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## Static and dynamic strain coupling behaviour of ferroic and multiferroic perovskites from resonant ultrasound spectroscopy

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#### Abstract

Resonant ultrasound spectroscopy (RUS) provides a window on the pervasive influence of strain coupling at phase transitions in perovskites through determination of elastic and anelastic relaxations across wide temperature intervals and with the application of external fields. In particular, large variations of elastic constants occur at structural, ferroelectric and electronic transitions and, because of the relatively long interaction length provided by strain fields in a crystal, Landau theory provides an effective formal framework for characterizing their form and magnitude. At the same time, the Debye equations provide a robust description of dynamic relaxational processes involving the mobility of defects which are coupled with strain. Improper ferroelastic transitions driven by octahedral tilting in KMnF<sub>3</sub>, LaAlO<sub>3</sub>, (Ca,Sr)TiO<sub>3</sub>, Sr(Ti,Zr)O<sub>3</sub> and BaCeO<sub>3</sub> are accompanied by elastic softening of tens of % and characteristic patterns of acoustic loss due to the mobility of twin walls. RUS data for ferroelectrics and ferroelectric relaxors, including BaTiO<sub>3</sub>, (K,Na)NbO<sub>3</sub>,Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> (PMN), Pb(Sc<sub>1/2</sub>Ta<sub>1/2</sub>)O<sub>3</sub> (PST), (Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>)<sub>0.955</sub>(PbTiO<sub>3</sub>)<sub>0.045</sub> (PZN-PT) and (Pb(In<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub>)<sub>0.26</sub>(Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>)<sub>0.44</sub>(PbTiO<sub>3</sub>)<sub>0.30</sub> (PIN-PMN-PT) show similar patterns of softening and attenuation but also have precursor softening associated with the development of polar nano regions. Defect-induced ferroelectricity occurs in KTaO<sub>3</sub>, without the development of long range ordering. By way of contrast, spin-lattice coupling is much more variable in strength, as reflected in a greater range of softening behaviour for Pr<sub>0.48</sub>Ca<sub>0.52</sub>MnO<sub>3</sub> and Sm<sub>0.6</sub>Y<sub>0.4</sub>MnO<sub>3</sub> as well as for the multiferroic perovskites EuTiO<sub>3</sub>, BiFeO<sub>3</sub>, Bi<sub>0.9</sub>Sm<sub>0.1</sub>FeO<sub>3</sub>, Bi<sub>0.9</sub>Nd<sub>0.1</sub>FeO<sub>3</sub>, (BiFeO<sub>3</sub>)<sub>0.64</sub>(CaFeO<sub>2.5</sub>)<sub>0.36</sub>, (Pb(Fe<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub>)<sub>0.4</sub>(Pb(Zr<sub>0.53</sub>Ti<sub>0.47</sub>)O<sub>3</sub>)<sub>0.6</sub>. A characteristic feature of transitions in which there is a significant Jahn-Teller component is softening as the transition point is approached from above, as illustrated by PrAIO<sub>3</sub>, and this is suppressed by application of an external magnetic field in the colossal magnetoresistive manganite  $Pr_{0.48}Ca_{0.52}MnO_3$  or by reducing grain size in  $La_{0.5}Ca_{0.5}MnO_3$ . Spin state transitions for  $Co^{3+}$  in LaCoO<sub>3</sub>, NdCoO<sub>3</sub> and GdCoO<sub>3</sub> produce changes in the shear modulus that scale with a spin state order parameter, which is itself coupled with the order parameter(s) for octahedral tilting in a linear-quadratic manner. A new class of phase transitions in perovskites, due to orientational or conformational ordering of organic molecules on the crystallographic A-site of metal organic frameworks, is illustrated for  $[(CH_3)_2NH_2]Co(HCOO)_3$  and  $[(CH_2)_3NH_2]Mn(HCOO)_3$  which also display elastic and anelastic anomalies due to the influence of intrinsic and extrinsic strain relaxation behaviour.

Keywords: phase transitions, elasticity, strain coupling

(Some figures may appear in colour only in the online journal)



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#### 1. Introduction

It is well understood that strain has a fundamental and pervasive influence on almost all types of phase transitions, either as the driving order parameter (acoustic mode instability) or by coupling with some other driving mechanism, which may be structural (soft mode, atomic ordering, hydrogen bonding, etc), ferroelectric (displacive, order/disorder, relaxor, etc), magnetic (ferro/antiferromagnetic, spin-glass, etc), or electronic (charge order, Jahn-Teller, spin state, superconducting, metal-insulator, etc). The most overt implications are, firstly, that the correlation length of the order parameter takes on the generally longer length scale of strain fields, secondly, that overlapping strains from otherwise separate order parameters can result in strong coupling between multiple instabilities and, thirdly, that transformation microstructures such as tweed and twin walls may interact strongly with defects. Some of the consequences relate to reduction of the Ginsburg temperature interval of critical fluctuations, an expectation that mean field models should provide effective descriptions of thermodynamic properties, a tendency for transitions which would otherwise be second order to become first order in character, interdependence of different physical properties such as ferroelectricity and magnetism, and control of the dynamics and mechanisms of switching by strain relaxation or defect pinning processes. Understanding the behaviour of bulk samples also feeds into considerations for thin film technologies since a key variable is the coherency strain of the film with its substrate. The choice of substrate is a choice of imposed strain which, in turn, drives a strain coupled order parameter in the film to some desired configuration and magnitude. There will be subtle differences, however, since the imposed strain will be homogeneous, whereas a bulk material containing ferroelastic twin walls or polar nano regions, for example, will contain strain heterogeneities at a local, mesoscopic length scale. In the context of multiferroic materials, direct magnetoelectric coupling tends to be weak, as represented by the small overlap of fields for ferro/antiferromagnetism and ferroelectricity in figure 1, but if both the ferroelectric dipole and the magnetic order parameter each couple with a co-elastic or ferroelastic strain the (indirect) coupling may be substantially increased.

Any change in strain state of a material will give rise to an associated change in elastic properties. Because the elastic constants are susceptibilities they can vary by tens of % and thus provide highly sensitive indicators of the strength and style of any strain coupling which may occur, even when the magnitudes of the strains themselves are on the order of or less than 1%o. This is quantifiable through the expression first introduced by Slonczewski and Thomas [1] for the variations of individual elastic constants,  $C_{ik}$ , as

$$C_{ik} = C_{ik}^{o} - \sum_{l,m} \frac{\partial^2 G_{\rm L}}{\partial e_i \partial q_l} \cdot R_{lm} \cdot \frac{\partial^2 G_{\rm L}}{\partial e_k \partial q_m},\tag{1}$$

where  $C_{ik}^{0}$  represents elastic constants without the influence of a phase transition,  $G_{L}$  is the excess free energy due to the transition  $e_i$ ,  $e_k$  are strains, and  $q_l$ ,  $q_m$  are components



**Figure 1.** Relationships between ferroic properties in terms of coupling effects. Direct magnetoelectric coupling is generally considered to be weak. Coupling between ferroelectric polarization and strain is typically strong, leading to strains of up to a few %. The strength of magnetoelastic coupling is highly variable from zero/undetectable up to a few %. Strong coupling of both magnetic and electric dipoles to some common strain provides, in principle, a mechanism for strong magnetoelectric coupling.

of the order parameter. The matrix  $R_{lm}$  is strictly the inverse of the matrix,  $\partial^2 G / \partial q_m \partial q_n$ , i.e.

$$\sum_{m} R_{lm} \frac{\partial^2 G}{\partial q_m \partial q_n} = \delta_{ln}.$$
 (2)

The order parameter and spontaneous strains depend on symmetry such that the form of coupling between them is also determined by symmetry. A wide variety of patterns of evolution with temperature, pressure and applied field is possible and, in principle, should provide insights into the strength, mechanisms and dynamics of strain coupling for any particular material of interest (e.g. [2–4]). Equation (1) generally describes elastic softening due to relaxation of the order parameter, but stiffening is also observed in a relatively small number of cases and points to different behaviour in terms of how the order parameter responds to an imposed stress. Non-relaxational contributions can occur, for example, from biquadratic coupling,  $\lambda e^2 q^2$ , and would be expected to scale with  $q^2$ .

Most methods of measuring elastic moduli are dynamic and the best analogy is with measurements of dielectric properties. The dynamically applied field is stress (electric field) and the response has real and imaginary components which are typically used to evaluate the elastic compliance (dielectric permittivity) and acoustic loss (dielectric loss) as functions of temperature and frequency. However, while the frequency of an electric field can be adjusted continuously through many orders of magnitude, there is no single experimental method for measuring elastic properties over a wide frequency interval. Instead, as illustrated in figure 2, a number of different methods are used in relatively narrow frequency windows. Resonant ultrasound spectroscopy (RUS)



**Figure 2.** Characteristic frequency ranges for different experimental methods used to measure elastic and anelastic properties.

has proved to be a powerful method for investigating elastic and anelastic anomalies associated with phase transitions due to its simplicity in terms of sample size and mounting. In addition, it appears that the frequency range near 1 MHz, combined with small imposed stresses, provides a particularly sensitive window on microstructure dynamics. The induced strains are estimated to be in the vicinity of  $10^{-7}$ , in comparison with  $\sim 10^{-3}-10^{-5}$  for dynamical mechanical analysis (DMA), for example [5]. The purpose of the present paper is to provide an overview of strain relaxation behaviour which is emerging from recent RUS studies of perovskites with diverse structural, ferroelectric, magnetic and electronic phase transitions.

#### 2. Resonant ultrasound spectroscopy

Details of the RUS method have been described extensively elsewhere [6-14]. The underlying principle is that a small sample, a few mm across and typically cut in the shape of a rectangular parallelepiped, is set lightly between two piezoelectric transducers and made to resonate at frequencies which fall in the range  $\sim 0.1-2$  MHz. The resonant modes are dominated by shearing motions but may also have a small component of breathing. The elastic constant or combination of elastic constants determining each resonance scales with the square of the resonant frequency, f. Acoustic loss is measured in terms of the inverse mechanical quality factor,  $Q^{-1}$ , generally taken to be  $\Delta f/f$ , where  $\Delta f$  is the width at half maximum height of the resonance peak. Measurements of f for samples with known shape and mass can be used to compute a full set of elastic constants in the case of a single crystal or the bulk and shear moduli in the case of an isotropic ceramic.

Because there is no glue involved in attaching the sample to transducers or buffer rods, it is a straightforward matter to make *in situ* measurements over a wide temperature interval. In the helium flow cryostat used in Cambridge to collect data in the temperature interval  $\sim$ 5–310 K [15], the sample sits directly between the transducers. In the high temperature instrument ( $\sim$ 300–1600 K [16]) the sample sits between the tips of alumina buffer rods inserted into a horizontal resistance furnace and the transducers are attached to the other end of the rods, outside the furnace. Experience has shown that spectra can be obtained from samples with dimensions in the size range  $\sim$ 0.5–5 mm. While the objective may be to determine



**Figure 3.** RUS data from a single crystal sample of KMnF<sub>3</sub> [23]. (*a*) Segments of spectra stacked in proportion to the temperature at which they were collected. Obvious frequency minima for the individual resonance peaks occur at 185 and 83 K. Between these temperatures broadening of resonance peaks signifies strong attenuation. (*b*)  $f^2$  (filled circles) and  $Q^{-1}$  (open circles) data for selected resonances. (Note that  $f^2$  values from different resonances have been scaled to overlap at high and low temperatures, as set out in [23]). The  $Pm\bar{3}m-I4/mcm$  phase transition at 185 K is first order. The *I*4/*mcm* (paramagnetic)–*Cmcm* (antiferromagnetic) transition at ~87 K is not accompanied by any obvious elastic anomalies. A Debye loss peak at ~130 K is attributed of freezing of ferroelastic domain wall motion.

absolute values of the elastic constants in some cases, the most straightforward experiment is to follow acoustic loss and relative changes in shear elastic constants using a sample with some irregular shape which requires minimal preparation. Again because of the relative simplicity of the experimental set up, it is possible to add an external electric field (e.g. [17]) or magnetic field (e.g. [18–20]). In a further development, the mechanical resonances of piezoelectric materials can be excited by applying an ac electric field directly to the sample instead of to the exciting transducer (resonant piezoelectric spectroscopy, RPS) [21, 22]. The second transducer still acts as the detector.

An illustration of the data obtained by automatic collection of RUS spectra through a sequence of phase transitions is provided in figure 3 for KMnF<sub>3</sub> (after [23]). Individual spectra from an irregularly shaped single crystal, with mass 0.3354 g and approximate dimensions  $10 \times 10 \times$ 1 mm<sup>3</sup>, are stacked in proportion to the temperature at which they were obtained. The sequence of transitions is  $Pm\bar{3}m$  (paramagnetic)–I4/mcm (paramagnetic) at ~185 K,



**Figure 4.** Variations in bulk (*K*) and shear (*G*) moduli with temperature through the known sequence of octahedral tilting transitions in SrZrO<sub>3</sub> obtained from a polycrystalline sample with dimensions  $1.861 \times 2.922 \times 4.699 \text{ mm}^3$ , mass 0.1352 g and  $\sim 2.8\%$  porosity [26]. The *Pm*3m–*14/mcm* and *Imma*–*Pnma* transitions are close to tricritical in character while the *I4/mcm*–*Imma* transition does not involve a group–subgroup relationship and is necessarily first order.

