On the compression mechanism of FeF$_3$

J.-E. Jørgensen^a* and R. I Smith^b

^{a}Department of Chemistry, University of Aarhus, DK-8000 Århus C, Denmark, and ^{b}ISIS Neutron Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, England

Correspondence e-mail: jenserik@chem.au.dk

The structure of FeF$_3$, iron trifluoride, has been studied in the pressure range from ambient to 8.28 GPa by time-of-flight neutron powder diffraction. No structural phase transitions were found within the investigated pressure range, and least-squares refinements of the crystal structures were performed in the space group $R\bar{3}c$ for all recorded data sets. It was found that volume reduction is achieved through rotation of the FeF$_6$ octahedra, and the Fe—F—Fe bond angle decreases from 152.5 (2) to 134.8 (3)$^\circ$ within the investigated pressure range. A small octahedral strain was found to develop during compression, which reflects an elongation of the FeF$_6$ octahedra along the c axis. The zero-pressure bulk modulus B_o and its pressure derivative B'_o were determined to be 14 (1) GPa and 12 (1), respectively.

1. Introduction

Many metal trifluorides have the VF$_3$ structure, including the title compound, FeF$_3$ (Leblanc *et al.*, 1985). These compounds are composed of corner-sharing MF$_6$ octahedra and are therefore structurally related to perovskite-type compounds AMX_3, as well as to ReO$_3$ (Meisel, 1932). A non-distorted perovskite-type compound is cubic with the space group $Pm\bar{3}m$, while the VF$_3$ structure is rhombohedral with the space group $R\bar{3}c$. The X atoms of a non-distorted perovskite compound occupy a configuration of the cubic lattice complex J (*International Tables for Crystallography*, 1992, Vol. A), which corresponds to a sphere packing of type 8/3/c2 with eight nearest-neighbour contacts per sphere (Fischer, 1973). The 8/3/c2 sphere packing of the X atoms constitutes a framework containing cubo-octahedral voids occupied by A atoms and octahedral voids occupied by M atoms. The VF$_3$ and ReO$_3$ structures are examples of cubic perovskite-related compounds with empty cubo-octahedral voids. The VF$_3$ structure is derived from the ReO$_3$ structure by coupled rotations of the octahedra around one of the cubic body diagonals as $R\bar{3}c$ is a subgroup of $Pm\bar{3}m$. The empty cubo-octahedral voids enable relatively large tilts and rotations of the octahedra in the ReO$_3$ structure, and the degree of space filling of an 8/3/c2 sphere packing can therefore be increased by rotating the octahedra around one of the body diagonals of the cubic unit cell. The octahedral voids are maintained during the rotation, while the empty cubo-octahedral voids will distort and diminish their volume. This type of deformation of the 8/3/c2 sphere packing suggests the simplest conceivable compression mechanism for an MX_3 compound with the space group $R\bar{3}c$. Rotation of the MX_6 octahedra around the c axis will diminish the length of the a axis, and thereby the volume, while the length of the c axis is maintained during the rotation (assuming undistorted octahedra and hexagonal setting of the space group). The compressibility in the a-axis direction is

expected to be high as the restoring force is due to bending of the $M-X-M$ bonds.

A 30° rotation around one of the body diagonals of the $Pm\bar{3}m$ structure causes the $M-X-M$ bond angle in the cubic structure to decrease from 180 to 131.8° and leads to hexagonal close packing of the framework atoms X, at which point an abrupt decrease in the compressibility should occur. Further rotation of the octahedra leads to a 'super dense' sphere packing of the X atoms containing groups of three squeezed X atoms. Calcite, $CaCO_3$, is an example of such a compound as carbon is located between three squeezed O atoms.

