CoF$_2$: a model system for magnetoelastic coupling and elastic softening mechanisms associated with paramagnetic ↔ antiferromagnetic phase transitions

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Abstract
Resonant ultrasound spectroscopy has been used to monitor variations in the elastic and anelastic behaviour of polycrystalline CoF$_2$ through the temperature interval 10–290 K and in the frequency range $\sim$0.4–2 MHz. Marked softening, particularly of the shear modulus, and a peak in attenuation occur as the Néel point ($T_N = 39$ K) is approached from both high and low temperatures. Although the effective thermodynamic behaviour can be represented semiquantitatively with a Bragg–Williams model for a system with spin 1/2, the magnetoelastic coupling follows a pattern which is closely analogous to that of a Landau tricritical transition which is co-elastic in character. Analysis of lattice parameter data from the literature confirms that linear spontaneous strains scale with the square of the magnetic order parameter and combine to give effective shear and volume strains on the order of 1%/\textdegree. Softening of the shear modulus at $T > T_N$ is attributed to coupling of acoustic modes with dynamical local ordering of spins and can be represented by a Vogel–Fulcher expression. At $T < T_N$ the coupling of strains with the antiferromagnetic order parameter leads to softening of the shear modulus by up to $\sim$2%, but this is accompanied by a small and frequency-dependent acoustic loss. The loss mechanism is attributed to spin–lattice relaxations under the influence of externally applied dynamic shear stress. CoF$_2$ provides a reference or end-member behaviour against which the likely antiferromagnetic component of magnetoelastic behaviour in more complex multiferroic materials, with additional displacive instabilities, Jahn–Teller effects and ferroelastic microstructures, can be compared.

Keywords: elasticity, phase transition, antiferromagnetic, magnetoelastic coupling, anelastic loss

(Some figures may appear in colour only in the online journal)
The RUS method has been described in detail elsewhere [42]. A small sample, usually in the shape of a parallelepiped with dimensions in the range ~1–5 mm, is held lightly between two piezoelectric transducers. The first transducer is excited at constant amplitude across a range of frequencies in the vicinity of 1 MHz, which in turn causes the sample to resonate at particular frequencies. The second transducer detects these resonances, or normal modes of vibration of the sample. The square of a given resonance frequency is directly proportional to the elastic constants associated with the normal mode involved [42]. In the low temperature head of the Cambridge
followed by 110 K in 30 K steps with a 20 min settle time for thermal equilibration. Each spectrum contained 65,000 data points in the frequency range 100–1200 kHz. Data collection for sample 2 followed exactly the same temperature steps, except that 130,000 data points were collected in the frequency range 100–2000 kHz.

Bulk ($K$) and shear ($\mu$) moduli were determined by matching observed peak frequencies with calculated frequencies using the DRS software [42] and assuming an isotropic medium. The result of fitting to the frequencies of 26 resonance peaks in a spectrum collected at 284 K from sample 2 was $\mu = 38.51 \pm 0.03$ GPa and $K = 103 \pm 1$ GPa, with an rms error on the fitting of 0.25%. This compares with 39, 83.6 GPa (Hashin–Shtrikman bounds from single crystal data of [44] in [45]) and 37.7, 110.4 GPa (Voigt–Reuss–Hill values from single crystal data listed in [46]). The density from the dimensions and mass of the sample was 4.493 g cm$^{-3}$, implying a porosity (which includes some contribution of slightly damaged edges of the parallelepipeds) of 2.2% when compared with a theoretical density of 4.592 g cm$^{-3}$ calculated from lattice parameters. Correction for this using the equations of Ledbetter et al. [47] gave $\mu = 40.1$, $K = 110.0$ GPa as the best estimate of absolute values for a fully dense polycrystalline sample. Determination of absolute values of the elastic properties was not a prime consideration in the present study, so the porosity correction was not made to all the data. Similarly, no correction was made for thermal expansion of the sample because the change would be very small and the effects of magnetic ordering can be seen in the uncorrected data.

All spectra were transferred to the software package Igor Pro (WaveMetrics) for analysis. Peak positions and widths at half height were determined for a selection of peaks by fitting with an asymmetric Lorentzian function. The mechanical quality factor, $Q$, was calculated using the relationship $Q = f/\Delta f$, where $f$ is the peak frequency and $\Delta f$ is the width of the peak at half its maximum height. The inverse of the mechanical quality factor, $Q^{-1}$, is a measure of acoustic dissipation in the sample.

Figure 1 shows the evolution with temperature of $f^2$ and $Q^{-1}$ for several representative peaks at different frequencies in spectra collected from sample 2. Their $f^2$ values have been scaled to be the same at room temperature, for easy comparison, and since the resonances mainly involve shearing motions, they are indicative primarily of the evolution of...
the square of the peak frequency, $f^2$, and the inverse mechanical quality factor, $Q^{-1}$, for a selection of resonance peaks, scaled to a constant value at 300 K. Their actual frequencies at room temperature are given in the caption. The broken line at 39.5 K is taken to mark the Néel point. High values of $Q^{-1}$ for the 445 and 860 kHz peaks at $T > 100$ K are artefacts which occur when the amplitude of resonances is large and the amplifier became saturated.

**Figure 3.** Changes in the bulk and shear moduli as a function of temperature from both samples. A vertical line marks the expected Néel point which has been placed at 39.5 K.

