] directions, the displacements are toward the centres of the cube edges, [110]. The 65 meV mode cannot be determined from

symmetry alone, since there are three different normal modes of symmetry  $F_{1u}$  ( $\Gamma_{15}$ ). However, since these three modes are widely separated in frequency, any reasonable force-constant model can be used to identify them to a good approximation. The highest of the three  $F_{1u}$  modes (near  $560\text{ cm}^{-1}$ ) is essentially a Ti–O stretching mode in which the titanium ion and nearest neighbour oxygens move out of phase; the second highest (at  $178\text{ cm}^{-1}$ ) is a Ti–O bend in which the four planar oxygen ions move up and the oxygens above and below the titanium move down. The lowest energy  $F_{1u}$  (at approximately  $40\text{ cm}^{-1}$ ) has the  $\text{TiO}_2$  cation move against the Sr ion.

We note empirically that the energies  $U_1 = 33\text{ meV}$  and  $U_2 = 62\text{ meV}$  of the two dielectric relaxations described above, obtained from fitting their relaxation times, are in proportion to the thermal energies  $kT_1$  and  $kT_2$  (37 K and 65 K) at which they occur. The ratio  $U/kT = 11.3 \pm 4$  in each case.

We also note that Chen Ang *et al* [1–3] have in fact observed dielectric relaxation peaks at five different temperatures, only two of which have been fitted to Arrhenius activation energies  $U - 1$  from (1). Three other peaks lie at 8 K, 18 K and 30 K. The 23 K peak is from ultrasonic attenuation [14]. We observe in table 1 that, empirically, the energy of each of these peaks satisfies a similar relationship with a known  $q = 0$  optical phonon, the energies of which are discussed above. The ratio of temperatures at which dielectric loss peaks to known  $q = 0$  transverse optical phonons (note, no longitudinal modes) suggests that the series of five loss peaks reported by Chen Ang *et al* [1–3] are due to a single kind of defect (identified as oxygen site only from the  $268\text{ cm}^{-1}$  mode), which, as temperature increases, undergoes successive relaxations involving the known long-wavelength phonons. Hence, instead of requiring five different physical relaxation mechanisms (Mizaras and Loidl [32], Viana *et al* [33], Chen Ang *et al* [1–3]), we invoke a single polar cluster interaction with five known  $q = 0$  optical phonon modes as temperature is increased. This empirical observation has the virtue of simplicity.

Note, however, that the present analysis has no microscopic physical explanation for the empirical relationship between  $kT_i$  loss peak temperatures and their activation energies  $U_i$ ; the ratio  $U/kT = 11.4$  is unexplained. However, we note that in other sub-disciplines in solid-state physics, the temperatures  $kT_i$  at which dynamic losses occur are typically an order of magnitude lower than the optical-phonon driven activation energy for the loss [34]; as one example we note that the three internal friction peaks of Zr–H impurity pairs in Nb occur [35] at  $T_i = 100\text{ K}$ ,  $130\text{ K}$  and  $160\text{ K}$  and exhibit activation energies  $U_i/K_B$ , respectively, of 800 K, 1670 K and 2000 K—ratios of 8:1, 12.8:1 and 12.5:1, quite comparable to that of 11.3:1 in the present study (1670 K corresponds to the Zr–H vibrational frequency at approximately  $1900\text{ cm}^{-1}$ ). Similarly, the Ni–Cr alloy internal friction peak at  $T_i = 950\text{ K} = 82\text{ meV}$  has [36] an activation energy  $U_i = 2.92\text{ eV}$  for a ratio of 35:1. A third example is in the very recent spin-relaxation study of Zhai *et al* [37] on ‘SrCaCuO’— $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ , it is found that  $kT_i = 160\text{ K}$ , whereas the activation energy  $U_i$  comes from optical phonons at about 400 K. In general, the ratio of these energies  $kT_i/U_i$  arises from the coupling coefficient; that is, in SrCaCuO there is a coupling of a spin-system to optical phonons, and in the case of strontium titanate there is a dipolar-defect mode, which couples to optical phonons. The temperature at which this coupled mode exhibits maximum dielectric loss involves both the optical phonon energy and the coupling constant. Thus, in table 1, the parameter  $U/kT = 11.4$  may be regarded as the coupling constant in our case and the results show that the coupling constant is the same for all  $q = 0$  optical phonons in strontium titanate (a nice simplification). Of course, it is still possible, instead, that the temperatures at which  $\epsilon''$  exhibits peaks may arise from apparently unrelated effects, such as optic mode crossing at 37 K or domain wall freezing, but the rather exact ratio of 0.088 for  $kT_i/U_i$  in each case for which the phonon energies are accurately known looks suspicious, and suggests that one should invoke a single mechanism in all cases.

We draw the following conclusions.

- (1) The dielectric relaxation at 37 K in strontium titanate involves a single long-wavelength optical phonon mode. This is the 'silent'  $F_{2u}(\Gamma_{25})$  mode in the cubic phase representation. The eigenvector of this mode is known exactly since it is the only mode having this irreducible representation. The interaction of this mode with polar clusters, probably of oxygen vacancies, to produce dielectric relaxation involves no long-range Coulombic field (Frohlich interaction), only short-range deformation-potential effects. This mode is not related to the tetragonal phase transition dynamics in any way. Its eigenvector rigorously involves only oxygen motion (no Sr or Ti displacements). Therefore, it most probably involves an oxygen-vacancy-mediated relaxation process.
- (2) The dielectric relaxation at 65 K in strontium titanate involves a single optical phonon mode, a mode that would be described as  $F_{2g}(\Gamma'_{25})$  at the R-point zone boundary in the cubic representations, but becomes  $q = 0$  in the doubled-cell tetragonal phase. This mode couples to long-wavelength fluctuations only below the phase transition at 105 K and its coupling is proportional to the order parameter for that transition (out of phase rotation of  $\text{TiO}_6$  octahedra). It has no dipole above 105 K and its interaction is therefore also not long range. It was originally interpreted in terms of domain-wall dynamics [32].
- (3) The six dielectric and ultrasonic loss peaks from 8 K to 65 K in strontium titanate can be interpreted as a single polar entity (probably clusters of oxygen vacancies) sequentially coupling to six different  $q = 0$  long-wavelength optical phonons *with the same coupling constant* as temperature is increased.

The problem of a charged, localized centre (or cluster) interacting with optical phonons is well known in a different context. In the strong-coupling limit (which would be appropriate for F-centres) there are intense multi-phonon contributions [38–40]. Since these are not observed in  $\text{SrTiO}_3$  we assume that the weak-coupling one-phonon limit is suitable. In the review of Pryce [41] it is pointed out that there are generally no wave-vector restrictions on the phonon relaxations and that LO modes should couple more strongly than TO modes, so that the relaxation spectrum against frequency looks like a LO one-phonon density of states. This is also in disagreement with the present experimental results, where the observed  $q = 0$  transverse phonon relaxations suggest that the charge centre responsible for the relaxations is an extended defect, or alternatively, that the electrons are highly correlated. Pryce develops a formalism for linear coupling with an arbitrary phonon spectrum at frequencies  $f_i$ . However, this gives only a monotonic temperature dependence and does not predict dielectric relaxation peaks at temperatures which are some fixed fraction of  $hf_i/k_B$  (1/11.4 in our case).

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