The non-distorted $Pm\bar{3}m$ structure is optimal for an MX_3 compound from an electrostatic point of view, as shown by Herzig & Zemann (1993). However, experimentally it is found that many metal trifluorides, MF_3, crystallize in the space group $R\bar{3}c$ with $M-F-M$ bond angles in the range 131.8–180°. ScF_3 is an example of a trifluoride close to the ReO_3 structure with an $Sc-F-Sc$ bond angle of 175.8°, and the space group was found to be $R32$ (Lösch et al., 1982). RhF_3 represents the other extreme, with hexagonally close packed fluoride ions (Hepworth et al., 1957). However, a small deviation from hexagonal close packing was later observed by Grosse & Hoppe (1987). Bonding effects such as the polarizability of the fluorine ions as well as covalency were suggested to be responsible for the deviation from the non-distorted $Pm\bar{3}m$ structure (Herzig & Zemann, 1993).

Sowa & Ahsbahs (1998) studied the two VF_3-type compounds TiF_3 and FeF_3 by high-pressure X-ray diffraction and showed that a pressure-induced octahedral strain devel-oped in both compounds. In addition, a high-pressure X-ray diffraction study of ReO_3 suggested that compression of the $R\bar{3}c$ high-pressure phase takes place through rotation of the ReO_6 octahedra and that the O atoms become hexagonally close packed at 38 GPa, resulting in an abrupt decrease in the compressibility (Jørgensen et al., 2000). However, no refinement of the crystal structure of the $R\bar{3}c$ phase was carried out in the studies of TiF_3, FeF_3 and the $R\bar{3}c$ phase of ReO_3. The structure of the $R\bar{3}c$ high-pressure phase of NbO_2F, in which the O and F atoms are statistically distributed, has been studied by high-pressure X-ray diffraction and Rietveld refinements. This study showed that compression of NbO_2F involved not only tilting of the $Nb(O/F)_6$ octahedra, but also compression of the $Nb-(O/F)$ distance (Carlson et al., 2000). Recently, CrF_3 has been studied by time-of-flight high-pressure neutron powder diffraction (Jørgensen et al., 2004). Rietveld refinements of the crystal structure as a function of pressure showed that the structural changes of the CrF_6 octahedra are minor during compression. However, a small but significant octahedral strain was found to develop during compression. The aim of the present study was to obtain detailed structural information on the compression mechanism of FeF_3 for comparison with the earlier high-pressure studies of the isostructural compounds TiF_3 and CrF_3, as well as with the $R\bar{3}c$ high-pressure phase of ReO_3.

2. Experimental

The FeF_3 samples used in the present work were obtained from Alfa Aesar (catalogue number 11487). High-pressure time-of-flight neutron powder diffraction data were collected on the Polaris diffractometer at the UK pulsed spallation source ISIS using the Paris–Edinburgh pressure cell (Besson et al., 1992). A fully deuterated 4:1 methanol–ethanol mixture was used as the pressure-transmitting medium. The sample was contained within a TiZr encapsulated gasket (Marshall & Francis, 2002). The combined use of the methanol–ethanol mixture and the encapsulated gasket meant that near-hydrostatic compression of the sample was ensured up to pressures of at least 9 GPa. Nine powder patterns of FeF_3 were recorded in the pressure range from ambient pressure to 8.28 GPa. The pressure was determined from a series of six measurements in the pressure range from ambient to 9.13 GPa on a mixed-phase sample with NaCl added as an internal stan-
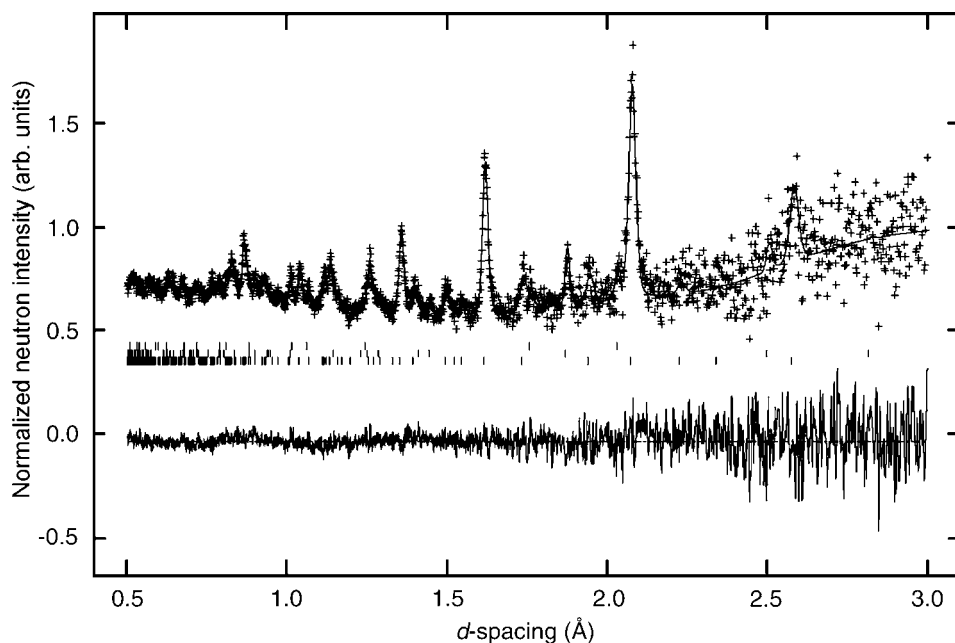
Figure 1
Selected part of the powder neutron diffraction pattern obtained from FeF_3 at 8.28 GPa. The crosses and the solid line represent the measured and calculated patterns, respectively. The lower curve shows the difference between observed and calculated intensities. From bottom to top, the vertical tick marks shown represent the Bragg reflection positions for FeF_3, WC and Ni, respectively. The weak contributions to the pattern from WC and Ni arise from the anvils of the pressure cell.

