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Multiferroic (ferroelastic/ferromagnetic/ferrimagnetic) aspects of phase transitions in RCo$_2$ Laves phases

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Received 21 October 2013, revised 28 November 2013
Accepted for publication 28 December 2013
Published 16 January 2014

Abstract

Magnetic phase transitions in RCo$_2$ Laves phases with R as a rare earth element are accompanied by changes in crystallographic space group. For purely structural transitions they would be described as improper ferroelastic and therefore fulfil the condition for multiferroic phase transitions in combining two out of three properties, ferro/antiferromagnetism, ferroelectricity and ferroelasticity. Here lattice parameter data from the literature and new measurements of elastic and anelastic properties, by resonant ultrasound spectroscopy, for NdCo$_2$ and ErCo$_2$ have been analysed from this perspective. The temperature dependence of symmetry-breaking shear strains is consistent with the cubic $\leftrightarrow$ tetragonal transition in NdCo$_2$ being close to tricritical in character and the cubic $\leftrightarrow$ rhombohedral transition in ErCo$_2$ being first order. Elastic softening and acoustic loss within the stability ranges of the ferroelastic phases can be understood in terms of a combination of intrinsic softening due to strain/order parameter coupling and ferroelastic twin-wall motion. Softening ahead of the transitions does not fit with standard macroscopic descriptions of dynamic effects from other systems but, rather, in the case of NdCo$_2$, might be attributed to the involvement of a second zone centre order parameter related to a separate instability driven by cooperative Jahn–Teller distortions. In ErCo$_2$, acoustic loss in the temperature interval above the transition point is discussed in terms of a possible tweed microstructure associated with strain coupling to local magnetic ordering. The overall multiferroic behaviour can be understood in terms of a single magnetic order parameter (irrep $m T_4^+$ of magnetic space group $Fd\bar{3}m$) which couples with a structural order parameter (irrep $\Gamma_3^0$ or $\Gamma_4^2$). The coupling is linear/quadratic which, in the case of two separate instabilities, causes them to combine in a single multiferroic phase transition.

Keywords: Laves phase, Griffiths phase, magnetic transitions, elasticity, strain relaxation

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

An important theme in the current intense focus on multiferroic materials is the nature of coupling. Direct coupling between ferroelectric and (anti)ferromagnetic order parameters is generally found to be weak but is likely to be enhanced if the separate effects are each coupled to strain such that the coupling occurs via common strain effects. As a consequence, ferroelastic properties are in some senses just as important as the primary magnetic/electric dipoles which would be made use of in device applications. In this context, the coupling of strain with a ferroelectric order parameter is rather well understood because the polarization typically develops by atomic displacements which must necessarily also give rise to changes in unit cell dimensions. Depending on the symmetry change, the material may also be ferroelastic without the need for some separate intrinsic instability. Magnetoelastic coupling can be rather more subtle, however, because changes in spin state may not require any changes in atomic coordinates and will not invariably show overt, i.e. easily measurable, coupling with strain, therefore.

If it is argued that a ‘good’ multiferroic material requires strong magnetoelastic coupling, one fertile avenue of investigation is into the mechanism of magnetoelastic coupling in materials where changes in magnetic structure are accompanied by relatively large lattice relaxations. An obvious corollary of this relates to switching behaviour through the movement of domain walls. In particular, magnetic ordering in a material which is also ferroelastic will contain domain walls whose structure contains gradients in both magnetic order and strain. It is possible that these will be pinned to different extents by defects, in comparison with domain walls which are purely magnetic or purely ferroelastic, and they will respond to both magnetic and stress fields imposed externally. In the present study, elastic and anelastic relaxations arising from magnetoelastic coupling in two materials which are known to have strong spin–lattice coupling have been investigated by resonant ultrasound spectroscopy (RUS).

$\text{RCO}_2$ Laves phases, with R as a rare earth element, form part of a class of materials in which ferromagnetic (or ferrimagnetic) phase transitions are accompanied by symmetry-breaking spontaneous strains and are therefore also ferroelastic. A comprehensive review of their physical properties and of thermodynamic models for their magnetic phase transitions has been given by Duc and Goto [1]. Figure 1 shows their characteristic pattern of transitions with changing number of 4f electrons, assuming all the ions to be in their usual $3+\text{ state}$. The paramagnetic high temperature parent cubic structure gives way to ferromagnetic ($\text{R} = \text{Pr, Nd, Sm}$) or ferrimagnetic ($\text{R} = \text{Gd, Tb, Dy, Ho, Er, Tm}$) ordered structures at phase transitions which are marked also by symmetry-breaking shear strains and positive volume strains [2–7]. The magnetism is dominated by the R sublattice, with essentially temperature-independent magnetic moments. Below the cubic to tetragonal or rhombohedral transitions shown in figure 1, the Co magnetic sublattice orders parallel/antiparallel to the R magnetic moment for light/heavy lanthanides. The magnetic ordering temperatures are proportional to the de Gennes factor, $(g - 1)^2J(J + 1)$, although the proportionality constant is different for the heavy and light rare earths [8]. The axis of magnetization is along [111], [110] or [001] of the parent cubic phase, giving rhombohedral, orthorhombic or tetragonal structures, respectively. Some of the transitions are first order in character and some are thermodynamically continuous.

For the present study, NdCo$_2$ and ErCo$_2$ were chosen as being representative of the ferromagnetic and ferrimagnetic groups, respectively. With respect to multiferroic systems more generally, RCo$_2$ Laves phases display two out of the three important ‘ferro-’ properties, namely ferroelasticity and ferro(ferri)magnetism. A contributory factor for the development of strong magnetoelastic coupling effects would be the existence of a separate structural instability somewhere nearby in parameter space, and it is proposed that in some cases the mechanism of strain relaxation might involve coupling with an order parameter due to cooperative Jahn–Teller distortions of the rare earth, as occurs in some rare earth vanadates and arsenates, for example [9–11]. The overall behaviour can then be understood from the perspectives of strain and elasticity as if they are simply ferroelastic materials in which one of two symmetry-breaking order parameters just happens to be magnetic.

The most recent crystallographic studies of NdCo$_2$, based on powder neutron diffraction, show a sequence with falling temperature of structures with crystallographic space groups $Fd\bar{3}m \rightarrow I4_1/amd \rightarrow Imma$ [6, 7]. The cubic $\leftrightarrow$ tetragonal transition occurs at $\sim 100$ K and the tetragonal $\leftrightarrow$ orthorhombic transition at $\sim 42$ K. Xiao et al [7] also included refinements of the magnetic moments. Powder neutron diffraction observations have confirmed crystallographic space group $R\bar{3}m$ for the magnetically ordered structure of ErCo$_2$ below the first-order cubic $\leftrightarrow$ rhombohedral transition at $\sim 32$ K [12]. Additional attention has related to the discovery of a Griffiths-like phase which develops in a temperature interval of $\sim 50$ K above the phase transition in ErCo$_2$ [12–16]. This phase contains local clusters with short range magnetic order on a length scale of

![Figure 1. Summary of magnetic phase transitions in RCo$_2$ Laves phases; data for GdCo$_2$, TbCo$_2$, DyCo$_2$, HoCo$_2$ and ErCo$_2$ from [3], data for PrCo$_2$, SmCo$_2$ and TmCo$_2$ from [4], data for NdCo$_2$ from [7].](attachment:image.png)
Figure 2. Phase diagram showing stability limits for ferrimagnetic, parimagnetic and paramagnetic phases of ErCo obtained from x-ray magnetic circular dichroism (XMCD) and ac susceptibility data [13].

~7 Å, within which Co moments are, on average, oriented antiparallel to the Er moments. The term ‘parimagnetic’ has been coined to distinguish it from normal patterns of paramagnetism [12, 13]. Dynamic properties of the clusters, as probed in an ac magnetic field, were found to be consistent with a freezing process which follows Vogel–Fulcher dynamics and an effective (zero-frequency) freezing temperature of ~70 K. Stability limits for the parimagnetism with respect to temperature and a static magnetic field are shown in figure 2.

