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Elastic and anelastic anomalies associated with the antiferromagnetic ordering transition in wüstite, Fe\textsubscript{x}O

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Abstract

The elastic and anelastic properties of three different samples of Fe\textsubscript{x}O have been determined in the frequency range 0.1–2 MHz by resonant ultrasound spectroscopy and in the range 0.1–50 Hz by dynamic mechanical analysis in order to characterize ferroelastic aspects of the magnetic ordering transition at \( T_N \sim 195 \) K. No evidence was found of separate structural and magnetic transitions but softening of the shear modulus was consistent with the involvement of bilinear coupling, \( \lambda e_4 q \), between a symmetry-breaking strain, \( e_4 \), and a structural order parameter, \( q \). Unlike a purely ferroelastic transition, however, \( C_{44} \) does not go to zero at the critical temperature, \( T_c^\ast \), due to the intervention of the magnetic ordering at a higher temperature. The overall pattern of behaviour is nevertheless consistent with what would be expected for a system with separate structural and magnetic instabilities, linear–quadratic coupling between the structural (\( q \)) and magnetic (\( m \)) driving order parameters, \( \lambda q m^2 \), and \( T_N > T_c^\ast \). Comparison with data from the literature appears to confirm the same pattern in MnO and NiO, with a smaller difference between \( T_N \) and \( T_c^\ast \) in the former and a larger difference in the latter. Strong attenuation of acoustic resonances at high frequencies and a familiar pattern of attenuation at low frequencies suggest that twin walls in the rhombohedral phase have typical ferroelastic properties. Acoustic dissipation in the stability field of the cubic phase is tentatively attributed to anelastic relaxations of the defect ordered structure of non-stoichiometric wüstite or of the interface between local regions of wüstite and magnetite, with a rate controlling step determined by the diffusion of iron.

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

1. Introduction

Wüstite, Fe\textsubscript{x}O, grown under most laboratory conditions is non-stoichiometric with some iron deficiency (0.88 < \( x < 1 \)). It is one end member of the (Mg, Fe)O solid solution, which is abundant in the lower mantle of the Earth, and potentially a chemical component of the inner core of the Earth (e.g. Ringwood 1977, Ohtani and Ringwood 1984, Kato and Ringwood 1989, Knittle and Jeanloz 1991, Jacobsen et al 2005, Asahara et al 2007, Ozawa et al 2008, Fischer et al 2011b). Over the years extensive efforts have been made to understand its diverse structural, magnetic, electrical, thermal and elastic properties (e.g. Jette and Foote 1933, Bizette and Tsai 1943, Chen and Peterson 1975, Jeanloz and Hazen 1983, McCammon and Liu 1984, Fei and Mao 1994, Zhang 2000, Zhang and Zhao 2005, Ono et al 2007, Ovsyannikov et al 2011a).
and polycrystalline Fe in 1980, Berger et al., has used a multi-function Kappabridge. A superconducting quantum interference device (SQUID) and magnetic properties have been checked independently using measurements made somewhere through the frequency should be a crossover between relaxed and unrelaxed states if as proposed, there can be a separate stability field for a cubic antiferromagnetic structure, it follows that there may be separate phase transitions which are primarily magnetic or structural in character. A formal Landau description of two distinct but coupled instabilities has recently been compared with strain and magnetic order parameter data from the literature to test this possibility (Carpenter et al. 2012). It is clear that there must be coupling between the magnetic and structural order parameters, but the data do not have sufficient resolution to indicate unambiguously that they ever develop at separate transition points. A better test of the model would be provided by comparison of observed and predicted elastic constants since the variation of these is known to be a highly sensitive indicator of the transition mechanism in materials with spontaneous strain/order parameter coupling (e.g. Carpenter and Salje 1998).

The second issue addressed here relates to anelastic properties. Kantor et al. (2008) have proposed that, following the initial suggestion of Jeanloz and Hazen (1983), discrepancies between measurements of bulk modulus by static and dynamic methods are due to the relaxation of defect clusters in non-stoichiometric samples. Data presented in support of this argument were obtained under static conditions (equation of state from diamond anvil cell experiments) from ultrasonic interferometry at GHz frequencies and from inelastic x-ray scattering at phonon frequencies. If the discrepancy is due to anelasticity, as proposed, there should be a crossover between relaxed and unrelaxed states in measurements made somewhere through the frequency range 0–10^5 Hz. Resonant ultrasound spectroscopy (RUS) at ~0.1–2 MHz and dynamic mechanical analysis (DMA) at 0.1–50 Hz have therefore been used to explore both the elastic and anelastic properties of FeO at ambient pressure. Results for three different samples are presented: single-crystal FeO, polycrystalline FeO, and a polycrystalline mixture of 69 wt% FeO + 31 wt% Fe2O4. Their magnetic properties have been checked independently using a superconducting quantum interference device (SQUID) and a multi-function Kappabridge.


2. Sample preparation and experimental details

The first sample used in this study was a single crystal with composition FeO. This was part of the same crystal as used by Jackson et al. (1990) for measurements of ultrasonic velocity in the [100] direction. It had the form of a cylinder ~5 mm in diameter and mass 0.5836 g, with parallel faces cut at an angle to the cylinder axis ~4.4 mm apart. The two other samples were prepared from FeO powder purchased from Sigma-Aldrich. The powder was ground in acetone at 600 rpm for 1 h using a Fritsch Pulverisette 7 agate mill. Approximately 1 g and 3 g of powder were pressed into cylindrical pellets of diameters ~6 mm and ~13 mm, respectively, under ~1800 psi pressure for 5 min. The pellets were vacuum sealed in fused quartz tubes, sintered at 1223 K for 48 h and then quenched into water. Rectangular parallelepipeds for RUS and DMA measurements were cut from the pellets using an annular diamond saw lubricated with paraffin. An offcut of each pellet was crushed and ground using a mortar and pestle, and then investigated by x-ray diffraction using a Bruker D8 diffractometer with Cu Kα radiation at 40 kV and 40 mA. The diffraction angle 2θ was scanned from 10° to 120°. Steps were in increments of 0.007°, and intensities were counted for 10 s at each step. For the pellet of diameter ~6 mm, the diffraction pattern was consistent with the cubic Fe3O4 structure of FeO, without any detectable impurity phase. On the other hand, for the pellet of diameter ~13 mm, the diffraction...
pattern indicated a mixture of wüstite and magnetite (Fe₃O₄). Rietveld refinements of the x-ray diffraction patterns using GSAS and EXPGUI (Larson and Von Dreble 2000, Toby 2001) showed that the polycrystalline sample had lattice parameter \( a = 4.3103 \pm 0.0001 \) Å and the mixture was composed of 69 wt% Fe₃O₄ with \( a = 4.2914 \pm 0.0001 \) Å plus 31 wt% Fe₃O₄ with \( a = 8.3973 \pm 0.0004 \) Å. McCammon and Liu (1984) reported the dependence of the lattice parameter on composition as \( a = 3.856 + 0.478x \), giving \( x = 0.950 \) for the single-phase sample and 0.911 for Fe₃O₄ in the two-phase mixture.