The onset of softening with falling temperature in the stability field of the high temperature phase occurs between $\sim 100$ and $\sim 150$ K. At first view, differences between $f^2$ data for the separate resonance peaks do not appear to depend systematically on frequency and are probably due in part to different contributions from breathing modes, related to the bulk modulus. Variations in $Q^{-1}$ are limited to a slight premonitory effect within a few degrees above $T_N$, a steep increase at the transition point and then a decay back to the same low values as for the high temperature structure by $\sim 20$ K. The magnitude of the peak in $Q^{-1}$ at $\sim 39$ K varies systematically with the frequency of the resonance peak from which the values were determined, with the largest maximum value at the highest frequency and the lowest maximum value at the lowest frequency.

Figure 3 shows the variation of the bulk and shear moduli as a function of temperature for both samples. Rms errors for the fits using 15–20 peaks were $< \sim 0.5\%$ and estimated uncertainties for $K$ and $\mu$ were $\pm 1.5\%$ and $\pm 0.15\%$, respectively. As expected, the shear modulus shows the same pattern of softening associated with the antiferromagnetic ordering transition as is seen for individual resonance peaks.
in figure 2. The maximum amount of softening is ~2.5% but this reduces to ~0.5% at ~10 K. The evolution of $\mu$ below $T_N$ is essentially the same in both samples. Data for $K$ are more scattered, with the observed anomalies below $T_N$ close to the level of the estimated experimental uncertainties and apparently not reproducible. In particular, they provide no obvious evidence for softening of the bulk modulus on either side of the transition point.

4. Strain analysis, order parameter evolution and elastic softening below $T_N$

Although there are insufficient data to produce a quantitative description of the elastic anomalies, their form can at least be predicted on the basis of a conventional Landau expansion in the magnetic order parameter, $Q_m$, and coupling with spontaneous strains. In order for the structure to become antiferromagnetic with spins parallel to the $c$-axis and no breaking of crystallographic symmetry, the transition must proceed according to irrep $m1\overline{2}$ of parent magnetic space group $P4_{2}mnm1'$, leading to magnetic sub group $P4_{2}m/mmm$. The group theory program ISOTROPY [48] has been used to determine the permitted terms in a conventional Landau expansion for the excess free energy, $G$, due to this symmetry change as

$$G = \frac{1}{2}aT_s \left( \coth \left( \frac{\Theta_s}{T} \right) - \coth \left( \frac{\Theta_s}{T_c} \right) \right) Q_m^2 + \frac{1}{2}bQ_m^2 + \frac{1}{5}cQ_m^6 + \lambda_1 (e_1 + e_2) Q_m^2 + \lambda_2 (e_1 - e_2) Q_m^2 + \lambda_3 e_1^2 Q_m^2 + \lambda_4 (e_1^2 + e_2^2) Q_m^2 + \frac{1}{2}(C_{11}^o + C_{12}^o)(e_1 + e_2)^2 + \frac{1}{2}(C_{11}^o - C_{12}^o)(e_1 - e_2)^2 + C_{13}^o (e_1 + e_2)^2 + C_{15}^o (e_1 + e_2)^2 + \frac{1}{2}C_{44}^o (e_1^2 + e_2^2) + \frac{1}{2}C_{66}^o e_3^2, \tag{1}$$

where $a$, $b$ and $c$ are normal Landau coefficients, $T_c$ is the critical temperature, $e_1 - e_6$ are spontaneous strains, $\lambda_1 - \lambda_6$ are strain/order parameter coupling coefficients, and $C_{ik}^o$ are the bare elastic constants, i.e. those excluding the effect of the phase transition. $\Theta_s$ is a saturation temperature giving the correct form of variation as $T \to 0$ K [49].

The spontaneous strains are expected to evolve with $Q_m$ according to

$$e_3 = \frac{2\lambda_1 C_{13}^o - \lambda_3 (C_{11}^o + C_{12}^o)}{C_{33}^o (C_{11}^o + C_{12}^o) - 2C_{13}^o} Q_m^2 \tag{2}$$

$$e_1 + e_2 = \frac{2\lambda_1 C_{13}^o - \lambda_3 (C_{11}^o + C_{12}^o)}{C_{33}^o (C_{11}^o + C_{12}^o) - 2C_{13}^o} Q_m^2, \tag{3}$$

and these relationships can be tested with measurements of lattice parameters as a function of temperature. Data of Chatterji et al [19] have been reanalysed in this context, as set out in the appendix, to show that the observed strains have values up to 0.001, that they scale with the intensities of superlattice reflections in powder neutron diffraction patterns ($\propto Q_m^2$), and that the order parameter follows a pattern which can be described effectively as being close to tricritical (figures A.1–A.3). In addition, there is a clear tail in $e_1$ which extends to ~70 K above $T_N$, indicative of a degree of short range ordering ahead of the phase transition (figure A.2).

Softening of the shear modulus appears to be typical of a phase transition with strain/order parameter coupling, and can be tested against the normal expectations predicted using the equation of Slonczewski and Thomas [50]:

$$C_{ik} = C_{ik}^o - \sum_{r,s} \frac{\partial^2 G}{\partial e_r \partial Q_r} \cdot \left( \frac{\partial^2 G}{\partial Q_r \partial Q_s} \right)^{-1} \cdot \frac{\partial^2 G}{\partial e_k \partial Q_s}. \tag{4}$$