*I4/mcm* (paramagnetic)–*Cmcm* (antiferromagnetic) at ~87 K, *Cmcm* (antiferromagnetic)–*Pnma* (canted antiferromagnetic) at ~83 K. Substantial softening, evident as shifts to lower frequencies of individual resonance peaks, and an increase in loss in the stability field of the *I4/mcm* structure, evident as peak broadening, are confirmed in the variations of  $f^2$  and  $Q^{-1}$ shown in figure 3(*b*). Softening of the elastic constants by up to ~40% is due to the development of shear strains associated with the octahedral tilting transitions but there is no overt evidence of contributions from magnetoelastic relaxations. The Debye-like loss peak centred on ~130 K has been attributed to freezing of ferroelastic twin walls due to pinning by F vacancies or dumbbell pairs of F interstitials [23–25].

Figure 4 shows an example of quantitative results for the bulk, *K*, and shear, *G*, moduli for a polycrystalline sample of SrZrO<sub>3</sub> through the sequence of octahedral tilting transitions  $Pm\bar{3}m-14/mcm-Imma-Pnma$  [26]. Experimental uncertainties obtainable for samples of this type are ~0.1% for *G*, and ~1% for *K*, though these become higher in the vicinity of transition points where the number of measurable resonance peaks reduces due to acoustic attenuation. The phase transitions are accompanied by characteristic patterns of elastic softening and stiffening, up to ~45%, due to coupling of shear and volume strains with the tilt order parameters.

#### 3. Ferroelastic transitions

The Landau free energy expansion for combined M-point and R-point (improper ferroelastic) tilting transitions in perovskites, with all low order couplings to strain, is (after [26–28])

$$G_{\rm L} = \frac{1}{2} a_1 \Theta_{\rm s1} \left( \coth\left(\frac{\Theta_{\rm s1}}{T}\right) - \coth\left(\frac{\Theta_{\rm s1}}{T_{\rm c1}}\right) \right) \left(q_1^2 + q_2^2 + q_3^2\right) \\ + \frac{1}{2} a_2 \Theta_{\rm s2} \left( \coth\left(\frac{\Theta_{\rm s2}}{T}\right) - \coth\left(\frac{\Theta_{\rm s2}}{T_{\rm c2}}\right) \right) \left(q_4^2 + q_5^2 + q_6^2\right)$$

$$\begin{aligned} &+\frac{1}{4}b_{1}\left(q_{1}^{2}+q_{2}^{2}+q_{3}^{2}\right)^{2}+\frac{1}{4}b_{1}'\left(q_{1}^{4}+q_{2}^{4}+q_{3}^{4}\right) \\ &+\frac{1}{4}b_{2}\left(q_{4}^{2}+q_{5}^{2}+q_{6}^{2}\right)^{2}+\frac{1}{4}b_{2}'\left(q_{4}^{4}+q_{5}^{4}+q_{6}^{4}\right) \\ &+\frac{1}{6}c_{1}\left(q_{1}^{2}+q_{2}^{2}+q_{3}^{2}\right)^{3}+\frac{1}{6}c_{1}'\left(q_{1}q_{2}q_{3}\right)^{2}+\frac{1}{6}c_{1}''\left(q_{1}^{2}+q_{2}^{2}+q_{3}^{2}\right) \\ &\times\left(q_{1}^{4}+q_{2}^{4}+q_{3}^{4}\right)+\frac{1}{6}c_{2}\left(q_{4}^{2}+q_{5}^{2}+q_{6}^{2}\right)^{3}+\frac{1}{6}c_{2}'\left(q_{4}q_{5}q_{6}\right)^{2} \\ &+\frac{1}{6}c_{2}''\left(q_{4}^{2}+q_{5}^{2}+q_{6}^{2}\right)\left(q_{4}^{4}+q_{5}^{4}+q_{6}^{4}\right)+\lambda_{q}\left(q_{1}^{2}+q_{2}^{2}+q_{3}^{2}\right) \\ &\times\left(q_{4}^{2}+q_{5}^{2}+q_{6}^{2}\right)+\lambda_{q}'\left(q_{1}^{2}q_{4}^{2}+q_{2}^{2}q_{5}^{2}+q_{3}^{2}q_{6}^{2}\right) \\ &+\lambda_{1}e_{a}\left(q_{1}^{2}+q_{2}^{2}+q_{3}^{2}\right)+\lambda_{2}e_{a}\left(q_{4}^{2}+q_{5}^{2}+q_{6}^{2}\right) \\ &+\lambda_{3}\left[\sqrt{3}e_{o}\left(q_{2}^{2}-q_{3}^{2}\right)+e_{t}\left(2q_{1}^{2}-q_{2}^{2}-q_{3}^{2}\right)\right] \\ &+\lambda_{5}\left(e_{4}q_{4}q_{6}+e_{5}q_{4}q_{5}+e_{6}q_{5}q_{6}\right)+\lambda_{6}\left(q_{1}^{2}+q_{2}^{2}+q_{3}^{2}\right) \\ &\times\left(e_{4}^{2}+e_{5}^{2}+e_{6}^{2}\right)+\lambda_{7}\left(q_{1}^{2}e_{6}^{2}+q_{2}^{2}e_{4}^{2}+q_{3}^{2}e_{5}^{2}\right) \\ &+\frac{1}{4}\left(C_{11}^{o}-C_{12}^{o}\right)\left(e_{o}^{2}+e_{t}^{2}\right)+\frac{1}{6}\left(C_{11}^{o}+2C_{12}^{o}\right)e_{a}^{2} \\ &+\frac{1}{2}C_{44}^{o}\left(e_{4}^{2}+e_{5}^{2}+e_{6}^{2}\right)\right). \end{aligned}$$

 $q_1 - q_3$  are components of the M-point order parameter,  $q_4 - q_6$  are components of the R-point order parameter,  $T_c$ 's are critical temperatures, a, b, b' are Landau coefficients,  $\Theta_s$ represents order parameter saturation temperatures,  $\lambda_i$  are coupling coefficients,  $e_4$ ,  $e_5$ ,  $e_6$  are shear strain components,  $e_a = (e_1 + e_2 + e_3)$ ,  $e_0 = (e_1 - e_2)$  and  $e_t = (1/\sqrt{3})(2e_3 - e_1 - e_2)$  are symmetry adapted combinations of linear strain components  $e_1$ ,  $e_2$  and  $e_3$ , and  $C_{ik}^o$  are elastic constants of the cubic parent structure (the 'bare' elastic constants). Expressions for the elastic constants of the tetragonal phase can be derived from this by applying equations (1) and (2) and have been listed in [28]. As seen in figure 5, they provide an effective quantitative description of the second order, R-point tilting transition in LaAlO<sub>3</sub> [29].

In reality it is now the deviations from these expected patterns which are of more interest since they reveal contributions of other, mainly dynamical, effects. Softening as  $T \rightarrow T_c$  from above is typically interpreted in terms of fluctuations related to the soft mode and conforms to a power law

$$\Delta C_{ik} = A_{ik} \left( T - T_c \right)^{-\kappa}, \qquad (4)$$

where  $A_{ik}$  is a material property and  $\kappa$  depends on the pattern of dispersion of the soft mode around the critical point in reciprocal space. For the case of LaAlO<sub>3</sub>, experimental values of  $\kappa$  for the separate elastic constants are in the vicinity of 1–1.3, which is consistent with softening of branches of the soft mode predominantly in two dimensions away from the R-point [30]. Additional softening below  $T_c$ , in excess of that expected for a classical second order transition, is due to coupling of the acoustic modes with a central peak mode seen in Brillouin scattering data. This is interpreted in terms of dynamical flipping of clusters of tilted octahedra between different orientations [29].



Figure 5. Comparison of elastic constants calculated using a fully calibrated Landau expansion (solid lines) with experimental values of single crystal elastic constants of LaAlO<sub>3</sub> [29]. Dashed lines represent values of the bare elastic constants extrapolated from high temperatures into the stability field of the rhombohedral structure. Open symbols are experimental values from RUS data; filled symbols are values from Brillouin scattering.

Acoustic loss in LaAlO<sub>3</sub> is indicated by an abrupt disappearance of resonance peaks from spectra collected below  $T_c$  (817 K) and is attributed to the motion under external stress of ferroelastic twin walls in the rhombohedral structure (figure 6(a)) [30]. This complete attenuation ('superattenuation') implies maximum values of  $Q^{-1}$  greater than  $\sim 0.02$  and continues until the resonance peaks gradually reappear below  $\sim 600$  K when the mobile twin walls become pinned by interaction with defects. In the case of tilting transitions in perovskites, the principal pinning mechanism is believed to involve oxygen vacancies (e.g. [31, 32]). The expected pattern of loss behaviour for a second order transition is seen in data from measurements of tan  $\delta$  by DMA, where  $\delta$  is the phase angle [31, 33]. A steep increase immediately below the transition point is followed by a plateau, marking relatively free motion in an effectively viscous medium (figure 6(b)). There is then a Debye peak marking the frequency dependent freezing interval, below which the twin walls are no longer able to escape from their pinning points. The RUS data for  $Q^{-1}$ are shifted to higher temperatures, as expected for a change in frequency from  $\sim 10^{-1}$ – $10^2$  Hz (DMA) to  $\sim 10^5$ – $10^6$  Hz (RUS), but this has turned out not to be quantitative in relation to the known dispersion behaviour at low frequencies. It



Figure 6. Acoustic loss behaviour of single crystal LaAlO<sub>3</sub> [30]. (a) Segments of RUS spectra stacked in proportion to the temperature at which they were collected. Resonances disappear abruptly below  $T_c = 817 \text{ K}$  (superattenuation) and reappear as broad peaks below ~600 K. (b) Variation of  $Q^{-1}$  from RUS spectra (left axis, joined up data points), compared with the variation of  $tan\delta$ from DMA data (right axis, dashed curve). The pattern of loss is qualitatively similar but the freezing temperatures are not consistent with a single mechanism. It seems likely that the relatively high stress in DMA causes movement of the tips of needle domains while the relatively low stress conditions of RUS result in local displacements of twin walls by a ledge mechanism.

400

Т (K)

600

800

1000

.....

200

appears, therefore, that there is more than one loss mechanism and, hence, more than one mechanism for twin wall motion and pinning.

The relatively high stress and low frequency conditions of a DMA experiment cause the forward and back movement, primarily, of the tips of needle twins, while the relatively low stress and high frequency conditions experienced by a resonating sample in an RUS experiment probably favour a local bowing mechanism. For thin walls, i.e. with thicknesses of less than a few unit cells as is generally the case for ferroelastic twins at temperatures away from transition point, this probably involves migration of ledges in directions parallel to the walls [34]. A ledge mechanism is also supported by simulations [35]. As with mechanisms of plastic deformation, therefore, there are regions of parameter space in which different mechanisms will operate and these can be represented in anelasticity maps of the form shown schematically for LaAlO<sub>3</sub> in figure 7.

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**Figure 7.** Anelasticity maps for LaAlO<sub>3</sub>, with possible fields of parameter space for different loss mechanisms associated with twin wall mobility [30, 34].

The pattern of softening and acoustic loss shown by LaAlO<sub>3</sub> is probably quite general for improper ferroelastic tilting transitions in perovskites, though with material specific details such as the precise pinning mechanisms and thickness of twin walls (e.g. SrTiO<sub>3</sub> [6, 36], (Ca,Sr)TiO<sub>3</sub> [5, 32, 37], Sr(Ti,Zr)O<sub>3</sub> [26, 38], BaCeO<sub>3</sub> [39], (La,Pr)AlO<sub>3</sub> [40], KMnF<sub>3</sub> [23], EuTiO<sub>3</sub> [41]). However, the softening expected with falling temperature predictable on the basis of equations (1)-(3) for a single (R-point) instability actually becomes stiffening when the second, M-point, instability gives rise to the *Pnma* structure (table 1, figure 4, and see [39]). It is possible that elastic stiffening in systems with two discrete order parameters occurs instead of softening because the coupled order parameters lock together in a way that does not allow them to relax in response to an applied stress. For perovskites, at least, it is more likely that the difference arises because of the way that strain couples with the M-point and R-point order parameters. In particular, a marked reduction in the tetragonal shear strain occurs when the transformation is from structures with R-point only tilts to the Pnma structure, as in CaTiO<sub>3</sub> [27], SrZrO<sub>3</sub> [26] and BaCeO<sub>3</sub> [39]. In other words,

**Table 1.** Order parameter components for selected symmetry subgroups of  $Pm\bar{3}m$  associated with special points  $M_3^+$  and  $R_4^+$  (after [27, 42]). The system of reference axes for these components is that used in [43] and the group theory program ISOTROPY.

Space group	Order parameter components		Relationships between order parameter
	$\overline{M_3^+}$	R <sub>4</sub> <sup>+</sup>	components
Pm3m	000	000	
I4/mcm	000	$q_{4}00$	
Imma	000	$q_4 0 q_6$	$q_4 = q_6$
R3c	000	$q_4 q_5 q_6$	$q_4 = q_5 = q_6$
Pnma	$0q_{2}0$	$q_4 0 q_6$	$q_2 \neq q_4 = q_6$

the strength of the net coupling to two order parameters is less than it is to only one.

