

## On the anomalous temperature-dependent magnetostriction in intermetallic DyFe<sub>2</sub>

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 2437

(<http://iopscience.iop.org/0953-8984/16/13/021>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 14:13

Please note that [terms and conditions apply](#).

# On the anomalous temperature-dependent magnetostriction in intermetallic DyFe<sub>2</sub>

G J Bowden<sup>1</sup>, P A J de Groot, J D O'Neil, B D Rainford and A A Zhukov

School of Physics and Astronomy, University of Southampton, Southampton SO17 1BJ, UK

E-mail: [gjb@phys.soton.ac.uk](mailto:gjb@phys.soton.ac.uk)

Received 9 December 2003

Published 19 March 2004

Online at [stacks.iop.org/JPhysCM/16/2437](http://stacks.iop.org/JPhysCM/16/2437) (DOI: 10.1088/0953-8984/16/13/021)

## Abstract

The anomalous temperature dependence of the magnetostriction in single-crystal DyFe<sub>2</sub> has been an unsolved problem in magnetism for some 27 years. In this paper, it is shown that an explanation can be provided, within the constraints of the Callen and Callen model, provided changes in the second-, fourth- and sixth-order crystal field energies of the rare earth ion are all taken into account. In particular, it is shown that the peculiar temperature dependence of the magnetostriction in DyFe<sub>2</sub> is due to competition between  $n = 2, 4$  and 6 crystal field distortions, whose temperature dependence can be accurately modelled using the Callen and Callen model.

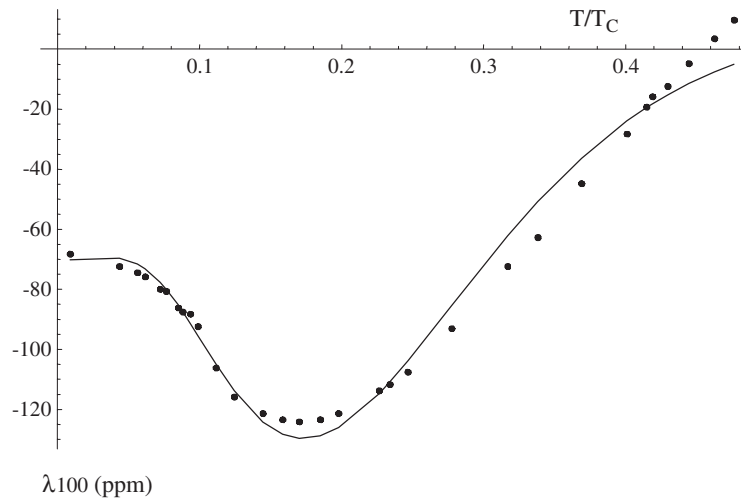
## 1. Introduction

Since the early 1970s it has been known that the rare-earth-iron (REFe<sub>2</sub>) intermetallic compounds exhibit giant magnetostriction (Clark and Belson 1972). Moreover, because of their high Curie temperatures, the magnetostriction is appreciable even at room temperature. As a result, the optimized binary intermetallic Tb<sub>0.3</sub>Dy<sub>0.7</sub>Fe<sub>1.9</sub> (Terfenol-D) has found many applications (e.g. Clark 1979, Greenough *et al* 1991, Claeysen *et al* 1997).

However, rather surprisingly, the curious temperature dependence of the magnetostriction in single-crystal DyFe<sub>2</sub> has never been given an explanation (Clark *et al* 1977, Clark 1979). At first sight DyFe<sub>2</sub> seems to fly in the face of the Callen and Callen model (CCM), which provides a satisfactory explanation of the temperature dependence of the magnetostriction, not only for TbFe<sub>2</sub> (Clark *et al* 1977) and TmFe<sub>2</sub> (Abbundi and Clark 1978, Bleaney *et al* 1981), but also for many other ferromagnetic compounds (Callen and Callen 1963, 1965a, 1965b). In all of the above-cited compounds the magnetostriction falls monotonically with increasing temperature, in complete contrast to that of DyFe<sub>2</sub> shown in figure 1.

In this paper, an explanation of the magnetostriction in single-crystal DyFe<sub>2</sub> is provided, within the constraints of the CCM. It is shown that it is necessary to take into account not only

<sup>1</sup> Author to whom any correspondence should be addressed.



**Figure 1.** The temperature dependence of the  $\lambda_{100}$  magnetostriction of  $\text{DyFe}_2$ , after Clark *et al* (1977). The full curve is a theoretical fit to the data based on (i) additional magnetostrictive terms arising from higher-order crystal field gradients and (ii) 'volume conservation', as discussed in the text.

the appearance of the quadratic crystal field terms as the lattice distorts, but also changes in the energies of the fourth-order and sixth-order crystal field terms. The latter possess a much faster temperature dependence than their quadratic counterparts and it is these terms that give rise to the curious temperature behaviour of  $\text{DyFe}_2$  below 120 K.

The structure of this paper is as follows. Firstly, we give a brief description of the CCM, as it applies to the  $\text{REFe}_2$  intermetallic compounds. Secondly, we detail some results of the point charge model (PCM) in the presence of uniform distortions. Thirdly, we apply our results to the easy axis [111] intermetallic  $\text{TbFe}_2$  which is known to follow the CCM. Finally, we address the more difficult problem of the magnetoelastic behaviour of the easy axis [001] intermetallic  $\text{DyFe}_2$ .