This gives the expressions for individual elastic constants listed in table 1 (following [39, 51]). Coupling terms of the form $e^2 Q^2$, such as $\lambda_6 e_3^2 Q_m^2$, give the variation of the elastic constants more simply by applying $C_{ik} = \partial^2 G / \partial e_i \partial e_k$, hence giving $C_{66} = C_{66}^o + 2\lambda_6 Q_m^2$. Expressions for the Voigt limit, $\mu_V$ and $K_V$, illustrate how the separate coupling parameters contribute to the softening:

$$m_V = \frac{1}{30} \left( m + 3((C_{11}^o - C_{12}^o) + 4\lambda_2 Q_m^2) \right)$$

$$+ 12(C_{44}^o + 2\lambda_4 Q_m^2) + 6(C_{66}^o + 2\lambda_6 Q_m^2) \tag{5}$$

where

$$m = C_{11}^o + C_{12}^o + 2C_{33}^o - 4C_{13}^o$$

$$- 8Q_m^2 (\lambda_1^2 + \lambda_3^2 + 2\lambda_1 \lambda_3), \tag{6}$$

and

$$K_V = \frac{1}{6} (2(C_{11}^o + C_{12}^o) + C_{33}^o + 4C_{13}^o$$

$$- 4Q_m^2 (4\lambda_1^2 + \lambda_3^2 + 4\lambda_3 \lambda_3)). \tag{7}$$

Terms originating from coupling of the form $\lambda e^2 Q^2$ would be expected to contribute to softening or stiffening in proportion to $Q_m^2$ but this is usually a small effect in comparison to terms originating from coupling of the form $\lambda e Q^2$ which include the inverse susceptibility, $\chi (= (\partial^2 G / \partial Q_m^2)^{-1})$. For a second order transition, $Q^2 \chi$ is constant and the softening is therefore expected to be discontinuous by a fixed amount. For a tricritical transition softening at the transition point is also expected to be discontinuous, but with a non-linear recovery as temperature reduces in the stability field of the

| Table 1. Variations of single crystal elastic constants derived from equation (1). |
| --- |
| $C_{11} = C_{22} = C_{11}^o - 4\lambda_1^2 Q_m^2 \chi + 2\lambda_2 Q_m^2$ |
| $C_{33} = C_{33}^o - 4\lambda_3^2 Q_m^2 \chi$ |
| $C_{12} = C_{12}^o - 4\lambda_2 Q_m^2 \chi - 2\lambda_2 Q_m^2$ |
| $C_{13} = C_{13}^o - 4\lambda_3 Q_m \chi$ |
| $C_{44} = C_{44}^o + 2\lambda_4 Q_m^2$ |
| $C_{66} = C_{66}^o + 2\lambda_6 Q_m^2$ |
| $(C_{11} - C_{12}) = (C_{11}^o - C_{12}^o) + 4\lambda_2 Q_m^2$ |
| $(C_{11} + C_{12}) = (C_{11}^o + C_{12}^o) - 8\lambda_1^2 Q_m^2 \chi$ |
low symmetry phase. The amount of softening in the present case clearly depends on the coefficients, $\lambda_1$ and $\lambda_3$, and values of these can be estimated from equations (2) and (3) by taking low temperature limiting values for strains $e_3$ and $(e_1 + e_2)$, room temperature values of elastic constants from Gerlich et al [46] to represent bare elastic constants ($C_{11}^0 = 128.1$ GPa, $C_{12}^0 = 100$ GPa, $C_{13}^0 = 88.1$ GPa, $C_{33}^0 = 197.1$ GPa) and setting the order parameter to equal 1 in the low temperature limit. This gives values for the coupling coefficients as $\lambda_1 = -0.127$ and $\lambda_3 = 0.028$ GPa. The data in figure 3 are of sufficient precision to show that the pattern of softening predicted on this overall basis for the shear modulus is consistent with a strain/order parameter relaxation mechanism at a phase transition which is approximately tricritical in character.

Discrimination between models for the evolution of the order parameter, as shown in figure A.3, depends in part on the form of the excess entropy, $\Delta S$. Equation (1) is based on the assumption of displacive character, for which

$$\Delta S = \frac{1}{2} a Q_m^2.$$  

(8)

The order/disorder limit would have the excess entropy as purely configurational, for which higher order terms in $Q_m$ are required if it is to be expressed as a series expansion. As set out in the appendix, heat capacity data from Catalano and Stout [24] have been reanalysed and used to confirm that the thermodynamic behaviour is indeed well represented by order/disorder character, the order parameter evolution is similar in form to that of Landau tricritical, and there is a degree of precursor ordering ahead of the Néel point.

5. Precursor effects at $T > T_N$

Tails in the data for $e_1$ (figure 5(b)) and $C_p$ (figure A.4) at $T > T_N$ signify premonitory effects, indicative of short range ordering that has stronger correlations within the $a$-$b$ plane than in the c-direction [19]. This premonitory ordering is presumed also to account for the elastic softening evident in the data shown in figures 2 and 3 over the same temperature interval. In order to characterize the softening more quantitatively, excess values of the shear modulus have been obtained by first fitting a baseline, $f_0^2$, with the form of equation (A.1) to $f^2$ data in the temperature interval 128–286 K for the resonance mode with frequency $\sim 445$ kHz at room temperature (figure 2). Differences between this fit, extrapolated down to 10 K, and the observed values are shown as $|\Delta f^2/f_0^2|$ in figure 4. Values of the saturation temperature, $\theta_s$, from the fitting were 157 K for the 445 kHz peak and between 241 and 253 K for the other peaks. In this context equation (A.1) merely provides a convenient description of reducing slope as $T \rightarrow 0$ K, which is comparable in form to a description by the Varshni equation (e.g. see [52]). Data for $\Delta Q^{-1}$, the excess of $Q^{-1}$ with respect to a straight line fit to values above $\sim 50$ K, have been added to figure 4, excluding high values that were due to saturation of the amplifier.