SrTiO<sub>3</sub> was the first perovskite to be examined by RUS [6] and is unique in the extent to which the twin walls remain mobile down to at least  $\sim 5 \text{ K}$  at RUS frequencies [38]. There is also no detectable freezing interval in mechanical spectroscopy data collected at  $\sim 1-50 \,\text{Hz}$  [44-47]. RPS spectra reveal a piezoelectric response below  $\sim 80 \,\mathrm{K}$  which becomes stronger below  $\sim 40 \text{ K}$  and has been interpreted as the development of electric polarity within the twin walls themselves [22]. An unusual pattern of acoustic resonances in SrTi<sup>18</sup>O<sub>3</sub> has also been considered to reflect the proximity to a ferroelectric instability [36]. The pattern of variations in LaAlO<sub>3</sub> discussed above seems to be more typical of what is expected for perovskites with tilting instabilities only. Relatively high values of  $Q^{-1}$ , or superattenuation, point to twin wall mobility under low applied stress in some interval below the transition point followed by pinning in both the  $R\bar{3}c$  structure of (La,Pr)AlO<sub>3</sub> [40] and the *I*4/*mcm* structure of (Ca,Sr)TiO<sub>3</sub> [5, 34, 37, 48]. High values of  $Q^{-1}$  relative to those of the parent cubic phase are also seen in the I4/mcm and Imma stability fields of Sr(Zr,Ti)O<sub>3</sub> but without any evidence of a specific freezing interval [26, 38]. In marked contrast,  $Q^{-1}$  values tend to be low for the *Pnma* structure, consistent with DMA measurements showing that twin walls become totally immobilized almost immediately that two tilt systems are present [5, 26, 32, 34, 38, 49, 50]. This cannot be a general rule, however, because strong attenuation continues through the stability fields of R3c and Imma structures of BaCeO<sub>3</sub>, down to  $\sim 200$  K in the stability field of the *Pnma* structure. There is no sign of the typical twin wall mobility related interval of high acoustic loss for the I4/mcm phase of EuTiO<sub>3</sub> below  $T_c = 284 \text{ K}$  [41], while the freezing interval for twin walls in the I4/mcm structure is centred on  $\sim 130$  K in KMnF<sub>3</sub> [23].

#### 4. Ferroelectrics and relaxors

Ferroelectric dipoles typically develop in perovskites due to displacements of cations following the evolution of order parameter components that belong to the irreducible representation  $\Gamma_4^-$  of parent space group $Pm\bar{3}m$ . As well as being ferroelectric, the transitions are (improper) ferroelastic and the influence of strain/order parameter relaxation is expected to be fundamentally the same as for tilting transitions.



**Figure 8.**  $f^2$  data for a resonance mode from RUS spectra collected as a function of increasing temperature through the transition sequence of a ceramic sample of BaTiO<sub>3</sub> (unpublished). Estimates of the transition temperatures for this sample (285, 329, 377 K) are based on the points at which there are minima or obvious breaks in slope.

The classic sequence of BaTiO<sub>3</sub> is Pm3m-P4mm-Amm2-R3m with falling temperature, and RUS data from a ceramic sample shown in figure 8 display a pattern in elastic properties which is similar to the analogous sequence seen in SrZrO<sub>3</sub> (figure 4). Softening at the cubic-tetragonal transition has a form consistent with the effects of classical strain/order parameter coupling and the subsequent first order transitions have softening as the transition points are approached from either side (e.g. kHz frequencies [51], 0.1–1 MHz [52, 53]). This pattern is probably quite general and is seen also, for example, through the Pm3m-P4mm-Pm transitions in members of the (K,Na)NbO<sub>3</sub> solid solution [54–56].

When the possibility of cation ordering on crystallographic B-sites with symmetry of irreducible representation  $R_1^+$  is included, i.e. alternating cations in three dimensions, the appropriate Landau expansion which gives the additional structure types relevant for relaxors and listed in table 2 becomes (after [57])

$$\begin{split} G_{\rm L} &= \frac{1}{2} a_{\Gamma} \Theta_{\rm s\Gamma} \left( \coth \left( \frac{\Theta_{\rm s\Gamma}}{T} \right) - \coth \left( \frac{\Theta_{\rm s\Gamma}}{T_{\rm c\Gamma}} \right) \right) \left( q_1^2 + q_2^2 + q_3^2 \right) \\ &+ \frac{1}{4} b_{\Gamma} \left( q_1^2 + q_2^2 + q_3^2 \right)^2 + \frac{1}{4} b_{\Gamma}' \left( q_1^4 + q_2^4 + q_3^4 \right) \\ &+ \frac{1}{6} c_{\Gamma} \left( q_1^2 + q_2^2 + q_3^2 \right)^3 + \frac{1}{6} c_{\Gamma}' \left( q_1 q_2 q_3 \right)^2 + \frac{1}{6} c_{\Gamma}'' \left( q_1^2 + q_2^2 + q_3^2 \right) \\ &\times \left( q_1^4 + q_2^4 + q_3^4 \right) + \lambda_{1\Gamma} e_{\rm a} \left( q_1^2 + q_2^2 + q_3^2 \right) \\ &+ \lambda_{2\Gamma} \left[ \sqrt{3} e_{\rm o} \left( q_1^2 - q_2^2 \right) + e_{\rm t} \left( 2q_3^2 - q_1^2 - q_2^2 \right) \right] \\ &+ \lambda_{3\Gamma} \left( e_4 q_3 q_2 + e_5 q_3 q_1 + e_6 q_1 q_2 \right) + a_{\rm R} \Theta_{\rm sR} \left( \coth \left( \frac{\Theta_{\rm sR}}{T} \right) \right) \\ &- \coth \left( \frac{\Theta_{\rm sR}}{T_{\rm cR}} \right) \right) q_{\rm R}^2 + \frac{1}{4} b_{\rm R} q_{\rm R}^4 + \lambda_{1\rm R} e_{\rm a} q_{\rm R}^2 + \lambda_{2\rm R} \left( e_{\rm o}^2 + e_{\rm t}^2 \right) \\ &\times q_{\rm R}^2 + \lambda_{3\rm R} \left( e_4^2 + e_5^2 + e_6^2 \right) q_{\rm R}^2 + \frac{1}{4} \left( C_{11}^{\rm o} - C_{12}^{\rm o} \right) \left( e_{\rm o}^2 + e_{\rm t}^2 \right) \\ &+ \frac{1}{6} \left( C_{11}^{\rm o} + 2C_{12}^{\rm o} \right) e_{\rm a}^2 + \frac{1}{2} C_{44}^{\rm o} \left( e_4^2 + e_5^2 + e_6^2 \right) \\ &+ \lambda_{\Gamma\rm R} \left( q_1^2 + q_2^2 + q_3^2 \right) q_{\rm R}^2. \end{split}$$

**Table 2.** Order parameter components for the symmetry subgroups of  $Pm\bar{3}m$  associated with special points  $\Gamma_4^-$  and  $R_1^+$  (after [58]). The system of reference axes for these components is that used in [43] and the group theory program ISOTROPY.

Space group	Order parameter components		Relationships between order parameter
	$\Gamma_4^-$	$\mathbf{R}_1^+$	components
Pm3m	000	0	
$P4_{mm}$	$00q_{3}$	0	
$Amm_2$	$q_1 q_2 0$	0	$q_1 = q_2$
R3m	$q_1 q_2 q_3$	0	$q_1 = q_2 = q_3$
Pm	$q_1 q_2 0$	0	$q_1 \neq q_2$
Ст	$q_1 q_2 q_3$	0	$q_1 = q_2 \neq q_3$
<i>P</i> 1	$q_1 q_2 q_3$	0	$q_1 \neq q_2 \neq q_3$
Fm3̄m	000	$q_{ m R}$	
I4mm	$00q_{3}$	$q_{\mathrm{R}}$	
Imm2	$q_1 q_2 0$	$q_{ m R}$	$q_1 = q_2$
R3m	$q_1 q_2 q_3$	$q_{ m R}$	$q_1 = q_2 = q_3$
Cm	$q_1 q_2 0$	$q_{ m R}$	$q_1 \neq q_2$
Ст	$q_1 q_2 q_3$	$q_{\mathrm{R}}$	$q_1 = q_2 \neq q_3$
<i>P</i> 1	$q_1 q_2 q_3$	$q_{ m R}$	$q_1 \neq q_2 \neq q_3$

Subscripts  $\Gamma$  and R and used to refer to parameters belonging to the  $\Gamma_4^-$  and  $R_1^+$  order parameters.

Precursor elastic softening not predicted by equation (5) relates to the properties and behaviour of short range ordering or polar nanoregions (PNRs) in the parent cubic structure because local electric dipoles generate local strains. In this regard the softening appears to be essentially the same whether it precedes a ferroelectric transition, as in BaTiO<sub>3</sub>, or ahead of relaxor-like freezing, as in  $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN). Precursor softening in BaTiO<sub>3</sub> begins at ~600 K which is  $\sim$ 50 K above the Burns temperature,  $T_{\rm d} \sim 550$  K, and  $\sim$ 200 K above the cubic-tetragonal ferroelectric transition, ~395 K [52, 53, 59–61]. In PMN  $T_{\rm d}$  is ~630 K [62] and the softening starts near 650 K [63], with frequency-dependent freezing occurring in the interval  $\sim 230-370 \text{ K}$  [64]. In both materials there is an intermediate temperature,  $T^* \sim 500$  K, at which acoustic emission indicates that the PNRs acquire a static or quasi-static component component [61,65]. In  $Pb(Sc_{1/2}Ta_{1/2})O_3$  (PST), precursor softening of the shear modulus according to equation (4) occurs with  $\kappa = -0.5$ , consistent with the local fluctuations being three dimensional in character [21]. The twin walls between  $180^{\circ}$  ferroelectric domains do not have any shear strain contrast across them and will not move when subject to some externally applied stress, but 90° twin walls in tetragonal structures and 71°/109° walls in rhombohedral structures are ferroelastic as well as being ferroelectric. Anelastic losses in these materials should provide insights into twin wall dynamics which are slightly different from but complementary to conventional information that is obtained from studies of dielectric loss, therefore.

PMN is generally taken as the model of end-member relaxor behaviour, with no long range order of Mg and Nb between crystallographic B-sites ( $q_R = 0$ ) and local rhombohedral symmetry below the freezing interval (recent reviews include [57,66]). The freezing process follows



**Figure 9.** (*a*), (*b*) RUS and dielectric data from a single crystal of PMN [63]. The patterns of variation through the freezing interval of both elastic compliance and capacitance (*a*) and acoustic loss and dielectric loss (*b*) are closely similar, signifying close coupling between strain and ferroelectric polarization. (*c*) Single crystal elastic constants show the onset of softening below  $T_d$ , no obvious anomalies in the vicinity of  $T^*$  or  $T_c$  and rounded minima through the freezing interval.

Vogel–Fulcher dynamics [64, 67–74]

$$\tau = \tau_{\rm o} \exp\left(\frac{U}{k_{\rm B} \left(T - T_{\rm f}\right)}\right),\tag{6}$$

in which relaxation time,  $\tau$ , is related to the inverse of attempt frequency,  $\tau_0$ , an effective activation energy, U, and a freezing temperature,  $T_f$ . If strain is coupled strongly to the electric dipoles and relaxations of both occur on the same timescale, the evolution of the elastic compliance, s, should be indistinguishable from the real part of the capacitance, C'. As shown in figure 9(*a*) (after [63]) this is close to being the case, with frequency-dependent peaks in both C' and  $1/f^2(\alpha s)$  where f is the frequency of a predominantly shear mode in RUS spectra. The relaxation times of PNRs

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below  $T_{\rm d}$  must be less than  $\sim 10^{-6}$  s as there is no evidence until  $\sim 300$  K for their influence on either  $Q^{-1}$  or the dielectric loss, tan $\delta$ , measured at ~1 MHz. The frequency-dependent maxima in both  $Q^{-1}$  and tan  $\delta$  in the freezing interval also have closely similar forms (figure 9(b)). In detail the dielectric and strain relaxation behaviour is not quite identical but the differences are only in values of the effective Vogel-Fulcher parameters. The response to an ac electric field is most likely dominated by flipping of 180° domains and migration of 180° domain walls while the response to an alternating stress field is likely to be flipping between 71°/109° domains and motion of the equivalent domain walls either within or between PNRs. From the evidence of RUS it appears that the strain flipping process is limited by a slightly lower activation energy barrier than straight dipole flipping. This is consistent with a slightly lower activation calculated for motion of 90° (ferroelastic/ferroelectric) twin walls than for motion of 180° (ferroelectric) twin walls in PbTiO<sub>3</sub> [75]. A summary of the overall pattern of elastic softening and stiffening in PMN in given in figure 9(c), showing shallow rounded minima through the freezing interval rather than the sharp minima observed at discrete ferroelectric and ferroelastic transitions (from [63]).

There is no sign at RUS frequencies of the properties and behaviour of PNR's in PMN changing at  $T^*$  (figure 9). The same applies for PST ahead of the weakly first order cubic-rhombohedral transition at 300 K in a sample with a high degree of B-site cation order ( $q_{\rm R} = 0.65$ ) [21], but RPS measurements show that there is a piezoelectric component present in the structure up to  $\sim$ 425 K. The onset of precursor softening, presumed to correspond with  $T_d$ , was found to be  $\sim$ 650 K. RPS measurements show also that a piezoelectric component persists in BaTiO<sub>3</sub> up to 613 K, which is above previously reported values of  $T_d$  [52]. Neither of these materials would be expected to have PNRs in the generally understood sense which depends on local chemical heterogeneity associated with cation disorder and yet they contain local dipoles without breaking of the macroscopic symmetry. Instead, there is the possibility or likelihood that the microstructure is a tweed texture characteristic of materials held in the close vicinity of a ferroelastic phase transition [21, 52, 53]. This tweed microstructure is likely also to be dynamic.