## 2. The Callen and Callen model

Following Bowden *et al* (1968), Atzmony and Dariel (1973, 1976), the Hamiltonian for a RE ion subject to both exchange and crystal field terms can be written:

$$\mathcal{H} = \mathcal{H}_{\text{EX}} + \mathcal{H}_{\text{CF}} \quad (1)$$

where the magnetic exchange is given by

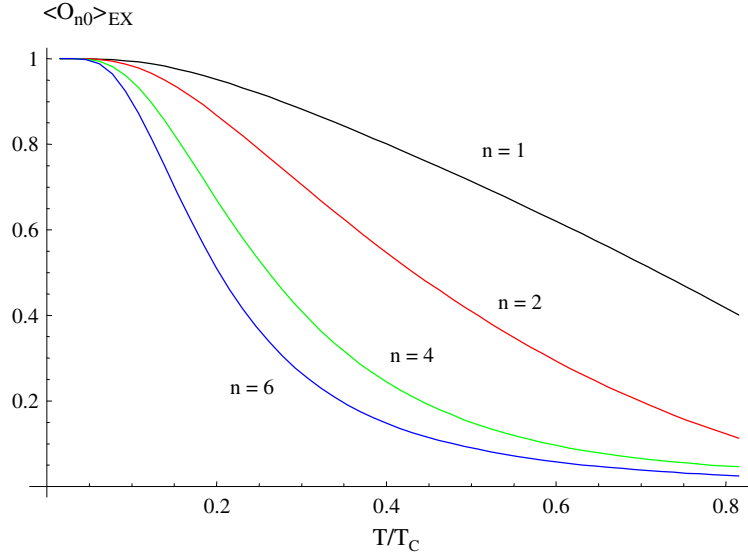
$$\mathcal{H}_{\text{EX}} = g\mu_{\text{B}}B_{\text{EX}}(T)J_Z \quad (2)$$

and

$$\mathcal{H}_{\text{CF}} = B_4[O_{40} + 5O_{44}^c] + B_6[O_{60} - 21O_{64}^c] \quad (3)$$

is the cubic crystal field Hamiltonian. Here

- (i) the temperature dependence of the RE–Fe exchange field  $B_{\text{EX}}(T)$  is assumed to follow that of the  $^{57}\text{Fe}$  magnetic hyperfine field,
- (ii) estimates of the cubic crystal field coefficients  $B_4$  and  $B_6$  have been given by Atzmony and Dariel (1973, 1976), and



**Figure 2.** Normalized expectation values of  $\langle O_{n0} \rangle_{\text{EX}}$  for  $n = 1, 2, 4,$  and  $6$ , as a function of reduced temperature, after Bowden *et al* (1968).

(This figure is in colour only in the electronic version)

(iii) the crystal field parameters and operators  $B_{40}$ ,  $O_{40}$ , etc, are defined, for example, by Hutchings (1964).

In the CCM, it is assumed that the magnetic exchange term is dominant. Thus to first order, the free energy can be written:

$$F = F_{\text{EX}} + \langle \mathcal{H}_{\text{CF}} \rangle_{\text{EX}} \quad (4)$$

where the crystal field term  $\langle \mathcal{H}_{\text{CF}} \rangle_{\text{EX}}$  is evaluated using the simple Zeeman wavefunctions appropriate to  $\mathcal{H}_{\text{EX}}$ . Note that, if the direction of magnetization is [001], only the diagonal terms in the crystal field Hamiltonian contribute to the first-order change in the free energy. Thus

$$\langle \mathcal{H}_{\text{CF}} \rangle_{\text{EX}} = B_4 \langle O_{40} \rangle_{\text{EX}} + B_6 \langle O_{60} \rangle_{\text{EX}}. \quad (5)$$

In figure 2 we show the temperature dependence of the normalized expectation values  $\langle O_{n0} \rangle_{\text{EX}}$  for  $n = 1, 2, 4$  and  $6$ . Note that  $\langle O_{n0} \rangle_{\text{EX}}$  falls more rapidly with increasing temperature, as  $n$  is increased. In obtaining these results we have used the  $T = 0$  K exchange Hamiltonian given by Bowden *et al* (1968)

$$\mathcal{H}_{\text{EX}} = 135 J_Z \text{ (K)} \quad (6)$$

together with a Curie temperature  $T_C = 635$  K (Buschow 1977). Atzmony and Dariel (1973, 1976) have given a smaller value of the exchange field ( $100 J_Z$ ). However, if we use this value we do not obtain good agreement between theory and experiment (see figure 1 of this paper and figure 6 of Bowden *et al* (1968)).

So far we have ignored magnetostriction. In addition to the crystal field terms  $\mathcal{H}_{\text{CF}}$  it is necessary to add both the magnetoelastic terms and elastic energy terms:

$$E_{\text{ME}} = b_1(\alpha_x^2 \varepsilon_{xx} + \alpha_y^2 \varepsilon_{yy} + \alpha_z^2 \varepsilon_{zz}) + b_2(\alpha_x \alpha_y \varepsilon_{xy} + \alpha_x \alpha_z \varepsilon_{xz} + \alpha_y \alpha_z \varepsilon_{yz}) \quad (7)$$

$$E_{\text{Elas}} = \frac{1}{2} C_{11}[e_{xx}^2 + e_{yy}^2 + e_{zz}^2] + \frac{1}{2} C_{44}[e_{xy}^2 + e_{xz}^2 + e_{yz}^2] + C_{12}[e_{xx} e_{yy} + e_{xx} e_{zz} + e_{yy} e_{zz}] \quad (8)$$

**Table 1.** Dominant second-order crystal field terms for specific distortions, together with their appropriate crystal field operators expressed in tesseral harmonic form. All distortions, except those shown explicitly, are zero.