RUS measurements were made on the single-crystal sample without any further preparation. The parallellepped of polycrystalline Fe₀.₉₅₀ for RUS measurements had dimensions \( 3.32 \times 2.73 \times 2.23 \) mm³, mass 0.098 g and density 4.83 g cm⁻³, which is 82% of the theoretical density 5.91 g cm⁻³ (Katsura et al 1967). The parallellepped of the mixture of 69 wt% Fe₀.₉₁₁ and 31 wt% Fe₃O₄ had dimensions \( 2.73 \times 2.01 \times 0.71 \) mm³, mass 0.0175 g and density 4.49 g cm⁻³. RUS data were collected between 5 and 305 K using a dynamic resonance system (DRS), a factor of \( \sim \) to the square of the amplitude, but the difference is only other measures of damping should be obtained from fitting.

Values of the inverse quality factor, \( Q^{-1} \), were determined by fitting 27 resonance peaks in RUS spectra. Data were collected during cooling at 5 K and was tested by three-point bending over 80 and 280 K in an applied field of 711 A m⁻¹ (i.e. 9 Oe).

### 3. Results

Figure 1 shows the temperature dependences of \( \chi \) from the three samples. For single-crystal Fe₀.₉₄₅ and single-phase polycrystalline Fe₀.₉₅₀, the maximum in susceptibility occurred at 195 ± 1 K, which has been taken as the value of \( T_N \). The Fe₀.₉₄₅ single crystal was used without further preparation. The magnetic measurements on Fe₀.₉₅₀ and Fe₀.₉₁₁+Fe₃O₄ were made on 0.120 and 0.113 g of powder, respectively. Susceptibility \( \chi \) was determined from \( \chi = M/H \). Separate measurements of susceptibility of 0.052 g powdered Fe₀.₉₅₀ and 0.089 g Fe₀.₉₁₁+Fe₃O₄ were made using a multi-function Kappabridge between 80 and 280 K in an applied field of 711 A m⁻¹ (i.e. 9 Oe).

\[
E = \beta F_d \exp(i\delta) / (4\pi^2 \omega_d),
\]

where \( h \) is the height of the sample, 2.69 mm, and \( A \) is the base area of the sample, 0.746 mm². For three-point bending

\[
E = \beta F_d \exp(i\delta) / (4\pi^2 \omega_d),
\]

where \( l \) is the spacing between the two bottom knife edges, 5.00 mm, \( t \) is the thickness of the sample, 0.29 mm, and \( w \) is the width of the sample, 2.01 mm. Data were collected during continuous cooling and heating at 1 K min⁻¹ with a sampling time of 3 s. The displacement amplitude was 5 \( \mu \)m. Absolute values of \( E' \) were not expected to be reliable, but the main interest was in relative changes of \( E' \) and \( \tan \delta \).

Magnetic moment \( M \) was measured using a SQUID magnetometer from Quantum Design Inc. in the temperature range 5–330 K, with a heating and cooling rate of 2 K min⁻¹ and an applied field, \( H \), of \( 1.99 \times 10^5 \) A m⁻¹ (i.e. 2500 Oe). The Fe₀.₉₄₅ single crystal was used without further preparation. The magnetic measurements on Fe₀.₉₅₀ and Fe₀.₉₁₁+Fe₃O₄ were made on 0.120 and 0.113 g of powder, respectively. Susceptibility \( \chi \) was determined from \( \chi = M/H \). Separate measurements of susceptibility of 0.052 g powdered Fe₀.₉₅₀ and 0.089 g Fe₀.₉₁₁+Fe₃O₄ were made using a multi-function Kappabridge between 80 and 280 K in an applied field of 711 A m⁻¹ (i.e. 9 Oe).
Table 1. Summary of density and elastic constants of polycrystalline (PC) and single-crystal (SC) Fe$_x$O as measured by dynamic methods at ambient conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ρ (g cm$^{-3}$)</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
<th>$K$ (GPa)</th>
<th>$\mu$ (GPa)</th>
<th>$E$ (GPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{0.95}$O (PC)</td>
<td>4.83</td>
<td>85.9</td>
<td>34.2</td>
<td>90.7</td>
<td>34.2</td>
<td>90.7</td>
<td>This study</td>
<td></td>
</tr>
<tr>
<td>Fe$_{0.911}$O + Fe$_3$O$_4$ (PC)</td>
<td>4.49</td>
<td>78.0</td>
<td>32.3</td>
<td>84.9</td>
<td>32.3</td>
<td>84.9</td>
<td>This study</td>
<td></td>
</tr>
<tr>
<td>Fe$_{0.95}$O (PC)</td>
<td>5.51</td>
<td>125.7</td>
<td>44.9</td>
<td>120.4</td>
<td>44.9</td>
<td>120.4</td>
<td>Akimoto (1972)</td>
<td></td>
</tr>
<tr>
<td>Fe$_{0.95}$O (SC)</td>
<td>5.68</td>
<td>228.5</td>
<td>128.6</td>
<td>162.0</td>
<td>48.1</td>
<td>131.3</td>
<td>Sumino et al (1980)</td>
<td></td>
</tr>
<tr>
<td>Fe$_{0.95}$O (SC)</td>
<td>5.68</td>
<td>239.6</td>
<td>139.6</td>
<td>173.0</td>
<td>48.3</td>
<td>132.6</td>
<td>Sumino et al (1980)</td>
<td></td>
</tr>
<tr>
<td>Fe$_{0.945}$O (SC)</td>
<td>5.71</td>
<td>218.4</td>
<td>123.0</td>
<td>154.8</td>
<td>46.4</td>
<td>126.6</td>
<td>Jackson et al (1990)</td>
<td></td>
</tr>
<tr>
<td>Fe$_{0.945}$O (SC)</td>
<td>5.71</td>
<td>218.4</td>
<td>123.0</td>
<td>154.8</td>
<td>46.4</td>
<td>126.6</td>
<td>Jackson et al (1990)</td>
<td></td>
</tr>
<tr>
<td>Fe$_{0.95}$O (SC)</td>
<td>217.0</td>
<td>121.0</td>
<td>45.9</td>
<td>153.0</td>
<td>46.8</td>
<td>127.4</td>
<td>Sumino et al (1980)</td>
<td></td>
</tr>
<tr>
<td>Fe$_{0.95}$O (SC)</td>
<td>217.0</td>
<td>121.0</td>
<td>45.9</td>
<td>153.0</td>
<td>46.8</td>
<td>127.4</td>
<td>Sumino et al (1980)</td>
<td></td>
</tr>
</tbody>
</table>