There are differences in the elastic and anelastic properties of poled and depoled (Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>)<sub>0.955</sub>(PbTiO<sub>3</sub>)<sub>0.045</sub> (PZN-PT) which relate to the onset of quasi-static correlations between PNRs and the dynamics of twin walls with ferroelastic components. The sequence of ferroelectric transitions with falling temperatures in single crystals is  $Pm\bar{3}m-P4mm$ -R3m [78–81]. RUS spectra from a single crystal poled parallel to [001]<sub>cubic</sub> at room temperature show that the shear elastic constant  $\frac{1}{2}(C_{11} - C_{12})$  has the expected minima at the transition points (figure 10(a), from [82]. On cooling of the depoled crystal, these become smoothed out. The change is due to the difference between the macroscopic properties of individual tetragonal or rhombohedral twin domains in comparison with the effectively cubic elastic constants of a crystal in which there are equal proportions of twin domains randomly distributed between different twin axes. However,

![](_page_9_Figure_1.jpeg)

**Figure 10.** Patterns of elastic softening and acoustic loss through ferroelectric transitions in poled and depoled crystals of (*a*) PZN-PT [82] and (*b*), (*c*) PIN-PMN-PT [88]. In PZN-PT a divergence between poled and depoled states occurs below  $T^*$  rather than at the cubic–tetragonal transition point. In PIN-PMN-PT, poling parallel to  $[1 \ 1 \ 1]_{cubic}$  reduces the acoustic loss in the stability field of the rhombohedral phase in comparison with the depoled crystal. For both materials, increasing acoustic loss below ~200 K is attributed to freezing of ferroelastic/ferroelectric twin walls. Elastic softening below ~700 K in PIN-PMN-PT is attributed to the development of PNRs.

this difference would be expected to be observed only below the cubic–tetragonal transition point,  $T_c = 419 \pm 1$  K, whereas it actually becomes established below ~475 K (figure 10(*a*)). In other words, while the average electric polarization becomes lost at 419 K, some memory of local poling is retained within the macroscopically cubic crystal. This is clearly related to  $T^*$ (~500 K) from acoustic emission [83, 84], below which quasistatic PNRs are believed to become stable.  $T_d$  is PZN and PZN-PT has been reported to be in the vicinity of 650–740 K [85– 87]. Some aspect of the microstructure between  $T_c$  and  $T^*$ must still be mobile, as there is an increase in  $Q^{-1}$  below ~450 K, but the acoustic loss is not as great as below  $T_c$  where ferroelastic twins become established. The marked changes in elastic properties at  $T^*$ , between poled and depoled crystals, are perhaps most obvious in PZN-PT because the degree of softening due to strain/order parameter coupling is so large. It is remarkable that  $\frac{1}{2}(C_{11} - C_{12})$  (figure 10(*a*)), reduces to significantly less than 50% of its value for the cubic parent structure due to the development of the quasi-static PNRs alone.

The transition sequence in  $(Pb(In_{1/2}Nb_{1/2})O_3)_{0.26}(Pb$  $(Mg_{1/3}Nb_{2/3})O_3)_{0.44}(PbTiO_3)_{0.30}$  (PIN-PMN-PT) is again  $Pm\bar{3}m-P4mm-R3m$  [89], with elastic softening as the transitions are approached both from above and below [88]. Figures 10(b) and (c) show the variations of  $f^2$  and  $Q^{-1}$  from a resonance peak in RUS spectra collected from a single crystal which had been poled by application of an electric field parallel to [111]<sub>cubic</sub> at room temperature. Softening below 700 K  $(\sim T_{\rm d})$  is accompanied by a small increase in  $Q^{-1}$  below  $\sim$ 480 K, which is  $\sim$ 35–50 K above the maximum of dielectric permittivity measured at 1 kHz and  $\sim$ 50 K above the cubictetragonal transition. As expected if the acoustic loss is due to mobility of 79°/109° twin walls and poling substantially reduces their density,  $Q^{-1}$  is much lower for the poled crystal than the depoled crystal. However, Debye-like loss peaks in the vicinity of 110K show that freezing of some related defect motion occurs in both the poled and depoled states (figure 10(b)). By analogy with octahedral tilting transitions, the loss peak is most likely to be due to pinning of the ferroelastic twin walls by defects. The presence of loss peaks in data from the poled crystal can then be understood as being due to final freezing of walls between PNRs which persist locally even in a poled crystal. Poling and persistence of PNRs could in turn account for memory effects in relaxor ferroelectrics such that a tetragonal phase with low acoustic loss can be obtained from a rhombohedral crystal poled along [001]<sub>cubic</sub> [88].

Strain coupling with polar defects in a perovskite which remains macroscopically cubic can also lead to 'defect-induced ferroelectricity', as in the case of KTaO<sub>3</sub> [90]. The presence of these defects is most clearly seen as an increase in the amplitude of resonant modes at low temperatures when the excitation is achieved electrically (RPS) rather than mechanically (RUS). Freezing of the defect motion below ~60 K is also apparent as Debye loss peaks in  $Q^{-1}$  data from the RUS spectra.

#### 5. Magnetoelastic coupling

In principle, coupling of strain with magnetic order parameters should provide the same mechanisms for elastic softening and acoustic loss as apply in structural and ferroelectric phase transitions, but there are some subtle differences. The effect of time reversal is that contributions to the excess free energy of odd order terms in the order parameter, M, are not allowed [91–94]. Bilinear coupling of M with a strain only occurs in piezomagnetic materials and is restricted to antiferromagnetically ordered phases with specific magnetic symmetry [95]. Linear-quadratic coupling,  $\lambda eM^2$ , is expected to be typical and, as with other types of transitions, an applied stress will induce a strain which, in turn, is expected to induce a relaxation of the order parameter. The resulting elastic softening as a function of temperature or pressure would be expected to depend on  $\lambda^2$  and the order parameter susceptibility according to equation (1). Strain components which remain strictly zero in the low symmetry phase couple as  $\lambda e^2 M^2$  in lowest order and the related elastic constant will soften or stiffen, depending on the sign of  $\lambda$ , in proportion to  $\lambda M^2$ . If the timescale for relaxation is long in comparison with the timescale of the measurement, only stiffening or softening due to this biquadratic coupling will be seen.

Strains coupled to the magnetic order parameter may be symmetry-breaking, as in the cubic-tetragonal/orthorhombic/ rhombohedral transitions of RCo2 Laves phases [96] and the hexagonal-monoclinic transition of hematite [97], in which case the predicted elastic anomalies will be those expected for improper ferroelastic transitions. If the order parameters transform only as the identity representation, the form of softening will be that expected for a co-elastic transition, as in the case of the tetragonal-tetragonal transition in  $CoF_2$  [98]. In comparison with structural and ferroelectric transitions, the strength of coupling between the (magnetic) order parameter and strain is highly variable. For example, in the RCo<sub>2</sub> Laves phases, shear and volume strains amount to a few % [96], which is within the range typically observed for tilting transitions in perovskites, less than 0.001 for antiferromagnetic ordering in CoF<sub>2</sub> [98], and not detectable for antiferromagnetic ordering in Pr<sub>0.48</sub>Ca<sub>0.52</sub>MnO<sub>3</sub> [99]. Finally, even if the coupling is strong (large values of  $|\lambda|$ ), the amount of softening may be small due to the difference in entropy changes between order/disorder and displacive systems. Linear-quadratic coupling  $(\lambda e M^2)$  is expected on the basis of equation (1) to give rise to softening of individual elastic constants according to

$$C_{ik} - C_{ik}^{\rm o} = -4\lambda^2 M^2 \chi, \tag{7}$$

where  $\chi$  is the order parameter susceptibility. The magnitude of the inverse susceptibility,  $\chi^{-1}$ , scales approximately with excess entropy through the Landau *a* coefficient. For the displacive tilting transitions in SrTiO<sub>3</sub> and LaAlO<sub>3</sub> a = 0.65 and 3.90 J mole<sup>-1</sup> K<sup>-1</sup>, respectively [28, 29, 100], in comparison with  $a = 2R \ln 2 = 11.5 \text{ J} \text{ mole}^{-1} \text{ K}^{-1}$  as an approximation for the limiting case of a one site order/disorder transition. As a consequence, the amount of softening associated with magnetic transitions in perovskites is expected to be smaller than that seen at tilting transitions. Precursor softening is still expected to reflect precursor fluctuations of the magnetic order parameter and magnetic twin walls which are also ferroelastic are expected to give rise to acoustic losses below the transition point.

The elastic and anelastic properties of  $KMnF_3$  measured at RUS frequencies (figure 3) are dominated by the influence of octahedral tilting transitions and no evidence has been found for coupling of shear strain with magnetic order parameters for the antiferromagnetic or canted ferromagnetic structures. In the absence of such strain coupling, it seems likely also that coupling between the magnetic and tilt order parameters will be weak [23].

There are no obvious anomalies in the elastic or anelastic properties through the Néel point of  $Pr_{0.48}Ca_{0.52}MnO_3$ , confirming that the antiferromagnetic order parameter couples only weakly, if at all with shear strain. Figure 10(*a*) shows the variation of  $f^2$  ( $\propto$  shear modulus) and  $Q^{-1}$  through

![](_page_10_Figure_8.jpeg)

**Figure 11.** (*a*) Variation of *G* (shear modulus) and  $Q^{-1}$  through the incommensurate charge ordering transition at 235 K and the Néel point at 180 K for a polycrystalline sample of Pr<sub>0.48</sub>Ca<sub>0.52</sub>MnO<sub>3</sub> [19]. There is no obvious elastic anomaly associated with antiferromagnetic ordering. The red solid curve is a fit of equation (10) to the Debye loss peak at ~75 K, with  $U = 7 \text{ kJ} \text{ mole}^{-1}$  if  $r_2(\beta) = 1$ . (*b*) The integral autocorrelation ( $\Psi$ ) from the same spectra, which includes contributions from the background as well as individual resonance peaks, reveals a distinct change in properties at the Néel point attributed to dynamical coupling of the antiferromagnetic order with strain [101].

the antiferromagnetic transition at  $T_{\rm N} = 180$  K and the incommensurate charge ordering transition at  $T_{\rm c} = 235$  K [19]. The obvious anomalies are associated with the charge ordering transition and there is a Debye loss peak due to a freezing process in the vicinity of 75 K. However, evidence for dynamic magnetoelastic coupling is present in the background of the RUS spectra, as revealed by autocorrelation analysis using the function [101]

$$A_{\rm corr}(x) = \frac{\int A(\omega - x) A(\omega)}{\int A^2(\omega)} d\omega$$
(8)

where A is amplitude and  $\omega$  is frequency. This decays symmetrically with displacement x and, in most cases,  $A_{\text{corr}}(x)$ is Gaussian around x = 0 [102–104]. Integration over the autocorrelation spectrum gives a parameter  $\Psi$  where

$$\Psi = \int A_{\rm corr}(x) dx. \tag{9}$$

The temperature dependence of  $\Psi$  (figure 11(*b*), after [101] determined from RUS spectra from Pr<sub>0.48</sub>Ca<sub>0.52</sub>MnO<sub>3</sub>reveals a distinct peak at 180 K, in addition to features at ~75 and ~235 K which were already visible from the analysis of individual resonance peaks given in figure 11(*a*). This feature would appear in  $f^2$  or  $Q^{-1}$  if it was from the discrete mechanical resonances but, as it does not, must come from

the background. Background excitations include transient processes, such as spikes during front propagation [101]. In the present case, the mechanism may be due to dynamical coupling of the antiferromagnetic order parameter with strains, due say to clustering or antiphase domain boundaries, which causes disruption of the standing waves of the mechanical resonances. The nature and strength of magnetoelastic coupling can have other subtle dependences which are not fully understood, however, since small anomalies (stiffening of  $\frac{1}{2}$  ( $C_{11} - C_{12}$ ), softening of the bulk modulus with falling temperature) have been seen at the Néel point of the commensurately ordered phase of Pr<sub>0.65</sub>Ca<sub>0.35</sub>MnO<sub>3</sub> [105].

The Debye loss peak at 75 K is attributed to freezing of domain wall motion with a rate limiting step that depends on the mobility of polarons. It can be represented quantitatively by [106, 107]

$$Q^{-1}(T) = Q_{\rm m}^{-1} \left[ \cosh \left\{ \frac{U}{{\rm R}r_2\left(\beta\right)} \left( \frac{1}{T} - \frac{1}{T_{\rm m}} \right) \right\} \right]^{-1}, \quad (10)$$

where U is an activation energy,  $Q_m^{-1}$  is the maximum value of  $Q^{-1}$  occurring at temperature  $T_m$ , and  $r_2(\beta)$  is a parameter that reflects the width of a Gaussian distribution of relaxation times.