Shear distortion	Crystal field terms	Tetragonal distortion	Crystal field terms
$\varepsilon_{xy} = \varepsilon_{yx}$	$B_{22}^S(\varepsilon_{xy})$	$\varepsilon_{xx}$	$B_{20}(\varepsilon_{xx}), B_{22}^C(\varepsilon_{xx})$
$\varepsilon_{xz} = \varepsilon_{zx}$	$B_{21}^C(\varepsilon_{xz})$	$\varepsilon_{xx}$	$B_{20}(\varepsilon_{xx}), B_{22}^C(\varepsilon_{xx})$
$\varepsilon_{zy} = \varepsilon_{yz}$	$B_{21}^S(\varepsilon_{zy})$	$\varepsilon_{yy}$	$B_{20}(\varepsilon_{yy}), B_{22}^C(\varepsilon_{yy})$
$B_{21}^C(\varepsilon) = B_{21}^S(\varepsilon) = 2B_{22}^S(\varepsilon)$		$B_{20}(\varepsilon_{xx}) = B_{20}(\varepsilon_{yy}) = -\frac{1}{2}B_{20}(\varepsilon_{zz})$	
Crystal field operators			
$O_2^0 = [3J_z^2 - J(J+1)]$			
$O_{21}^C = \frac{1}{2}[J_z J_x + J_x J_z]$		$O_{21}^S = \frac{1}{2}[J_z J_y + J_y J_z]$	
$O_{22}^C = [J_x^2 - J_y^2] = \frac{1}{2}[J_+^2 + J_-^2]$		$O_{22}^S = [J_x J_y + J_y J_x] = \frac{1}{2i}[J_+^2 - J_-^2]$	

where (i)  $b_1$  and  $b_2$  are the lowest-order magnetoelastic constants, (ii)  $\alpha_x$ , etc, are the direction cosines, (iii)  $e_{\alpha\alpha} = \varepsilon_{\alpha\alpha}$  ( $\alpha = x, y, z$ ) and  $e_{\alpha\beta} = (\varepsilon_{\alpha\beta} + \varepsilon_{\beta\alpha})$ , etc, are the strains defined, for example, by Kittel (1971), and (iv)  $C_{11}$ ,  $C_{44}$  and  $C_{12}$  are the elastic constants (Blessing 1976). In the past, equations (7) and (8) have been used as the starting point for many authors (e.g. Clark 1979, de la Fuente *et al* 2001). But in this paper we will show that equations (7) and (8) are insufficient to describe the magnetostriction in DyFe<sub>2</sub>.

### 3. The point charge model

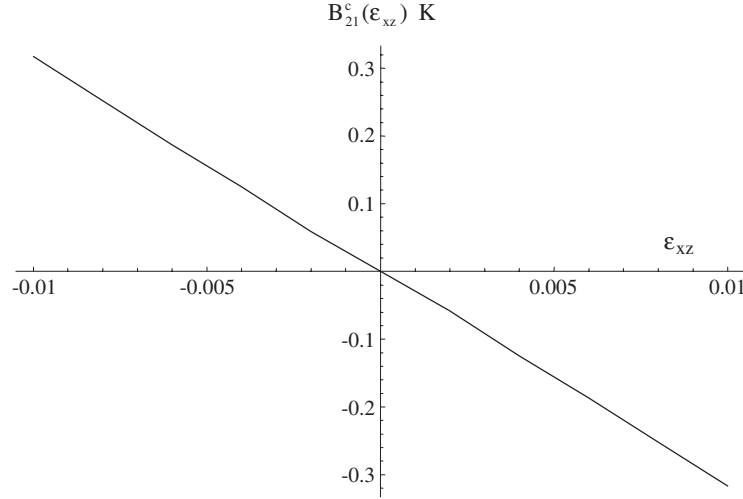
Magnetoelasticity in REFe<sub>2</sub> compounds takes place because the distortion lowers the symmetry at the RE ion and hence its crystal field energy. In this paper, we use the PCM to identify the changes in the crystal-field Hamiltonian  $\mathcal{H}_{CF}$ , following uniform distortions of the lattice. It is, of course, well known that, while the PCM model correctly predicts the symmetry of the problem, it is unlikely to yield quantitative values of, say, the crystal field parameters  $B_4$  and  $B_6$ . Nevertheless, it can be used to correctly identify the additional crystal field terms that arise as a result of magnetostriction. As we shall see the crystal field gradients  $\partial B_n / \partial \varepsilon$  can then be used as parameters to fit the experimental data. For a full review of the PCM model the reader is referred to Hutchings (1964).

Following Kittel (1971), for small uniform distortions of the cubic lattice we write

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} 1 + \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & 1 + \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & 1 + \varepsilon_{zz} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad (9)$$

where it is understood that the distortions  $\varepsilon_{\alpha\alpha}$  are small ( $<1\%$ ). The diagonal distortions  $\varepsilon_{xx}$ , etc, refer to extensions along the  $x$ ,  $y$  and  $z$  axes of the cubic lattice, which give rise to tetragonal distortions. However, the off-diagonal elements  $\varepsilon_{xy}$ , etc, the so-called shear terms, give rise to rhombohedral type distortions of the cubic lattice provided we set  $\varepsilon_{xy} = \varepsilon_{yx}$ , etc. In table 1, we summarize the various second-rank crystal field terms that arise, and their appropriate Steven's crystal field operators, for specific distortions.

In practice, calculations show that linear superposition holds well. For example, if we set  $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = 0$  and  $\varepsilon_{xy} = \varepsilon_{xz} = \varepsilon_{yz} = \varepsilon$ , for a rhombohedral distortion, the PCM shows that all three coefficients  $B_{22}^S$ ,  $B_{21}^C$  and  $B_{21}^S$  are now non-zero, but with practically the



**Figure 3.**  $B_{21}^c(\varepsilon_{xz})$ , for the RE lattice only, as a function of the tetrahedral distortion  $\varepsilon_{xz}$ .

same values as those obtained independently of each other. Thus for a rhombohedral shear distortion, an additional strain-dependent crystal field Hamiltonian:

$$\begin{aligned} \mathcal{H}'_{\text{CF}} &= B_{22}^S(\varepsilon)O_{22}^S + B_{21}^C(\varepsilon)O_{21}^C + B_{21}^S(\varepsilon)O_{21}^S \\ &= B_{21}^c(\varepsilon)\left\{\frac{1}{2}[J_x J_y + J_y J_x] + \frac{1}{2}[J_x J_z + J_z J_x] + \frac{1}{2}[J_y J_z + J_y J_z]\right\} \end{aligned} \quad (10)$$

must be taken into account. Note that, on comparing equations (7) and (10), there is a one-to-one correspondence between  $B_{21}^c(\varepsilon)$  and the usual magnetostrictive coefficient  $b_2$ , provided we replace the dimensionless products such as  $(\alpha_x \alpha_y \propto xy)$  by  $\frac{1}{2}[J_x J_y + J_y J_x]/J(J+1)$ .