Note that data given as being from Sumino et al (1980) have been recalculated from the list of resonance frequencies given in their table 2 with an overall root mean square error for the fitting of 0.3%.

Figure 1. Temperature dependences of magnetic susceptibility $\chi$ for single-crystal (SC), Fe$_{0.945}$O, polycrystalline (PC), Fe$_{0.95}$O powder, and a mixture (Mix) of Fe$_{0.911}$O and Fe$_3$O$_4$ determined by a multi-functional Kappabridge (Bridge) and SQUID. The magnetic properties of the two-phase mixture (b) are dominated by the properties of magnetite obscuring the magnetic ordering of Fe$_{0.911}$O. The vertical dotted line marks the expected temperature for the Verwey transition in magnetite (120 K) and the dashed–dotted line shows the maximum in susceptibility for the single-crystal and single-phase polycrystalline sample (195 ± 1 K).

lower frequencies with decreasing temperature and disappear below ~187 K. For Fe$_{0.911}$O + Fe$_3$O$_4$, the resonance peaks shift to lower frequencies with decreasing temperature and then slightly shift to higher frequencies below ~180 K.

Figure 2. RUS spectra of wüstite samples. (a) Single-crystal Fe$_{0.945}$O. (b) Polycrystalline Fe$_{0.95}$O. (c) Mixture of Fe$_{0.911}$O (69 wt%) + Fe$_3$O$_4$ (31 wt%). The y axis is amplitude, but the spectra have been offset in proportion to the temperature at which they were collected, and consequently the axis is labelled as temperature.

Data for normalized frequency squared $(f/f_0)^2$ and $Q^{-1}$ from selected resonances in the primary RUS spectra are shown as a function of temperature in figure 3. $f_0$ is the resonance frequency at 300 K. Figure 3(a) contains data from the single-crystal sample. All the resonances show some softening with falling temperature and all continue to soften through the Néel temperature (195 K). $Q^{-1}$ has small values above 195 K but there is then a steep increase beginning either
at 195 K or a few degrees above it. This steep increase in peak widths means that it is not possible to follow individual resonances to temperatures below 187 K, with the exception of one near 0.52 MHz at room temperature which has a distinct minimum in \(f\) at \(\sim 175\) K, followed by a steady recovery to higher values with falling temperature. Even this peak was hard to follow, however, and the frequencies shown in figure 3(a) are uncertain at the lowest temperatures.

Figure 3(b) shows similar data for the polycrystalline \(\text{Fe}_{0.92}\text{O}\) sample. In this case, values for the shear modulus \(\mu_{\text{cal}}\) and bulk modulus \(K_{\text{cal}}\) were also obtained by the fitting of 27 resonance peaks, with an overall root mean square error of \(\sim 0.3\%\). These are shown in figure 3(c). As with the single crystal, elastic softening with falling temperature continued through \(T_N\) (=195 K) before the resonance peaks disappeared at \(\sim 190\) K. In contrast with the single-crystal data, however, \(Q^{-1}\) shows barely any change at \(T_N\) and the steep rise begins at \(\sim 190–192\) K. Also in contrast with the single-crystal data, there is some dispersion in \(Q^{-1}\) above 195 K, such that a peak near \(\sim 0.35\) MHz has a steady increase with increasing temperature and perhaps a maximum at 295 K, the peak near 0.47 MHz has a smaller increase and the peak near 1.54 MHz shows only a slight increase. It was not possible to follow any resonance to low temperatures. Values of the bulk and shear moduli derived from single-crystal measurements on \(\text{Fe}_{0.92}\text{O}\) (Sumino et al 1980) have been added to figure 3(c) for comparison with the new data for \(\text{Fe}_{0.95}\text{O}\). They show rather similar dependences. The new data for \(K\) show a slight decrease with falling temperature.

\(Q^2\) and \(Q^{-1}\) data for the mixture of \(\text{Fe}_{0.91}\text{O}\) and \(\text{Fe}_3\text{O}_4\) are shown in figure 3(d). Although it was not possible to get an independent measurement of \(T_N\) for this sample, due to the overwhelming magnetic properties of magnetite, the compilation of data in McCammon (1992) gives an expected value of \(\sim 205\) K. All three of the resonance peaks analysed in detail soften in the same manner with \(T\to T_N\) from above, and then more steeply through 205 K. They have a minimum at \(\sim 180\) K and then recover to some extent. Two of the peaks give \(Q^{-1}\) values which increase steeply below \(\sim 205\) K, and there is perhaps an intermediate peak in the \(Q^{-1}\) variation with temperature at \(\sim 190–195\) K.