Table 1
Structural parameters for FeF$_3$.

Space group $R\bar{3}c$ Fe: 6(b) (0 0 0) and F: 18(e) ($-x$ 0 3/4).

P (GPa)	a (Å)	c (Å)	x	$100\langle u_{Fe}^2\rangle$ (Å^2)	$100\langle u_{F}^2\rangle$ (Å^2)	R_{wp}
0.0001	5.1980 (5)	13.338 (2)	0.4122 (7)	0.24 (7)	0.92 (8)	0.0446
0.54	5.1144 (5)	13.347 (2)	0.3940 (7)	0.21 (7)	0.69 (9)	0.0453
1.46	5.0094 (5)	13.397 (2)	0.3805 (7)	0.49 (9)	0.59 (8)	0.0460
1.98	4.9636 (5)	13.419 (2)	0.3744 (6)	0.56 (8)	0.43 (7)	0.0423
2.59	4.9190 (5)	13.431 (2)	0.3675 (7)	0.43 (7)	0.40 (7)	0.0394
3.95	4.8400 (4)	13.441 (2)	0.3592 (7)	0.18 (6)	0.34 (6)	0.0367
5.57	4.7683 (5)	13.439 (2)	0.3527 (9)	0.33 (6)	0.33 (6)	0.0379
7.00	4.7202 (5)	13.411 (2)	0.348 (1)	0.21 (6)	0.32 (6)	0.0380
8.28	4.6866 (6)	13.368 (3)	0.344 (1)	0.24 (7)	0.38 (7)	0.0446

dard (Decker, 1971). The uncertainties of the determined pressures were estimated to be ±0.02 GPa. Data analysis was performed by use of the Rietveld method using the *GSAS* suite of programs (Larson & Von Dreele, 1987).[1]

3. Results and discussion

The recorded diffraction profiles of FeF$_3$ gave no indication of a structural phase transition within the investigated pressure range and therefore all Rietveld refinements were performed in the space group $R\bar{3}c$. Small scattering contributions from WC and Ni originating from the anvils of the pressure cell were also included in the Rietveld refinements. Fig. 1 shows the observed, calculated and difference (obs − calc) powder neutron diffraction profiles of FeF$_3$ at 8.28 GPa, and the refined structural parameters at each of the measured pressures are given in Table 1. For all pressures up to 8.28 GPa the parameters in Table 1 were refined using data collected from the pure FeF$_3$ loading. The structural parameters for FeF$_3$ obtained at ambient pressure are in fair agreement with earlier results obtained by Leblanc *et al.* (1985).