This paper is divided into five main sections. The starting point for the description of a typical ferroelastic transition would be an analysis of changes of lattice parameters in terms of spontaneous strain and its coupling with the driving order parameter (see e.g. [17]). The magnetic order parameter contains three components and coupling of these with the strains is set out in a conventional Landau expansion in section 2. Data from the literature are used to follow the strain variations in an appendix. Sections 3 and 4 contain details of the RUS measurements made in the frequency range 0.05–1.2 MHz. Previous elasticity data for both NdCo₂ and ErCo₂, measured by pulse–echo ultrasonics at 10 MHz, show extensive elastic softening both above and below the transition points [18], but there do not appear to be any data in the literature relating to acoustic loss. In section 5, the elastic softening is interpreted in terms of normal patterns of ferroelastic behaviour and acoustic loss is interpreted in terms of the relaxation properties of ferroelastic twin walls. Acoustic loss in the stability interval of the Griffiths-like phase of ErCo₂ may be indicative of the development of a twinned microstructure ahead of a first-order ferroelastic phase transition.

2. Symmetry and strain analysis

Elastic anomalies associated with phase transitions can usually be attributed predominantly to the effects of strain coupled to the driving order parameter, for which a convenient and frequently robust description is provided by Landau theory [11, 17, 19–21]. The magnetic space group of the parent structure of RCo₂ Laves phases is $Fd\bar{3}mI'$ and the magnetic order parameter of the known ordered structures has the symmetry of the irreducible representation $m\Gamma_{44}^i$, with three components, $m_i$ ($i = 1–3$). The group theory program ISOTROPY [22] gives the full Landau expansion for the excess free energy, $G$, as

\[ G = \frac{1}{2} A\Theta_s \left( \coth \left( \frac{\Theta_s}{T_c} \right) - \Theta_s \right) \left( m_1^2 + m_2^2 + m_3^2 \right) \]

\[ + \frac{1}{4} B(m_1^2 + m_2^2 + m_3^2)^2 + \frac{1}{4} B'(m_1^2 + m_2^2 + m_3^2) \]

\[ + \frac{1}{6} C(m_1^2 + m_2^2 + m_3^2)^3 + \frac{1}{6} C'(m_1m_2m_3) \]

\[ + \frac{1}{6} C''(m_1^6 + m_2^6 + m_3^6) + \lambda_1 e_4(m_1^2 + m_2^2 + m_3^2) \]

\[ + \lambda_2 \left[ \sqrt{3}e_6(m_1^2 - m_2^2) + e_1(2m_3^2 - m_1^2 - m_2^2) \right] \]

\[ + \lambda_3 (e_6 m_1 m_2 + e_4 m_2 m_3 + e_6 m_1 m_3) \]

\[ + \frac{1}{4}(C_{11} - C_{12}) (e_6^2 + e_1^2) + \frac{1}{5}(C_{11}^o + 2C_{12}^o) e_2^2 \]

\[ + \frac{1}{4} C_{44}^o (e_3^2 + e_2^2 + e_1^2) \]

(1)

Here $A$, $B$, $B'$, $C$, $C'$, $C''$ are standard Landau coefficients, $T_c$ is a critical temperature, $\lambda_1$, $\lambda_2$, $\lambda_3$ are coupling coefficients, $\Theta_s$ is the order parameter saturation temperature and $C_{11}^o$, $C_{12}^o$, $C_{44}^o$ are elastic moduli of the cubic structure, usually referred to as the bare elastic moduli. The symmetry-adapted strains are given in terms of the linear strain components, $e_1$, $e_2$ and $e_3$, of the strain tensor in table A.1 in the appendix as volume ($e_2$), orthorhombic shear ($e_4$), and tetragonal shear ($e_5$) strains, while $e_4$, $e_5$, $e_6$ are off-diagonal (shear) components of the strain tensor. In the general case, relationships between strains and order parameter components are given by the equilibrium condition, $\partial G/\partial e = 0$, and these are also listed in table A.1.

Substituting strain terms in (1) gives the renormalized form of the Landau expansion as

\[ G = \frac{1}{2} A\Theta_s \left( \coth \left( \frac{\Theta_s}{T_c} \right) - \Theta_s \right) \left( m_1^2 + m_2^2 + m_3^2 \right) \]

\[ + \frac{1}{4} B^*(m_1^2 + m_2^2 + m_3^2)^2 + \frac{1}{4} B'^*(m_1^2 + m_2^2 + m_3^2) \]

\[ + \frac{1}{6} C(m_1^2 + m_2^2 + m_3^2)^3 + \frac{1}{6} C'(m_1m_2m_3) \]

\[ + \frac{1}{6} C''(m_1^6 + m_2^6 + m_3^6) + \lambda_1 e_4(m_1^2 + m_2^2 + m_3^2) \]

\[ + \lambda_2 \left[ \sqrt{3}e_6(m_1^2 - m_2^2) + e_1(2m_3^2 - m_1^2 - m_2^2) \right] \]

\[ + \lambda_3 (e_6 m_1 m_2 + e_4 m_2 m_3 + e_6 m_1 m_3) \]

\[ + \frac{1}{4}(C_{11} - C_{12}) (e_6^2 + e_1^2) + \frac{1}{5}(C_{11}^o + 2C_{12}^o) e_2^2 \]

(2)

where

\[ B^* = B - \frac{\lambda_1^2}{C_{44}^o} = -\frac{2\lambda_1^2}{3(C_{11}^o + 2C_{12}^o)} + \frac{4\lambda_2^2}{5(C_{11}^o - C_{12}^o)} \]

(3)

\[ B'^* = B' + \frac{\lambda_1^2}{C_{44}^o} = \frac{12\lambda_2^2}{5(C_{11}^o - C_{12}^o)} \]

(4)

These relationships have the same form as for octahedral tilting transitions associated with the R point of the Brillouin zone of perovskites [23–26].

Solutions to (2) give the different possible equilibrium magnetic structures in table 1, which includes all possible combinations of the non-zero order parameter components. The first three magnetic subgroups in the list give structures which have been reported for NdCo₂ (tetragonal and orthorhombic) [7] and ErCo₂ (rhombohedral) [12]. The starting Landau equation applies to displacive transitions, in which the excess entropy is expected to scale with the square of
the order parameter. This is not correct for the entropy of an order–disorder system which requires higher order terms. In treatments of magnetic ordering, explicit temperature dependences are assigned to the higher order Landau coefficients (see e.g. [1, 27–30] and references therein). The coupling behaviour will still be correctly described and the general phenomenology will also be essentially the same, however, so generalities which follow from earlier work on displacive systems [23–26, 31–34] still apply.

If the excess free energy is dominated by the second- and fourth-order terms, such that the expansion can be truncated to exclude sixth-order terms, only the tetragonal and rhombohedral structures can be stable. For the expansion given here, \( B^+ < 0 \) gives the former as being stable, \( B^+ > 0 \) gives the latter and the orthorhombic form is always intermediate in energy between the two. The influence of sixth-order terms is such that each of the three structures can be stable, depending on the actual values of the coefficients [31, 34], and a sequence of transitions cubic \( \rightarrow \) tetragonal \( \rightarrow \) orthorhombic \( \rightarrow \) rhombohedral may develop with falling temperature for \( (B^+ + B^+) < 0, B^+ > 0 \). There is still only one intrinsic instability, however. Higher order terms are required for the stability range of a monoclinic phase to appear [34], a result which is equivalent to the assessment of Atzmony and Daniel [35] that higher order terms in power series of direction cosines are required to stabilize easy magnetization axes which are other than major symmetry axes of a parent cubic structure. For real magnetic systems, temperature dependences of the fourth-order coefficients may be relevant, but an important contributory factor for these different stabilities and transition sequences must be the strength of coupling of the order parameters with shear strains, as defined by values of the coupling coefficients \( \lambda_2 \) and \( \lambda_3 \). All three of the known magnetic structures appear in the phase diagram of (Tb, Ho)Co\(_2\), with a crossover from the rhombohedral structure being stable in TbCo\(_2\) to the tetragonal structure being stable in HoCo\(_2\) [36]. The same crossover occurs in the phase diagram of (Tb, Dy)Co\(_2\), though in this case an intermediate stability range for the orthorhombic structure was not reported [37].

Lattice parameter data from the literature have been used here to follow the evolution of strains and, hence, of the magnetic order parameter as a function of temperature for NdCo\(_2\) and ErCo\(_2\), as set out in the appendix. The patterns of strain and order parameter evolution show that the cubic \( \leftrightarrow \) tetragonal transition in NdCo\(_2\) is close to Landau tricritical and the cubic \( \leftrightarrow \) rhombohedral transition is first order. There is only one instability, which gives rise to the hierarchy of transitions.