 $Sm_{0.6}Y_{0.4}MnO_3$  (SYM0.4) is a perovskite with Rand M-point tilting (Pnma) which develops a sinusoidally modulated antiferromagnetic structure below  $T_{\rm N1} = 50 \,\rm K$ and a ferroelectric cycloidally modulated antiferromagnetic structure below  $T_{\rm N2}~\approx~27\,{\rm K}$ , without any changes in crystallographic point group [108, 109]. These magnetic transitions are co-elastic but the changes in shear modulus and acoustic dissipation differ from the pattern shown, for example, at the  $\beta - \alpha$  transition in quartz which also does not have a symmetry-breaking shear strain. Instead of softening below the transition point seen in a polycrystalline sample of quartz and changes in  $Q^{-1}$  only through the transition point itself (figure 7 of [16]), the main features are a small, continuous increase in  $f^2$  (proportional to the shear modulus) and a change from relatively high  $Q^{-1}$  values in the stability field of the para phase to low values through  $T_{\rm N1}$  (figure 12, from [110]. Changes to the shear strains  $e_{tx}$  and  $e_4$ , superimposed on the strains due to octahedral tilting, are close to or within the limits of experimental uncertainty but there is a small volume strain below  $T_{\rm N1}$  which reaches a maximum value of  $\sim -0.0008$ (figure 5 of [110]). Slight stiffening of the shear modulus is consistent with a mechanism described by  $\lambda e^2 M^2$  where the shear strains, e, are small or zero. The drop in  $Q^{-1}$  signifies that a loss mechanism in the paramagnetic structure becomes suppressed in the antiferromagnetic phases and this is mostly likely to relate to dynamical disordering of spin states which are weakly coupled with the small volume strains. Above  $T_{N1}$ relaxation times of the local dynamical strains must be not too dissimilar from  $\sim 10^{-6}$  s, whereas long range magnetic order below  $T_{\rm N1}$  must be static or nearly so. In effect, the ordering of the magnetic moments leads to a small additional bracing of the structure with respect to external stress in much the same way as occurs for hydrogen bonding in the mineral lawsonite [15].

![](_page_11_Figure_8.jpeg)

**Figure 12.**  $f^2$  and  $Q^{-1}$  data from three different resonances in RUS spectra from a single crystal of SYM0.4 [110]. The  $f^2$  data have been scaled to overlap at 300 K (red triangles ~600 kHz, blue circles ~760 kHz, green squares ~950 kHz). The overall trend is of slight stiffening below the two magnetic ordering temperatures, consistent with weak magnetoelastic coupling. The main acoustic loss occurs above  $T_{\rm N1}$  in the stability field of the paramagnetic phase and is most likely due to precursor fluctuations/clustering involving local electric/magnetic dipoles.

#### 6. Multiferroics

EuTiO<sub>3</sub> has essentially the same  $Pm\bar{3}m-I4/mcm$  octahedral tilting transition as occurs in SrTiO<sub>3</sub>, with  $T_{\rm c} \sim 282$  K [111– 114]. In addition, it becomes antiferromagnetic below  $T_{\rm N} \sim$ 6K [115, 116] and has a polar soft optic mode which makes it an incipient ferroelectric [117, 118].  $T_c$  can shift by a few degrees when an external magnetic field is applied [119] and magnetoelectric effects have been demonstrated at low temperatures [120–123], signifying that there is coupling between the three ferroic properties shown in figure 1. Elastic softening through  $T_c$  from RUS measurements on a single crystal (figures 13(a) and (b), after [41]; see also [124]) has the steep softening expected for an improper ferroelastic transition which is close to second order in character. However, the decrease in  $Q^{-1}$  below its peak at ~280 K implies that the ferroelastic twins do not have any significant interval of mobility and quickly become pinned with falling temperature.

In contrast with antiferromagnetic ordering in SYM0.4, there is slight softening and an increase in  $Q^{-1}$  below  $T_N$  in EuTiO<sub>3</sub> (figure 13(c)). In other words, there is some significant coupling between the magnetic order parameter and strain though perhaps the form of softening might be due to the biquadratic coupling term,  $\lambda e^2 M^2$ . Additional anomalies in  $f^2$  and  $Q^{-1}$  at ~3 K (figure 13(c)) have the same form as seen at the Morin transition in hematite, Fe<sub>2</sub>O<sub>3</sub> [97] and are due to the (first order) change in easy magnetization direction known to occur at this temperature [112].

Anomalies in elastic properties associated with the magnetic transitions shift in temperature as a function of magnetic field [125], confirming that there is significant magnetoelastic coupling in EuTiO<sub>3</sub>. Magnetoelectric coupling might therefore also be expected to be relatively strong via a common strain mechanism. It is certainly the case that strain modifies the magnetic ordering behaviour because thin films with an imposed strain from the substrate become both

![](_page_12_Figure_1.jpeg)

**Figure 13.**  $f^2$  and  $Q^{-1}$  data from selected resonances in RUS spectra from single crystals of EuTiO<sub>3</sub>. Resonances (with their values scaled so as to overlap in each case) which are tentatively assigned to being determined predominantly by  $C_{44}(a)$  and  $(C_{11} - C_{12})$  (b) show 20–30% softening due to the octahedral tilting transition at  $\sim$ 284 K as expected for the effects of classical strain/order parameter coupling [41].  $Q^{-1}$  has a peak immediately below the transition point but diminishes rapidly with falling temperature, indicating low mobility of ferroelastic twin walls, in marked contrast with SrTiO<sub>3</sub>. (c) Distinct elastic and anelastic anomalies accompany the magnetic transitions at 5.6  $(T_N)$  and 2.8 K  $(T_{\rm tr})$ , indicative of some degree of magnetoelastic coupling [125]. data have been scaled to 1 at the lowest temperature (blue circles  $f \sim 990$  kHz, green triangles  $\sim 1170$  kHz, red squares  $\sim 1780$  kHz). (d) Data collected with and without application of a 10 T magnetic field show little or no change in  $f^2$  but  $Q^{-1}$  diminishes with applied field. The change in acoustic loss is interpreted in terms of the presence of magnetic defects which have a component of strain.

ferroelectric and ferromagnetic [126–128]. The effect of applied magnetic field at  $T_{\rm N} < T < T_{\rm c}$  is mainly to reduce  $Q^{-1}$  without inducing much change in  $f^2$  for individual resonances (figure 13(*d*)), suggesting a loss mechanism related to the presence of magnetic defects which might also have a role in pinning the ferroelastic domain walls [125], and, perhaps, in stabilizing the incommensurate structure known to occur under some conditions [113, 129].

BiFeO<sub>3</sub> is another perovskite of intense current interest in the context of single phase multiferroics (e.g. [130-134]). The first order paraelectric-ferroelectric transition at ~1100 K is between a structure with *Pnma* symmetry  $(M_3^+ + R_4^+ \text{ tilts})$  to one with R3c symmetry ( $\Gamma_4^-$  polar displacements +R<sup>+</sup><sub>4</sub> tilts). In addition to the incommensurate cycloidal antiferromagnetic structure which develops below  $\sim$ 650 K, there are further more subtle changes at lower temperatures which have not all been fully characterized, as summarized by Park et al [134]. Small changes in lattice parameters below  $\sim 650 \text{ K}$  [135–137] show that there are shear and volume strains of up to a few per mil at room temperature (based on the data in figure 4 of [136]) due to coupling with the magnetic order parameter. There is also a softening by  $\sim 4\%$  of the longitudinal elastic constant below  $\sim$ 700 K, as measured at 10 MHz in a polycrystalline sample [138], with a step-like form which could be consistent with classical strain relaxation arising from  $\lambda eM^2$  coupling at a co-elastic transition.

As with other phase transitions, anelastic properties are as illuminating of the role of strain as the effects of static elastic relaxations. The microstructure of BiFeO<sub>3</sub> potentially contains ferroelastic/(71°/109°) ferroelectric twin walls, 180° ferroelectric twin walls and magnetic domain boundaries relating to the cycloidal structure. A classical Debye loss peak between 200 and 225 K has been observed in DMA data collected from a ceramic sample in the frequency range 0.6– 18 Hz [139] and a similar peak is present near 350 K in the 10 MHz pulse-echo ultrasonic data of [138]. In combination, the temperatures,  $T_{\rm m}$ , at which the attenuation is a maximum ( $\omega \tau = 1$ , where the angular frequency  $\omega$  is  $2\pi f$ ) can be described with the simplest Arrhenius relationship

$$\tau = \tau_{\rm o} \exp\left(\frac{U}{{\rm R}T}\right),\tag{11}$$

with  $U = 0.65(1) \text{ eV} (63(1) \text{ kJ mole}^{-1}), \tau_0 = 1.04 \times 10^{-17} \text{ s.}$ Redfern et al [139] obtained 0.59(9) eV (57(9) kJ mole<sup>-1</sup>) for the DMA data alone. By analogy with similar loss patterns in PZT [140] it is likely that the loss mechanism relates to pinning of the ferroelastic twin walls by oxygen vacancies. However, 0.6 eV (58 kJ mole<sup>-1</sup>) is slightly lower than expected for a pinning mechanism that involves oxygen vacancies, which is typically  $\sim 0.9-1.1 \text{ eV} (86-106 \text{ kJ mole}^{-1})$  for purely ferroelastic twin walls in oxide perovskites [31] and  $\sim 1 \text{ eV}$ for 90° twin walls in PZT [140]. The value of  $\tau_0$  is also rather small in comparison with  $\sim 10^{-11}$ - $10^{-13}$  s given in [31, 32, 140] for oxide perovskites. If the observed parameters have a classical physical meaning, a second possibility is that the relaxation involves changes in the repeat distance of the incommensurate magnetic structure which become pinned by interaction with point defects. By interpolation, the same

![](_page_13_Figure_1.jpeg)

**Figure 14.** (a)  $f^2$  and  $Q^{-1}$  data from selected resonances in RUS spectra from a polycrystalline sample of BiFeO<sub>3</sub> (unpublished data for the same sample as used by Redfern *et al* [139]). The  $f^2$  data for three resonances have been scaled to overlap at 295 K; actual room temperature values of f are 240 kHz (brown circles), 573 kHz (green triangles), 887 kHz (blue squares).  $Q^{-1}$  generally increases with increasing temperature, with a break in slope at ~140 K and slight anomalies at ~180, ~220 and ~260 K. Calculated values of  $Q^{-1}$  using equation (10), with  $Q_m^{-1}$  =0.006,  $T_m$  = 310 K, U = 63 kJ mole<sup>-1</sup>,  $r_2(\beta)$  = 1, are shown as a red curve. (b)  $f^2$  and  $Q^{-1}$  data from selected resonances in RUS spectra from a polycrystalline sample of Bi<sub>0.9</sub>Sm<sub>0.1</sub>FeO<sub>3</sub> [142]. The predominant features in  $Q^{-1}$  are a slight increase below ~30 K and a sharp break in slope at ~250 K.  $f^2$  data show a change in trend at ~200 K.

loss behaviour would be expected to occur in the vicinity of 300 K at frequencies of ~100–500 kHz, and  $Q^{-1}$  from RUS spectra indeed starts to increase from below room temperature ([141], figure 14(*a*)). However,  $Q^{-1}$  calculated using equation (10), with  $Q_m^{-1} = 0.006$ ,  $T_m = 310$  K, U = 63 kJ mole<sup>-1</sup>,  $r_2(\beta) = 1$ , clearly does not reproduce the width of the temperature dependence of the loss behaviour. This indicates that a different loss mechanism or set of mechanisms is being sampled, and a likely explanation is a set of overlapping loss peaks, including at ~180 and ~220 K. The relationships of these to a surface transition proposed to occur at ~140 K and glassy freezing of the magnetic structure below ~200 K [141] are not understood. Small anomalies in the temperature dependence of  $f^2$  (figure 14(*a*)) are also consistent with loss mechanisms that involve only small changes in shear modulus.

Stoichiometric BiFeO<sub>3</sub> decomposes at high temperature but substitution of ions such as  $Nd^{3+}$ ,  $Sm^{3+}$  or  $Gd^{3+}$  for  $Bi^{3+}$  on the crystallographic A-site has proved effective for producing more stable materials with closely related physical properties. In  $Bi_{0.9}Sm_{0.1}FeO_3$  (BSFO10)the structural/ferroelectic [143]

and magnetic [144] transitions may almost coincide at  $\sim$ 640 K. Resonance peaks in RUS spectra from a polycrystalline sample show softening of  $f^2$  by  $\sim 7\%$  with falling temperature at about the same point [142]. Strong dissipation occurs below  $\sim$ 420 K, and is presumed to be due to the same loss mechanism(s) as in BiFeO<sub>3</sub>. The first order structural/ferroelectric transition in Bi<sub>0.9</sub>Nd<sub>0.1</sub>FeO<sub>3</sub> (BNFO10) is at  $\sim$ 850 K and the magnetic transition is at  $\sim$ 700 K [145]. RUS data perhaps show a slight stiffening of the shear modulus below 650 K but do not extend to high enough temperatures to be sure of the trend for the paramagnetic rhombohedral structure [142]. Increasing acoustic loss below  $\sim$ 420 K is much the same as for BSFO10. The onset of increasing loss with increasing temperature is at  $\sim$ 250 K in both cases, which is again essentially the same as in BiFeO<sub>3</sub> itself. This aspect of the anelastic behaviour therefore seems to be common to all the compositions so far investigated. Both BSFO10 and BNFO10 show a continuous trend of additional stiffening (up to  $\sim$ 1–2%) below  $\sim$ 200 K (figure 14(b), after [142]) which correlates with small changes in magnetization. Together with other small variations of  $Q^{-1}$  these point to further magnetoelastic coupling and adjustments in magnetic structure but, as with BiFeO<sub>3</sub> itself, characterization of their origin remains incomplete.

