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Comment on "Intrinsic dielectric frequency dependent spectrum of a single domain tetragonal BaTiO3" [J. Appl. Phys. 112, 014108 (2012)]

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Additional information on J. Appl. Phys.

Comment on "Intrinsic dielectric frequency dependent spectrum of a single domain tetragonal BaTiO₃" [J. Appl. Phys. 112, 014108 (2012)]

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In a recent publication, Liu *et al.* [Appl. Phys. **112**, 014108 (2012)] proposed a model for evaluating the dielectric function along the ferroelectric axis in the tetragonal phase of barium titanate, ε_c. In what follows, however, we argue that their interpretation of this model is physically inconsistent. © *2013 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4798231]

The coexistence of order-disorder and displacive features in typical ferroelectrics has been a controversial issue for decades. Barium titanate (BTO) is frequently quoted in this context. Recently, such a coexistence was clearly revealed in this compound,[2] which has thence triggered a flurry of work aiming at unraveling the nature of the underlying phonon modes.[3–6] The work by Liu *et al.*[1] makes an interesting contribution in this respect.

The directly measured ε_c has been long known at variance with the contributions as estimated via Lyddane-Sachs-Teller relation from ordinary optical phonon modes, namely the so-called Last mode, Axe mode, and Slater mode.[7,8] The discrepancy can be understood in terms of an additional Debye mode, which has evaded all efforts until very recently.[2] Both computer simulations[2] and atomistic considerations[5] suggest that the Slater mode and the Debye mode probably originate from the same polar degree of freedom. In particular, the latter may be linked with the Ti flips between the P and $-P$ direction. Here, P denotes the spontaneous polarization of the ferroelectric phase. The simulated flipping frequency of a single Ti ion seems somewhat bigger than the relaxation rate of the Debye mode.[2] However, the flipping frequency of a Ti cluster should be smaller and a better representation of this rate.

The above physical picture is in accord with Comes' eight-site model,[9] which has been studied in various ways.[3,4,10–14] In this model, a Ti ion is supposed to flutter among eight equivalent sites that are cubically distributed about the center of the corresponding oxygen cage. A phase transition is characterized by a change in the symmetry of the pattern in which these sites are populated. In cubic phase, all sites are equally populated. In tetragonal phase, however, the presence of molecular field lowers the population symmetry. As a result, a Ti ion preferentially visits the four sites (privileged sites) that are along the P direction. Consequently, a Ti ion spends most time hopping within these privileged sites. This hopping was associated by Liu *et al.* to the relaxation mode Hlinka *et al.* discovered in ε_c. In tetragonal phase, such hopping represents motions perpendicular to the ferroelectric axis, namely along a-direction (see Fig. 1 in Ref. 1).

The expression of ε_c given by Liu *et al.*, Eq. (4) in their work,[1] implies two different contributions from the abovementioned Ti hopping mode. The first contribution corresponds to the second term in their Eq. (4). It is of the standard Debye form with finite oscillator strength. The second contribution is contained in the third term in Eq. (4). This term also includes contributions from the ordinary phonon modes. In the second contribution, vanishing bare oscillator strength was assumed for the hopping mode but its coupling to ordinary phonon modes affords it a finite spectral weight.

However, their formula contradicts the following fact: the Ti hopping has no direct coupling to an electric field applied in the ferroelectric axis and therefore cannot make any direct contribution to ε_c. In other words, as required by the oscillator strength sum rule,[15] the spectral weight integrated over the entire frequency range should be regardless of the Ti hopping. Consequently, the second term in Eq. (4) makes redundant contribution given the form of the third term. The latter has already captured the contributions from all modes under their consideration, including the hopping and ordinary phonon. The second term would exist only if there existed direct coupling between the Ti hopping and external electric field.

Another moot point may be raised by noting that the Ti hopping mode should actually be responsible for the tetragonal-orthorhombic transition that takes place at about 290 K. Near structural instability, we may assume the average hopping time of a simple Debye form: $\tau \approx \tau_0 \frac{T_0}{T-T_0}$, where T_0 is the extrapolated Curie temperature (slightly below 290 K since the transition is of first order). As temperature is decreased toward T_0, the hopping time tends to diverge, a phenomenon known as "critical slowing down." At room temperature ($T - T_0 \approx 10$K), Liu *et al.* took the hopping rate, $\gamma = \tau^{-1}$, to be about 100 cm^{-1}, which would mean that the hopping rate had to decrease to zero at a rate of 10 cm^{-1} K^{-1}. This seems too larger: typically this quantity should be around 1 cm^{-1} K^{-1}.

An alternative to interpret their Eq. (4) is to take the second term as a contribution from the Ti flipping mode, as in Refs. 2 and 5. In this scenario, the third term then gives the contributions from the ordinary phonon that is renormalized by the hopping mode. The oscillator strength sum rule can be obeyed by noting that, the flipping mode and the Slater mode are associated with the same coordinate, and thus, due to spectral weight transfer, their individual oscillator strengths cannot be constants any more but the sum should be.

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In conclusion, we have shown that the interpretation given by Liu *et al.* of Eq. (4) and of the relaxation mode in ε_c is physically inconsistent.

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