It is a straightforward matter to predict the evolution of individual elastic constants as a function of temperature through the phase transitions and, hence, to predict the form of evolution of the bulk and shear moduli for a polycrystalline sample. Softening in the stability range of the cubic phase ahead of the first transition is not predicted, but the effect of the linear/quadratic strain/order parameter coupling is expected to be discontinuous softening of all the individual elastic constants at the transition point. The order parameter relaxes in response to an applied stress and the amount of softening scales with the square of the strain/order parameter coupling coefficients [38]. For a tricritical transition, there is then some non-linear recovery (stiffening) of the elastic constants below the transition point, as seen in the bulk and shear moduli of SrZrO\(_3\), for example [39]. If the same mechanism applies, with relaxation of the magnetic order parameter occurring on a timescale that is shorter than the timescale of an applied stress, exactly the same pattern should be expected for the elastic constants of RCo\(_2\) phases.

3. Experimental details

Polycrystalline ingots of ErCo\(_2\) and NdCo\(_2\) were prepared following a standard procedure. The primary metals (99% purity) were melted together in an electric arc furnace under a controlled Ar atmosphere to prevent oxidation. Since some amount of rare earth is evaporated during the melting process, an excess of 1% was added to obtain a final sample with the correct stoichiometry. Once the alloy was formed, the samples were wrapped in tantalum foil, encapsulated under Ar atmosphere in a sealed silica tube and homogenized by annealing at 850 °C for twelve days. X-ray diffraction analysis on powdered samples was performed in a Rigaku RTO 500RC diffractometer with Bragg–Brentano geometry using Cu \( K\alpha \) radiation at room temperature. Rietveld analysis demonstrated very well crystallized samples, as shown in previous work [13], and no impurities above the 1% detection limit of powder diffraction methods.

The samples used for RUS measurements were irregularly shaped, with approximate dimensions \( 2 \times 1 \times 1 \) mm\(^3\) and mass 0.0855 g (ErCo\(_2\)) and \( 3 \times 2 \times 2 \) mm\(^3\), 0.2498 g (NdCo\(_2\)). The scientific basis of RUS measurements has been described in detail in a number of places, including Migliori and Sarrao [40]. In the high temperature instrument used in

<table>
<thead>
<tr>
<th>Magnetic space group</th>
<th>Order parameter components ((m_1, m_2, m_3))</th>
<th>Lattice vectors</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I4_1/amd' )</td>
<td>((a, 0, 0))</td>
<td>((0, 1/2, −1/2), (0, 1/2, 1/2), (1, 1, 0))</td>
<td>((-1, 1/4, −1/4))</td>
</tr>
<tr>
<td>( 1mm'd' )</td>
<td>((a, a, 0))</td>
<td>((1/2, 1/2, 0), (1/2, −1/2, 0), (0, 0, −1))</td>
<td>((0, −1/4, −1/4))</td>
</tr>
<tr>
<td>( R3m' )</td>
<td>((a, a, a))</td>
<td>((1/2, 0, −1/2), (0, −1/2, 1/2), (−1, −1, −1))</td>
<td>((0, 0, 0))</td>
</tr>
<tr>
<td>( C2'/c' )</td>
<td>((a, b, 0))</td>
<td>((0, 1, 0), (0, 0, −1), (−1/2, 1/2, 0))</td>
<td>((0, 1/4, −1/4))</td>
</tr>
<tr>
<td>( C2'/m' )</td>
<td>((a, a, b))</td>
<td>((1/2, 1/2, 1), (1/2, −1/2, 0), (1/2, 1/2, 0))</td>
<td>((0, 0, 0))</td>
</tr>
<tr>
<td>( P\tilde{1} )</td>
<td>((a, b, c))</td>
<td>((0, 2/1, 0), (1/2, 0, 1/2), (0, −1/2, −1/2))</td>
<td>((0, 0, 0))</td>
</tr>
</tbody>
</table>
Cambridge, a sample rests lightly between the tips of alumina rods which protrude into a horizontal Netzsch 1600 °C resistance furnace. The piezoelectric transducers are at the other end of the rods, outside the furnace [41]. In the low temperature instrument the sample rests directly between the transducers and is suspended in a helium flow cryostat, with an atmosphere of a few mbar of helium to allow heat transfer [42].

Spectra containing 65,000 data points in the frequency range 50–1200 kHz were collected from the ErCo$_2$ sample at low temperatures in cooling and heating sequences. Cooling from 280 to 40 K was carried out in 30 K steps, with a 15 min settle time for thermal equilibration before each spectrum was collected. The second stage was 40–20 K in 1 K steps, with a 10 min settle time, and the final stage was 20–5 K in 5 K steps, with 15 min settle time. The heating sequence was: 5–19 K in 2 K intervals, 15 min settle, 19–42 K in 1 K intervals (10 min settle), 42–110 K in 2 K intervals (10 min settle), 110–295 K in 5 K intervals (15 min settle). For the NdCo$_2$ sample, low temperature spectra were collected in the frequency range 50–1200 kHz, with each spectrum containing 130,000 data points. A thermal equilibration time of 15 min was allowed at each step. Spectra were collected at 30 K intervals during cooling from room temperature to 10 K. In the subsequent heating sequence, spectra were collected over four stages: 10–90 K at 5 K intervals, 90–105 K at 1 K intervals, 105–125 K at 2 K intervals, 125–295 K at 5 K intervals. After completion of the low temperature runs, high temperature spectra (50–1200 kHz, 130,000 data points) were collected from the NdCo$_2$ sample in an argon atmosphere, with nominal steps of 20 K during heating and cooling between 287 K and 600 K and 15 min for thermal equilibration.

Data collected from each experiment were transferred to the IGOR PRO (Wavemetrics) software package, and each resonance peak was fitted using an asymmetric Pearson VII function to extract values for the peak frequency, $f$, and the width at half of the maximum height, $\Delta f$. The elastic constants of a resonating sample scale with $f^2$ and for a polycrystalline sample the main contribution comes from the shear modulus. The inverse mechanical quality factor, $Q^{-1}$, is a measure of acoustic attenuation and is usually given by $Q^{-1} = \Delta f / f$.

4. Results

4.1. NdCo$_2$

Figure 3 shows segments of primary spectra from the NdCo$_2$ sample stacked in proportion to the temperature at which they were collected during a heating sequence from ~10 to ~292 K. All the resonance peaks had the same decrease in frequency with decreasing temperature ahead of the cubic $\leftrightarrow$ tetragonal transition, as seen for the single peak shown. An abrupt drop in frequency below ~98 K was accompanied by an abrupt increase in peak width. No peaks were detectable below ~40 K, the expected temperature of the tetragonal $\leftrightarrow$ orthorhombic transition, though sharp resonances reappeared below ~20 K.

Figure 4 contains segments of spectra collected above room temperature in the stability range of the cubic phase. The peak frequencies clearly increased slightly with increasing temperature, but there is also a hysteresis. During heating the resonance peaks occur at slightly lower frequencies than during cooling. There is also a marked increase in peak widths near 400 K in the heating sequence. There was no measurable change in mass of the sample before and after heating, so a change in composition of the sample can be ruled out as a
Changes in $Q^{-1}$ (blue filled circles) and $f^2$ (red crosses) with temperature for the lowest frequency resonance mode of NdCo$_2$ (shown in figure 3). The dashed line at 98 K marks the transition between tetragonal (B) and cubic (C) phases, while the dashed line at 40 K marks the assumed transition between orthorhombic (A) and tetragonal phases. $Q^{-1}$ remained low at high temperatures before increasing abruptly at 98 K, with further increases ahead of the second transition point. The value of $f^2$ slowly decreased with decreasing temperature from room temperature and then more steeply below 98 K. Individual resonance peaks were too broad to be detected in spectra collected in the range 36–21 K.

4.2. ErCo$_2$

Segments of spectra collected during heating of the ErCo$_2$ sample are shown as a stack in figure 7. The distinctive features are softening in the stability range of the cubic phase in an interval of ~100 K above the cubic ↔ rhombohedral transition point, and clear peak broadening within ~50 K of the transition. On the basis of the observation of complete disappearance of resonance peaks in spectra collected at and below 33 K, the rhombohedral phase is seen to be strongly attenuating, though a few relatively sharp resonances may just about be distinguishable from background noise in the lowest temperature spectra.

Figure 5. Changes in $Q^{-1}$ (blue filled circles) and $f^2$ (red crosses) with temperature for the lowest frequency resonance mode of NdCo$_2$ between room temperature and 600 K. Data for $f^2$ from the cooling sequence have been rescaled so as to overlap at room temperature and indicate that a more normal pattern of elastic softening with increasing temperature would probably become established above ~600–700 K.
Figure 7. Part of a stack of RUS spectra for ErCo$_2$, collected between 7 and 291 K, and displaced up the y-axis in proportion to the temperature at which they were collected. The spectrum shown as a thick (black) line indicates the assumed transition temperature of 33 K. The unusual peak shape for strong resonances at higher temperature is an artefact from saturation of the amplifier.