More extensive solid solution away from BiFeO<sub>3</sub> results in suppression of the R3c ferroelectric structure but not necessarily of magnetic ordering. In the case of replacement of Bi<sup>3+</sup> by a combination of Ca<sup>2+</sup> and oxygen vacancies, G-type antiferromagnetic ordering with  $T_{\rm N} \sim 650 \,{\rm K}$  persists (figure 15(*a*)). RUS spectra collected from a sample with composition  $(BiFeO_3)_{0.64}(CaFeO_{2.5})_{0.36}$ (BCFO36), which is metrically tetragonal or orthorhombic at room temperature, have allowed the influence of magnetic ordering to be examined separately from the ferroelectric transition [146]. The topology of the phase diagram, with apparently little influence of changes in structure, ferroelectric order and oxygen vacancy ordering on  $T_N$ , suggests that the antiferromagnetic order parameter is only weakly (if at all) coupled to the other order parameters of the system. If this is the case, it is likely that coupling between the magnetic order parameter and strain is also weak. Figure 15(b) shows that there is a small stiffening (increasing  $f^2$ ) associated with antiferromagnetic ordering. It was found that the excess stiffening ( $\Delta f^2$ ) scales approximately with the square of the magnetic order parameter for a sample with closely similar composition, consistent with coupling of the form  $\lambda e^2 M^2$  [146]. There is a significant loss peak between ~300 and  $\sim 750$  K (figure 15(b)) but this may well be due to a change in mobility of oxygen vacancies, as suggested by changes in electrical conductivity [146].

At low temperatures in BCFO36 there is a rather similar pattern of stiffening and acoustic loss (figure 15(c)), but without evidence of a phase transition. The peak in  $Q^{-1}$  has its maximum at ~110 K and is almost indistinguishable from dielectric loss peaks measured at the same frequencies. Taking the value of U = 0.22 eV (21 kJ mole<sup>-1</sup>) extracted from dielectric loss measurements [147], which also gave  $\tau_0 = 5.3 \times 10^{-15} \text{ s}$ , leads to a fit value of  $r_2(\beta) \sim 5.5$  [146] in equation (10). The classical Debye pattern of acoustic loss

![](_page_14_Figure_1.jpeg)

Figure 15. Elastic and anelastic anomalies from RUS data for a polycrystalline sample of (BiFeO<sub>3</sub>)<sub>0.64</sub>(CaFeO<sub>2.5</sub>)<sub>0.36</sub> [146]. (a) Subsolidus phase relations for BiFeO<sub>3</sub>–CaFeO<sub>2.5</sub>. (b)  $f^2$  and  $Q^{-1}$  data for high temperatures from a resonance peak with frequency near 320 kHz. A small break in slope of  $f^2$  coincides with  $T_{\rm N} = 645$  K. The steep increase in  $Q^{-1}$  between  $\sim 300$  and  $\sim$ 700 K is perhaps related to the mobility of oxygen vacancies under applied stress. (c)  $f^2$  and  $Q^{-1}$  data for low temperatures from a resonance peak with frequency near 300 kHz. The break in slope in  $f^2$  and a peak in  $Q^{-1}$  at ~130 K can be accounted for by classical Debye loss behaviour using equation (10) (black curve and dashed lines for baselines).

and elastic stiffening is due to freezing of the motion of defects which are coupled with strain, and oxygen vacancies with a range of local environments are the most likely candidates for this.

Another potentially important family of single phase multiferroic perovskites includes solid solutions between  $Pb(Fe_{0.5}Nb_{0.5})O_3$  (PFN) or  $Pb(Fe_{0.5}Ta_{0.5})O_3$  (PFT) and Pb(Zr,Ti)O<sub>3</sub> (PZT) [148–151]. Magnetic properties derived from the iron-bearing end member are effectively combined with ferroelectric properties of PZT. In order to maximize the variations in dielectric properties, compositions close to the morphotropic phase boundary have been chosen. Amongst these, a ceramic sample with nominal composition (Pb(Fe<sub>0.5</sub>Ta<sub>0.5</sub>)O<sub>3</sub>)<sub>0.4</sub>(Pb(Zr<sub>0.53</sub>Ti<sub>0.47</sub>)O<sub>3</sub>)<sub>0.6</sub>

![](_page_14_Figure_5.jpeg)

**Figure 16.**  $f^2$  and  $Q^{-1}$  data from selected resonances in RUS spectra from a polycrystalline sample with nominal composition  $(Pb(Fe_{0.5}Ta_{0.5})O_3)_{0.4}(Pb(Zr_{0.53}Ti_{0.47})O_3)_{0.6}$  [152]. (a) The variation of  $f^2$  through the expected transition point, ~475 K, is typical of other cubic-tetragonal transitions in perovskites. (b) The hysteresis in  $f^2$  between ~160 and 235 K is attributed to a first order structural transition (green diamonds = cooling, red triangles = heating). Increasing values of  $f^2$  with falling temperature below  $\sim 50 \text{ K}$ coincide with changes in magnetic susceptibility which may be related to the development of spin or cluster glass ordering.

 $(=Pb(Fe_{0.20}Ta_{0.20}Zr_{0.32}Ti_{0.28})O_3)$ , which is both ferroelectric and ferromagnetic at room temperature, was recently examined by RUS [152]. Sanchez et al [149] had previously reported tetragonal-orthorhombic and orthorhombicrhombohedral transitions with transition temperatures of  $\sim$ 475 and  $\sim$ 250 K. For a homogeneous sample with this nominal composition the first transition would more likely have been cubic (paraelectric)-tetragonal (ferroelectric) based on extrapolation between  $\sim 660$  K for the Pm3m-P4mm transition in Pb(Zr<sub>0.53</sub>Ti<sub>0.47</sub>)O<sub>3</sub> [153] and  $\sim$ 270 K in Pb(Fe<sub>0.5</sub>Ta<sub>0.5</sub>)O<sub>3</sub> [154, 155]. The actual composition was  $Pb(Fe_{0.17}Ta_{0.27}Zr_{0.30}Ti_{0.17})O_3$  [156].

Figure 16 shows variations of  $f^2$  and  $Q^{-1}$  below room temperature from [152]. Softening of individual resonances above and through  $\sim 450 \text{ K}$  (figure 16(*a*)) indicates softening of the shear modulus ( $\propto f^2$ ) by ~30% and follows a pattern which is typical of transitions between cubic, tetragonal, rhombohedral and orthorhombic phases driven by octahedral tilting or by ferroelectric displacements (e.g. figures 3, 4, 8, 10 and 13). The sample has an open magnetic hysteresis loop at room temperature but no overt evidence has been seen in the RUS data for a discrete para-ferromagnetic transition. This would be difficult to detect in the interval ~405–472 K where attenuation is high, however. The  $f^2$  data display a clear hysteresis between heating and cooling in the

temperature interval ~160–235 K (figure 16(*b*)), which has been interpreted as being due to a first order transition. Based on the structural sequence in PFT [155], this is most likely to involve the symmetry change *P4mm–Cm* associated with a change in orientation of the ferroelectric dipole (table 2). However, although the low temperature (monoclinic) phase is slightly stiffer than the tetragonal phase, there is no sign of the softening as the transition point is approached from either side that is seen at transitions between structures with different orientations of ferroelectric dipoles in the ferroelectric materials described above or between structures with different directions of octahedral rotations. The changes in  $f^2$  are also not accompanied by marked changes in acoustic loss, though  $Q^{-1}$  values for the low temperature structure are clearly lower than for the high temperature structure.

Below ~50 K changes of  $f^2$  in Pb(Fe<sub>0.20</sub>Ta<sub>0.20</sub>Zr<sub>0.32</sub>Ti<sub>0.28</sub>) O<sub>3</sub> (figure 16(*b*)) correlate with changes in magnetic susceptibility. The origin of this low temperature behaviour in terms of either a magnetic transition, clustering or glassy behaviour has not yet been established but the key point is that the RUS and magnetic data together provide evidence for significant magnetoelastic coupling. Thus, in this first sample examined from the PFT-PZT system, there is clearly coupling of strain with ferroelectric and magnetic ordering, providing the possibilities for strong magnetoelectric coupling which should be tunable by choice of composition. The presence of ferroelastic, ferroelectric and magnetic domain walls also provides possibilities for generating materials with a diversity of microstructures with their own unique properties.

#### 7. Jahn-Teller

Although transitions driven by cooperative Jahn-Teller distortions are restricted to phases with a limited number of cations which have particular occupancies of electron orbitals, they can have a special significance because the Jahn-Teller effect links changes in electronic configuration to changes in structural state. Distortions of individual octahedra can lead to macroscopic strains of up to a few % and variations in elastic properties by tens of %. Coupling between the order parameters for cooperative Jahn-Teller and octahedral tilting transitions is inevitable and there are possibilities also for enhanced magnetoelastic coupling. Group-theoretical formalities for multiple instabilities involving octahedral tilting and different Jahn-Teller order parameters are set out in [157, 158] and including cation or charge order in [159]. Attention is drawn here to elastic and anelastic anomalies accompanying combined  $R_4^+$  tilting plus  $\Gamma_3^+$  Jahn-Teller transitions in PrAlO<sub>3</sub> and Jahn–Teller ( $M_2^+$  and  $\Gamma_3^+$ ) plus charge ordering ( $\Sigma_1$  and  $\Sigma_2$ ) in the tilted ( $M_3^+$  and  $R_4^+$ ) structure of Pr<sub>0.48</sub>Ca<sub>0.52</sub>MnO<sub>3</sub>.

The most recent neutron powder diffraction studies show that PrAlO<sub>3</sub> undergoes a sequence of transitions  $Pm\bar{3}m$ - $R\bar{3}c$  (second order at ~1864 K),  $R\bar{3}c$ -Imma (first order at 210–220 K), Imma–C2/m (second order at ~151 K) [160, 161]. The first transition is driven by octahedral tilting but the orthorhombic phase is believed to be stabilized in part by Jahn–Teller distortions and the third entirely be Jahn– Teller distortions around  $Pr^{3+}$  [162]. A thermodynamic description of the combined instabilities is provided by a free energy expansion in  $\Gamma_3^+$  ( $q_{oz}, q_{tz}$ ) and  $R_4^+$  order parameters, ( $q_1, q_2, q_3$ ), plus coupling with volume ( $e_a$ ) and shear strains ( $e_{tz}, e_{oz}, e_4, \ldots$ ) [160]

$$\begin{aligned} G_{\rm L} &= \frac{1}{2} a \Theta_{\rm s} \left( \coth\left(\frac{\Theta_{\rm s}}{T}\right) - \coth\left(\frac{\Theta_{\rm s}}{T_{\rm c}}\right) \right) \left(q_{1}^{2} + q_{2}^{2} + q_{3}^{2}\right) \\ &+ \frac{1}{4} b \left(q_{1}^{2} + q_{2}^{2} + q_{3}^{2}\right)^{2} + \frac{1}{4} b' \left(q_{1}^{4} + q_{2}^{4} + q_{3}^{4}\right) + \lambda_{1} e_{\rm a} \left(q_{1}^{2} + q_{2}^{2} + q_{3}^{2}\right) \\ &+ q_{3}^{2} \right) + \lambda_{2} \left(e_{\rm t} \left(2q_{1}^{2} - q_{2}^{2} - q_{3}^{2}\right) + \sqrt{3} e_{\rm o} \left(q_{2}^{2} - q_{3}^{2}\right)\right) \\ &+ \lambda_{3} \left(e_{4}q_{1}q_{3} + e_{5}q_{1}q_{2} + e_{6}q_{2}q_{3}\right) + \frac{1}{2} a_{\rm JT} \Theta_{\rm s,JT} \left( \coth\left(\frac{\Theta_{\rm s,JT}}{T}\right) \right) \\ &- \coth\left(\frac{\Theta_{\rm s,JT}}{T_{\rm c,JT}}\right) \right) \left(q_{\rm oz}^{2} + q_{\rm tz}^{2}\right) + \frac{1}{3} u_{\rm JT} \left(q_{\rm tz}^{3} - 3q_{\rm tz}q_{\rm oz}^{2}\right) \\ &+ \frac{1}{4} b_{\rm JT} \left(q_{\rm oz}^{2} + q_{\rm tz}^{2}\right)^{2} + \lambda_{\rm t} \left(q_{\rm oz}e_{\rm o} - q_{\rm tz}e_{\rm t}\right) + \lambda_{\rm a}e_{\rm a} \left(q_{\rm oz}^{2} + q_{\rm tz}^{2}\right) \\ &+ \lambda_{\rm e} \left(q_{\rm tz} \left(2e_{\rm f}^{2} - e_{\rm fz}^{2} - e_{\rm fz}^{2}\right) - \sqrt{3}q_{\rm oz} \left(e_{\rm fz}^{2} - e_{\rm fz}^{2}\right)\right) + \frac{1}{4} \left(C_{11}^{\rm o} - C_{12}^{\rm o}\right) \left(e_{\rm o}^{2} + e_{\rm t}^{2}\right) + \frac{1}{6} \left(C_{11}^{\rm o} + 2C_{12}^{\rm o}\right) e_{\rm a}^{2} + \frac{1}{2}C_{44}^{\rm o} \left(e_{\rm fz}^{2} + e_{\rm fz}^{2} + e_{\rm fz}^{2}\right). \end{aligned}$$

The coefficients are for standard Landau terms (a, b, ...) or for coupling terms  $(\lambda_1, \lambda_2, ...)$ .  $C_{ik}^o$  are elastic constants of the reference cubic phase and  $\Theta_s$ ,  $\Theta_s$ , JT are order parameter saturation temperatures. A central feature of this description is the combination of pseudoproper ferroelastic behaviour represented by the Jahn–Teller order parameters, with bilinear coupling between order parameter components and strain, and improper ferroelastic behaviour represented by the tilt order parameters, with linear–quadratic coupling.