The complete data in figure 4 show that the evolution of changes in $f^2$, i.e. changes predominantly in the shear modulus, is independent of frequency at $T > T_N$ and that the softening is not accompanied by any detectable increase in acoustic loss. For improper ferroelastic or co-elastic transitions driven by a soft optic phonon, such softening is generally understood in terms of local fluctuations and can be described by a power law of the form $\Delta C_{ik} = A_{ik}|T - T_c|^\alpha$ [53–57].
Log–log plots of the data for $|\Delta f^2/f_o^2|$ and $(T - 39.5)$, are distinctly non-linear in the present case, however. An alternative variation due to short range ordering is shown by relaxor ferroelectrics, such as Pb(Mg1/3Nb2/3)O3 (PMN), where the softening is attributed to coupling between dynamical polar nano-regions and acoustic phonons. As a pure piece of empiricism it was found that softening at high temperatures in PMN can be described using a Vogel–Fulcher type of equation that is usually used to describe a freezing process according to

$$\tau = \tau_0 \exp \left( \frac{U}{k_B(T - T_1)} \right). \quad (9)$$

$\tau$ is a relaxation time, $\tau_0$ is the inverse of the attempt frequency, $U$ is an effective activation energy, $k_B$ is the Boltzmann constant and $T_1$ is a characteristic freezing temperature. In this case, the low loss implies $\omega T \ll 1$, where $\omega(=2\pi f)$ is the angular frequency at which the measurement was made. For PMN the relaxation time was replaced by the change in shear modulus (figure 10 of [58]). For CoF$_2$ the change in $f^2$ of a single RUS mode is used in place of the change in shear modulus, but the same empiricism provides an equally good description of the premonitory softening in CoF$_2$. The black curve in figure 4 is for $|\Delta f^2/f_o^2| = 0.0001\exp(95/(T - 15))$. In the absence of any physical justification, this has not been explored further but, if real, the value of $U/k_B = 95$ K would imply an effective activation energy barrier of $\sim 0.8$ kJ mol$^{-1}$ or $\sim 0.008$ eV, with an effective zero-frequency freezing temperature of $\sim 15$ K.

The form and magnitude of dynamical local ordering at $T > T_N$ which gives rise to the elastic softening also gives the tail in strain, $e_1$, and the two effects are closely interdependent. As shown in figure 5, $e_1^2$ scales closely with $|\Delta f^2/f_o^2|$, implying a relationship $e_1^2 \propto \Delta \mu \propto |\Delta f^2/f_o^2|$. The macroscopic order parameter $Q_m$ is strictly zero, but the average degree of local ordering can be represented by a short range order parameter, $\sigma_m$. In the simplest case, both the strain and the elastic softening would behave as excess properties and would then be expected to scale in some simple way with $\sigma_m$. There is no change in symmetry involved, so there are no constraints on the form of coupling between $\sigma_m$ and $e_1$ or $e_3$, which can be $\lambda_1\sigma_m e_1^2$, $\lambda_2\sigma_m e_2^2$, $\lambda_3\sigma_m e_3^2$, etc. A term $\lambda_1\sigma_m e_1^2$ added to the elastic energy $\frac{1}{2}C_{11}^0\epsilon_1^2$ will cause a renormalization of the elastic constant, $C_{11}$, as

$$C_{11} = C_{11}^0 + 2\lambda_1\sigma_m. \quad (10)$$

The observed relationships in figure 5 could then result if the contribution to softening of the shear modulus comes mainly from $C_{11}$ (together with $C_{22}$ and $C_{12}$) and if the same coupling term gives rise to a dependence $\sigma_m \propto e_1^2$. There is no equivalent tail in $e_3$, implying that the coupling coefficient for an equivalent term $\lambda_1\sigma_m e_1^2$ is small and, presumably, that the softening of $C_{33}$ would also be small. According to this treatment, the tail in $e_1^2$ and the variation of $|\Delta f^2/f_o^2|$ are measures of the dynamical average of the degree of short range order as $T \rightarrow T_N$. It should also be pointed out that additional contributions to the shear modulus may come from $C_{44}$, $C_{66}$, etc., through terms such as $\lambda_2\sigma_m e_1 e_2^2$ and $\lambda_3\sigma_m e_1 e_3^2$, but in MnF$_2$ at least, the precursor softening of $C_{44}$ and $C_{66}$ is very small [59].

6. Acoustic attenuation

Attenuation of acoustic waves in the vicinity of a magnetic ordering transition might be expected to follow a power law dependence on the reduced temperature as [1, 52],

$$\alpha \propto \omega^2 \left( \frac{T - T_N}{T_N} \right)^{-\eta}. \quad (11)$$

where $\alpha$ is the attenuation coefficient ($\propto Q^{-1}$). This has been used to describe the pattern of attenuation in a temperature interval of up to a few degrees above the Néel point of MnF$_2$, for example, where values of $\eta \approx 0.1$–0.5 have been reported [1, 60–66]. The present data show constant and very low values of $Q^{-1}$ from $\sim 50$ K up to room temperature (figures 2 and 4). Linear fits to data between 39.7 and 52.2 K on plots of $\ln \Delta Q^{-1}$ against $\ln((T - 39.5)/39.5)$ give values of $\eta = 0.9$–1.1 for the resonance peaks near 487, 860, 1300 and 1882 kHz, which depend most strongly on the shear modulus. Data from the same temperature interval for the peak near 445 kHz, which includes a larger dependence on the bulk modulus, give $\eta = 0.6$. The attenuation mechanism, at least for temperatures within $\sim 1$ K of $T_N$, has been attributed to energy density fluctuations [3]. Over the relatively narrow range of frequencies observed in the present study, there is too much scatter in the data to test the expected frequency dependence, but the $\omega^2$ dependency has been observed for MnF$_2$ (e.g. [1, 60]).