Figure 4 shows the temperature dependences of the storage modulus \(E'\), loss modulus \(E''\) and energy dissipation \(\tan\delta\) determined by DMA at low frequencies (0.1–50 Hz) for polycrystalline \(\text{Fe}_{0.95}\text{O}\) with parallel plate compression geometry. Marked elastic softening occurs through the Néel point (195 K), reaching a minimum between \(\sim 185\) and 190 K. Data for \(\tan\delta\) are rather scattered but there is a steep increase below \(\sim 190–195\) K and a maximum at \(\sim 170–190\) K for most frequencies. \(\tan\delta\) values are markedly lower at 0.1 and 1 Hz than at higher frequencies, however. There do not appear to be systematic variations of the observed properties below the Néel point but, at higher temperatures, \(\tan\delta\) appears to have a maximum in the vicinity of 10–20 Hz (figure 5).

DMA data for the mixture of \(\text{Fe}_{0.91}\text{O}\) and \(\text{Fe}_3\text{O}_4\), in three-point bending geometry, are shown in figure 6. With falling temperature, there is first a slight increase in \(E''\) in the vicinity of 240 K, followed by a steep reduction through the expected Néel temperature (\(\sim 205\) K). A minimum occurs at \(\sim 160\) K, followed by slight stiffening. \(\tan\delta\) increases with falling temperature and two peaks can be observed. The first, \(P_1\), occurs at \(\sim 230–254\) K and shifts to higher temperature with increasing frequency. Estimates of the temperature of the peak values of \(\tan\delta\) at each frequency conform to an Arrhenius relationship, \(\ln(\tan) = \ln(\tan_0) - E_a/(RT)\) (figure 7) with an activation energy, \(E_a\), of \(57 \pm 13\) kJ mol\(^{-1}\), and an attempt frequency, \(f_0\), of \(5.6 \times 10^{13}\) Hz (with large uncertainty). The expected Néel point (\(\sim 205\) K) appears to be marked by an increase in \(\tan\delta\), though the change in slope.
is not as abrupt as for the other two samples. Below the transition, tan δ appears to define a second Debye peak, $P_2$, though data would be needed at lower temperatures to be sure that this is a well-defined dissipation peak.

4. Discussion

In reviewing data from the literature for the phase transition in Fe$_x$O with a range of values of $x$, Carpenter et al (2012) showed that the variation of the magnetic order parameter $m$ with temperature $T$ changes from $\sim m^8 \propto (T_N - T)$ for $x = 0.99$ to $\sim m^4 \propto (T_N - T)$ for $x = 0.94$ and $\sim m^2 \propto (T_N - T)$ for $x = 0.92$. There are issues with resolution for the determinations of the shear strain, $e_4$, accompanying the magnetic ordering, but for present purposes the available data can be interpreted as implying a single phase transition with $e_4 \propto m^2$. $T_N$ values obtained from two of the three samples in the present study are within experimental error of values in the literature (see the compilations of McCammon 1992 and Carpenter et al 2012) and there is no reason to suppose that the value of $T_N$ for the third sample would differ from that of other samples with similar compositions. Thus, the expectation is that the elastic and anelastic behaviour reported here can be interpreted in terms of well-characterized magnetic behaviour. The focus of discussion is on variations of the elastic constants that are due to strain/order parameter coupling and variations of $Q^{-1}$ and tan δ that are due to defects in the cubic structure or to twin walls in the rhombohedral structure.

4.1. Comparison of observed and predicted elastic constants

Softening of elastic constants associated with structural phase transitions characteristically arises as a consequence of coupling between strain and the driving order parameter, and the patterns of softening depend on the form of the coupling terms (e.g. Rehwald 1973, Lüthi and Rehwald 1981, Carpenter and Salje 1998, Salje and Carpenter 2011). The underlying premise is that changes in the order parameter are rapid in comparison with changes in strain so that the observed strain response to a given applied stress includes relaxation of the order parameter. Coupling terms in the Landau expansion for a linear/quadratic coupling model of the combined structural/magnetic transition in Fe$_x$O given by Carpenter et al (2012) provide a basis for predicting the form of elastic softening expected in the limiting cases of the transition being driven only by magnetic ordering or by the structural instability. Variations of the bulk modulus would be due to $\lambda e_4 m^2$ and $\lambda e_4 q^2$, where $\lambda$ describes the strength of
with $m^2$ from the coupling term $\lambda e^2_4 m^2$ (figure 7(b)). In most systems, some softening also occurs in the elastic constants as $T \to T_N$ from above due to the influence of fluctuations or clustering (e.g. Carpenter and Salje 1998).

The bilinear term $\lambda e^4 q$ should give softening of the form typical of a pseudopure ferroelastic transition, as shown in figure 7(c). Note that for this case the transition has been shown as occurring at $T^*_c$ to include renormalization of the critical temperature, $T^*_c$, by the bilinear coupling. Single-crystal data of Sumino et al (1980) for Fe$_{0.92}$O have been reproduced in figure 9 and an expression of the form of equation (13) from Carpenter et al (2012):

$$C_{44} = C^0_{44} \left( \frac{T - T^*_c}{T - T^*_c} \right)^4,$$

has been fitted to values at temperatures above the expected Néel temperature of $\sim 201$ K. There are correlations between the fitted parameters, but one possible set of parameters is $C^0_{44} = 51$ GPa (the elastic constant in the absence of any phase transition), $T^*_c = 36$ K and $T^*_N = 71$ K. The pattern of softening is essentially as expected for a structural instability which would occur below $T^*_N$ if magnetic ordering did not occur (figure 8(c)). According to this model, $T^*_N$ is greater than $T^*_c$ and a schematic pattern of elastic stiffening at $T < T^*_N$ might be as shown by the dotted line in figure 8(c). The shear modulus depends on both $C_{44}$ and $\frac{1}{2} (C_{11} - C_{12})$, but the latter is almost independent of temperature between 195 and 300 K (data of Sumino et al 1980 in figure 9) so that the softening of $\mu$ is due essentially to $C_{44}$. All the new RUS and DMA data are consistent with this pattern of softening in the stability field of the cubic structure, as are data for $E$ from Koch and Fine (1967) and for $C_{44}$ from Berger et al (1983), covering a range of compositions from Fe$_{0.91}$O to Fe$_{0.95}$O.