Figure 8 contains data for $f^2$ and $Q^{-1}$ from the fitting of selected peaks in the primary spectra. In the case of $f^2$, absolute values have been rescaled so as to be superimposed at room temperature. Above $\sim 175$ K, the trend is of increasing stiffness with falling temperature, effectively of the shear modulus, as normally expected. The onset of softening ahead of the cubic ↔ rhombohedral transition then becomes established below $\sim 150$ K. $Q^{-1}$ remains low in the stability range of the cubic phase but then increases markedly below $\sim 80$ K with a peak either at or near to 33 K, which is taken as the transition temperature.

5. Discussion

5.1. Ferroelastic properties of NdCo$_2$

Although the driving mechanism for phase transitions in NdCo$_2$ and ErCo$_2$ is magnetic ordering, they display typical ferroelastic behaviour as regards the evolution of symmetry-breaking and non-symmetry-breaking strains, elastic softening and acoustic losses, through a combination of strain/order parameter coupling and mobile twin walls. From the perspective of strain and elasticity, they are more or less indistinguishable from improper ferroelastic phase transitions driven by ferroelectric displacements or octahedral tilting in perovskites, for example. Spontaneous shear strains described in section 2 and the appendix are consistent with a Landau description of tricritical or first-order transitions, and the symmetry hierarchy, due to a single instability, is closely analogous to the transition sequences in BaTiO$_3$ or SrZrO$_3$. As in a ferroelectric material which is also ferroelastic, there is no strain contrast across twin walls between domains in which the polarization is rotated through 180°, and these will not move under application of an external stress. 90° walls are both magnetic and ferroelastic, however, and it is these which will be responsible for the observed acoustic loss behaviour.

Elastic softening associated with an improper ferroelastic transition would be expected to follow, in the simplest form [11, 19, 21],

$$C_{ik} - C_{ik}^0 = -4\lambda^2 q^2 \chi,$$

where $C_{ik}$ is an elastic constant related to the symmetry-breaking strain of the low symmetry phase, $C_{ik}^0$ is the same elastic constant of the high symmetry phase extrapolated through the transition point, $q$ is the order parameter and $\chi$ is the order parameter susceptibility. For the simplest case of a second-order phase transition at $T < T_c$,

$$\chi^{-1} = 2A \frac{B}{B^c} (T_c - T) = 2Bq^2,$$

(6)
and the amount of softening would therefore be constant, at \(2\lambda^2/B\). For a tricritical transition the amount of softening is expected to reduce non-linearly with falling temperature. In SrTiO\(_3\), the symmetry-breaking shear strain reaches \(\sim 0.001\) and the softening of the shear modulus is \(\sim 20\%\) [23], while equivalent strains and softening values are up to \(\sim -0.003, \sim -0.002\) and \(\sim 40\%, \sim 25\%\) for LaAlO\(_3\) and SrZrO\(_3\), respectively [24, 38, 43]. Rather than reducing with falling temperature, as would be expected for classical order parameter relaxation in response to an induced strain, however, the amount of softening of the shear modulus of NdCo\(_2\) increases with falling temperature. This pattern and magnitude of softening is more reminiscent of superelastic softening due to displacement of ferroelastic twin walls, as seen in low frequency experiments on SrTiO\(_3\) [44], KMn\(_{1-x}\)Ca\(_3\)F\(_3\) [45] and LaAlO\(_3\) [46].

There are insufficient data available to quantify fully the extent of the intrinsic softening of individual shear elastic constants due to the strain/order parameter coupling in NdCo\(_2\), but smaller effects would generally be expected for magnetic ordering than for displacive transitions because the inverse susceptibility, \(\chi\), scales approximately with the excess entropy, \(S\), through the value of the Landau A coefficient (\(B/B^* = 1\) in equation (6)), which Landau theory gives as \(S = -\frac{1}{2}Aq^2\). For example, values of \(A\) for the tilting transitions in SrTiO\(_3\) and LaAlO\(_3\) are 0.65 J mol\(^{-1}\) K\(^{-1}\) and 3.90 J mol\(^{-1}\) K\(^{-1}\) [23, 24, 47], in comparison with \(A\sim 11.5\) J mol\(^{-1}\) K\(^{-1}\) expected for the simplest case of order/disorder where \(S = -R\ln 2\) at \(q = 1\). On this basis, it has been assumed that the contribution of intrinsic effects to the observed softening of the shear modulus would be correspondingly smaller for NdCo\(_2\). Following the approach of Harrison and Redfern [46] and Schranz et al [48], data from figure 5 have been replotted as \(1/f^2\), which scales with the elastic compliance, in figure 9. A linear baseline, as an approximation for a small intrinsic softening effect, has been subtracted so as to ascribe the remaining ‘excess’ to motion of twin walls. According to Harrison and Redfern [46] and Schranz et al [48] this excess should scale with \(q^2\) if the number of ferroelastic twin walls does not vary with temperature. The observation of (excess compliance)\(^2\) \(\propto\) temperature (figure 9) is then consistent with the tricritical character deduced from the strain variation in figure A.1 (\(\epsilon_T^2 \propto q^4 \propto (T_c - T)\)).

The pattern of increasing acoustic loss in the stability range of the tetragonal phase of NdCo\(_2\) (\(Q^{-1}\) in figure 5) is also similar to the pattern of loss attributed to twin-wall motion in LaAlO\(_3\) at lower frequencies (figure 5(d) of [46]). The twin walls move in an effectively viscous medium and the steep increase of \(Q^{-1}\) below \(\sim 60\) K probably signifies the onset of some pinning process. Although the tetragonal ↔ orthorhombic transition then intervenes, superattenuation of resonance peaks over an interval of \(\sim 20\) K into the stability range of the orthorhombic phase is most likely a continuation of this process as the mobility of ferroelastic twin walls becomes further restricted by pinning. The return to sharp resonances at some temperature between 21 and 16 K then marks the temperatures below which the twin walls become effectively immobile. (Evidence of domain wall pinning from magnetic measurements, at about this same temperature, has been reported within the stability range of the rhombohedral phase of ErCo\(_2\) [49]. Evidence of twin-wall freezing, i.e. a return to distinct sharp resonance peaks, has not been conclusively identified in the RUS data for ErCo\(_2\), however.)

Finally, in making comparisons between NdCo\(_2\) and improper ferroelastic tilting transitions in perovskites, it is worth noting that the patterns of softening and loss are similar for high frequencies and relatively low stress in the case of NdCo\(_2\), from the present study, in contrast with low frequencies (\(\sim 1\) Hz) and relatively high stress (three-point bending in dynamical mechanical analysis) for the perovskites [45, 46, 48, 50]. The elastic properties of LaAlO\(_3\) measured at RUS frequencies are dominated by intrinsic effects from strain/order parameter coupling and the anelastic losses have been understood in terms of local and rather limited displacements of the twin walls [43]. Twin walls in purely ferroelastic materials tend to have thicknesses corresponding to just a few unit cells [51], whereas magnetic domain walls are typically much thicker than this. If there is any coupling between a magnetic order parameter and strain, it is inevitable that the twin walls which separate domains that are both magnetic and ferroelastic will involve some combination of these limiting cases. It is known that thin walls will interact with point defects to a greater extent than thick walls, so thicker walls are generally expected to be more mobile and less susceptible to pinning [52]. Relatively high mobility of ferroelastic twin walls in NdCo\(_2\) would naturally follow if their...
widths are effectively increased by coupling with variations in magnetic order across them, and this is likely to be a general property of ferroelastic walls in magnetic materials.

5.2. Parimagnetic ordering in ErCo$_2$

The parimagnetic Griffiths-like phase of ErCo$_2$ may involve another typical aspect of ferroelastic behaviour, in the form of a tweed microstructure. In metals the development of tweed microstructure is a characteristic pretransition effect ahead of martensitic transitions (e.g. as modelled recently in [53] and [54]), and can also be associated with magnetic ordering (see e.g. [55]). Magnetic ordering in RC$_2$ phases is accompanied by strain and it is inevitable that local magnetic clusters in ErCo$_2$, whether static or dynamic, would be accompanied by local strain variations. Local ordering mediated by shear strain characteristically gives rise to some degree of self-organization determined by minimization of elastic energies and the most likely form that this would take is a tweed texture, involving two interacting strain modulations $90^\circ$ apart [56, 57].

