

## The magnetoelastic effect in $\text{CoF}_2$ investigated by means of neutron powder diffraction

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

2010 J. Phys.: Condens. Matter 22 096001

(<http://iopscience.iop.org/0953-8984/22/9/096001>)

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 30/05/2010 at 07:24

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

# The magnetoelastic effect in $\text{CoF}_2$ investigated by means of neutron powder diffraction

Tapan Chatterji<sup>1</sup>, Bachir Ouladdiaf<sup>2</sup> and Thomas C Hansen<sup>2</sup>

<sup>1</sup> JCNS, Forschungszentrum Jülich Outstation at Institut Laue-Langevin, BP 156, 38042 Grenoble Cedex 9, France

<sup>2</sup> Institut Laue-Langevin, BP 156, 38042 Grenoble Cedex 9, France

Received 14 October 2009, in final form 1 December 2009

Published 10 February 2010

Online at [stacks.iop.org/JPhysCM/22/096001](http://stacks.iop.org/JPhysCM/22/096001)

## Abstract

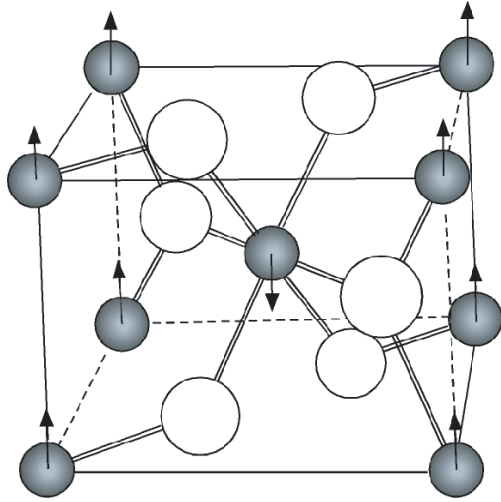
We have investigated the magnetoelastic effects in  $\text{CoF}_2$  associated with the antiferromagnetic phase transition temperature  $T_N \approx 39$  K by means of neutron powder diffraction. The temperature variation of the lattice parameters and the unit cell volume has been determined accurately with small temperature steps. From the temperature variation of the lattice parameter  $c$  we extracted the lattice strain  $\Delta c$  associated with the antiferromagnetic phase transition. Rietveld refinement of the crystal and magnetic structure from the diffraction data at 2.2 K gave a magnetic moment of  $2.57 \pm 0.02 \mu_B$  per Co ion. We determined the temperature variation of the intensity of the 100 magnetic Bragg reflection, which is proportional to the square of the order parameter of the phase transition. We established that the lattice strain  $\Delta c$  couples linearly with the square of the order parameter of the antiferromagnetic phase transition in  $\text{CoF}_2$ .

(Some figures in this article are in colour only in the electronic version)

The coupling between the spin and lattice degree of freedom is an important topic in condensed matter physics especially in context with many novel electronic materials with potential industrial applications, for example, colossal magnetoresistive manganites and multiferroic materials. Below the magnetic ordering temperature the lattice tends to respond by distorting itself from that of the paramagnetic state. The distortion involves the lattice parameters with or without a change in symmetry. This magnetoelastic effect which is sometimes called magnetostriction or exchange striction is, however, often very small and therefore can only be detected with high resolution diffraction techniques. With the advent of the high resolution synchrotron x-ray and neutron diffraction techniques the magnetoelastic effects such as exchange striction can now be investigated. The temperature stability and the instrument resolution are also important requirements for such studies. In order to study the small magnetoelastic effects it is necessary have very fine temperature steps and for this a high-intensity x-ray or neutron beam is useful in order to complete the study in a finite time. The exchange striction has been investigated quite intensively in ferromagnets due to their industrial applications. There are several excellent review articles [1–6] on the magnetoelastic

effect that focus mainly on ferromagnetic materials. The magnetoelastic effects have been relatively less investigated in antiferromagnets. However, these effects have been thoroughly investigated in face centred cubic antiferromagnets such as simple transition metal oxide MnO and chalcogenide MnS [7]. The magnetoelastic effects in rare earth metals and compounds have also been reviewed [8, 9]. We recently reported [10, 11] magnetoelastic effects in  $\text{LaMnO}_3$  and  $\text{NdMnO}_3$  close to the Néel temperature. Here we report the results of our neutron diffraction investigation of the magnetostriction close to the antiferromagnetic phase transition in  $\text{CoF}_2$ .