The single-crystal elastic constants of Sumino et al (1980) do not show any sign of significant softening of $\frac{1}{2} (C_{11} - C_{12})$ for Fe$_{0.92}$O as $T \to T^*_N$ from above, though their data for $K$ and our RUS data for $K$ of Fe$_{0.95}$O (figure 3(c)) do show some slight softening. Softening of the bulk modulus above a phase transition is commonly observed and can be ascribed to fluctuations arising from interactions between...
Figure 8. Schematic patterns of variation of the elastic constants due to strain/order parameter coupling, including the coupling of spontaneous strains $e_s$ (volume strain), $e_t$ (tetragonal shear strain) and $e_4$ with magnetic ($m$) and structural ($q$) order parameters (after Carpenter and Salje 1998). (a) $\lambda e_s m^2$, $\lambda e_t q^2$, $\lambda e_4 m^2$. Dashed lines are for a second-order structural transition at $T = T_c$. The solid curve below $T_c$ is for a transition with a steeper variation of the order parameter, such as $q^4 \propto (T_c - T)$. The solid curve above $T_c$ includes some pretransition softening. The solid curves would also represent softening behaviour due to a purely magnetic transition at $T_N$. (b) $\lambda e_t m^2$; thermodynamically continuous magnetic transition at $T_N$. (c) $\lambda e_4 q$. Solid curves are for a classical second-order transition at $T = T_c^*$. The dotted line represents a hypothetical form of recovery of $C_{44}$ at $T < T_N$ ($T_N > T_c^*$).


Owing to the strong acoustic attenuation in rhombohedral crystals, there are rather few data for $T < T_N$ but those of Berger et al (1983) for $C_{11}$ and $(C_{11} + C_{12} + C_{44})$ show marked softening, with a nonlinear recovery in the latter (i.e. similar patterns to those shown in figure 8(a) for $C_{11}$ and $C_{12}$, and in figure 8(c) for $C_{44}$). A relatively steep recovery occurs in $E$ (Koch and Fine 1967), consistent with the influence of bilinear coupling being seen in $C_{44}$. This steep recovery is also seen in the DMA data for $E'$ from the polycrystalline Fe$_{0.95}$O sample (figure 4(a)). Data for a single resonance peak in RUS data from the single-crystal sample (figure 3(a)) and the mixture of Fe$_{0.91}$O + Fe$_{3}$O$_{4}$ (figure 3(d)) could represent a combination of the pattern in figure 8(a) expected for $\frac{1}{2}(C_{11} + C_{12})$ due to $\lambda e_t q^2$ and expected for $C_{44}$ below $T_N$ due to $\lambda e_4 q$ (figure 8(c)). Thus the overall pattern of softening is consistent with the conventional mechanism of strain/order parameter coupling, with relaxation of structural and magnetic order parameters on the timescale of strain relaxation in response to the applied dynamic stress. Softening ahead of the transition point has the typical pattern of a pseudoproper ferroelastic transition, but the antiferromagnetic ordering instability point is reached before the pure ferroelastic transition occurs.

The new DMA data (figures 4 and 6) and data in the literature (Koch and Fine 1967, Berger et al 1983) show...
softening continuing through the Néel point and reaching minimum values of the elastic constants at \( \sim 10-25 \) K below \( T_N \). The same pattern has been observed in association with a second-order improper ferroelastic transitions in the perovskite \( \text{BaCeO}_3 \) (Zhang et al 2010a). By way of contrast, the equivalent transition in \( \text{SrZrO}_3 \) is tricritical in character and the softening occurs only as a steep change immediately at the transition temperature (McKnight et al 2009a). This difference in behaviour could be due to the influence of a dynamic component to the transitions when the free energy potential is relatively flat and restoring forces are small just below \( T_c \). In the case of \( \text{LaAlO}_3 \), which has a second-order improper ferroelastic transition at \( 817 \) K, softening through and down to \( \sim 20 \) K below \( T_c \) is accompanied by steep variations in the intensity of a central peak in Brillouin spectra (Carpenter et al 2010a). These indicate local, dynamical flipping of the structure between different twin-related orientations. Coupling of the central peak mode with the acoustic modes gives rise to additional softening which is not accounted for in the conventional strain/order parameter coupling model. For \( \text{Fe}_{0.94}\text{O} \), the strain behaviour is close to \( e^{2}_{\perp} \propto (T_N - T) \) (data of Glazyrin et al 2011 in Carpenter et al 2012) and is therefore close to being second order in character with respect to ferroelastic properties. It might be that softening through \( T_N \) is due to the presence of local dynamical flip modes as well.

4.2. Anelasticity due to twin wall mobility

Strong acoustic attenuation is a characteristic feature of ferroelastic materials in a wide temperature interval below their transition temperatures and is due to mobility of twin walls under stress (e.g. in lead zirconate titanate: Postnikov et al 1970, Wang et al 2001, 2002, 2006, He et al 2000, Bourim et al 2002; \( \text{SrTiO}_3 \); Migliori et al 1993, Schranz et al 1999, Kityk et al 2000a, 2000b, Lemanov et al 2002, Scott et al 2011; \( \text{K MnF}_3 \): Schranz et al 2003, Schranz and Kityk 2008, Salje and Zhang 2009; (Ca, \( \text{Sr} \))\( \text{TiO}_3 \); Harrison et al 2003, Walsh et al 2006, Darakchiev et al 2006; \( \text{LaAlO}_3 \): Harrison and Redfern 2002, Harrison et al 2004a, 2004c, Carpenter et al 2010a; \( \text{Sr(} \text{Zr, Ti}) \text{O}_3 \); McKnight et al 2009a, 2009b, Zhang et al 2010b; \( \text{BaCeO}_3 \); Zhang et al 2010a; (La, Pr)\( \text{AlO}_3 \); Carpenter et al 2010b, Thomson et al 2010). The attenuation of shear waves occurs in rhombohedral \( \text{Fe}_2\text{O} \) at frequencies ranging from \( \sim 10 \) MHz (Berger et al 1983), through \( \sim 0.1-1 \) MHz (Sumino et al 1980, this study) to \( \sim 0.1-50 \) Hz (this study). In this respect the properties are dominated by ferroelastic aspects of the phase transition.