Finally, one further point should be made. Our calculations reveal that the coefficients  $B_{21}^c(\varepsilon)$  are, in general, linear functions of the distortion. An example is shown in figure 3.

On fitting such curves we find

$$B_{21}^c(\varepsilon_{xz}) = \frac{\partial B_{21}^c}{\partial \varepsilon_{xz}} \varepsilon_{xz} = \{q_{\text{RE}}(-31.5) + q_{\text{Fe}}(3.07)\} \varepsilon_{xz} \quad (11)$$

where  $q_{\text{RE}}$  and  $q_{\text{Fe}}$  are the point charges on the RE and Fe atoms, respectively. Within the constraints of the PCM therefore, the dominant contribution to  $B_{21}^c(\varepsilon_{xz})$  is from the RE lattice. This result is used in the following section to make an estimate of the magnetostriction in TbFe<sub>2</sub>, at 0 K.

#### 4. A PCM estimate of the magnetostriction in TbFe<sub>2</sub>

Unlike DyFe<sub>2</sub>, both TbFe<sub>2</sub> and TmFe<sub>2</sub> possess a [111] direction of easy magnetization, as dictated by the signs of the crystal field coefficients  $B_4$  and  $B_6$  (Bowden *et al* 1968). Moreover for both these compounds it is known that (i) the shear terms dominate the magnetostriction and (ii) the latter is well described by equations (7) and (8) (Abbundi and Clark 1978). In addition, we note that, if we set the diagonal terms equal to zero and the shear terms  $\varepsilon_{xy} = \varepsilon_{xz} = \varepsilon_{yz} = \varepsilon$ , the volume is conserved to second order in  $\varepsilon$ .

To make an estimate of the magnetostriction in TbFe<sub>2</sub>, it is necessary to recast equation (10) into a new frame of reference where the new  $z$  axis coincides with the [111] axis, the direction of preferred magnetization.

**Table 2.** Transformation of the rank 2 operators on rotating to a new coordinate system where the  $z$  axis is aligned with the [111] direction. After Arif *et al* (1975).

$$\begin{aligned}
 O_2^0 &\rightarrow O_2^2(c) - 2\sqrt{2}O_2^1(c) \\
 O_2^1(c) &\rightarrow \frac{1}{6} \left[ O_2^0 - \sqrt{2}O_2^1(c) + \sqrt{6}O_2^1(s) - O_2^2(c) + \sqrt{3}O_2^2(s) \right] \\
 O_2^1(s) &\rightarrow \frac{1}{6} \left[ O_2^0 - \sqrt{2}O_2^1(c) + \sqrt{6}O_2^1(s) - O_2^2(c) - \sqrt{3}O_2^2(s) \right] \\
 O_2^2(c) &\rightarrow -\frac{1}{\sqrt{6}}O_2^1(s) - \frac{1}{3}O_2^2(s) \\
 O_2^2(s) &\rightarrow \frac{1}{3} \left[ O_2^0 + 2\sqrt{2}O_2^1(c) + 2O_2^2(c) \right]
 \end{aligned}$$

Using the transformations set out in table 2, and keeping only the diagonal terms, we find

$$\langle \mathcal{H}'_{\text{CF}} \rangle_{\text{EX}} \rightarrow \frac{1}{2} \frac{\partial B_{21}^c}{\partial \varepsilon_{xz}} \langle O_{20} \rangle_{\text{EX}} \varepsilon. \quad (12)$$

To this we must add the elastic energy term:

$$E_{\text{Elas}} = 2C_{44}[\varepsilon_{xy}^2 + \varepsilon_{xz}^2 + \varepsilon_{yz}^2] = 6C_{44}\varepsilon^2. \quad (13)$$

Consequently, on minimizing with respect to  $\varepsilon$ , we find

$$\varepsilon = -\frac{\frac{\partial B_{21}^c}{\partial \varepsilon_{xz}} \langle O_{20} \rangle_{\text{EX}}}{24C_{44}}. \quad (14)$$

Thus the temperature dependence of  $\varepsilon$  follows that of  $\langle O_{20} \rangle_{\text{EX}} = \langle 3J_z^2 - J(J+1) \rangle_{\text{EX}}$  (see  $n = 2$  of figure 2), as expected (Clark 1979). Moreover, on using (i)  $C_{44} = 3.84 \times 10^{10}$  (J m<sup>-3</sup>) {=1.367 × 10<sup>5</sup> (K/ion)} (Blessing 1976) and (ii)  $\partial B_{21}^c / \partial \varepsilon_{xz} = \{q_{\text{RE}}(-31.5)\}$  (K/ion) (see equation (11), with  $q_{\text{RE}}$  set equal to +3), we find  $\varepsilon = 3024$  ppm at  $T = 0$  K. Finally, on noting that  $\partial \ell / \ell = 2\varepsilon$  for rhombohedral distortions, we conclude that  $\lambda_{111} = \partial \ell / \ell = 6048$  ppm. Rather surprisingly, this estimate compares favourably with the value given by Clark (1979) of  $\lambda_{111} = 4400$  ppm at 0 K. Alternatively, if we set  $\lambda_{111} = 4400$  ppm, the calculated field gradient is found to be  $\partial B_{21}^c / \partial \varepsilon_{xz} = -68.7$  (K/ion). Note, however, that the above treatment does not involve internal distortions, as discussed by Cullen and Clark (1977).

Finally, we note without proof that the PCM calculations also reveal that higher-order crystal field gradients  $\partial B_{n0} / \partial \varepsilon_{xz}$ , for  $n = 4$  and 6, are negligible. However, this is definitely not the case for the tetrahedral distortion discussed in the following section.