Fig. 2 shows the a and c lattice parameters and the relative volume V/V_o derived from data collected from the mixed FeF$_3$/NaCl sample and plotted as a function of pressure. The a lattice parameter decreases smoothly and it is reduced by 9.8% when the pressure is increased from ambient to 8.28 GPa. The c lattice shows much less pressure dependence on an absolute scale, but its pressure dependence is more complicated. It increases by 0.77% to its maximum value at 4 GPa and decreases again at higher pressures. The pressure dependence of the c axis is small but statistically significant, although the estimated standard deviations shown in Fig. 2(a) might be underestimated, as is often the case for Rietveld refinements. Increases in the c lattice parameter during compression were also observed in earlier studies of TiF$_3$ and FeF$_3$ (3.3 and 1.1%, respectively) by Sowa & Ahsbahs (1998). In the case of CrF$_3$, the c lattice parameter increased by 0.17%

and obtained its maximum value at 3.43 GPa (Jørgensen *et al.*, 2004). The increase in c is associated with small distortions of the FeF$_6$ octahedra as explained below, and the pressure dependence of the a and c lattice parameters for CrF$_3$, TiF$_3$ and FeF$_3$ show that volume reduction of these compounds takes place through rotation of the octahedra around the c axis.

The unit-cell volumes derived from the recorded diffraction data on the mixed FeF$_3$/NaCl sample were used for the determination of the bulk modulus B_o and its pressure derivative B'_o for FeF$_3$ by use of the third-order Birch–Murnaghan equation of state

$$P = \frac{3}{2} B_o \left(x^{-7/3} - x^{-5/3}\right)\left[1 - \frac{3}{4}(4 - B'_o)\left(x^{-2/3} - 1\right)\right], \quad (1)$$

where x denotes the volume ratio V/V_o (V_o being the volume at zero pressure), while B_o and B'_o are the isothermal bulk modulus at ambient pressure and its pressure derivative, respectively. The least-squares fit to the measured data yielded the following value for the bulk modulus: $B_o = 14$ (1) GPa and $B'_o = 12$ (1). In comparison, the values $B_o = 29.2$ (4) GPa and
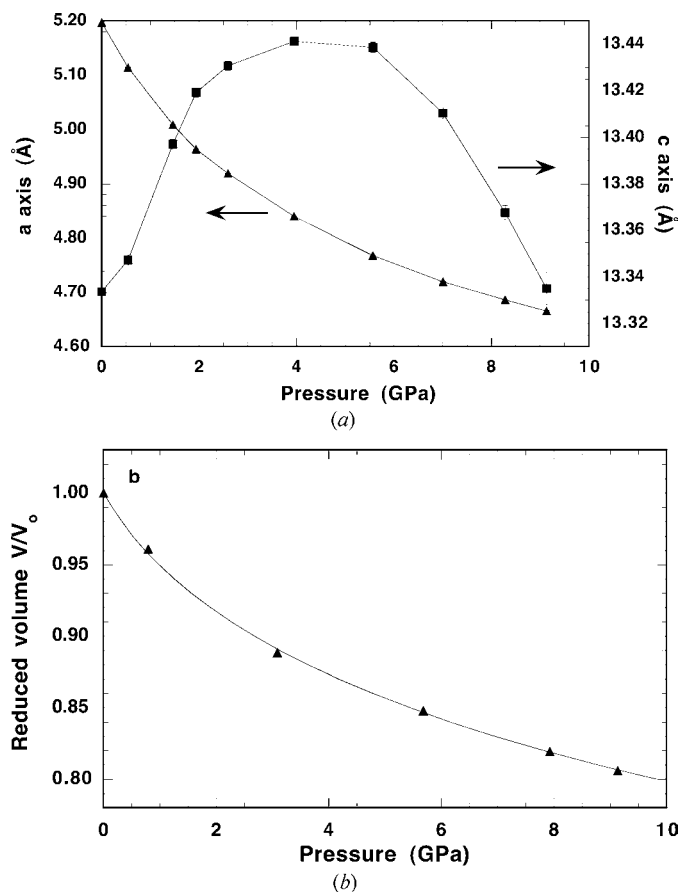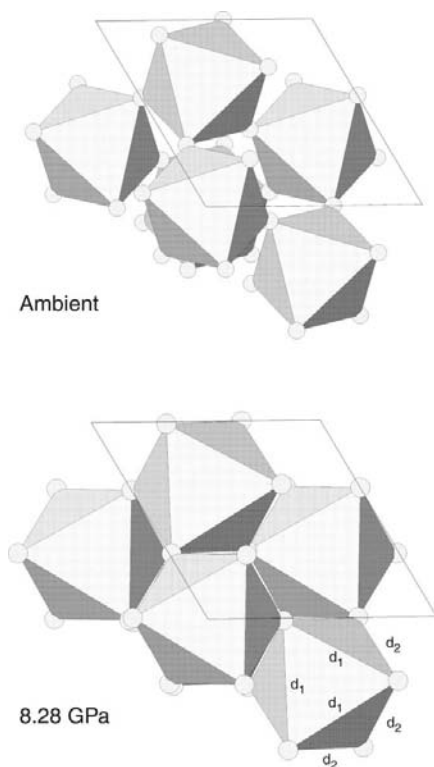