Previous studies of the local ordering in ErCo$_2$ have focused on magnetic properties, including magnetic susceptibility [12] and separate net magnetic moments of the Er and Co sublattices [13]. The imaginary component of the ac susceptibility measured in zero DC field was found to show a frequency-dependent Debye-like peak which shifts from $\sim$84 K in data collected at 1 Hz to $\sim$92 K when measured 1 kHz [12]. The loss behaviour was attributed to a relaxation process with some broad distribution of relaxation times which could be described in terms of Vogel–Fulcher dynamics and an effective zero-frequency freezing temperature of $\sim$70 K. In order to allow direct comparison with results from elasticity measurements obtained in the present study, data from figure 8 have been replotted in figure 10 along with magnetic susceptibility data for 100 Hz from Herrero-Albillos et al [12]. The real part of the magnetic susceptibility is analogous to elastic compliance and the ratio of imaginary and real parts is tan $\delta$, which is analogous to $Q^{-1}$.

The patterns of variation for the real part of the magnetic susceptibility and the elastic compliance are clearly related to the cubic $\leftrightarrow$ rhombohedral phase transition and are consistent with the simplest view that the transition involves long range magnetic ordering coupled with ferroelastic strain. The variations of tan $\delta$ and $Q^{-1}$ are quite different, however. If the loss behaviour had the same origin in both measurements, the increase in $Q^{-1}$ measured at $\sim$900 kHz would occur at a higher temperature than tan $\delta$ measured at 100 Hz, and this is the reverse of what is observed. The increase in acoustic loss occurs at and below the Vogel–Fulcher freezing temperature, coinciding almost exactly with the interval of parimagnetic ordering shown in figure 2. The actual acoustic loss mechanism, on a timescale of $\sim 10^{-5}$–$10^{-6}$ s, is therefore most likely to involve movement of boundaries between regions with different static short range order as part of a microstructure which is likely to be tweed. A stability interval for the parimagnetic configuration ahead of the cubic $\leftrightarrow$ tetragonal transition in HoCo$_2$, which is also first order in character, has recently been proposed as well [58], and the same arguments would apply to this.

Figure 10. Comparison of elasticity data for ErCo$_2$ from figure 8 ($1/f^2$ and $Q^{-1}$) measured at $\sim$922 and $\sim$1093 kHz, and ac magnetic data from Herrero-Albillos et al [12], measured at 100 Hz (tan $\delta$ and the green open circles). The dashed line placed at 33 K marks the transition between rhombohedral, ferrimagnetic (A) and cubic, parimagnetic (B) phases, whilst the dashed line at 80 K indicates the approximate temperature for onset of local, parimagnetic ordering within the cubic paramagnetic (C) phase.

5.3. Softening mechanisms in the stability range of the cubic phases

Strain/order parameter coupling, as expressed in a conventional Landau expansion with macroscopic parameters such as (1), is not expected to give rise to softening in the stability range of the high symmetry phase ahead of an improper ferroelastic phase transition [21]. Some softening is almost invariably observed, however, and is attributed to dynamical effects. The interval of premonitory softening is less than $\sim$50 K for octahedral tilting transitions, as in KMnF$_3$ [59], SrTiO$_3$ [23], SrZrO$_3$ [39], BaCeO$_3$ [60] and LaAlO$_3$ [43], for example, but extends to $\sim$200–300 K for ferroelectric and relaxor-ferroelectric phases, such as BaTiO$_3$ [61, 62], PMN (Pb(Mn$_{1/3}$Nb$_{2/3}$)O$_3$) [63], PZT–PT (Pb(Zn$_{1/3}$Nb$_{2/3}$)$_3$O$_3$–PbTiO$_3$) [61, 64], and PIN–PMN–PT (Pb(1/2Nb$_1$/2)O$_3$–Pb(Mn$_{1/3}$Nb$_{2/3}$)$_3$O$_3$–PbTiO$_3$) [65, 66]. From the present study, the same softening interval is $\gtrsim$500 K in NdCo$_2$ and $\sim$125 K in ErCo$_2$, and its form has the potential for providing some understanding of the nature of precursor ordering effects in magnetic systems.

Figure 11 shows the total softening in the stability ranges of the cubic phases, based on $f^2$ data for selected resonances and estimates of baseline values, $f_o^2$, which would represent
the expected pattern of stiffening with falling temperature in the absence of any magnetic ordering. A convenient baseline has the form of equation (12), which has been fitted to $f^2$ data for ErCo$_2$ between 173 and 291 K and extrapolated to 0 K (figure 11(a)). This gives essentially the same description as the equation of Varshni [67] for elastic moduli at low temperatures [68, 69]. To estimate a baseline for NdCo$_2$, which has $f^2$ almost independent of temperature above $\sim$500 K, it was simpler to use low temperature data for the shear modulus of YCo$_2$, which does not display magnetic ordering, taken from Klimker et al [18]. These were scaled so that a linear fit extrapolated to high temperatures matched $f^2$ data at $\sim$600 K (figure 11(b)). Differences between $f^2$ and $f_o^2$ are given as a fractional softening in figure 11(c), showing that the effect is much smaller in ErCo$_2$ than in NdCo$_2$.

The simplest description of precursor softening at a (displacive) ferroelastic transition is given by a power law

$$C_{ik} - C_{ik}^0 = \Delta C_{ik} = A_{ik} (T - T_c)^{-\kappa},$$

where $A_{ik}$ is constant and $\kappa$ can take values between 1/2 and 2 [21, 70–73]. This describes the softening ahead of octahedral tilting transitions in LaAlO$_3$ and KMnF$_3$ as well as within the stability range of the alpha phase at the $\alpha \leftrightarrow \beta$ coelastic transition in quartz, for example [3, 74, 75]. The underlying physics can be understood in terms of dispersion of a soft optic mode away from its special point in the Brillouin zone. For relaxor-ferroelectric materials the onset of softening appears to be associated with the development of atomic displacements of atoms which are sufficiently well correlated to give rise to local ferroelectric dipoles in polar nanoregions (PNRs). Evidence for dynamic effects comes in the form of central peaks in Raman and Brillouin spectra, as well as quasi-elastic scattering in inelastic neutron scattering spectra (e.g. in PMN [76–84]). The mechanism of softening is then likely to be coupling between central peak/quasi-elastic scattering mode(s) and acoustic phonons [85]. At least in the case of PMN [63], softening of the shear modulus can be described, as a piece of pure empiricism, by a Vogel–Fulcher expression

$$G - G^0 = \Delta G = A \exp \left( \frac{U}{k_B (T - T_1)} \right),$$

where $G$ is the observed shear modulus, $G^0$ is the shear modulus extrapolated from high temperatures, $A$ is a constant, $U$ is an activation energy, $T_1$ is a freezing temperature and $k_B$ is Boltzmann’s constant. However, neither of these expressions provides a good description of the softening observed in NdCo$_2$, but the same kind of empirical approach shows that an adequate description is provided by

$$f^2 - f_o^2 = A \exp \left( B (T - T_c) \right),$$

where $A$ and $B$ are constants, as shown in figure 12. This could perhaps arise from some progressive population of locally ordered or disordered states, but there is no independent evidence that it is dynamic in origin.

Resonances of a small sample depend primarily on shearing motions and, for a cubic material, the shear modulus in turn depends on $C_{44}$ and $\frac{1}{2}(C_{11} - C_{12})$. Softening of either or both of these could be responsible for the observed softening of ErCo$_2$ and NdCo$_2$. Single-crystal elastic constant data for CeAl$_2$ show precursor softening of $C_{44}$ only ahead of an antiferromagnetic ordering transition [86], while softening of both has been observed in TmAl$_2$ [87]. There do not appear to be equivalent single-crystal data available, as yet, for RCO$_2$ Laves phases but this style of softening of the shear