Figure 17 shows a stack of RUS spectra collected through the transition sequence from a single crystal of PrAlO<sub>3</sub> [163]. The  $R\bar{3}c$ -Imma transition is marked by softening of all the resonances from both sides, as appears to be characteristic of first order transitions between structures with different orientations of essentially the same order parameter such as the equivalent *I4/mcm*-Imma transition in SrZrO<sub>3</sub>. By way of contrast, the Imma-C2/m transition is marked by steep precursor softening of the lowest frequency resonance, while other resonance modes stiffen. The low frequency mode would extrapolate to zero at  $T_{c,JT}$  (151 K) for the Imma-C2/m transition, corresponding to the expected pseudoproper ferroelastic solution for a second order transition (leaving out the influence of saturation terms)

$$(C_{11} - C_{12}) = \left(C_{11}^{o} - C_{12}^{o}\right) \left(\frac{T - T_{c}^{*}}{T - T_{c}}\right).$$
(13)

 $T_c^*$  is the transition temperature as renormalized by bilinear coupling of the order parameter with the symmetry-breaking strain. The difference between  $T_c^*$  and  $T_c$ , 38 K, is a measure of the strength of the coupling  $(T_c^* - T_c = \lambda_t^2/(a_{\rm JT}\frac{1}{2}(C_{11}^0 - C_{12}^0)))$  and determines the steepness of curvature of the softening. Acoustic dissipation below

![](_page_16_Figure_1.jpeg)

**Figure 17.** RUS spectra from a single crystal of PrAlO<sub>3</sub>, stacked in proportion to the temperatures at which they were collected [163]. Phase transitions are easily identifiable by sharp minima in the frequencies of selected peaks at ~215 K ( $R\bar{3}c$ -Imma) and 151 K (Imma-C2/m). Superattenuation in the stability field of the C2/m structure is attributed to the mobility of ferroelastic twin walls, apart from in a small temperature interval just above 100 K where an accidental degeneracy occurs such that the shear strain goes to zero.

room temperature remains low (sharp resonance peaks) in the stability fields of the rhombohedral and orthorhombic phases but superattenuation occurs in the stability field of the monoclinic phase. In other words, twin walls due to the cooperative Jahn-Teller distortion are highly mobile while those due to tilting are pinned. Resonance peaks reappear in the spectra across a narrow temperature interval,  $\sim$ 90–116 K, which coincides with an accidental degeneracy in the strains such that the monoclinic shear strain contrast across the twin walls goes to zero. The twin walls do not move under the influence of an external stress in this circumstance. There is no evidence of domain wall freezing with further lowering of temperature, and the walls must remain mobile down to at least 10 K. PrAlO<sub>3</sub> remains paramagnetic but displays anomalous magnetic properties in the stability field of the monoclinic structure which could be explained in terms of reorientation of twin domains under the influence of an external magnetic field [163, 164]. This would be assisted by the easy mobility of the ferroelastic twin walls, in principle allowing poling of ferroelastic domains by a magnetic field. The same pattern of softening and loss extends into the LaAlO<sub>3</sub>-PrAlO<sub>3</sub> solid solution [40].

Half-doped manganites can develop a charge ordered structure in which a significant driving force is Jahn–Teller distortion around Mn in crystallographic B-sites (e.g. [165, 166]). Their remarkable magnetoresistance properties depend on competition between magnetic and structural instabilities and it is well understood that these effects can be mediated by strain. The commensurate  $Pnm2_1$  structure [167–170] is derived from the parent  $Pm\bar{3}m$  structure by a combination of irreducible representations [19, 99, 159] but,

![](_page_16_Figure_6.jpeg)

**Figure 18.** Variation in *G* (*a*) and  $Q^{-1}$  (*b*) through the incommensurate ordering transition ( $T_c = 235$  K in zero field) and the Néel point ( $T_N = 180$  K in zero field) for a polycrystalline sample of Pr<sub>0.48</sub>Ca<sub>0.52</sub>MnO<sub>3</sub> in progressively higher magnetic fields [19]. Softening as  $T_c$  is approached from above, due to the Jahn–Teller component, becomes suppressed at 15 T. Acoustic loss is also suppressed by increasing field.

in the present context, the key order parameters belong to  $\Gamma_3^+$  (Jahn–Teller) and  $\Sigma_1$ ,  $\Sigma_2$  (ordering). Changes in elastic properties associated primarily with the Jahn–Teller contribution have been observed by pulse-echo ultrasonics and Brillouin scattering in manganite solid solutions such as (Pr,Ca)MnO<sub>3</sub> and (La,Ca)MnO<sub>3</sub> [105, 171–178].

In Pr<sub>0.48</sub>Ca<sub>0.52</sub>MnO<sub>3</sub> the charge ordering process leads to an incommensurate structure, but  $\Gamma_3^+$  is still active and is expected to give the ordering transition an element of pseudoproper ferroelastic character. As seen in data for shear modulus and  $Q^{-1}$  from a polycrystalline sample in figure 11(a), [19] the *Pnma*-incommensurate transition at  $\sim$ 235 K is marked by softening from both sides. This is attributed to pseudoproper softening of  $\frac{1}{2}(C_{11}-C_{12})$  in the Pnma field followed by stiffening as the zone centre and zone boundary order parameters develop non-zero values. Application of an external magnetic field causes the charge ordered insulator phase to be replaced by one with metallic electrical conductivity, in effect because ferromagnetism and the cooperative Jahn-Teller distortions are incompatible. Suppression of the  $\Gamma_3^+$  order parameter is seen in the variation of the shear modulus when the same transition is followed in increasingly strong external magnetic fields: at 5 and 10 T there is still softening with falling temperature but at 15 T this part of the elastic anomaly has disappeared (figure 18(a)).

A further indication of the importance of a ferroelastic component is the pattern of acoustic loss in zero field (figures 11(a) and 18(b)), which is similar to the patterns observed at ferroelastic transitions. The increase in  $Q^{-1}$  below ~235 K

implies that some aspect of the incommensurate structure, most likely the domain walls, couples with strain and is mobile under the influence of an external stress. This mobility ends at a classical Debye loss peak centred on ~75 K which can be fit with  $U \sim 0.1$  eV and  $\tau_0 \sim 10^{-11} - 10^{-13}$  s (figure 11(*a*)) [19]. Under application of an external shear stress, the domain walls may change their spacing or rotate locally until they become pinned by defects or the rate limiting step, perhaps the mobility of polarons, becomes too slow in relation to the applied frequency. The acoustic loss disappears in a 15 T field (figure 18(*b*)), emphasizing the importance of Jahn–Teller distortions also in the structure of the incommensurate phase.

An alternative means of suppressing the Jahn–Teller component of a phase transition is to reduce the grain size since this acts to suppress the strain. The charge ordering transition in La<sub>0.5</sub>Ca<sub>0.5</sub>MnO<sub>3</sub> with grain sizes of  $\sim$ 75 and  $\sim$ 135 nm has pseudoproper ferroelastic softening but is significantly reduced at grain sizes of  $\sim$ 34 and  $\sim$ 42 nm [179].

#### 8. Spin state transitions

Changes in the spin states of cations do not result directly in discrete phase transitions in perovskites. Rather, their influence is seen in modifying structural evolution via the changes in radius ratios for cations on the A- and B-sites due to the associated changes in effective radii. For example, the radius of  $Co^{3+}$  is 0.61 Å in the high spin state and 0.545 Å in the low spin state [180]. This change in radii will also influence the magnitude of strains which accompany octahedral tilting, i.e. renormalizing the strain coupling coefficients,  $\lambda_i$ , to some extent. There remains some controversy with respect to the sequence of stable spin states for Co<sup>3+</sup> in LaCoO<sub>3</sub>, NdCoO<sub>3</sub> and GdCoO<sub>3</sub>, but recent work seems to be favouring low spin→low spin+high spin→intermediate spin with increasing temperature (e.g. [181–184]). The linkage between R-point tilting and spin configuration can be expressed in terms of a Landau expansion of the form [185]

$$\begin{aligned} G_{\rm L} &= \frac{1}{2}a\left(T - T_{\rm c}\right)\left(q_{1}^{2} + q_{2}^{2} + q_{3}^{2}\right) + \frac{1}{4}b\left(q_{1}^{2} + q_{2}^{2} + q_{3}^{2}\right)^{2} \\ &+ \frac{1}{4}b'\left(q_{1}^{4} + q_{2}^{4} + q_{3}^{4}\right) + \lambda_{1}e_{\rm a}\left(q_{1}^{2} + q_{2}^{2} + q_{3}^{2}\right) \\ &+ \lambda_{2}\left(e_{\rm t}\left(2q_{1}^{2} - q_{2}^{2} - q_{3}^{2}\right) + \sqrt{3}e_{\rm o}\left(q_{2}^{2} - q_{3}^{2}\right)\right) \\ &+ \lambda_{3}\left(e_{4}q_{1}q_{3} + e_{5}q_{1}q_{2} + e_{6}q_{2}q_{3}\right) + G\left(q_{\rm spin}\right) + \lambda_{4}e_{\rm a}q_{\rm spin} \\ &+ \lambda_{5}\left(e_{\rm o}^{2} + e_{\rm t}^{2}\right)q_{\rm spin} + \lambda_{6}\left(e_{4}^{2} + e_{5}^{2} + e_{6}^{2}\right)q_{\rm spin} + \frac{1}{4}\left(C_{11}^{\rm o} - C_{12}^{\rm o}\right) \\ &\times \left(e_{\rm o}^{2} + e_{\rm t}^{2}\right) + \frac{1}{6}\left(C_{11}^{\rm o} + 2C_{12}^{\rm o}\right)e_{\rm a}^{2} + \frac{1}{2}C_{44}^{\rm o}\left(e_{4}^{2} + e_{5}^{2} + e_{6}^{2}\right). \end{aligned}$$

 $G(q_{spin})$  is the free energy due to changes in spin state and can be described by Boltzmann partitioning between discrete energy levels.

For rhombohedral  $(R\bar{3}c)$  LaCoO<sub>3</sub>, the dominant strain coupled with  $q_{\text{spin}}$  is a volume strain and this leads to an effective linear-quadratic coupling between the two order parameters,  $\lambda_{\text{tilt,spin}}q_1^2q_{\text{spin}}$ , where  $\lambda_{\text{tilt,spin}} = -9\lambda_1\lambda_4/(C_{11}^\circ + 2C_{12}^\circ)$ . This in turn leads to a renormalization of the transition temperature for the  $Pm\bar{3}m-R\bar{3}c$  transition:

$$T_{\rm c}^* = T_{\rm c} + \frac{6\lambda_1 \lambda_4 q_{\rm spin}}{a \left( C_{11}^{\rm o} + 2C_{12}^{\rm o} \right)},\tag{15}$$

as seen through shear strain variations in LaCoO<sub>3</sub> [185].  $q_{spin}$  transforms as the identity representation and would be expected to renormalize the single crystal elastic constants quite simply according to, for example,

$$C_{44} = C_{44}^{\rm o} + 2\lambda_6 q_{\rm spin} \tag{16}$$

$$\frac{1}{2}\left(C_{11} - C_{12}\right) = \frac{1}{2}\left(C_{11}^{o} - C_{12}^{o}\right) + 2\lambda_5 q_{\rm spin}.$$
 (17)

The pattern of changes in the shear modulus of LaCoO<sub>3</sub> measured at RUS frequencies through the spin state transition temperatures of ~100 and ~500 K has indeed been found to reflect the pattern of changes of  $q_{spin}$  estimated from average Co–O bond lengths [185]. The correlation between these parameters is even closer in NdCoO<sub>3</sub> [186], which has both R-point and M-point tilts (*Pnma*). In GdCoO<sub>3</sub>, the shear strains coupled to octahedral tilting are larger, with the result that an applied stress is more likely to induce a relaxation of the spin state to give softening of the form implied by equation (1), i.e. with dependence on the order parameter susceptibility. Significant softening occurs below ~900 K where the changes in shear strain associated with changing  $q_{spin}$  are greatest [186].

Changes in  $q_{spin}$  can also modify the properties of ferroelastic twin walls and add to the number of possible mechanisms for thermally activated relaxation. By combining data from measurements from DMA, RUS, pulse-echo ultrasonics and Brillouin scattering at frequencies shown in figure 2, an Arrhenius map for the temperature and frequency dependence of four loss mechanisms has been proposed for  $LaCoO_3$  (figure 19(a), after [185]). The most obvious is relaxation of  $q_{spin}$  in response to the application of an external stress due to the coupling with strain. A second mechanism is revealed by DMA data collected at frequencies of 0.1-50 Hz which show a freezing interval attributed to pinning of ferroelastic twin walls in the temperature interval  $\sim 600-$ 650 K. The activation energy of 1.9(2) eV (182(19) kJ mole<sup>-1</sup>) is perhaps due to pinning by pairs of oxygen vacancies. An additional loss mechanism is reflected in the peak in  $Q^{-1}$ at  $\sim 100 \,\mathrm{K}$  (figure 19(b)) and has tentatively been attributed to relaxation of magnetic polarons [185]. This picks up on the suggestion that polarons can be bound up with spin state changes because of the possibility that defects next to Co<sup>3+</sup> stabilize the high spin state even when the matrix contains low spin states [187]. It then also follows that the ferroelastic twin walls could have discrete and interesting properties since they are accompanied by strain gradients. If there are strain gradients there must also be gradients in spin state and, because of their propensity for being pinned by oxygen vacancies, the twin walls may then also have locally high concentrations of magnetic polarons.