In the absence of any ferroelastic twin microstructure, the acoustic attenuation at $T < T_N$ is more likely to be intrinsic. A log–log plot for data between 12.8 and 38.8 K from the heating sequence (figure 6(a)) shows that a conventional power law does not provide a good description over the entire temperature range below $T_N$. The dashed line in figure 6(a) has a slope of 0.6 which provides a reasonable fit for $T \sim 28–39$ K, but this extends well away from the temperature interval expected for critical fluctuations. It compares with 0.29 $\pm$ 0.03 [60] and 0.13 [62] reported for immediately below $T_N$ from measurements at $\sim 10–60$ MHz in MnF$_2$ and 0.55 $\pm$ 0.06 at $\sim 0.1–1$ MHz in Fe$_2$O$_3$ [67]. In spite of the scatter in
the data, there appears to be a discernible dispersion with frequency, as shown by data for $\Delta Q^{-1}$ in figure 6(b) at three temperatures immediately below $T_N$ (37.6, 36.6, and 35.6 K). These variations are expected to conform to normal Debye-like behaviour, where

$$Q^{-1}(\omega \tau) = \Delta \frac{\omega \tau}{1 + (\omega \tau)^2}$$  \hspace{1cm} (12)

$$M(\omega \tau) = M_U - M_0 \Delta \frac{1}{1 + (\omega \tau)^2}$$  \hspace{1cm} (13)

and

$$\Delta = \frac{M_U - M_R}{M_0}. \hspace{1cm} (14)$$

$M_U$ is the unrelaxed modulus, $M_R$ the relaxed modulus and $M_0 = (M_U M_R)^{1/2}$. The observations are that $\Delta Q^{-1}$, the loss component associated with the antiferromagnetic structure, increases with increasing frequency in a manner that may not be far from linear (figure 6(b)), which is consistent with $\omega \tau \ll 1$. The relaxation time immediately above $T_N$ in MnF$_2$ is $\sim 3 \times 10^{-9}$, as determined by Kawasaki and Ikushima [68] and Moran and Lüthi [69] from measurements of acoustic velocity and attenuation at 10 MHz. At 1 MHz this would give $\omega \tau \approx 0.02$.

For a small change in the observed modulus, $\delta M = M_U - M(\omega \tau)$, equations (12)–(14) can be combined to give

$$\frac{Q^{-1}}{\delta M / M} \approx \omega \tau,$$  \hspace{1cm} (15)

which may be used to say something about the relaxation times at $T < T_N$. For direct comparability it is necessary to divide the values of $\Delta Q^{-1}$ given above by $\sqrt{3}$, to take account of the fact that $Q^{-1}$ obtained from widths of the amplitude of resonance peaks is a factor of $\sim \sqrt{3}$ larger than the true value [70–73]. Using $\Delta Q^{-1} = 0.0015/\sqrt{3}$ as representing $Q^{-1}$ at $T_N$ when measured at $\sim 1882$ kHz would give $\delta M / M = 0.02$ as the expected amount of anelastic softening if the relaxation time of the loss mechanism remained at $3 \times 10^{-9}$ s. However, this is an order of magnitude larger than the frequency-dependent variations of $\Delta f^2 / f_0^2$ shown in figure 6(b), signifying that the loss mechanism below $T_N$ has a relaxation time which is at least an order of magnitude slower than just above $T_N$. In order to obtain absolute values for $\tau$, it is necessary to estimate values for the equivalent of the unrelaxed modulus, $M_U$, but the data for $\Delta f^2 / f_0^2$ are too scattered for this. (A substantial part of the experimental uncertainty arises from the choice of $f_0$ and the relatively narrow range of frequencies which can be obtained by RUS.) Nevertheless, the relatively steep decline in $\Delta Q^{-1}$ with decreasing temperature in the interval of $\sim 20$ K below $T_N$ is most likely due to a significant lowering of the relaxation time with decreasing temperature and this is counter to what would be expected for a thermally activated loss mechanism. As also proposed by Moran and Lüthi [69], this is more in line with the Landau–Khalatnikov relation for critical slowing down [74]

$$\tau = \frac{\tau_0 T_c}{|T - T_c|}, \hspace{1cm} (16)$$

where $T_c$ is the critical temperature ($T_N$ in this case) and $\tau_0$ is a constant. If $\tau$ scales approximately with $\Delta Q^{-1}$, this would give a slope of $-1$ in figure 6(a) and a dashed line with this slope is included as a guide to the eye.

The inverse susceptibility, $\chi^{-1} = \partial^2 \tilde{G}/\partial \tilde{Q}_m^2$, would go linearly to zero at $T_N$ for an order parameter evolution which follows Landau tricritical behaviour and this could be the dominant factor in determining the temperature dependence of the relaxation time over a temperature interval of at least 20 K below $T_N$, which is well beyond the expected range of any critical fluctuations. The most straightforward model is then of spin–lattice coupling in which there is an adjustment of $Q_m$ to an applied stress through the strain/order parameter coupling terms. The restoring force would depend on $\chi^{-1}$, though a small thermal barrier could still operate. In other words, the small strain induced in the RUS experiment, which may be $\sim 10^{-6}$ [72], would simply cause an adjustment in the degree of magnetic order with a small phase lag.