![Figure 11. Elastic softening ahead of the magnetic ordering transitions in ErCo$_2$ and NdCo$_2$. Vertical dashed lines are at 33 and 98 K. (a) ErCo$_2$ data for a resonance peak with $f \sim 1$ MHz at room temperature. The curve represents baseline values, to exclude the influence of magnetic ordering, and is a fit of (12) to data between $\sim$173 and 291 K, with $a_1 = 8.973 \times 10^{11}$ Hz$^2$, $a_2 = -2.144 \times 10^{10}$ Hz$^2$, $\theta = 141.97$ K. (b) NdCo$_2$ data for a resonance peak with $f \sim 0.3$ MHz at room temperature. The straight line is an approximation for baseline values, to exclude the influence of magnetic ordering, based on the (weak) temperature dependence of the shear modulus of YCo$_2$ from Klimker et al [18]. The dash–dot curve is a fit of equation (10) to the data, with a constant value of $f^2 = 9.2 \times 10^{10}$ Hz$^2$ to represent $C_{ik}^0$, and $T_c = 39.3$ K, $T_c^* = 45.8$ K. (c) Resonance frequency data from (a) and (b) scaled with respect to baseline values, $f_o$, showing more precursor softening, over a wider temperature interval, in NdCo$_2$ than in ErCo$_2$.](image-url)
modulus has previously been seen in polycrystalline samples of RCo$_2$ with R = Pr, Nd, Dy, Ho, Er and Tm [18, 88]. The temperatures are not so far from the transition temperatures, \( \sim 10-35 \) K, of structural transitions in rare earth vanadates and arsenates for which the driving mechanism has been attributed to cooperative Jahn–Teller effects and which also show precursor softening of this type (as reviewed in [10] and [11]). If there is bilinear coupling between a strain and a separate structural order parameter with the same symmetry, behaviour comparable with that shown at a pseudoproper ferroelastic transition must be expected. Precursor softening of the corresponding elastic constant or combination of elastic constants would be expected to follow the usual solution [89, 90]

\[
C_{ik} = C_{ik}^{n} \left( \frac{T - T_{c}^{*}}{T - T_{c}} \right),
\]

where \( T_{c}^{*} \) is the critical temperature renormalized by the bilinear coupling according to

\[
T_{c}^{*} = T_{c} + \frac{\lambda^{2}}{AC_{ik}^{n}};
\]

\( \lambda \) is the coefficient for the coupling term \( \lambda eq_{\text{fit}} \), \( q_{\text{fit}} \) is the driving order parameter and \( e \) the (shear) strain with the same symmetry; \( A \) is the Landau coefficient for the term in \( q^{2} \). A fit of equation (10) to data for \( f^{2} \) (\( \propto \) shear modulus) is shown in figure 11(b) and has \( T_{c}^{*} = 45.8 \pm 1.5 \) K, \( T_{c} = 39.3 \pm 1.7 \) K. This would imply that there is a zone centre structural instability with a critical temperature of \( \sim 46 \) K and weak \( (T_{c}^{*} - T_{c} = 6.5 \) K) bilinear coupling between the tetragonal strain and a structural order parameter. Absolute values of these critical temperatures are not as well constrained as the fitting might imply because they are for the shear modulus, rather than for \( C_{44} \) or \( \frac{1}{2}(C_{11} - C_{12}) \), but the precursor softening can clearly be represented in these terms and the implications of this are considered in section 5.4.

5.4. Linear–quadratic coupling between Jahn–Teller and magnetic order parameters

A fundamental difference between the behaviour of RCo$_2$ phases and the improper ferroelastic behaviour at tilting and ferroelectric transitions could be the specific role of the rare earth atoms. Following the analysis of softening at \( T > T_{K} \) in terms of the existence of a zone centre structural instability, it is proposed here that they might contribute to the strain evolution through possible Jahn–Teller effects. These are expected to be much smaller in magnitude for the rare earth compared with transition metal cations but such effects are taken to be responsible for low temperature (range 12-35 K) tetragonal to orthorhombic structural phase transitions in certain rare earth vanadates, specifically DyVO$_4$, DyAsO$_4$ and TbVO$_4$ [9]. The cooperative Jahn–Teller effects in these and other materials, with considerable emphasis on the behaviour of rare earth ions, were comprehensively reviewed by Gehring and Gehring [10]. These authors pointed out that a necessary condition for a true Jahn–Teller effect was that the lowest lying state of the active ion should be either a non-Kramers doublet or a quartet state. For ions with an odd number of electrons, such as Nd$^{3+}$ and Er$^{3+}$ the doublets are always Kramers doublets, so the condition for a Jahn–Teller effect is that the lowest lying state should be a quartet state. Lea et al [91] have provided the requisite calculations for the triply ionized rare earth ions in the tetrahedral (site symmetry Td) environment of the R$^{3+}$ ions in the Laves phases. The free ion ground states of Nd$^{3+}$ and Er$^{3+}$ are \( ^{4}I_{9/2} \) and \( ^{4}I_{15/2} \) respectively (Hund’s rules; see also table 1 of [91]). As also shown in Lea et al [91] table 1, the \( J = 9/2 \) state splits under Td symmetry into a doublet and two quartets (\( \Gamma_{6} + 2\Gamma_{8} \)), whereas the \( J = 15/2 \) state splits into two doublets and three quartets (\( \Gamma_{6} + \Gamma_{7} + 3\Gamma_{8} \)). (The notation here is due to [92].) Lea et al [91] calculated and showed the energy levels, subject to scaling by a quantity \( W \), as a function of a quantity \( x \), which is a measure of the relative importance of the fourth-degree and sixth-degree terms in the crystal field potential. For Nd$^{3+}$ (\( J = 9/2 \)) \( W \) is negative (so the diagram of Lea et al [91], figure 8, must be inverted) and so too is \( x \), from which it can be deduced that the ground state is a quartet. For Er$^{3+}$ (\( J = 15/2 \)) \( W \) is positive but \( x \) is negative, and it can be seen (from figure 2 in Lea et al) that the ground state might be either \( \Gamma_{6} \) or \( \Gamma_{7} \), depending on the value of \( x \), both of these being Kramers doublets. Evidently Nd$^{3+}$ with its quartet ground state satisfies the necessary condition for a Jahn–Teller effect, but Er$^{3+}$ does not; this is at least consistent with the relatively larger precursor softening seen in NdCo$_2$ in comparison with ErCo$_2$. Furthermore, elastic softening is not seen in YCo$_2$ [18], which is consistent with the view that the effect is associated with the rare earth ion rather than Co.

A set of experimentally derived crystalline electric field (CEF) parameters for Nd$^{3+}$ in NdCo$_2$ was reported by Dublon et al [93]. With these parameters, we calculate that the Nd$^{3+}$ \( J = 9/2 \) state indeed gives a ground quartet, with another excited quartet at \( E_{9/2}/k_{B} = 390 \) K and a higher lying doublet at \( E_{11/2}/k_{B} = 560 \) K. This calculated full splitting is similar to Nd$^{3+}$ CEF splitting in other systems and similar in magnitude to that of Ho and Er in Co Laves phases (HoCo$_2$ [94], ErCo$_2$ [95]).
The general form of coupling (ignoring subscripts) between the magnetic order parameter and strain in (1) is \( \lambda \text{em}^2 \) but if there are correlations of crystal field splitting effects between adjacent atoms, the cooperative Jahn–Teller order parameter, \( q_{JT} \), would also operate. The three related structures arising from the latter alone would have crystallographic space group \( I4_1/amd \) for \( \Gamma_3^+ \) as the active irrep, and \( Imma \) or \( R\bar{3}m \) for \( \Gamma_5^+ \) as the active irrep. Direct coupling between \( m \) and \( q_{JT} \) or indirect coupling via common strains would give rise to linear–quadratic coupling terms of the form \( \lambda q_{JT}m^2 \), with significant implications for the evolution of structural, physical and magnetic properties. Whereas the general effects of bilinear and biquadratic coupling between order parameters in materials with two separate instabilities were established long ago (see e.g. [96] and [97]), a general treatment of linear–quadratic coupling has only recently been produced [98, 99]. In the linear–quadratic case a single transition will occur and the two order parameters would be expected to scale as \( q_{JT} \propto m^2 \) if the two instabilities have the same transition temperature or are strongly coupled. If the transition temperatures are different, various topologies become possible and there may be one or two transitions, depending on which is the higher. Magnetic ordering occurs first in NdCo\(_2\), with a transition temperature of \( \sim 98 \) K, and this would not be expected to be renormalized by the coupling (see figure 1 of [98]). From the fitting shown in figure 11(b), the critical temperature for the postulated cooperative Jahn–Teller transition appears to be \( \sim 45 \) K. The effect of coupling between the structural and magnetic order parameters will be to cause only a single transition, below which both take non-zero values, and, depending on the strength of this coupling, evolution of the two order parameters with temperature will then differ from that expected for the separate transitions.

