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**Citation for published version:**

Gehring, PM, Xu, Z, Stock, C, Xu, G, Parshall, D, Harriger, L, Gehring, CA, Li, X & Luo, H 2019, 'Comment on "Giant electromechanical coupling of relaxor ferroelectrics controlled by polar nanoregion vibrations"', Science Advances. <https://doi.org/10.1126/sciadv.aar5066>

**Digital Object Identifier (DOI):**

[10.1126/sciadv.aar5066](https://doi.org/10.1126/sciadv.aar5066)

**Link:**

[Link to publication record in Edinburgh Research Explorer](#)

**Document Version:**

Peer reviewed version

**Published In:**

Science Advances

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## FRONT MATTER

### Title

Comment on “Giant Electromechanical Coupling of Relaxor Ferroelectrics Controlled by Polar Nanoregion Vibrations”.

### Authors

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### Abstract

Manley *et al.* (Science Advances, 16 September 2016, p. e1501814) report the splitting of a transverse acoustic phonon branch below  $T_C$  in the relaxor ferroelectric  $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x]\text{O}_3$  with  $x = 0.30$  using neutron scattering methods. Manley *et al.* argue that this occurs because these phonons hybridize with local, harmonic lattice vibrations associated with polar nanoregions. We show that this splitting is absent when the measurement is made using a different neutron wavelength. It is therefore spurious.

## MAIN TEXT

Manley *et al.* (1) report neutron time-of-flight scattering measurements of the low-frequency lattice dynamics in the relaxor ferroelectric  $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x]\text{O}_3$  (PMN- $x$ PT) with Ti content  $x = 0.30$ . Above the Curie temperature  $T_C$  their data are consistent with a single transverse acoustic (TA) phonon branch measured at wave vectors  $\mathbf{Q} = (2+H, H-2, 0)$  for  $0.0 \text{ rlu} < H < 0.4 \text{ rlu}$  (reciprocal lattice units). Below  $T_C$  they observed a narrow dip in intensity located near the peak of the TA phonon lineshape for  $H = 0.25 \text{ rlu}$ . This was interpreted as evidence that the TA phonon branch had split into two branches that exhibit anti-crossing behavior.

We measured the neutron inelastic scattering from a  $10 \text{ cm}^3$  single crystal of PMN- $x$ PT with nominally identical composition ( $x = 0.29$ ) below  $T_C$  for  $H = 0.25 \text{ rlu}$ , i.e. at a constant wave vector  $\mathbf{Q} = (2.25, -1.75, 0)$ . These data, shown in the top panel of Fig. 1, were obtained using the NIST BT7 triple-axis spectrometer, which selects the incident and final neutron energies via Bragg diffraction rather than time-of-flight. But instead of collecting data with a fixed incident neutron energy of  $E_i = 25 \text{ meV}$  as done in (1), we employed a commonly used fixed final neutron energy  $E_f = 14.7 \text{ meV}$ . Our data show no evidence of this splitting. A least-squares fit to a single damped harmonic oscillator describes the TA phonon extremely well.

Since the purported phonon splitting varies with neutron wavelength, it is spurious. This begs the question of why it is seen in the configuration used by Manley *et al.* (1) ( $E_i = 25$  meV), but not in the one used by us ( $E_f = 14.7$  meV). We can explain why quantitatively via a double scattering process involving a phonon and a Bragg peak. Spurious features generated in this manner were termed “ghostons” by Ronnow *et al.* and used successfully to explain unexpected features observed in the neutron inelastic scattering from CuGeO<sub>3</sub> (2). In the bottom panel of Fig. 1 we have replotted the data published by Manley *et al.* (1) using the same energy scale to facilitate comparison between our datasets. Note that our data are plotted on a linear intensity scale whereas those of Manley *et al.* (1) are plotted on a log scale. We calculated ghoston energies for the case when  $E_i = 25$  meV using only the measured cubic lattice constant of 4.02 Angstroms. The energy of one ghoston (red arrow) coincides precisely with the anomalous intensity dip seen in the data for  $H = 0.25$  rlu (open purple circles), and it follows the dip to higher energy as  $H$  decreases. It is generated via phonon scattering followed by Bragg scattering from the (400) reciprocal lattice vector (both (202) and (20-2) yield the same ghoston energy). Ghostons can add or subtract intensity from a given location in reciprocal space; the magnitude and sign of the excess intensity depends on the sample and scattering geometries (3). In this case the “Bragg-last” ghoston reduces the intensity at this energy thereby producing a dip in the TA phonon lineshape.