## 5. Magnetostriction in DyFe<sub>2</sub>

In the case DyFe<sub>2</sub>, with a [001] easy axis, it is the tetragonal terms that come into play. For our purposes therefore we set the shear terms equal to zero. For the undistorted lattice, with the unit cell parameter  $a = 7.325$  Å, the PCM model yields

$$\begin{aligned}
 B_{40} &= q_{\text{RE}}[-6.66 \times 10^{-4}] + q_{\text{Fe}}[+8.75 \times 10^{-4}] \\
 B_{44}(c) &= 5B_{40} \\
 B_{60} &= q_{\text{RE}}[-3.62 \times 10^{-7}] + q_{\text{Fe}}[-1.65 \times 10^{-7}] \\
 B_{64}(c) &= -21B_{60}.
 \end{aligned} \quad (15)$$

These numbers can be compared with the estimates of Atzmony and Dariel (1973, 1976) for the crystal field parameters at the Dy site:

$$\begin{aligned}
 B_{40} &= -3.02 \times 10^{-3} \text{ K} \\
 B_{60} &= -7.22 \times 10^{-6} \text{ K}.
 \end{aligned} \quad (16)$$

**Table 3.** The PCM calculations of the crystal field coefficients  $B_{n0}$  and their gradients. The Lorentz sphere used to obtain these numbers was set at  $12a$ , with  $a = 7.325 \text{ \AA}$ .

Sublattice		
$B_{n0}$	$\varepsilon_{zz}$	$\varepsilon_{xx}$
RE	$B_{20} = q_{\text{RE}}[+3.27\varepsilon_{zz} + 26.0\varepsilon_{zz}^2]$	$q_{\text{RE}}[-1.64\varepsilon_{xx} - 13.0\varepsilon_{xx}^2]$
RE	$B_{40} = q_{\text{RE}}[-6.66 \times 10^{-4} + 7.36 \times 10^{-3}\varepsilon_{zz}]$	$q_{\text{RE}}[-6.66 \times 10^{-4} + 1.30 \times 10^{-3}\varepsilon_{xx}]$
RE	$B_{60} = q_{\text{RE}}[-3.62 \times 10^{-7} + 2.34 \times 10^{-6}\varepsilon_{zz}]$	$q_{\text{RE}}[-3.62 \times 10^{-7} + 9.86 \times 10^{-8}\varepsilon_{xx} + 1.57 \times 10^{-6}\varepsilon_{xx}^2]$
Fe	$B_{20} = q_{\text{Fe}}[-10.64\varepsilon_{zz}]$	$q_{\text{Fe}} 5.32\varepsilon_{xx}$
Fe	$B_{40} = q_{\text{Fe}}[+8.75 \times 10^{-4} - 2.53 \times 10^{-3}\varepsilon_{zz}]$	$q_{\text{Fe}}[+8.75 \times 10^{-4} - 9.18 \times 10^{-4}\varepsilon_{xx}]$
Fe	$B_{60} = q_{\text{Fe}}[-1.65 \times 10^{-7} - 7.45 \times 10^{-6}\varepsilon_{zz}]$	$q_{\text{Fe}}[-1.65 \times 10^{-7} + 4.30 \times 10^{-6}\varepsilon_{xx}]$
Isotropic compression		
	$B_{40} = q_{\text{RE}}[-6.66 \times 10^{-4} + 3.33 \times 10^{-3}\varepsilon] + q_{\text{Fe}}[+8.75 \times 10^{-4} - 4.37 \times 10^{-3}\varepsilon]$	
	$B_{60} = q_{\text{RE}}[-3.62 \times 10^{-7} + 2.54 \times 10^{-6}\varepsilon] + q_{\text{Fe}}[-1.65 \times 10^{-7} + 1.16 \times 10^{-6}\varepsilon]$	

Given equations (15) and (16) we can solve for  $q_{\text{RE}}$  and  $q_{\text{Fe}}$ , finding  $q_{\text{RE}} = +16.0$  and  $q_{\text{Fe}} = +8.7$ . Since we expect  $q_{\text{RE}} \sim +3$  and  $q_{\text{Fe}}$  perhaps negative (for charge neutrality), this calculation illustrates the difficulties associated with the PCM in providing quantitative estimates of the crystal field parameters  $B_{n0}$ . Nevertheless, the PCM does provide estimates whose absolute values can be believed to, say, within an order of magnitude.

In the presence of a tetragonal distortion, the quadratic crystal field terms  $B_{20}$  and  $B_{22}^C$  make their appearance. In addition, the coefficients  $B_{40}$  and  $B_{60}$  change slightly and the ratios  $B_{44}(c) = 5B_{40}$  and  $B_{64}(c) = -21B_{60}$  for cubic symmetry fail. A summary of the PCM calculations for the diagonal  $B_{n0}$  terms can be seen in table 3. In general, the gradients are found to be linear. But where there is noticeable curvature, a quadratic term has been included.

Note the dramatic change in  $B_{60}$  as a function of distortion  $\varepsilon_{\alpha\alpha}$ , for the Fe sublattice. Also included in table 3 are the calculated values of  $B_{40}$  and  $B_{60}$  for the isotropic compression  $\varepsilon$ .