Other systems in which linear–quadratic coupling is important are Fe\(_2\)O, MnO, (La, Pr)AlO\(_3\) and selected pnictides [99–106]. The topology of order parameter variations in NdCo\(_2\) is expected to be closely similar to that of Fe\(_2\)O, though the relevant instability in the latter may be due to a soft acoustic mode [99], rather than a cooperative Jahn–Teller distortion. Strikingly, the temperature dependence of the magnetic order parameter in Fe\(_2\)O can also be represented by the simple patterns expected from Landau theory for displacive systems. In NdCo\(_2\) this result would be obtained if the influence of a Jahn–Teller component of the mixed behaviour is dominant. It seems likely, also, that the shear strain would come overwhelmingly from coupling with the Jahn–Teller component. As in Fe\(_2\)O and MnO, separate coupling of the two order parameters with volume strains has the potential to give rise to a phenomenologically rich phase diagram in pressure–temperature space.

Evidence from variations of spontaneous strains and the shear modulus analysis (figures A.1 and 9) is that the cubic ↔ tetragonal transition in NdCo\(_2\) can be described quantitatively in terms of Landau tricritical behaviour. A complete description of the phase transition will require two separate contributions to the excess energy, related to the magnetic and Jahn–Teller order parameters, together with coupling between them, in the manner set out for magnetic order plus soft acoustic mode for Fe\(_2\)O [99] and for tilting plus Jahn–Teller effects in PrAlO\(_3\) [101]. In the limit of strong coupling the contributions of the separate order parameters become subsumed into the evolution of a single order parameter, with renormalized coefficients such that \( q_{JT} \) will scale with \( m^2 \). This is effectively what (1) includes, though by not including \( q_{JT} \) explicitly, the susceptibility for \( q_{JT} \) which leads to elastic softening at \( T > T_c \) has been omitted.

Coupling with the volume strain will tend to drive the magnetic ordering transition to become first order, as already discussed by Inoue and Shimizu [29] and Duc et al [30]. The orientation of easy magnetization, parallel to [001], [111] or [110] of the parent cubic structure, would depend on the preferred orientation of cooperative Jahn–Teller distortions. The energetics of the latter are subsumed, in particular, in the value of the coefficient \( B^* \) which depends on the balance of the strength of coupling of the order parameters with tetragonal and rhombohedral strains (equation (4)).

6. Conclusions

The distinction between ferromagnetism for the light rare earth elements and ferrimagnetism for the heavy elements, together with the increase and decrease of \( T \), is well known (figure 1) and they both correlate with the occupancy of 4f energy levels. Some of the ordered phases are tetragonal and some are rhombohedral, however, and there is no obvious pattern in this. Some develop from the parent cubic phase by first-order transitions and some by continuous transitions, but, according to the arguments presented here, the transitions are likely to all be close to tricritical in character, with stronger coupling to the volume strain driving them first order in some cases. The subsequent appearance of orthorhombic phases, via first-order transitions, can also be understood in terms of the values of Landau coefficients in the same way as for the transition hierarchy in BaTiO\(_3\). The specific conclusions drawn here from consideration of strain and elasticity behaviour of ErCo\(_2\) and NdCo\(_2\) are then as follows.

(1) Treatment of lattice parameter variations in terms of spontaneous strains coupled with magnetic order parameters shows a pattern of tricritical behaviour for NdCo\(_2\) and a small first-order discontinuity for ErCo\(_2\) associated with cubic ↔ rhombohedral/tetragonal transitions.

(2) Arising from the strain coupling there are marked changes in shear modulus which can be understood in terms of classic ferroelastic behaviour. In particular, continued softening in the stability interval of the tetragonal phase below the cubic ↔ tetragonal transition in NdCo\(_2\) is ascribed to a combination of strain relaxation due to \( \lambda \text{em}^2 \) coupling terms plus motion under external stress of ferroelastic twin walls.

(3) Precursor softening in the stability range of the cubic phase of NdCo\(_2\) does not match up with expected patterns related to a soft optic phonon or to Vogel–Fulcher dynamics of clustering/short range ordering. Rather, it fits with the influence of bilinear coupling between shear strains and an additional order parameter belonging to a zone centre irrep that has been attributed to a Jahn–Teller
cooperative distortion. Data for RCo$_2$ from the literature show that softening of the shear modulus occurs with falling temperature for $R = \text{Pr}, \text{Nd}, \text{Sm}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$ and Tm [18, 87]. Single-crystal data for TmCo$_2$ show softening of both $C_{44}$ and $\frac{1}{2}(C_{11} - C_{12})$ [87] which, in this context, would imply bilinear strain coupling with both $\Gamma^2_4$ and $\Gamma^2_5$ order parameters. The relevant shear strains would be $e_1$ and $(e_4, e_5, e_6)$, respectively.

(4) Softening ahead of the phase transition in ErCo$_2$ is less in extent than in NdCo$_2$ and may be influenced also by the development of the paramagnetic or Griffiths-like phase below $\sim 80$ K. The influence of the latter is more evident in a marked increase in acoustic loss, however, which does not correspond with loss behaviour in an ac magnetic field at lower frequencies. It is proposed that the paramagnetic phase may contain a static microstructure of strain modulations (tweed).

(5) The critical temperature for (zone centre) magnetic ordering in NdCo$_2$ is above that of the zone centre structural instability, but linear–quadratic coupling between the two order parameters gives a single instability below which both adopt non-zero values. Depending on the balance of energies between the two instabilities and the strength of coupling between them, this coupling will tend to give the overall pattern of evolution a component of displacive, as opposed to order/disorder, character.

(6) Acoustic loss below the transition points can be understood in terms of mobility of ferroelastic twin walls in an effectively viscous matrix. Evidence of the pattern of substantial softening shown by the tetragonal phase of NdCo$_2$ is that the walls are particularly mobile under the low stress and high frequency conditions of an RUS experiment. Increasing acoustic loss below $\sim 60$ K can be interpreted as the onset of domain wall freezing and this continues into the stability range of the orthorhombic structure. Below $\sim 20$ K an abrupt return to low loss, comparable with that of the parent cubic structure, signifies that the ferroelastic twin walls have become immobile.

(7) From the perspectives of strain and elasticity the phase transitions in RCo$_2$ Laves phases exhibit typical properties of ferroelastic materials. The ferroelastic twin walls must contain steep strain gradients, in the usual way, but because they are also ferrimagnetic or ferromagnetic, they must also contain gradients in the magnetic order parameters which might become steep due to coupling with the strain gradients. There are therefore possibilities for more complex relaxations within the twin walls than would occur with materials with magnetic or ferroelastic properties alone.

Acknowledgments

The RUS facilities in Cambridge were established and supported by grants from the Natural Environment Research Council (grant Nos NE/B505738/1, NE/F017081/1). The financial support of the Spanish MINECO MAT2011-23791 and Aragonesa DGA-IMANA (co-funded by the European Social Fund) projects is acknowledged.

Figure A.1. (a) Lattice parameter data for NdCo$_2$ from Xiao et al [7] and (b) and symmetry-adapted strains determined from them. The baseline, $a_0$, has fit parameters $a_1 = 7.2455$ Å, $a_2 = 0.036 13$ Å, $\theta_s = 212.1$ K in (12). The solid curve is a fit of $e^2_1 \propto T$ for values of the tetragonal phase, which extrapolates to zero at $T_c = 95.2$ K. The dotted curve is the same fit multiplied by $-0.5$ and nearly passes through values of $e_1$ for the orthorhombic phase below $\sim 42$ K.

Appendix.

General strain–order parameter relationships for the magnetic order parameters derived from equation (1) are listed in table A.1. Specific relationships for tetragonal, orthorhombic and rhombohedral structures are given in table A.2, together with the relationships between strain components and lattice parameters for each case (following [39] and [112]).

Figure A.1 shows lattice parameter data for NdCo$_2$ from Xiao et al [7] and spontaneous strains calculated from them. Figure A.2 contains equivalent results for ErCo$_2$, starting with the lattice parameters of Gratz and Lindbaum [5]. Values of the lattice parameter, $a_0$, of the reference state in each case were obtained by fitting the function

$$a_0 = a_1 + a_2 \coth \left( \frac{\theta_s}{T} \right)$$

(1)

to values of $a$ for the cubic phase; $a_1$ and $a_2$ are constants and $\theta_s$ is a saturation temperature. This expression provides a convenient description of the levelling off of thermal expansion as $T \to 0$ K [23, 107–111].