The RUS results show the onset of acoustic dissipation occurring at or very close to \( T_N \) in all three samples (figure 3), presumably marking the first appearance of rhombohedral twins. There is thus no evidence for a stability field of an antiferromagnetic (AFM) ordered phase with cubic lattice geometry, as proposed by Kantor et al (2005) for a sample with composition \( \text{Fe}_{0.92}\text{O} \). The pattern of maximum in tan \( \delta \) at \( \sim 10-20 \) K below the transition temperature followed by a plateau of relatively high values in DMA data (polycrystalline sample of \( \text{Fe}_{0.95}\text{O} \), figure 4) is also characteristic of a twin-wall loss mechanism in ferroelastic materials, as illustrated, for example, by Harrison et al (2004b) for \( \text{LaAlO}_3 \). The same plateau occurs in both acoustic and dielectric losses at ferroelastic transitions and is attributed to viscous movement of the twin walls, with the viscous drag being attributed to the disruption of phonons behind the moving walls (Combs and Yip 1983, Huang et al 1992, Wang et al 1996, Harrison et al 2004a). In the immediate temperature interval below the transition point, the strain contrast across the twin walls becomes small at a second-order transition, however, so the viscous coefficient and relaxation time of the twin-wall motion tend to zero (Wang et al 1996), with the result that the characteristic maximum in tan \( \delta \) occurs significantly below the transition point. These aspects of twin-wall dynamics are considered in detail by Huang et al (1992, 1997), Wang and Huang (1994) and Wang et al (1996, 2000). The data for tan \( \delta \) in figure 4 do not quite have sufficient resolution to determine whether the temperature of the peak below \( T_N \) is frequency-dependent but there is a systematic frequency dependence for the peak height. At \( 0.1 \) and 1 Hz, the peak is small and starts at \( \sim 187 \) K. The onset temperature at 5 Hz is about the same but the maximum of the peak is markedly higher. At 10, 20 and 50 Hz the onset point is close to \( T_N \) and peak height increases to its largest value at the highest measuring frequency. This can perhaps be understood if relaxation time is a controlling factor in determining the effective viscosity and is greater than \( \sim 1 \) s. For slow application of stresses, the twin-wall motion is sufficiently rapid that the overall response of the crystal is essentially elastic, but for faster stress rates the twin walls do not have sufficient time to fully relax and the response becomes anelastic.

A complete pattern of typical ferroelastic behaviour would include a Debye loss peak at lower temperatures where the twin walls would become pinned by defects. \( Q^{-1} \) remains too high for resonance peaks to be detected down to 5 K in any of the three samples examined by RUS, however, and there is no sign of such a peak in the DMA data down to \( \sim 135 \) K for the \( \text{Fe}_{0.95}\text{O} \) sample. For the present, therefore, it is not clear whether the ferroelastic twin walls in \( \text{Fe}_2\text{O} \) can be pinned.

DMA data for the \( \text{Fe}_{0.91}\text{O} + \text{Fe}_2\text{O}_4 \) sample (figure 6) appear at first sight to be quite different from those of the \( \text{Fe}_{0.95}\text{O} \) sample. An important distinction between the samples, however, is the different magnitude of the symmetry-breaking shear strain, \( e_4 \), accompanying the phase transition. The compilation of data from the literature in figure 9(a) of Carpenter et al (2012) shows that \( e_4 \) would not exceed \( \sim 0.001 \) for \( \text{Fe}_{0.91}\text{O} \), even at the lowest temperatures, which compares with \( \sim 0.008 \) for \( \text{Fe}_{0.95}\text{O} \). The strain contrast between twin domains will therefore be correspondingly smaller and the peak in tan \( \delta \) displaced to correspondingly lower temperatures below the transition point. This is more or less as observed. On this basis, the lack of any systematic frequency dependence to the peak \( P_2 \) in figure 6 would also suggest that at least some part of the relaxation time spectrum for viscous relaxations is at times greater than \( \sim 10 \) s. The additional peak, \( P_1 \), is attributed to the role of ordered defects in the cubic structure or to interfaces between intergrown magnetite and wüstite, as discussed in section 4.3.
4.3. Anelasticity due to the influence of defects

For all DMA frequencies and the lowest RUS frequencies, there are significant acoustic losses in polycrystalline samples at temperatures in the stability field of the cubic structure (figure 3, 4 and 6). These can be most obviously described in terms of a Debye peak for DMA data from the two-phase mixture of Fe$_{0.91}$O+$+$Fe$_2$O$_4$. The activation energy obtained from the relationship between peak temperature and frequency, $E_a = 57 \pm 13$ kJ mol$^{-1}$ (figure 7), is closer to the activation energy for the self-diffusion of iron in wüstite, e.g. $\sim 130$ kJ mol$^{-1}$ for Fe$_{0.95}$O and $\sim 105$ kJ mol$^{-1}$ for Fe$_{0.94}$O (Mrowec and Podgorecka 1987), than the activation energy for diffusion of oxygen vacancies, $\sim 330$ kJ mol$^{-1}$, reported by Ilschner et al (1964) based on creep experiments. The attempt frequency is subject to a large uncertainty and is not so helpful in suggesting the rate controlling step in the relaxation process which gives rise to the observed loss. DMA data for Fe$_{0.95}$O do not show such a clear pattern of losses but the absolute values of $\tan \delta$ do have a systematic dependence on frequency (figure 5). The angular frequency, $\omega$, at which maximum dissipation occurs ($\omega \tau = 1$) is $\sim 10$ Hz, implying relaxation times near $\tau = 1/\omega = 1/(2\pi f) = 0.02$ s. There is some evidence of frequency dependence in RUS data for polycrystalline Fe$_{0.95}$O and the mixture of Fe$_{0.91}$O+Fe$_2$O$_4$. Dissipation is larger at lower frequencies, but there is not a sufficiently wide range of frequencies to characterize it fully. From figure 7, the extrapolated temperature for maximum dissipation at 1 MHz would be $\sim 385$ K, so perhaps the RUS measurements near room temperature are just catching the tail of a Debye loss peak.