To reduce the number of parameters, it is helpful to try and establish relationships between the various gradients. For example, PCM calculations show that

$$\partial B_{20}/\partial \varepsilon_{xx} = \partial B_{20}/\partial \varepsilon_{yy} = -\frac{1}{2}\partial B_{20}/\partial \varepsilon_{zz}. \quad (17)$$

This is to be expected. If we compress the lattice equally in all directions  $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = \varepsilon$ , cubic symmetry is maintained and the total change in  $B_{20}$  must be zero. However, this conservation rule does not apply to  $B_{40}$  and  $B_{60}$ , both of which increase in magnitude as the lattice is compressed. Thus

$$\frac{\partial B_{40}}{\partial \varepsilon_{xx}} = \frac{1}{2} \left[ \frac{dB_{40}}{d\varepsilon} - \frac{\partial B_{40}}{\partial \varepsilon_{zz}} \right] \quad (18)$$

where  $(dB_{40}/d\varepsilon)$  is the change in  $B_{40}$  following isotropic compression. PCM calculations show that this indeed is the case, again demonstrating that the assumption of linear superposition is upheld. But there are no simple relationships between  $(\partial B_{40}/\partial \varepsilon_{zz})$  and  $(\partial B_{40}/\partial \varepsilon_{xx})$ , and  $(\partial B_{60}/\partial \varepsilon_{zz})$  and  $(\partial B_{60}/\partial \varepsilon_{xx})$ . Thus we are left with the rather disagreeable fact that five parameters may be required to fit the magnetoelastic data of DyFe<sub>2</sub>.

A possible way around this impasse can be devised by noting that within the PCM

$$B_{40} \propto 1/a^5 \quad \text{and} \quad B_{60} \propto 1/a^7 \quad (19)$$

where  $a$  is the value of the unit cell. This result can be used to show that

$$\frac{dB_{40}}{d\varepsilon} = -5B_{40} \quad \text{and} \quad \frac{dB_{60}}{d\varepsilon} = -7B_{60} \quad (20)$$



for isotropic compression, in agreement with the calculations set out in table 3. Thus, if we use the crystal field parameters given in equation (16), the problem can be reduced to the three parameters  $\partial B_{20}/\partial \varepsilon_{zz}$ ,  $\partial B_{40}/\partial \varepsilon_{zz}$  and  $\partial B_{60}/\partial \varepsilon_{zz}$ . However, such an approach remains heavily reliant on the predictions of the PCM, embodied in equations (19) and (20).

In summary, therefore, the crystal field energy associated with the tetragonal distortion is given by

$$E_{\text{ME}} = \frac{\partial B_{20}}{\partial \varepsilon_{zz}} \langle O_{20} \rangle_{\text{EX}} \varepsilon_{zz} + \frac{\partial B_{40}}{\partial \varepsilon_{zz}} \langle O_{40} \rangle_{\text{EX}} \varepsilon_{zz} + \frac{\partial B_{60}}{\partial \varepsilon_{zz}} \langle O_{60} \rangle_{\text{EX}} \varepsilon_{zz} \\ - \frac{1}{2} \frac{\partial B_{20}}{\partial \varepsilon_{zz}} \langle O_{20} \rangle_{\text{EX}} \varepsilon_{xx} + \frac{\partial B_{40}}{\partial \varepsilon_{xx}} \langle O_{40} \rangle_{\text{EX}} \varepsilon_{xx} + \frac{\partial B_{60}}{\partial \varepsilon_{xx}} \langle O_{60} \rangle_{\text{EX}} \varepsilon_{xx} \\ - \frac{1}{2} \frac{\partial B_{20}}{\partial \varepsilon_{zz}} \langle O_{20} \rangle_{\text{EX}} \varepsilon_{yy} + \frac{\partial B_{40}}{\partial \varepsilon_{xx}} \langle O_{40} \rangle_{\text{EX}} \varepsilon_{yy} + \frac{\partial B_{60}}{\partial \varepsilon_{xx}} \langle O_{60} \rangle_{\text{EX}} \varepsilon_{yy} \quad (21)$$

for an arbitrary tetrahedral distortion  $\varepsilon_{zz} \neq \varepsilon_{xx} = \varepsilon_{yy}$ . To this we must add the elastic energy:

$$E_{\text{Elas}} = \frac{1}{2} C_{11} [\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2] + C_{12} [\varepsilon_{xx} \varepsilon_{yy} + \varepsilon_{xx} \varepsilon_{zz} + \varepsilon_{yy} \varepsilon_{zz}]. \quad (22)$$

On minimizing with respect to the three distortions we find

$$\begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \end{pmatrix} = \frac{1}{\eta} \begin{bmatrix} C_{11} + C_{12} & -C_{12} & -C_{12} \\ -C_{12} & C_{11} + C_{12} & -C_{12} \\ -C_{12} & -C_{12} & C_{11} + C_{12} \end{bmatrix} \begin{pmatrix} d_x \\ d_y \\ d_z \end{pmatrix} \quad (23)$$

where

$$\eta = (C_{11} - C_{12})(C_{11} + 2C_{12}) \quad (24)$$

and

$$\begin{pmatrix} d_x \\ d_y \\ d_z \end{pmatrix} = \begin{pmatrix} +\frac{1}{2} \frac{\partial B_{20}}{\partial \varepsilon_{zz}} \langle O_{20} \rangle_{\text{EX}} & -\frac{\partial B_{40}}{\partial \varepsilon_{xx}} \langle O_{40} \rangle_{\text{EX}} & -\frac{\partial B_{60}}{\partial \varepsilon_{xx}} \langle O_{60} \rangle_{\text{EX}} \\ +\frac{1}{2} \frac{\partial B_{20}}{\partial \varepsilon_{zz}} \langle O_{20} \rangle_{\text{EX}} & -\frac{\partial B_{40}}{\partial \varepsilon_{xx}} \langle O_{40} \rangle_{\text{EX}} & -\frac{\partial B_{60}}{\partial \varepsilon_{xx}} \langle O_{60} \rangle_{\text{EX}} \\ -\frac{\partial B_{20}}{\partial \varepsilon_{zz}} \langle O_{20} \rangle_{\text{EX}} & -\frac{\partial B_{40}}{\partial \varepsilon_{zz}} \langle O_{40} \rangle_{\text{EX}} & -\frac{\partial B_{60}}{\partial \varepsilon_{zz}} \langle O_{60} \rangle_{\text{EX}} \end{pmatrix}. \quad (25)$$

Note that  $d_x = d_y$  and therefore  $\varepsilon_{xx} = \varepsilon_{yy}$ , as expected.