$\text{CoF}_2$  belongs to the family of transition metal difluoride, which have been the subject of intensive investigations [12–19].  $\text{CoF}_2$  along with other transition metal difluorides  $\text{MnF}_2$ ,  $\text{FeF}_2$  and  $\text{NiF}_2$ , crystallize with the tetragonal rutile-type structure in the  $P4_2/mnm$  space group. However the magnetic properties of  $\text{CoF}_2$  are more complex than those of isomorphous  $\text{MnF}_2$ , because the Co ion has unpaired angular momentum that plays an important role in determining its magnetic properties.  $\text{CoF}_2$  orders [20–24] below  $T_N \approx 39$  K with an antiferromagnetic structure [25] shown in figure 1 with the propagation vector  $\mathbf{k} = 0$ . The magnetic moments of Co ions at the corner (000) positions of the tetragonal unit cell

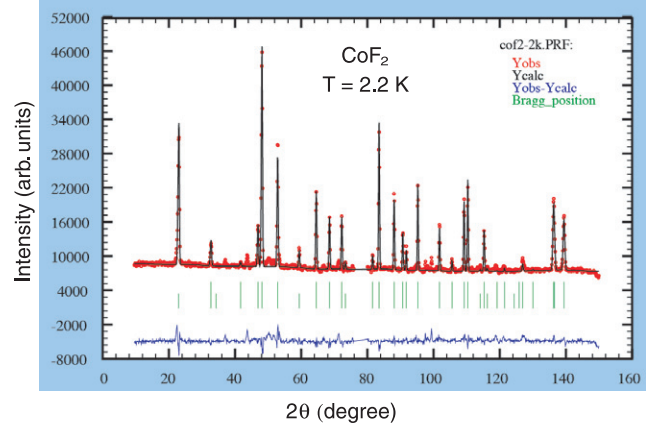


**Figure 1.** The antiferromagnetic structure adopted by 3d transition metal difluorides namely CoF<sub>2</sub> with the rutile-type crystal structure. The black circles represent the transition metal ion and the white circles represent the F ions. The arrows on the black circles represent moment direction of the transition metal ions below the Néel temperature [25].

are all parallel to the *c*-axis whereas that of the Co ions at the ( $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ ) positions are oppositely oriented. The presence of an orbital moment in CoF<sub>2</sub> makes it particularly interesting for the study of magnetoelastic coupling in this compound. We recently investigated [26] the hyperfine interaction in CoF<sub>2</sub> by high resolution neutron spectroscopy and concluded that the presence of unquenched orbital moment of the Co ion in CoF<sub>2</sub> leads to its anomalous behaviour compared to that of other Co-based compounds.

Powder neutron diffraction measurements were performed on CoF<sub>2</sub> using the high-intensity two-axis powder diffractometer [27] D20 at the Institut Laue-Langevin, Grenoble. The neutron wavelength was 1.868 Å. For enhanced resolution a Soller collimator with a divergence of 20' in the incident beam, and a monochromator aperture of 20 mm were used. Approximately a 3 g CoF<sub>2</sub> powder sample was placed inside a 8 mm diameter vanadium can, which was fixed to the sample stick of a standard <sup>4</sup>He cryostat. Figure 2 shows a typical diffraction diagram measured at *T* = 2.2 K along with the results of Rietveld refinement of the tetragonal *P*4<sub>2</sub>/*mnm* crystal structure and the antiferromagnetic structure described in the previous paragraph.

Figure 3 shows the temperature variation of the lattice parameters *a*, *c* and the unit cell volume *V* of CoF<sub>2</sub>. The lattice parameters *a* and *c* show strong anomalies close to *T*<sub>N</sub> ≈ 39 K. The lattice parameter *a* increases whereas the lattice parameter *c* decreases below *T*<sub>N</sub>. The effect of the antiferromagnetic transition on the lattice parameter *a* is particularly remarkable in that the increase of this lattice parameter with decreasing temperature starts below about *T* = 110 K, which is much higher than *T*<sub>N</sub> ≈ 39 K. The decrease in the lattice parameter *c* on the other hand starts below about *T* = 50 K, which is much closer to *T*<sub>N</sub>. It seems that the short-range magnetic correlations influence the lattice parameter *a* more than they