Combining expressions for strains in terms of order parameter components gives the relationships between symmetry-adapted strains and the magnetic order parameters listed in table A.2. On this basis, the strain variations show that the cubic $\leftrightarrow$ tetragonal transition in NdCo$_2$ is close to Landau tricritical ($e^2_1 \propto m^4_1 \propto (T_c - T)$, for $T_c \gg \theta_s$ in (2)), with
Table A.1. Strain–order parameter relationships derived from equation (1).

\[
\begin{align*}
e_a &= \frac{\lambda_1(m_1^2 + m_2^2 + m_3^2)}{4(C_{11} + 2C_{12})}, \\
e_0 &= \frac{\lambda_2 \sqrt{3}(m_1^2 - m_2^2)}{4(C_{11} - C_{12})}, \\
e_1 &= \frac{-\lambda_3}{4(C_{11} - C_{12})}, \\
e_2 &= \frac{-\lambda_3 m_3}{4}, \\
e_3 &= \frac{-\lambda_3 m_1 m_2}{4(C_{11} - C_{12})} \\
e_4 &= \frac{-\lambda_3 m_1 m_2}{4(C_{11} - C_{12})}, \\
e_5 &= \frac{-\lambda_3 m_1 m_2}{4(C_{11} - C_{12})}, \\
e_6 &= \frac{-\lambda_3 m_1 m_2}{4(C_{11} - C_{12})} \\
\end{align*}
\]

where \(e_a = (e_1 + e_2 + e_3)\), \(e_0 = (e_1 - e_2)\), \(e_1 = \frac{1}{\sqrt{3}}(2e_3 - e_1 - e_2)\).

Table A.2. Strain–order parameter relationships for tetragonal, orthorhombic and rhombohedral structures. Also given are definitions of strains in terms of lattice parameters a, b, c for the tetragonal and orthorhombic structures or a, α, α for the rhombohedral structure; \(a_0\) is the reference parameter of the parent cubic structure extrapolated into the ranges of stability of the low temperature structures.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Tetragonal</th>
<th>Orthorhombic</th>
<th>Rhombohedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m_3 \neq 0, m_1 = m_2 = 0)</td>
<td>(I4_1/md')</td>
<td>(I4_1/md')</td>
<td>(R3m')</td>
</tr>
<tr>
<td>(e_a)</td>
<td>(\frac{\lambda_1 m_1^2}{4(C_{11} + 2C_{12})})</td>
<td>(\frac{2\lambda_1 m_1^2}{4(C_{11} + 2C_{12})})</td>
<td>(\frac{3\lambda_1 m_1^2}{4(C_{11} + 2C_{12})})</td>
</tr>
<tr>
<td>(e_1)</td>
<td>(\frac{-2\lambda_2 m_1^2}{4(C_{11} - C_{12})})</td>
<td>(\frac{2\lambda_2 m_1^2}{4(C_{11} - C_{12})})</td>
<td>(\frac{3\lambda_2 m_1^2}{4(C_{11} - C_{12})})</td>
</tr>
<tr>
<td>(e_0)</td>
<td>(e_4 = e_5 = e_6 = 0)</td>
<td>(e_0 = e_4 = e_5 = 0)</td>
<td>(e_0 = e_1 = 0)</td>
</tr>
<tr>
<td>(e_1 = e_2 = \frac{\sqrt{2}a - a_0}{a_0})</td>
<td>(e_1 + e_2 = \frac{\sqrt{2}a - a_0}{a_0} + \frac{\sqrt{2}b - a_0}{a_0})</td>
<td>(e_1 = e_2 = e_3 = \frac{a - a_0}{a_0})</td>
<td></td>
</tr>
<tr>
<td>(e_3 = \frac{c - a_0}{a_0})</td>
<td>(e_3 = \frac{c - a_0}{a_0})</td>
<td>(e_4 = \frac{C_4}{4m_0} \cos \alpha)</td>
<td></td>
</tr>
</tbody>
</table>

\(T_c = 95\) K (figure A.1(b)). If there is only one instability, the magnitude of \(m_2^2\) for the tetragonal structure and \(2m_1^2\) for the orthorhombic structure should then evolve in the same manner and, indeed, there is no obvious break in the evolution of the volume strain, \(e_a\), at the tetragonal \(\leftrightarrow\) orthorhombic transition. On the same basis, the sign of \(e_1\) should reverse and be reduced by a factor of 2 on cooling through the transition. The solid curve in figure A.1(b) is for the tricritical solution, fitted to data for \(e_1\), and the dotted curve is the same fit multiplied by −0.5. The latter nearly passes through the data for \(e_1\) of the orthorhombic structure, confirming that these relationships provide a good representation of the overall behaviour. Forker et al.[113] reported that the cubic \(\leftrightarrow\) tetragonal transition is first order, which would put it just to the first-order side of tricritical ((\(B^a + B^c\) < 0), rather than being exactly tricritical ((\(B^a + B^c\) = 0)). Their conclusion is the subject of some debate, however [114–116].

The measured magnetization, \(M\), should be related to the magnetic order parameter according to \(M^2 \propto m_2^2\) for the tetragonal structure and \(M^2 \propto 2m_1^2\) for the orthorhombic structure. Hence, the strains should scale as \(M^2\). As shown in figure A.3, data from Xiao et al.[7] are consistent with the strain/order parameter relationships, bearing in mind that values of \(e_a\) are subject to relatively large uncertainties due to their sensitivity to the choice of baseline for \(a_0\).

The two magnetic transitions in NdCo2 can then be understood in terms of a single instability with \(T_c = 95\) K. Successive structures associated with irrep \(mGamma^4_4\) arise because of their change in relative stability with falling temperature, in a manner that is analogous to the hierarchy of cubic \(\rightarrow\) tetragonal \(\rightarrow\) orthorhombic \(\rightarrow\) rhombohedral ferroelectric (\(Gamma^4_4\) of \(Pm\bar{3}m\)) transitions in BaTiO3 analysed by Devonshire [31, 117, 118], even though the sequence is not quite complete in NdCo2. The same incomplete sequence is seen in the tilting transitions of Sr2ZnO3 (\(R3\) of \(Pm\bar{3}m\) [39]). Devonshire showed that the orthorhombic phase can only have an equilibrium stability interval if the fourth-order coefficient of the Landau expansion is negative (see, also, [33]), but the conventional expansion only applies strictly to the displacive limit. It is clear that for RCO2 phases the first transition with reducing temperature is either first order or close to tricritical, i.e. with the fourth-order coefficient negative or close to zero. A pattern of order parameter evolution which is not dissimilar to a Landau tricritical one is also obtained from the Bragg–Williams model of the order–disorder case (see e.g. [119]), so the Landau description can produce at least a semi-quantitative representation of the order parameter evolution even though the description of the excess entropy may be incorrect. A closely similar result has been obtained also for antiferromagnetic ordering in CoF2 [120].

The data of Gratz and Lindbaum [5] showed that the cubic \(\leftrightarrow\) rhombohedral transition at 32 K in ErCo2 is first order and this difference from the cubic \(\leftrightarrow\) tetragonal transition in NdCo2 can be understood in terms of the magnitudes of the volume strains. The fourth-order coefficients are renormalized by coupling with strain in the usual way and the volume

\[\bar{T}_c = 95\text{ K (figure A.1(b))}.\]
governed by a Landau expansion with the form of (1). phase, as would be expected for a system with only one instability of the orthorhombic phase are close to the fit to Figure A.3. Comparison of data for NdCo$_2$ from Xiao et al[7] for total magnetization, $M$, and from figure A.1 for symmetry-adapted strains. Straight lines, constrained to pass through the origin, have been fitted to $\varepsilon_a$ and $\varepsilon_t$ of the tetragonal structure and extrapolated for comparison with data for the orthorhombic phase. Data for $\sim -2\varepsilon_t$ of the orthorhombic phase are close to the fit to $\varepsilon_t$ for the tetragonal phase, as would be expected for a system with only one instability governed by a Landau expansion with the form of (1).

The vertical broken line marks the first-order cubic $\leftrightarrow$ rhombohedral transition at $\sim 32$ K.

the sign of $\mathcal{B}^{\nu*}$, which is sensitive to the relative magnitudes of $\lambda_2$ and $\lambda_3$ when $\mathcal{B}'$ is small.

References

[31] Devonshire A F 1949 Phil. Mag. 40 1040

Figure A.2. (a) Lattice parameter data for ErCo$_2$ from figure A.1(b) and A.2(b)). If all other parameters are more or less the same, the implication is that the value of $\lambda_1$ is greater for the former than the latter and, presumably, is then sufficient to cause the combined fourth-order coefficient in (2) to become negative. The relative stability of tetragonal and rhombohedral structures can also be understood in terms of

Figure A.3.
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[117] Devonshire A F 1951 Phil. Mag. 42 1065