Despite the complexity of equations (23)–(25), some salient facts can already be noted. Firstly, the temperature dependence of the magnetostriction now depends not only on  $\langle O_{20} \rangle_{\text{EX}}$  but also on  $\langle O_{40} \rangle_{\text{EX}}$  and  $\langle O_{60} \rangle_{\text{EX}}$ . Secondly, since the temperature dependence of the expectation values of the operators  $\langle O_{n0} \rangle_{\text{EX}}$  is faster for higher  $n$  (see figure 2), it is quite plausible that the  $\langle O_{60} \rangle_{\text{EX}}$  term is responsible for the fast temperature dependence of  $\lambda_{100}$  below 100 K. These points are taken further in the next section.

## 6. Volume conservation

So far, we have made no comments regarding volume conservation during the magnetostriction process. However, if the magnetostriction is driven solely by the quadratic crystal field term, it is easily shown that

$$\varepsilon_{zz} = \frac{1}{(C_{11} - C_{12})} \frac{\partial B_{20}}{\partial \varepsilon_{zz}} \langle O_{20} \rangle_{\text{EX}} \quad (26) \\ \varepsilon_{xx} = \varepsilon_{yy} = -\frac{1}{2} \varepsilon_{zz}.$$

Thus (i) volume is conserved and (ii) the magnetostriction follows the classic Callen and Callen prediction: namely that the magnetostriction decreases monotonically with increasing temperature according to  $\langle O_{20} \rangle_{\text{EX}}$ . Since this is not found experimentally in DyFe<sub>2</sub>, higher-order crystal field terms must be important.

In practice, there is only one way of incorporating the higher-order fourth- and sixth-order terms, while conserving volume at all temperatures. We must set

$$\frac{\partial B_{40}}{\partial \varepsilon_{xx}} = -\frac{1}{2} \frac{\partial B_{40}}{\partial \varepsilon_{zz}} \quad \text{and} \quad \frac{\partial B_{60}}{\partial \varepsilon_{xx}} = -\frac{1}{2} \frac{\partial B_{60}}{\partial \varepsilon_{zz}} \quad (27)$$

(see equation (32) below). However, in view of equations (18) and (20), this implies that the isotropic gradients  $dB_{40}/d\varepsilon$  and  $dB_{60}/d\varepsilon$  are zero. Nevertheless, as we shall see below, the constant volume approximation does provide a reasonable fit to the magnetostriction data.

Given equations (17) and (27) it is easily shown that

$$\varepsilon_{zz} = -\frac{1}{(C_{11} - C_{12})} \left[ \frac{\partial B_{20}}{\partial \varepsilon_{zz}} \langle O_{20} \rangle_{\text{EX}} + \frac{\partial B_{40}}{\partial \varepsilon_{zz}} \langle O_{40} \rangle_{\text{EX}} + \frac{\partial B_{60}}{\partial \varepsilon_{zz}} \langle O_{60} \rangle_{\text{EX}} \right] \quad (28)$$

$$\varepsilon_{xx} = \varepsilon_{yy} = -\frac{1}{2} \varepsilon_{zz}.$$

Thus the magnetostriction takes the form of a simple linear combination:

$$\varepsilon_{zz} = \alpha \langle O_{20} \rangle_n + \beta \langle O_{40} \rangle_n + \gamma \langle O_{60} \rangle_n \quad (29)$$

where the  $\langle O_{n0} \rangle_n$  are the normalized values of the  $\langle O_{n0} \rangle_{\text{EX}}$ , as shown in figure 2. From a least squares fit to the experimental data shown in figure 1 we find

$$\alpha = +220(15) \text{ ppm}; \quad \beta = -1048(11) \text{ ppm}; \quad \gamma = 758(4) \text{ ppm}. \quad (30)$$

The errors shown are only approximate. They are derived from computed fits where the RE exchange field Hamiltonian has been set to  $135(5)J_z$ . If the exchange term is set at a  $100J_z$  (the estimate of the RE exchange field given by Atzmony and Dariel (1973, 1976)), the minimum in the calculated magnetostriction moves noticeably towards a lower temperature.

From an examination of figure 1, it will be observed that the agreement between theory and experiment is very reasonable. Thus we are able, at last, to gain a detailed insight into the nature of the magnetostriction in DyFe<sub>2</sub>. At low temperatures the  $\partial B_{40}/\partial \varepsilon_{zz}$  term ( $\sim 1000$  ppm) is primarily responsible for the negative contraction, but this is offset by smaller positive expansions from both  $\partial B_{20}/\partial \varepsilon_{zz}$  and  $\partial B_{60}/\partial \varepsilon_{zz}$  terms. However, since the positive expansion originating from  $\partial B_{60}/\partial \varepsilon_{zz}$  falls off very rapidly with increasing temperature, this gives rise to a minimum in the contraction at about 120 K. Finally, at higher temperatures the  $\partial B_{20}/\partial \varepsilon_{zz}$  term dominates and gives rise to a small positive magnetostriction above room temperature.

Given the results embodied in equation (31), it is possible to deduce the three field gradients involved:

$$\frac{\partial B_{20}}{\partial \varepsilon_{zz}} = -0.579(39); \quad \frac{\partial B_{40}}{\partial \varepsilon_{zz}} = +1.772(20) \times 10^{-2}; \quad \frac{\partial B_{60}}{\partial \varepsilon_{zz}} = -2.329(12) \times 10^{-4} \quad (31)$$

where we have used, the stiffness constants  $C_{11} = 4.16 \times 10^5$  and  $C_{12} = 1.367 \times 10^5$  (K fu<sup>-1</sup>) (Blessing 1976). These field gradients, obtained from the magnetostriction data, should not be seen as being at odds with the predictions of the PCM. For example, if we use equations (16) and (20) we find the isotropic gradients  $dB_{40}/d\varepsilon = +1.51 \times 10^{-3}$  and  $dB_{60}/d\varepsilon = 5.44 \times 10^{-3}$ . Such numbers are consistent, within the accuracy afforded by the PCM.