**Figure 2.** The diffraction diagram of CoF<sub>2</sub> at *T* = 2.2 K with the result of the Rietveld refinement of the tetragonal *P*4<sub>2</sub>/*mnm* crystal structure and the antiferromagnetic structure.

do the lattice parameter *c*. The unit cell volume remains more or less constant below *T*<sub>N</sub>. This may suggest a strong anisotropy in magnetic correlations along the *a* and *c* axes above the Néel temperature. There is a slight tendency of the unit cell volume to increase at lower temperature but it is not very significant. We have extrapolated the temperature variation of the lattice parameter *c* in the temperature range 50–170 K to the low temperature range by fitting with polynomial function shown in figure 3 as red curves. We extrapolated the corresponding data for *a* and *V* similarly. We expect that this is how the lattice parameters *a* and *c* and the unit cell volume *V* would vary with temperature in the absence of any magnetic transition. However the extrapolated red curves for *a* and *V* are more uncertain than that of *c*. By subtracting the measured temperature variation of *a*, *c* and *V* from these curves we got the lattice strains Δ*a*, Δ*c* and Δ*V* due to the magnetostriction. Figure 4 shows the temperature variation of these lattice strains. The relative difference between observed and extrapolated curves in red colour

$$\lambda_a = \frac{a - a_0}{a_0}; \quad \lambda_c = \frac{c - c_0}{c_0} \quad (1)$$

are spontaneous linear magnetostrictive strains in basal plane and along the *c*-axis, respectively. They are temperature dependent and reach their maximum value at *T* = 0 K. The corresponding relative difference

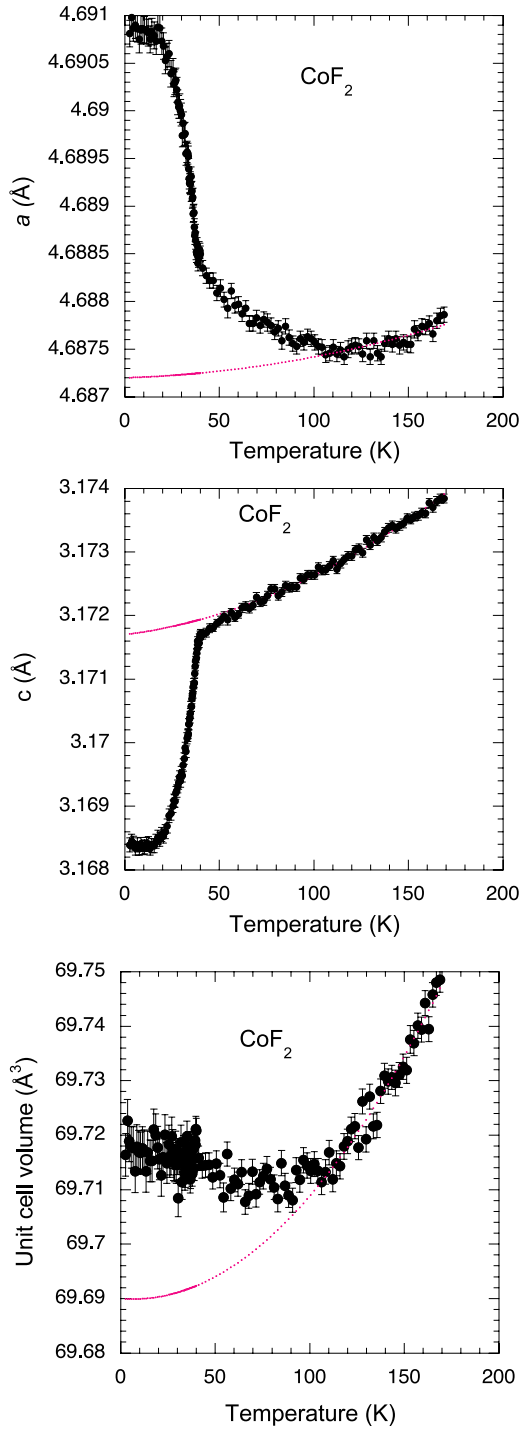
$$\omega_s = \frac{V - V_0}{V_0} \quad (2)$$

defines spontaneous volume magnetostriction. In the case of uniaxial lattices (i.e., tetragonal, hexagonal and rhombohedral)