The defects in non-stoichiometric wüstite are clusters of Fe$^{2+}$ vacancies and Fe$^{3+}$ interstitials (e.g. Andersson and Sletnes 1977, Welberry and Christy 1997). Andersson and Sletnes (1977) reported spinodal-like decomposition based on a study of Fe$_2$O and magnetite using transmission electron microscopy, and the ordering was enhanced on annealing below 573 K. It was suggested that the defect clusters in wüstite could be treated as magnetite-like microdomains (Jeanloz and Soto-Sorensen 1982). The form of defect structure changes with pressure (Ding et al 2005) and it follows, therefore, that a dynamic compressional stress would give rise to anelastic losses at frequencies which relate closely to the relaxation time for Fe diffusion across a magnetite/wüstite interface or for reordering in the clusters. Shear stresses would have the same effect if there is a local shear strain across the interfaces or associated with the ordering. The maximum change in elastic constants possible is the difference between relaxed, $C_R$, and unrelaxed, $C_U$, values and the acoustic loss would follow (from Nowick and Berry 1972):

$$\tan \delta = \frac{\Delta}{\sqrt{1+\Delta}} \frac{\omega \tau}{1+\omega^2 \tau^2} \approx \frac{\Delta \omega \tau}{1+\omega^2 \tau^2}. \tag{5}$$

for small $\Delta$, where

$$\Delta = (C_U - C_R)/C_R. \tag{6}$$

Again from extrapolation of the straight line in figure 7, the frequency for maximum loss at 300 K would be $\sim 6.4 \times 10^3$ Hz, so that there should be differences between values of the bulk and shear moduli measured at room temperature using dynamic methods at higher frequencies than this and values obtained from static equation of state methods, as proposed by Jeanloz and Hazen (1983) and Kantor et al (2008) for the bulk modulus. Taking the maximum value of $\tan \delta$ as 0.02 (at $\omega \tau = 1$) gives $\Delta = 0.04$. For a Young’s modulus of $\sim 60$ GPa, this gives a difference between relaxed and unrelaxed values of $\sim 3$ GPa, as observed for the wüstite + magnetite mixture (figure 6).

The Young’s modulus contains contributions from $\mu$ and $K$ according to equation (3) and a simple calculation is sufficient to show that the observed anelastic effect for $E$ would be sufficient to account for the anelastic softening of $K$ proposed by Jeanloz and Hazen (1983). If $\mu$ is not subject to anelastic loss and is assumed to be 47 GPa (see values in table 1), $K = 155$ GPa (representing the static value) gives $E = 128.1$ GPa. Taking an extreme value of $K = 180$ GPa to represent a dynamic measurement (e.g. see figure 1 of Jeanloz and Hazen 1983) gives $E = 129.7$ GPa. The difference, 1.8 GPa, is within the range expected on the basis of the values of $\tan \delta$ up to 0.02, with some scope also for anelastic softening of the shear modulus. This is at least consistent with the analysis both of Jeanloz and Hazen (1983) and of Kantor et al (2008) that relaxation of the defect ordered structure could account for the differences between $K$ measured in dynamic and static experiments using Fe$_2$O samples with significant non-stoichiometry. In other words, the relatively soft bulk modulus would include some degree of reorganization of the locally ordered defect structure. In (nearly) stoichiometric FeO, the bulk modulus would then revert to the higher values, presumably because of the absence of the defect structure, as reported by Zhang (2000). This simple empiricism is not valid, however, if there is the close agreement between dynamic and static values reported by Jackson et al (1990). In this case, the loss behaviour of the samples studied here would have to be due to some other mechanism.

4.4. Comparisons with MnO and NiO

MnO, NiO and CoO have antiferromagnetic ordered structures which differ from the magnetic structure of Fe$_2$O in the orientation of the Fe$^{2+}$ spin moments. In Fe$_2$O, the moments lie parallel and antiparallel to [111] (magnetic space group $R\bar{3}c$) (Shull et al 1951, Roth 1958). In the other three phases, the moments lie parallel and antiparallel to a direction which is allowed by symmetry to be tilted out of the (111) plane but which is close to [112] (magnetic space group $C_2$/c, Shull et al 1951, Roth 1958, Daniel and Cracknell 1969, Cracknell et al 1970, Hermann-Ronzaud et al 1978, Berger et al 1983, Goodwin et al 2006, Carpenter et al 2012). Note, however, that a definitive distinction between this structure and another slight variant with space group $C_{2/m}$ has not yet really been made for MnO (Carpenter et al 2012). In spite of these differences, the structural and magnetic behaviour of all four phases is closely similar.
MnO and NiO are permitted by symmetry to have monoclinic lattice geometry but are rhombohedral within experimental uncertainty. CoO differs by having an additional tetragonal lattice distortion, but this is due to the Jahn–Teller effect (Saito et al 1966, Rechtin et al 1970, Ding et al 2006). If, as set out in Carpenter et al (2012) there are two separate instabilities, one structural and the other magnetic, coupling of the two order parameters with strains will not be very different for the two magnetically ordered structures. Coupling of the structural order parameter, which has symmetry properties of irreducible representation $\Gamma^5_4$ of the parent $Fmm\bar{m}$ space group, would be the same. The only difference between strain coupling with the $mL^{+}_2$ (for Fe$_3$O) and $mL^{+}_4$ magnetic order parameters (MnO, NiO, CoO) is that coupling of the form $\lambda m^2 e_i$ is allowed in the latter but not in the former. However, non-zero values for the tetragonal strain, $e_1$, have not yet been observed for MnO and NiO, implying that the coupling coefficient for this term is negligibly small. In this case, the relevant strain coupling term is $\lambda m^2 e_2^2$. The Néel temperatures for MnO, Fe$_3$O and NiO are $\sim 118$, $\sim 195$ and $\sim 522$ K, respectively. Subtle differences between the spontaneous strains and elastic constant variations can be understood if they all would undergo a purely structural phase transition at some low temperature but, instead, they have a magnetic ordering instability at progressively higher temperatures which is, nevertheless, coupled to the structural instability.