7. Discussion

Apart from there being different driving mechanisms, i.e. antiferromagnetic ordering rather than softening of an optic
phonon, variations in the strain, elastic and anelastic properties which accompany the phase transition in CoF$_2$ are remarkably similar in form to those shown by quartz at the $\beta$ (hexagonal) $\leftrightarrow\alpha$ (trigonal) transition [51, 75, 76]. Both transitions are co-elastic, i.e. they do not involve a symmetry-breaking (shear) strain, both have non-symmetry-breaking strains which scale with the square of the order parameter, and the order parameter evolution with temperature in each case can be represented as being close to tricritical. Both show non-linear softening of elastic constants below the transition point and small increases in acoustic dissipation across a narrow temperature interval around the transition point. The Slonczewski–Thomas softening mechanism involves relaxation of the order parameter in response to changes of strain when an external stress is applied. To be observed, this relaxation must occur on a timescale which is shorter than that of the strain response, $\sim 10^{-6}$ s in this case. All the data presented here are consistent with this pattern of behaviour. The order parameter susceptibility would not be expected to be that for a displacive system, and an order–disorder model not dissimilar from the Bragg–Williams model of a spin 1/2 system would produce a more nearly quantitative alternative.

Differences in the magnitude of softening between quartz and CoF$_2$ ($\sim 2\%$ softening of the shear modulus of CoF$_2$ but $\sim 80\%$ and $\sim 8\%$ for $K$ and $\mu$, respectively, in quartz [76]), and between magnetic ordering versus displacive systems more generally, can be understood in terms of the strength of the strain coupling and the magnitudes of the entropies involved. For example, the amount of softening at a second order co-elastic transition scales with $\lambda^2/b$, where $b$ is the Landau fourth order coefficient, excluding renormalization by coupling with strain, and is close to being equal to $aT_c$ ($a$ is the Landau coefficient for the second order term, $T_c$ the transition temperature). For a tricritical transition, $b \approx 0$ and $c = aT_c$, where $c$ is the coefficient for the sixth order term. Spontaneous strains are about an order of magnitude larger in quartz than they are in CoF$_2$, so $\lambda^2$ will be approximately two orders of magnitude greater. In quartz, the total excess entropy is $\sim 4.9 \, J \, K^{-1} \, mol^{-1}$ [75], in comparison with a total excess entropy for CoF$_2$ of $\sim 4 \, J \, K^{-1} \, mol^{-1}$ so, as a first approximation, the $a$ coefficients will be similar. $T_c$ for the quartz transition is $\sim 840$ K, in comparison with 39 K, so the $c$ coefficient will be comparably larger, and this will reduce the difference in expected softening by approximately one order of magnitude, which is not far from what is observed.

Displacive systems more typically have smaller excess entropies and strains of a few $\%$. For example, symmetry-breaking shear strains up to $\sim 0.002$ and volume strains up to $\sim 0.005$ accompany the (soft mode) octahedral tilting transition in LaAlO$_3$, and the total excess entropy is $< 2 \, J \, K^{-1} \, mol^{-1}$ [77]. Softening of the shear and bulk moduli below the second order transition at $T_s = 817$ K amounts to $\sim 40\%$ and $\sim 25\%$ respectively [72]. Tilting transitions in SrZrO$_3$ are accompanied by shear and volume strains of up to $\sim 0.003$, $\sim 0.002$, respectively, together with softening of the shear and bulk moduli by up to $\sim 40\%$ and $\sim 8\%$ [78]. The effective (non-symmetry-breaking) shear strain accompanying antiferromagnetic ordering in CoF$_2$ can be expressed in terms of the tetragonal strain $e_t = \frac{1}{2}(2e_3 - e_1 - e_2)$ which reaches a maximum value of $\sim 0.002$, and the volume strain $(2e_1 + e_3)$ reaches a maximum value of $\sim 0.001$. Thus the shear strains are comparable, but the volume strain is smaller. The associated elastic anomalies should be smaller, due to the larger excess entropy, but greater for the shear modulus than for the bulk modulus, exactly as observed.

Given that the general pattern of softening shown by the bulk elastic properties of CoF$_2$ conforms to the Slonczewski–Thomas mechanism, it must be expected that the variations of single crystal elastic constants at $T < T_N$ will be described correctly by the equations in table 1. While there are no available single crystal data for CoF$_2$, data for effectively the same transition in MnF$_2$ [59] support this view. Each of $C_{44}$, $C_{66}$ and 1/2 ($C_{11} - C_{12}$) show continuous variations through the Néel point with increasing differences from the bare elastic constants which would scale with $Q^2$, but $C_{11}$ and $C_{13}$ show the characteristic dip due to the influence of the inverse susceptibility, $\chi$. Some influence of pseudopropor ferroelastic softening of 1/2 ($C_{11} - C_{12}$), across a temperature interval of at least $\sim 300$ K as $T \rightarrow T_N$ from above, is also seen however. This is attributable to the $P_{42/mnm} \leftrightarrow P_{nmm}$ instability somewhere not far away in pressure–temperature parameter space, since a soft optic mode has been observed by Schleck et al [79]. Contributions from Jahn–Teller cooperative transitions to the elastic softening can be ruled out in the light of the structural data which shows significant distortions of the CoF$_6$ octahedra that are closely similar at 15 and 300 K [17].