A second ghoston (black arrow), generated by “Bragg-first” scattering from (-2-20), coincides precisely with the energy of the purported lower phonon branch identified by Manley *et al.* (1). It shifts to higher energy too as  $H$  decreases but does so more rapidly. This ghoston adds to the spectral weight already present at this energy, thereby enhancing the illusion of a split TA phonon branch. The red and black arrows for  $H = 0.25$  rlu are reproduced in the top panel of Fig. 1 to emphasize that these ghostons are absent at these energies when  $E_f = 14.7$  meV.

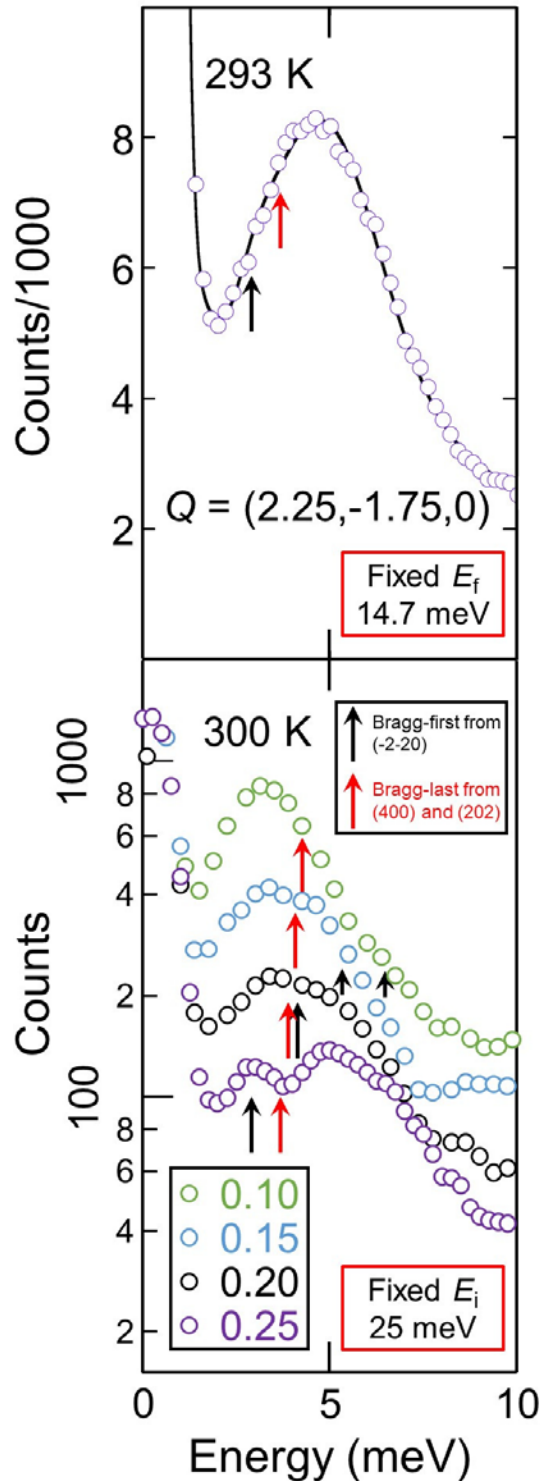
Three questions remain: (a) why does this feature vanish above  $T_C$ , (b) why is it observed in the (1-10) Brillouin zone, and (c) why is it affected by an external electric field? The answers are (a) primary extinction (4), (b) ghostons exist in all zones (2), and (c) electric fields strongly affect PMN-xPT Bragg intensities (5). In the cubic perovskite structure, Bragg reflections having all even Miller indices ( $hkl$ ) have the largest structure factor. Therefore they (and all related ghostons) suffer the greatest extinction on heating above  $T_C$  (4). This effect is large: the (200) Bragg intensity in our crystal decreases by a factor of six between 300 K and 500 K. In the (1-10) zone, ghostons generated by (2-20) and (0-40) have energies close to those in the (2-20) zone for  $E_i = 25$  meV. And, as shown in Fig. 2, we observed no TA splitting at  $\mathbf{Q} = (1.25, 0.75, 0)$  when  $E_f = 13.7$  meV (another common configuration). Thus, the splitting in this zone is also spurious. Finally, applied electric fields are known to affect Bragg intensities; for this reason, they necessarily affect any associated ghoston intensities.