$$\omega_s = 2\lambda_a + \lambda_c. \quad (3)$$

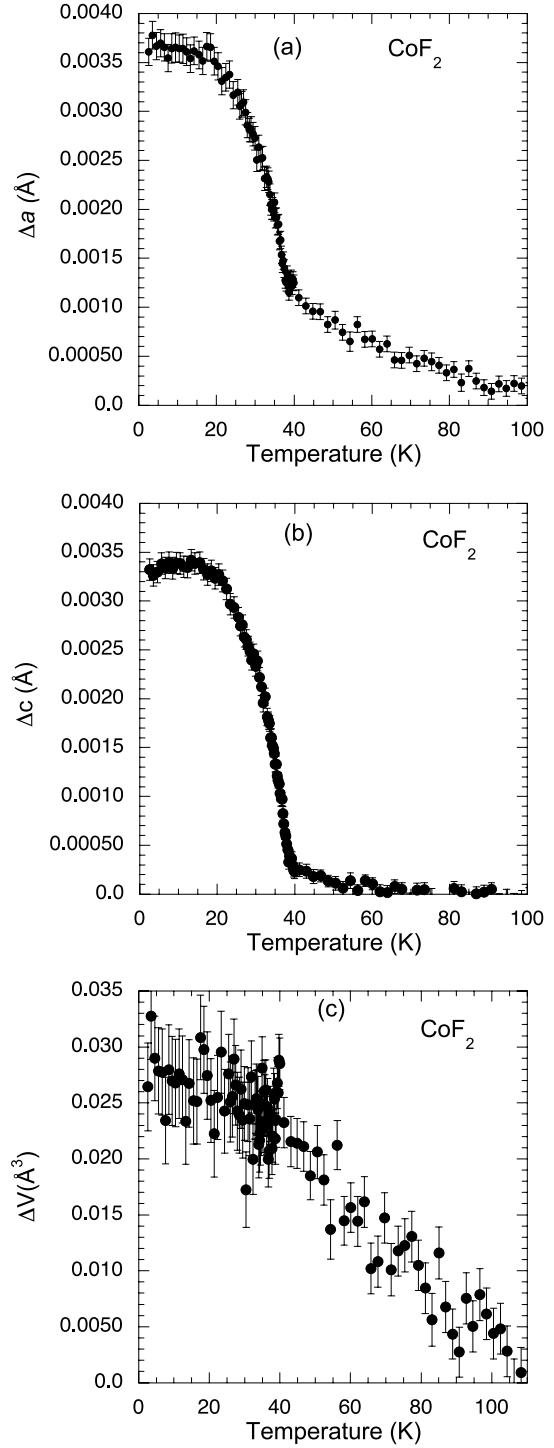
In the case of uniaxial crystals, the linear magnetostriction up to second-order terms can be described by [28]

$$\begin{aligned} \lambda = & \lambda_1^{\alpha,0}(\beta_x^2 + \beta_y^2) + \lambda_2^{\alpha,0}\beta_z^2 + \lambda_1^{\alpha,2}(\beta_x^2 + \beta_y^2)(\alpha_z^2 - 1/3) \\ & + \lambda_2^{\alpha,2}\beta_z^2(\alpha_z^2 - 1/3) + \lambda^{\gamma,2}[0.5(\beta_x^2 + \beta_y^2)(\alpha_x^2 - \alpha_y^2) \\ & + 2\alpha_x\beta_x\alpha_y\beta_y] + 2\lambda^{\epsilon,2}(\alpha_x\beta_x + \alpha_y\beta_y)\alpha_z\beta_z. \end{aligned} \quad (4)$$