Acoustic dissipation associated with shear modes at the $\beta \leftrightarrow \alpha$ transition in polycrystalline quartz is also low, and, as in CoF$_2$, rises to a distinct maximum at the transition temperature [76]. Softening as $T \rightarrow T_c$ from above is not accompanied by any obvious tail in the strain [75], however, and the power law dependency is entirely consistent with a phonon mechanism and fluctuations. In contrast, the pattern of softening in CoF$_2$, which occurs in the temperature interval where there is a tail in the strain, is represented better by a Vogel–Fulcher expression. The softening mechanism is presumed to involve dynamical order/disorder of spin orientations which couple with the acoustic modes, perhaps with a low thermal barrier for reversal of some spin orientations within relatively well ordered clusters. The drop in relaxation time below $T_N$ is consistent with a different loss mechanism operating, and the simplest mechanism which might give the observed temperature dependence would involve spin–lattice coupling and restoring forces responding to an applied stress which depend substantially on the susceptibility of the magnetic order parameter.

Finally, an additional magnetoelastic contribution could be due to piezomagnetism. Previous theoretical studies [80] have predicted that CoF$_2$ might have a significant piezomagnetic effect based on considerations of the crystal symmetry [81]. A linear compression in the $a$–$b$ plane would give rise to a magnetization along the $c$–axis, which is also the axis for sublattice alignment in the antiferromagnetic state. Recently it was suggested that the piezomagnetic effect might cause a linear relationship between the strain and the induced ferromagnetic moment [82]. If this holds true for the
present case, the relationship between the antiferromagnetic order parameter, $Q_{\text{AFM}}$, and induced ferromagnetic order parameter, $Q_{\text{FM}}$, would be $Q_{\text{FM}} \propto Q_{\text{AFM}}^2$, since the strain is proportional to the square of the antiferromagnetic order parameter. However there is no direct evidence for a separate contribution from piezomagnetism in the data presented here.

8. Conclusions

In combination, elastic and anelastic properties measured by RUS for CoF$_2$ in the present study, together with lattice parameter and heat capacity data from the literature, reveal patterns of spin–lattice coupling and dynamics which are likely to be characteristic of aspects of magnetic transitions in insulating oxides. In particular:

(1) Elastic softening at $T < T_N$ can be understood in terms of the same phenomenological strain/order parameter coupling as occurs in displacive systems. Although the order parameter relates to spin ordering, it evolves in a manner that is not far from the Landau tricritical solution for a displacive system. Differences in the magnitudes of the softening can then be understood in terms simply of differences in the strength of coupling, which tends to be weaker in magnetic systems than for displacive transitions.

(2) It is proposed that elastic softening, $\Delta C$, at $T > T_N$ can be understood in terms of dynamical ordering of spin orientations, possibly with a small activation energy barrier for local reorientations, and coupling of these with acoustic modes. The short range ordering is sufficient to give a measurable tail in strain, $e$, which scales simply as $e^2 \propto \Delta C$.

(3) Relaxation times for spin–lattice coupling associated with the antiferromagnetic ordering transition in CoF$_2$ are sufficiently fast that, when measured at $\sim 1$ MHz by RUS, there is no evidence of acoustic attenuation in the dynamical region above $T_N$. Slowing down of the spin–lattice coupling as $T \rightarrow T_N$ is sufficient to result in a small but significant peak in acoustic attenuation. At $T < T_N$, the relaxation times appear to show a weak temperature dependence which correlates, at least qualitatively, with the intrinsic order parameter susceptibility.

(4) CoF$_2$ provides a model for the likely antiferromagnetic part of magnetoelastic behaviour in more complex ferroic materials with additional displacive instabilities, Jahn–Teller effects and ferroelastic microstructures. A complete understanding of this behaviour remains incomplete, however, in view of the fact that in other selected systems, such as hexagonal YMnO$_3$ [83] and the organic radical $\beta$-p-NCC6F4CNSSN [82], antiferromagnetic ordering is accompanied by elastic stiffening, rather than softening.

Appendix. Strain coupling and order parameter evolution

In order to analyse the spontaneous strains associated with antiferromagnetic ordering in CoF$_2$, a baseline of the form [49, 84]

$$a_0 = a_1 + a_2 \theta_s \coth \left( \frac{\theta_s}{T} \right) \quad (A.1)$$

was first fit to the $c$ lattice parameter data from Chatterji et al [19]. This provided a constrained value for $\theta_s$ to use in the subsequent fitting of the $a$ parameter (figure A.1).

Values of $e_1$ and $e_3$ were calculated in the usual way from the excess in the lattice parameters below the magnetic transition, i.e. $e_1 = (a - a_0)/a_0$, $e_3 = (c - c_0)/c_0$, and are given in figure A.2. Data for the intensities of antiferromagnetic superlattice reflections from neutron diffraction experiments ($I_{100} \propto Q_{m}^2$, data of [19]), have been added to confirm that this treatment gives the expected dependence on $Q_{m}^2$. The correlation for $e_3$ is close over the entire temperature interval, while $e_1$ correlates closely below $\sim 38$ K but has a tail above $T_N$ that extends up to $\sim 120$ K. Correlations between the trends shown for $e_1$ and $e_3$ with respect to $I_{100}$ are more robust than in the original analysis of Chatterji et al [19] probably because of the choice of baseline used here for calculating the strains.