![](_page_18_Figure_1.jpeg)

**Figure 19.** (*a*) Arrhenius plot for thermally activated relaxational processes in LaCoO<sub>3</sub> [185]. (*b*) Variation of  $Q^{-1}$  from resonance peaks in the frequency range 200–450 kHz, showing the additional loss peak at ~100 K which has been tentatively ascribed to coupling of strain with magnetic polarons [185].

#### 9. Metal organic frameworks

A new class of perovskite structures has organic molecules in a metal organic framework. For example,  $[(CH_3)_2NH_2]M$ (HCOO)<sub>3</sub> corresponds to ABO<sub>3</sub> in which the dimethylammonium cation occupies the A-site, the B-site is effectively a metal-oxygen octahedron (M = Zn, Co, Mn, Ni, Fe) and the oxygen linkages are replaced by formate anions [188–191]. In  $[(CH_2)_3NH_2]M(HCOO)_3$  (M = Mn, Cu, Zn) the A-sites are occupied by azetidinium cations [189, 192-194]. In addition to tilting and magnetic transitions, orientational ordering or conformational changes of the A-site cation and associated changes in hydrogen bonding lead to an additional set of phase transitions which do not occur in conventional oxide or halide perovskites. Freezing of the ring-puckering motion of the azetidinium groups in [(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>]Mn(HCOO)<sub>3</sub> is associated with the X-point of the Brillouin zone and gives a symmetry change Pnma-P2<sub>1</sub>/n [193, 194]. Orientational ordering of the dimethylammonium cation in [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]Mn(HCOO)<sub>3</sub> results in a change of space group from  $R\bar{3}c$  to Cc [191]. This Cc structure is no. 47 in the list of Stokes et al [195]. It contains ferroelectric displacements belonging to irrep  $\Gamma_4^-$  plus octahedral tilts belonging to irrep  $R_4^+$  of space group  $Pm\bar{3}m$ with a unit cell of  $\sim \sqrt{6a} \times \sqrt{2a} \times \sqrt{2a}$  and monoclinic angle

~125°, where  $a \sim 6$  Å is the dimension of the basic cubic structure (C J Howard, personal communication). Markedly different styles of elastic anomalies observed in these materials reflect the markedly different driving mechanisms and dynamics of the additional improper ferroelastic phase transitions [194, 196].

Figure 20(a) shows the variations of  $f^2$  and  $Q^{-1}$  for resonances in RUS spectra collected from two different single crystals of [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]Co(HCOO)<sub>3</sub> [196]. Instead of low acoustic loss above and high loss below the transition temperature ( $T_c \sim 165 \,\mathrm{K}$ ) plus softening with falling temperature through  $T_c$ , as seen in oxide perovskites with improper ferroelastic transitions, the most prominent feature is a Debye peak in  $Q^{-1}$  and associated stiffening at  $\sim 200$  K. The measuring frequency, f = 370 kHz, gives a relaxation time,  $\tau$ , of  $4.3 \times 10^{-5}$  s from the condition  $\omega \tau = 1 (\omega = 2\pi f)$ . Fits to the data shown in figure 20(a) are based on equation (10) with  $U = 0.21 - 0.26 \text{ eV} (20-25 \text{ kJ mole}^{-1})$  if it is assumed that there is a single relaxation time  $(r_2(\beta) = 1)$ . Equation (11) then gives the inverse of the attempt frequency  $\tau_{a}$  as  $2.6 \times 10^{-12}$  s for U = 0.21 eV. This relaxation behaviour and its implied coupling with strain are presumed to be due to the dynamical disorder of the dimethylammonium cations above  $T_{\rm c}$ , with relaxation times that pass through  $\sim 10^{-7}$  s ahead of the phase transition. The phase transition itself involves development of hydrogen bonds and the observed activation energy must relate to breaking and reforming of multiple hydrogen bonds between the A-site cation and the framework. Low  $Q^{-1}$  values below  $T_c$  imply that there is no movement either of ferroelastic twin walls or of the dimethylammonium cations on the timescale of mechanical resonances excited in the RUS experiment. In the equivalent manganese structure, a hysteresis of  $\sim 10$  K for the transition temperature of  $\sim 185$  K signifies first order character [190] and there is then an abrupt decrease in acoustic loss with falling temperature [196]. An anomaly in the dielectric constant above the transition point observed at 100 kHz disappears from data collected at lower frequencies and is likely to be due to the same mechanism of dynamical disordering of the A-cation with relaxation times in the vicinity of  $\sim 10^{-6}$  s ahead of the transition itself. Integration of the excess heat capacity through the transition gives an entropy change of  $\sim 1 \text{ J} \text{ mole}^{-1} \text{ K}^{-1}$  instead of the ideal value of  $R \ln 3 = 9.1 \,\mathrm{J} \,\mathrm{mole}^{-1} \,\mathrm{K}^{-1}$  expected for a pure order/disorder process [190], again signifying that the freezing process is spread over a wider temperature interval. Alternatively, it is also possible that the transition mechanism is displacive but there appear to be, as yet, no reports of a soft mode.

Figure 20(*b*) shows  $f^2$  and  $Q^{-1}$  for resonances in RUS spectra collected from a single crystal of [(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>]Mn(HCOO)<sub>3</sub> [194]. The transition at ~272 K is known to be weakly first order and is characterized by a minimum in  $f^2$ . There is also an increase in acoustic loss below the transition point. The excess entropy obtained from integration of the excess heat capacity in the vicinity of the transition point, 3.4 J mole<sup>-1</sup> K<sup>-1</sup>, is sufficiently close to the expected value of  $R \ln 2 = 5.8 \text{ J mole}^{-1} \text{ K}^{-1}$  to be consistent with a view that the change in conformation of

![](_page_19_Figure_1.jpeg)

**Figure 20.**  $f^2$  and  $Q^{-1}$  from single crystals of metal organic frameworks with the perovskite structure. (*a*) [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]Co(HCOO)<sub>3</sub> displays a Debye loss peak at ~200 K attributed to slowing down of dynamical disordering of the dimethylammonium cations on the A-site ahead of the phase transition at ~165 K. There is a small change in  $f^2$  associated with the magnetic transition at ~15 K, signifying only very weak magnetoelastic coupling [196]. (*b*) [(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>]Mn(HCOO)<sub>3</sub> has minima in  $f^2$  and, hence, in single crystal elastic constants at ~272 K, together with a peak in loss and elastic stiffening below the transition due to conformational ordering of the azetidinium cation on the A-site [194].

the azetidinium cations from flat, on average, to puckered is close to order/disorder in character. Softening of the single crystal elastic constants, as represented by reducing frequency of all the resonance modes with falling temperature towards the transition point implies that the softening mechanism is related to fluctuations, in much the same way as for oxide perovskites, though the fluctuations are related primarily to the conformation of the A-site cation. Stiffening below the transition point resembles the pattern of stiffening seen in the mineral lawsonite,  $CaAl_2Si_2O_7(OH)_2 \cdot H_2O_7$ , in which phase transitions are driven by changes in hydrogen bonding, and follows from coupling terms of the form  $\lambda e^2 Q^2$  [15]. The peak in  $Q^{-1} \sim 50 \,\mathrm{K}$  below the transition point is most likely related to freezing of ferroelastic twin walls, which will require changes in topology of the puckered azetidinium cations. Dielectric losses also reduce below  $\sim 180 \text{ K}$  [193], consistent both with strong coupling between shear strain and the puckering transition and with freezing of twin wall motion as temperature falls below this.

In contrast with the clear influence of strain coupling to dynamical behaviour of the A-site cations in the two metal organic frameworks, magnetic transitions in the vicinity of 10 K barely show up in the RUS data [194, 196]. Given that the metal cations are separated by longer distances in these materials than in conventional perovskites, it is not surprising that magnetic interactions should be weak and that spin–lattice coupling should also be weak. The existence of only weak magnetoelastic effects is likely to place constraints on the extent to which the metal organic frameworks might display magnetoelectric properties.

#### 10. Summary

Changes in elastic properties arise as a consequence of coupling of strain with static order parameters and with dynamical processes which occur as precursors to phase transitions, as intrinsic aspects of the transitions themselves or related to the mobility of associated microstructures. As seen from this review of diverse phase transitions in perovskites, RUS provides a convenient method of following these changes routinely over wide temperature intervals and with externally applied fields. In addition, the RPS method allows detection of the first appearance of locally piezoelectric domains or of piezoelectric domain walls in paraelectric host phases. In principle it should be possible to detect transitions in thin films, with the best chance to be gained by using a thin substrate. It is also possible to follow strain coupling phenomena associated with phase transitions in powder samples, down to the nanoscale, by making a pellet from a mixture of the powder and an appropriate binding material such as CsI.

Elastic relaxations accompanying tilting transitions with a single tilt system appear to follow the patterns expected on the basis of Landau theory quantitatively, apart from precursor effects and the influence of central peak modes in the vicinity of the transition points. The same can be concluded for ferroelectric transitions arising by the operation of a soft mode, though variations for a complete elastic tensor have not yet been determined quantitatively for a perovskite. Pseudoproper ferroelastic behaviour driven by cooperative Jahn-Teller distortions also appears to follow the pattern predicted from classical strain/order parameter coupling. Quantitative descriptions of the elastic softening associated with transitions involving two coupled instabilities have not yet been achieved, although it is straightforward to derive the appropriate Landau expansions with linearquadratic or biquadratic coupling. In this context, a slight mystery is that coupling between two tilt systems results in elastic stiffening with falling temperature rather than softening.

The forms of coupling permitted by symmetry between strain and magnetic order parameters are equally straightforward to predict but the strength of coupling is more variable than for structural transitions. Spin–lattice coupling can be so weak that there is no detectable elastic anomaly in the vicinity of the transition point but examples of slight softening or stiffening are also observed. Stiffening effects most likely point to contributions from terms  $\lambda e^2 M^2$ , rather than  $\lambda e M^2$ . With respect to the search for materials with strong strain mediated magnetoelectric coupling, as implied by figure 1, the most suitable candidates would probably have a Jahn–Teller component coupled with magnetic ordering so as to give rise to an effectively large magnetoelastic coupling.

Precursor softening effects can be represented on a phenomenological basis but this does not discriminate between different physical origins such as dispersion of the soft optic mode, tweed and PNRs. They appear, in general, to occur over a wider temperature interval above  $T_c$  for ferroelectric transitions (~250-450 K in PMN, BaTiO<sub>3</sub>, PZN-PT, PIN-PMN-PT) than for octahedral tilting transitions ( $\sim$ 50–100 K in  $(La,Pr)AlO_3$ ,  $KMnF_3$ ,  $Sr(Zr,Ti)O_3$ ). The absence of significant acoustic loss associated with the softening indicates relaxation times which are significantly less than  $\sim 10^{-6}$  s, though in the particular case of relaxors the pattern of loss closely mirrors the dielectric loss seen through the Vogel-Fulcher freezing interval. In all cases, changes of the elastic properties are indicative of the existence of strain coupling with the local order parameter(s).

In spite of the relatively narrow frequency interval over which RUS measurements can be made, an increasing number of possible loss mechanisms is being recognized. The most characteristic of these is due to ferroelastic twin walls which give rise to a steep rise in dissipation near  $T_c$ , followed by a plateau, followed by a Debye freezing peak. The pinning mechanism is believed to be due to oxygen (or fluorine) vacancies though there is a spread of activation energies. In this context, an important development is the proposal of a ledge mechanism for twin wall motion. Such ledges can allow small displacements of twin walls under very low stress conditions, in comparison with collective movements of the tips of needle twins, and probably account for most of the increase in  $O^{-1}$  seen below ferroelastic transition points in perovskites. Different loss patterns for different perovskites obtained under the same conditions of frequency and load should reflect different dynamics and pinning properties of the twin walls themselves, whether due to the different wall thicknesses and variations in structure of the walls or different defect energies and densities. No perovskite exists without extrinsic defects and these too can have a disproportionate effect on the macroscopic properties, such as the polar defects in KTaO<sub>3</sub> which lead to piezoelectric effects [90], and on pinning of microstructures. These properties are relevant in the context of domain boundary engineering to create materials with distinctive characteristics for device materials (e.g. [197–199]), and will vary in parameter space represented by anelasticity maps.

Finally, in the search for perovskites with novel properties, tuning by chemistry has been a primary tool. The choice of end members for multi component solid solutions is used to create single phases, thin films or heterostructures with particular combinations of magnetic, ferroelectric and electronic instabilities. A further refinement is that changes in cation order can be used to control the length scales over which local states of order are coherent. The tendency for materials with progressively more complex chemistry and local order of this type is that they will develop interesting glass-like behaviour due to competition between order parameters which is unfavourable. If there are local variations in the magnitudes and orientations of different order parameters it follows that there will be heterogeneities in local strain states. Variations of elastic and anelastic properties at low temperatures, such as occur in PZT-PFT (figure 16), should be diagnostic of these and are increasingly likely to appear.

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