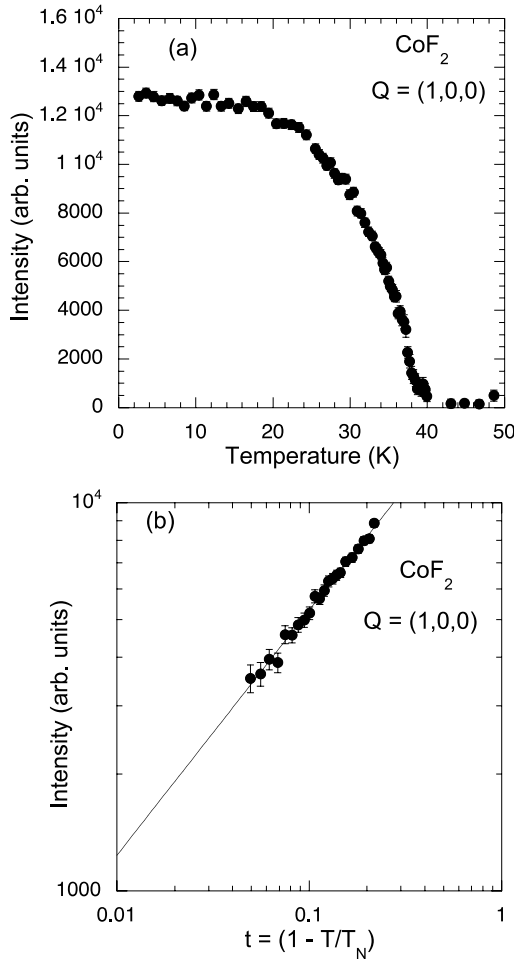
**Figure 3.** Temperature variation of the lattice parameters  $a$ ,  $c$  and the unit cell volume  $V$  of  $\text{CoF}_2$ . The red curves are extrapolated  $a$ ,  $c$  and  $V$  from the high temperature lattice parameters and unit cell volume and represent their temperature variation in the absence of magnetic ordering.

The  $z$ -axis coincides with the  $c$ -axis of the crystal. Here  $\alpha_i$  denote the direction cosines of the magnetisation with respect to the crystal axes and  $\beta_i$  are the direction cosines of the strain measurement direction with respect to the crystal axes. The magnetostriction constants with index  $\alpha$  ( $\alpha$ -magnetostriction) do not reduce the lattice symmetry and describe the changes in interatomic distance within the



**Figure 4.** Temperature variation of (a)  $\Delta a$ , (b)  $\Delta c$  and (c)  $\Delta V$ .

basal plane ( $\lambda_1^\alpha$ ) and along the  $c$ -axis ( $\lambda_2^\alpha$ ). The terms with zero-order  $\alpha$ -magnetostriction constant  $\lambda_1^{\alpha,0}$  and  $\lambda_2^{\alpha,0}$  do not depend on the magnetization direction and represent the isotropic (with respect to the magnetization direction) part of magnetostriction. The second-order  $\alpha$ -magnetostriction has anisotropic character and reflects the change in interatomic distances within the basal plane ( $\lambda_1^{\alpha,2}$ ) and along the  $c$ -axis ( $\lambda_2^{\alpha,2}$ ), when the magnetization rotates in the crystal under the action of magnetic field or during a spontaneous



**Figure 5.** (a) Temperature variation of the magnetic 100 reflection. (b) Log–log plot of the intensity of the 100 magnetic peak versus reduced temperature  $t = (T_N - T)/T_N$  that yield the critical exponent  $\beta = 0.315 \pm 0.007$ .