Elastic-inelastic double scattering processes are generally extremely weak, but Ronnow *et al.* (2) note that even 1 cm<sup>3</sup> crystals can produce ghostons. As the PMN-xPT crystal used by Manley *et al.* (1) has a volume of order 20 cm<sup>3</sup>, such effects should be expected. In fact, scattering studies of large single crystals of relaxors are particularly problematic: the unusually broad phonon energy widths greatly enhance the chances of observing ghostons because the strict constraint imposed by energy conservation is much easier to satisfy (6).

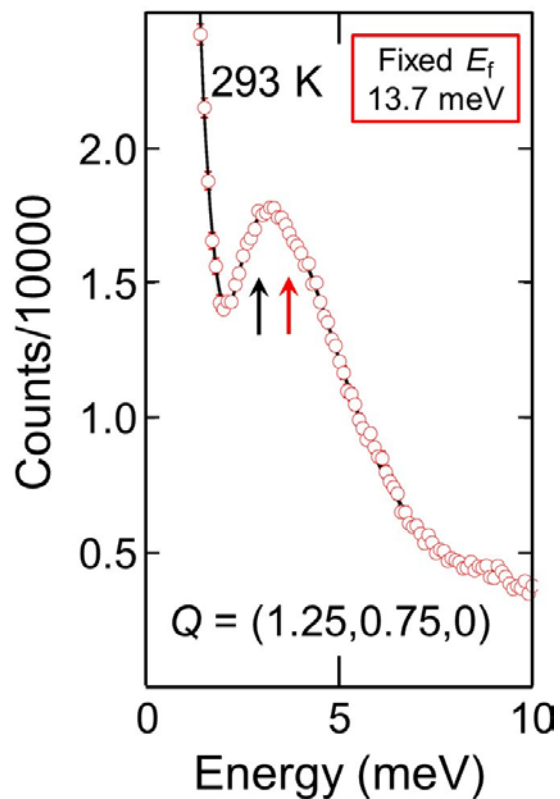
We have shown that the purported TA phonon splitting depends on the choice of neutron energy. We can account for this anomaly quantitatively using a ghoston double-scattering model. We conclude that the evidence supporting the anti-crossing model of Manley *et al.* (1) is spurious.

## References and Notes

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**Fig. 1. TA mode in (2-20) Brillouin zone.** (Top panel) Energy scan at  $Q = (2.25, -1.75, 0)$  showing an unsplit TA phonon lineshape in PMN- $x$ PT with  $x = 0.29$ . Solid line is a fit to a single damped harmonic oscillator. Data were measured with  $E_f = 14.7$  meV. Errors bars represent  $\pm\sqrt{N}$ , where  $N$  is the total number of counts. (Bottom panel) Energy scans from Manley *et al.* (1) for  $Q = (2+H, H-2, 0)$  using  $E_i = 25$  meV. Ghostons are indicated by arrows for each value of  $H$ .



**Fig. 2. TA mode in (110) Brillouin zone.** Energy scan at  $Q = (1.25, 0.75, 0)$  in PMN- $x$ PT with  $x = 0.29$ . Solid line is a fit to a single damped harmonic oscillator lineshape. These data were measured on the NIST BT4 triple-axis spectrometer with  $E_f = 13.7$  meV. Errors bars represent  $\pm\sqrt{N}$ , where  $N$  is the total number of counts.