Finally, we note that further progress can be made by dropping the volume conserving restriction imposed by equation (27). However, this inevitably leads to coupling between the  $\varepsilon_{zz}$  and  $\varepsilon_{xx}$  ( $=\varepsilon_{yy}$ ) strains via

$$\begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{zz} \end{pmatrix} = \frac{1}{\eta} \begin{pmatrix} C_{11} & -C_{12} \\ -2C_{12} & C_{11} + C_{12} \end{pmatrix} \begin{pmatrix} d_x \\ d_z \end{pmatrix}. \quad (32)$$

Thus the problem becomes less transparent. Moreover, in place of three parameters, five crystal field gradients are now required to fit the magnetostrictive data. In practice, of course, it is

always possible to increase the agreement between theory and experiment simply by increasing the number of adjustable parameters. However, before this is attempted, simultaneous measurements of both  $\varepsilon_{zz}$  and  $\varepsilon_{xx}$  should be made. This information could then be used to place constraints on the relationship between the crystal field gradients  $\partial B_{n0}/\partial\varepsilon_{xx}$  and  $\partial B_{n0}/\partial\varepsilon_{zz}$ , for  $n = 4$  and  $6$ .

## 7. Discussion and conclusions

In this paper an explanation has been given for the anomalous temperature dependence of the magnetostriction in single-crystal DyFe<sub>2</sub>, within the canons of the CCM. Provided higher-order crystal field terms are taken into account, it is possible to fit the magnetoelastic data with just three field gradients. Indeed the problem can be turned on its head and the measured magnetostriction used to calculate the crystal field gradients  $\partial B_{n0}/\partial\varepsilon_{\alpha\alpha}$  for the REFe<sub>2</sub> intermetallic compounds. As expected, these experimentally determined gradient values differ from the predictions of the simple PCM model. Clearly a more refined *ab initio* model is needed to calculate the crystal field coefficients  $B_4$  and  $B_6$  and their gradients  $\partial B_{n0}/\partial\varepsilon_{\alpha\beta}$ , etc. One possibility is to use a first principles density functional approach. This has been used, for example, to calculate the crystal field coefficients for hexagonal SmCo<sub>5</sub> (Richter *et al* 1992). But to the authors' knowledge no such calculations have been performed for the gradients  $\partial B_{n0}/\partial\varepsilon_{\alpha\beta}$ .

Finally, some cautionary remarks should be made. In the above treatment it has been assumed that the stiffness constants  $C_{11}$ , etc, are all temperature-independent. This is unlikely to be the case. Both Young's modulus and the shear modulus have been measured and are known to be temperature-dependent, particularly in those REFe<sub>2</sub> alloys which exhibit magnetic compensation (see the review by Clark 1979). In particular, the Young's modulus in DyFe<sub>2</sub> falls by some 10% as the temperature is raised from 0 to 300 K (Klimker *et al* 1974). Similar comments also apply of course to the field gradients  $\partial B_{n0}/\partial\varepsilon$ , which are unlikely to remain constant as the lattice expands on warming. However the essential physics of the magnetostrictive processes in DyFe<sub>2</sub> have been identified, and a 27 year problem in magnetism laid to rest.

## References

- Abbundi A and Clark A E 1978 *J. Appl. Phys.* **49** 1969–71  
 Arif S K, Bunbury D St P, Bowden G J and Day R K 1975 *J. Phys. F: Met. Phys.* **5** 1037–47  
 Atzmony U and Dariel M P 1973 *Phys. Rev. B* **7** 4220–32  
 Atzmony U and Dariel M P 1976 *Phys. Rev. B* **13** 4006–14  
 Bleaney B, Bowden G J, Cadogan J M, Day R K and Dunlop J B 1981 *J. Phys. F: Met. Phys.* **12** 795–811  
 Blessing G 1976 *Acoustical Society of America, Bulletin 92nd Mtg (San Diego, CA, Nov. 1976)*  
 Bowden G J, Bunbury D St P, Guimares A and Snyder R E 1968 *J. Phys. C: Solid State Phys.* **1** 1376–87  
 Buschow K H J 1977 *Rep. Prog. Phys.* **40** 1179–256  
 Callen E and Callen H B 1963 *Phys. Rev.* **129** 578–93  
 Callen E and Callen H B 1965a *Phys. Rev. A* **139** 455–71  
 Callen H B and Callen E 1965b *J. Phys. Chem. Solids* **27** 1271–85  
 Claeysen F, Lhermet N, de Letty R and Bouchilloux P 1997 *J. Alloys Compounds* **258** 61–73  
 Clark A E 1979 *Handbook on the Physics and Chemistry of the Rare Earths* vol 2, ed K A Gschneider Jr and L Eyring (Amsterdam: North-Holland) pp 231–58  
 Clark A E, Abbundi R, Savage H T and McMasters O D 1977 *Physica B* **86–88** 73–4  
 Clark A E and Belson H H 1972 *Phys. Rev. B* **5** 3642–4  
 Cullen J R and Clark A E 1977 *Phys. Rev. B* **15** 4510–5  
 de la Fuente C, Arnaudas J I, Ciria M and Moral A del 2001 *Phys. Rev. B* **63** 054417  
 Greenough R D, Jenner A G I, Schulze M P and Wilkinson A J 1991 *J. Magn. Magn. Mater.* **101** 75–80  
 Hutchings M T 1964 *Solid State Phys.* **16** 2227–73  
 Kittel C 1971 *Introduction to Solid State Physics* 4th edn (New York: Wiley)  
 Klimker H, Rosen M, Dariel M P and Atzmony U 1974 *Phys. Rev. B* **10** 2968–72  
 Richter M, Oppeneer P M, Eschrig H and Johansson B 1992 *Phys. Rev. B* **46** 13919