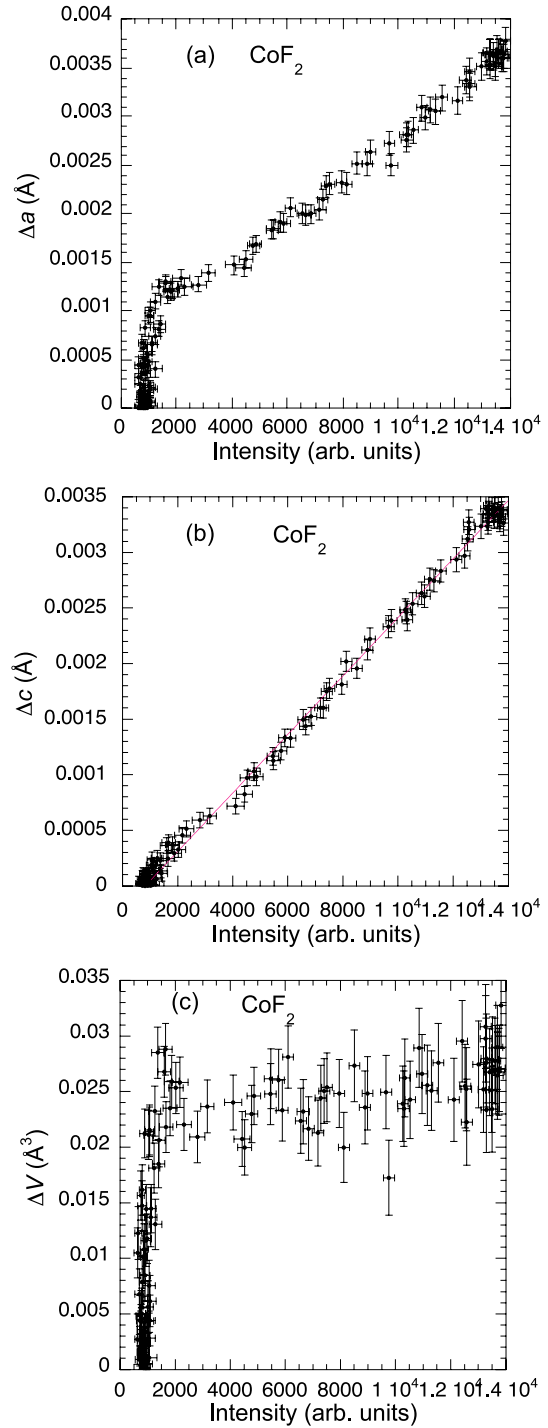
spin reorientation. The quantity  $\lambda^\gamma$  ( $\gamma$ -magnetostriction) describes an orthorhombic distortion in the basal plane when the magnetization direction does not coincide with the  $c$ -axis. The quantity  $\lambda^\epsilon$  describes a deviation of the angle between the basal plane and the  $c$ -axis from  $90^\circ$ .

The magnetovolume effect  $\omega_s$  and the atomic magnetic moment  $\mu$  for a single sublattice ferromagnet are connected by the following phenomenological expression:

$$\omega_s = kC\mu^2 = n\mu^2, \quad (5)$$

where  $k$  is the compressibility and  $C$  is the magnetoelastic-coupling constant. The magnetoelastic-coupling coefficient  $n = kC$  is used when the factor  $k$  and  $C$  cannot be found separately. We will show in the following that the above expression seems also to be valid for the two sublattice antiferromagnet  $\text{CoF}_2$ .

We investigated the antiferromagnetic phase transition in  $\text{CoF}_2$  at  $T_N$ . Figure 5(a) shows the temperature dependence of the intensity of the 100 magnetic reflection that is proportional to the square of the magnetic moment of the Co ion or the square of the order parameter of the antiferromagnetic phase



**Figure 6.** Plot of the lattice strains (a)  $\Delta a$ , (b)  $\Delta b$  and (c)  $\Delta V$  against the intensity of the 100 magnetic reflection.

transition. From the Rietveld refinement of the diffraction intensities at  $T = 2.2$  K (figure 2) the magnetic moment of the Co ion was determined to be  $2.57 \pm 0.02 \mu_B$ . The magnetic moment determined agrees well with that determined by Jauch *et al* [24] who found a moment  $2.60 \pm 0.04 \mu_B$  per Co ion. The Néel temperature was determined from the temperature variation of the intensity of the 100 magnetic reflection to be  $T_N = 39.0 \pm 0.4$  K. To determine the critical exponent we did a log–log plot (figure 5(b)) of the intensity of the 100

magnetic reflection close to  $T_N$  versus the reduced temperature  $t = (1 - T/T_N)$ . This gave the critical exponent  $\beta = 0.315 \pm 0.007$  which is quite close to the three-dimensional Ising value  $\beta = 0.326$  and is also consistent with previous neutron diffraction results [22, 23]. However, this agreement could be accidental because we did not have enough data points close to  $T_N$ .

In order to check how the lattice strains  $\Delta a$ ,  $\Delta c$  and  $\Delta V$  couple to the order parameter we plotted these against the intensity of the 100 magnetic reflection shown in figure 6. As we already commented that the intensity of the 100 magnetic reflection is proportional to the square of the order parameter or to the square of the magnetic moment of the Co ion. The linear plot shows that the lattice strain  $\Delta c$  couples linearly with the square of the order parameter. The linearity is quite obvious for  $\Delta c$  but it is much less so for  $\Delta a$  and perhaps questionable for  $\Delta V$ . The quadratic relationship between the lattice strain and the order parameter is expected for a single sublattice ferromagnet as shown in equation (5). But figure 6 shows that equation (5) is also valid for the two sublattice antiferromagnet  $\text{CoF}_2$ . It is not clear what determines the coupling between the lattice strain and the order parameter. Completely different results were obtained by us [10, 11] in  $\text{LaMnO}_3$  and  $\text{NdMnO}_3$ . In  $\text{NdMnO}_3$  the lattice strain along the  $c$ -axis was found to couple linearly with the order parameter whereas in  $\text{LaMnO}_3$  the coupling was neither linear nor quadratic. In order to ascertain what really determines the coupling we plan to study systematically the magnetoelastic effect in a number of simple antiferromagnets.