Variations of the equilibrium order parameter derived from equation (1) have the form [49, 84, 85]

$$Q_{m}'' = \Lambda \frac{\Theta_{s}}{T_c} \left( \coth \left( \frac{\Theta_{s}}{T} \right) - \coth \left( \frac{\Theta_{s}}{T_c} \right) \right), \quad (A.2)$$

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Figure A.2. Comparison of spontaneous strains calculated from the data shown in figure A.1 with intensities of the 100 Bragg peak ($\propto Q_{2m}^2$) in powder neutron diffraction patterns (from original data of Chatterji et al [19]; intensities have been corrected to account for nuclear contributions).

where $A$ is a constant, and $n = 2$ for a second order transition or $n = 4$ when it is tricritical. Using $I_{100}$ to represent $Q_{2m}^2$, fits of equation (A.2) in figure A.3(a) show that the evolution of the order parameter can be adequately represented by a Landau tricritical solution with $\Theta_s = 95$ K. Order parameter variations derived from the Brillouin function for systems with spin $3/2$ or spin $1/2$ [86, 87] do not fit the data as well (figure A.3(b)). A second order solution ($n = 2$) does not quite give as good a description as the tricritical solution ($n = 4$). Also shown are equivalent intensity data for the antiferromagnetic transition in FeF$_2$ from Chatterji et al [19], which can be described using the same function for tricritical character, with $\Theta_s = 60$ K ($T_c = 79$ K). Strempfer et al [16] showed that Ising behaviour also provides a reasonable representation of the sublattice magnetization (their figure 4).

Equation (A.2) represents the solution for a displacive system but, in this case, the behaviour is close to the order/disorder limit as can be shown from considerations of the excess entropy. Heat capacity data from Catalano and Stout [24] have been used to determine the observed excess entropy associated with the magnetic phase transition. A baseline of the form of equation (A.1) was fit to the low temperature heat capacity data as shown in figure A.4. This gave an excess heat capacity, $\Delta C_p$, from which the excess entropy and enthalpy were calculated as

$$\Delta S = \int \frac{\Delta C_p}{T} \, dT$$

(A.3)

$$\Delta H = \int \Delta C_p \, dT.$$  

(A.4)

Figure A.3. Fits of equation (A.2) to neutron diffraction intensity data ($I_{100} \propto Q_{2m}^2$) for CoF$_2$ (red crosses) and FeF$_2$ (blue circles), for $n = 4$ (a) and $n = 2$ (b). For CoF$_2$ the fit was to data from figure A.2 between 2.5 K and $T_c = 39$ K, giving a proportionality constant (with $I_{100}$ in place of $Q_{2m}^2$) of $3.5794 \times 10^5$ and $\Theta_s = 95.48$ K ($n = 4$) or $2.827 \times 10^5$, 90.70 K ($n = 2$). Intensity data for FeF$_2$ were taken from Chatterji et al [19]; the fit for $n = 4$ gave a proportionality constant of $1.7763 \times 10^9$ and $\Theta_s = 60.17$ K. Also shown (right axis, bottom) are solutions to the Brillouin function for systems with $S = 3/2$ and $1/2$.

Variations of the excess entropy and enthalpy obtained in this way are shown in figures A.5(a) and (b), respectively, along with $I_{100} \propto Q_{2m}^2$.

The measured excess entropy does not scale linearly with the measured variation of $Q_{2m}^2$ and the susceptibility, $\chi$, derived from equation (1) would not provide a quantitative description of the elastic softening, therefore. The simplest model which would reproduce, semiquantitatively, the variations of $Q_{2m}^2$, $\Delta H$ and $\Delta S$ is one site (spin $1/2$, $n = 1$) Bragg–Williams ordering. The order parameter would be expected to vary according to

$$Q_m = \tanh \left( \frac{T_c Q_m}{T} \right)$$

(A.5)

which is the solution derived from the Brillouin function for spin $1/2$ and is closer to the variation of Landau tricritical than Landau second order [88]. Addition of saturation to the Landau expansion would make the variation of tricritical and Bragg–Williams solutions even more similar. The excess enthalpy would be expected to scale linearly with $Q_{2m}^2$. 

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Figure A.4. Heat capacity data taken from Catalano and Stout [24] fitted with a baseline of the form of equation (A.1) in the temperature range 0–80 K. Fit coefficients are $a_1 = -14.647$ J K$^{-1}$ mol$^{-1}$, $a_2 = 0.485$ J mol$^{-1}$ and $\theta_s = 30$ K.

Figure A.5. Variation of the excess entropy (a) and excess enthalpy (b) from integration of the excess heat capacity in figure A.4. The intensity of antiferromagnetic superlattice reflections ($I_{100} \propto Q_m^2$) is shown for comparison (right axis). Also shown is the excess entropy for the Bragg–Williams description of a one site ordering system, $\Delta S_{BW}$, calculated using equation (A.7) and values of $Q_m$ determined from $I_{100}$ values scaled to 1 at low temperature. According to

$$\Delta H_{BW} = -\frac{n}{2}RT_c Q_m^2$$

(A.6)

and the excess entropy would vary with $Q_m$ according to

$$\Delta S_{BW} = \frac{nR}{2}((1 + Q_m) \ln(1 + Q_m)$$

$$+ (1 - Q_m) \ln(1 - Q_m))$$

$$= -\frac{nR}{2} \left( Q_m^3 + \frac{1}{6}Q_m^4 + \frac{1}{15}Q_m^6 + \cdots \right)$$

(A.7)

where $n = 1$ and $R$ is the gas constant. Values of $Q_m$ estimated from the $I_{100}$ data, scaled to 1 at low temperature, have been used to calculate $\Delta S_{BW}$ as shown in figure A.5(a). Although the model values are somewhat higher than values derived from the excess heat capacity (figure A.5(b)), the form of variation is correct. Using $T_c = 39$ K and $Q_m = 1$ for complete order, equation (A.4) gives $|\Delta H_{BW}| = 162$ J mol$^{-1}$. This is higher than ‘observed’ but the form is again correct. A degree of short range ordering ahead of the Néel point, not included because of the choice of baseline used to determine $\Delta C_p$, would contribute to the differences between observed and calculated values for both the excess enthalpy and entropy.

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