Figure 9 shows the temperature dependences of $C_{44}$, $\Delta(C_{11} - C_{12})$ and $K$ for NiO, Fe$_3$O and MnO single crystals, from Plessis et al (1971) and Sumino et al (1980). All show some softening of $C_{44}$ as $T \to T_N$ from above but the extent of this is very slight in NiO. The amount of softening is greatest for MnO, which has the lowest value of $T_N$, and intermediate for Fe$_3$O. Similarly, the value of $e_4$ at 5 K is smallest for NiO ($\sim 0.001$, data of Cheetham and Hope 1983), and largest for MnO ($\sim 0.01$, data of Kantor et al 2005). Another way of writing equation (4) for the softening of $C_{44}$ in the stability field of the cubic structure is (e.g. see Carpenter and Salje 1998)

$$C_{44} = C^0_{44} - \frac{\lambda^2 e_2^2}{a(T - T_c)}.$$

The coupling coefficient here is for the bilinear term, $\lambda e_2^2$, and describes the strength of coupling between the structural order parameter and the symmetry-breaking shear strain. Variations in the steepness of the softening can therefore be attributed to variations in the strength of this coupling. The very small anomaly due to the phase transition at 522 K (figure 9, data of Plessis et al 1971) confirms that the coupling is indeed weak in NiO. The reverse is also evident, that strong coupling and a large degree of softening go together in MnO. Finally, the lack of effective coupling of the form $\lambda e_2^2 m^2$ is confirmed by the temperature dependence of $\frac{1}{2}(C_{11} - C_{12})$ below $T_N^*$ in both MnO and NiO, which follows the pattern of variation shown in figure 8(b) due to $\lambda e_2^2 m^2$ (figure 9, data of Plessis et al 1971, Sumino et al 1980). The variation of $C_{11}$ in MnO and $\frac{1}{2}(C_{11} + C_{12} + C_{44})$ in NiO follow the pattern shown in figure 8(a) (Cracknell et al 1970, Plessis et al 1971, Palmer and Waintal 1980, Seino 1982).

A general model would have a low temperature for the structural instability in MnO, Fe$_3$O and NiO but progressively higher temperatures for the magnetic instability. The effective strength of $\lambda e_2^2$ ferroelastic coupling diminishes with increasing temperature differences between the two instabilities, such that the overall pattern of behaviour in NiO is overwhelmingly dominated by the magnetic ordering. For Fe$_3$O, the two instability temperatures would be closer together and, based on the fit to $C_{44}$ using equation (4) shown in figure 9, the structural instability would occur by itself at $\sim 71$ K. Similar fitting to $C_{44}$ data in figure 9 gives $\sim 101$ K as the possible structural instability temperature for MnO, i.e. the closest to being coincident with $T_N$. Because $T_N$ is greater than $T^*_N$ for all three phases, there will only be one phase transition in each system, as discussed for the most general cases of linear–quadratic coupling by Salje and Carpenter (2011).

5. Conclusions

From the perspectives of strain, elastic softening and anelastic losses, the phase transition in Fe$_3$O near 195 K has most of the characteristics of a pseudopropert ferroelastic phase transition. By themselves, the observed changes in the elastic constants do not necessarily allow discrimination between thermodynamically continuous and discontinuous mechanisms but spontaneous strain variations, together with data for magnetic ordering from heat capacities and intensities of superlattice reflections (Carpenter et al 2012) are all consistent with thermodynamically continuous behaviour. However, if the transition was driven by a ferroelastic structural instability alone, it would be expected to be first order in character due to the contribution of a third-order term in the Landau free energy expansion (Carpenter et al 2012). There is no direct evidence for two separate structural and magnetic instabilities, but the pattern of $C_{44}$ softening is permissive of this being the case. If there are indeed two separate instabilities with critical temperatures $T_N$ and $T^*_N$, the elastic softening is consistent with $T_N$ ($\sim 201$ K) being greater than $T^*_N$ ($\sim 71$ K) by $\sim 130$ K for Fe$_{0.92}$O. The separate order parameters can be coupled directly or indirectly by the common strain, $e_4$, according to $\lambda q m^2$. In general, this linear–quadratic coupling gives a single phase transition when the magnetic transition occurs at a higher temperature than the structural transition would occur by itself.

Anelastic behaviour in the stability field of the cubic structure of Fe$_3$O is consistent with a loss mechanism that might involve relaxations of the local defect structure in response to an applied stress. Local reordering of cations or movement of interfaces between magnetite-like ordered regions appears to have diffusion of iron as the rate controlling step. This is at least consistent with the analysis of Jeanloz and Hazen (1983), Kantor et al (2008) that differences between values of the bulk modulus measured at room temperature by static and dynamic methods could be anelastic in origin.
Finally, the systematic variations of $T_N$, $e_4$, and $C_{44}$ softening between MnO, Fe$_2$O$_3$, and NiO are consistent with all three structures having some relatively low value of $T'_c$ but increasing values of $T_N$. The increasing difference, $T_N - T'_c$, in a system with linear–quadratic coupling and $T_N > T'_c$ would cause the single phase transition at high temperatures to become more like a co-elastic magnetic transition and less like a pseudoproper ferroelastic structural transition, as is indeed observed.

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