In conclusion we investigated the magnetoelastic effects in the simple antiferromagnet  $\text{CoF}_2$  close to  $T_N$  by neutron powder diffraction and have established that the lattice strain  $\Delta c$  couples linearly with the square of the order parameter of the antiferromagnetic phase transition.

## References

- [1] Mayergoyz I D 2000 *Handbook of Giant Magnetoresistive Materials* (San Diego, CA: Academic)
- [2] du Tremolet de Lacheisserie E 1993 *Magnetostriction: Theory and Application of Magnetoelasticity* (Boca Raton, FL: CRC Press)
- [3] Morin P and Schmitt D 1990 *Ferromagnetic Materials* vol 5, ed K H J Buschow and E P Wohlfarth (Amsterdam: Elsevier) p 59
- [4] Andreev S 1990 *Ferromagnetic Materials* vol 5, ed K H J Buschow and E P Wohlfarth (Amsterdam: Elsevier) p 237
- [5] Wassermann E F 1990 *Ferromagnetic Materials* vol 5, ed K H J Buschow and E P Wohlfarth (Amsterdam: Elsevier) p 1
- [6] Clark A E 1980 *Ferromagnetic Materials* vol 1, ed E P Wohlfarth (Amsterdam: North-Holland) p 531
- [7] Morosin B 1970 *Phys. Rev. B* **1** 236
- [8] Doerr M, Rotter M and Lindbaum A 2005 *Adv. Phys.* **54** 1
- [9] Lindbaum A and Rotter M 2002 *Handbook of Magnetic Materials* vol 14, ed K H J Buschow (Amsterdam: Elsevier) p 307
- [10] Chatterji T, Henry P F and Ouladdiaf B 2008 *Phys. Rev. B* **77** 212403
- [11] Chatterji T, Ouladdiaf B and Bhattacharya D 2009 *J. Phys.: Condens. Matter* **21** 306001
- [12] Staut J W and Griffel M 1949 *Phys. Rev.* **76** 144
- [13] Ohlmann R C and Tinkham M 1961 *Phys. Rev.* **123** 425
- [14] Kieffer F 1952 *Phys. Rev.* **87** 608
- [15] Nakamura T and Taketa H 1955 *Prog. Theor. Phys.* **13** 129
- [16] Staut J W and Matarrese L M 1953 *Rev. Mod. Phys.* **25** 338
- [17] Moriya T 1959 *J. Phys. Chem. Solids* **11** 73
- [18] Jaccarino V 1959 *Phys. Rev. Lett.* **2** 163
- [19] Jaccarino V 1959 *J. Chem. Phys.* **30** 1627
- [20] Erickson R A 1953 *Phys. Rev.* **90** 779
- [21] Martel P, Cowley R A and Stevenson R W H 1968 *Can. J. Phys.* **46** 1355
- [22] Cowley R A, Buyers W J L, Martel P and Stevenson R W H 1973 *J. Phys. C: Solid State Phys.* **6** 2997
- [23] Strempler J, Rütt U, Bayracki P S, Brückel T and Jauch W 2004 *Phys. Rev. B* **69** 014417
- [24] Jauch W, Reehuis M and Schultz A J 2004 *Acta Crystallogr. A* **60** 51
- [25] Chatterji T (ed) 2006 *Neutron Scattering from Magnetic Materials* (Amsterdam: Elsevier)
- [26] Chatterji T and Schneider G J 2009 *J. Phys.: Condens. Matter* **21** 436008
- [27] Hansen T C, Henry P F, Fischer H E, Torregrossa J and Convert P 2008 *Meas. Sci. Technol.* **19** 034001
- [28] Clark A E, de Savage B and Bozorth R 1965 *Phys. Rev.* **138** A216