Figure 2
Lattice parameters a and c (a) and the relative volume V/V_o (b) plotted as a function of pressure. The solid curve for the relative volume represents a fit to the third-order Birch–Murnaghan equation of state with bulk modulus $B_o = 14$ (1) GPa and its pressure derivative $B'_o = 12$ (1) as described in the text. The estimated standard deviations of a, c and V/V_o are smaller than the plotted symbols for most of the points, and the solid curves for the lattice parameters a and c are guides to the eye.

$B'_o = 10.1$ (3) were obtained for CrF_3 (Jørgensen *et al.*, 2004). The low values of B_o obtained for both compounds show that CrF_3 and FeF_3 are relatively soft compounds. Compression of FeF_3 and CrF_3 is achieved through bending of chemical bonds, which yields larger compressibilities than when compression takes place through compression of chemical bonds, as discussed by Jørgensen *et al.* (2004). The obtained B'_o value of 12 (1) for FeF_3 is reasonable as most materials have values between 2 and 12 with soft materials having large B'_o values as opposed to the normal typical $B'_o \simeq 4$ results.

Fig. 3 shows the FeF_3 structure at ambient pressure and 8.28 GPa. Symmetry allows for two independent F—F distances, d_1 and d_2, within each FeF_6 octahedron but only one Fe—F distance. The short and long F—F distances d_1 and d_2 are found within and out of the basal plane, respectively. Figs. 4 and 5 show the structural changes of FeF_3 during compression. From Fig. 4(*a*) it is seen that the structural changes of the FeF_6 octahedra are minor during compression. However, d_1 and d_2 are seen to become significantly different at pressures above 0.54 GPa, and d_2 undergoes very little change up to 2.6 GPa, while d_1 decreases significantly in the same pressure range. This result indicates that the FeF_6 octahedra are becoming squeezed in the *ab* plane, while their dimension along the *c* axis is almost unchanged. Furthermore, d_1 exhibits a change in slope at 2.6 GPa, while d_2 starts decreasing at this
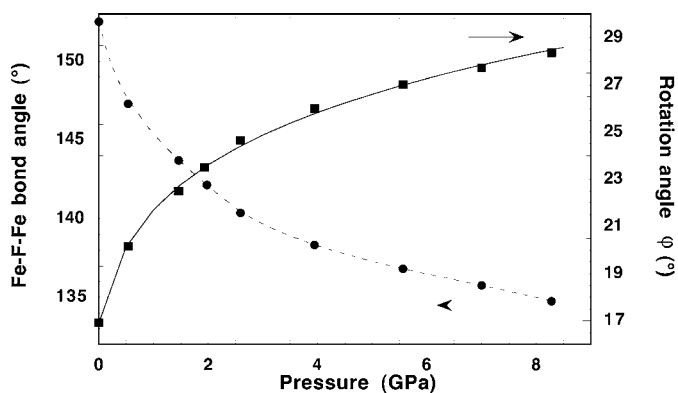
pressure. d_1 and d_2 are reduced by 2.0 and 0.50%, respectively, while the Fe—F bond is shortened by 1.2%. The distortion of the FeF_6 octahedra can be expressed in terms of an octahedral

(a)

(b)
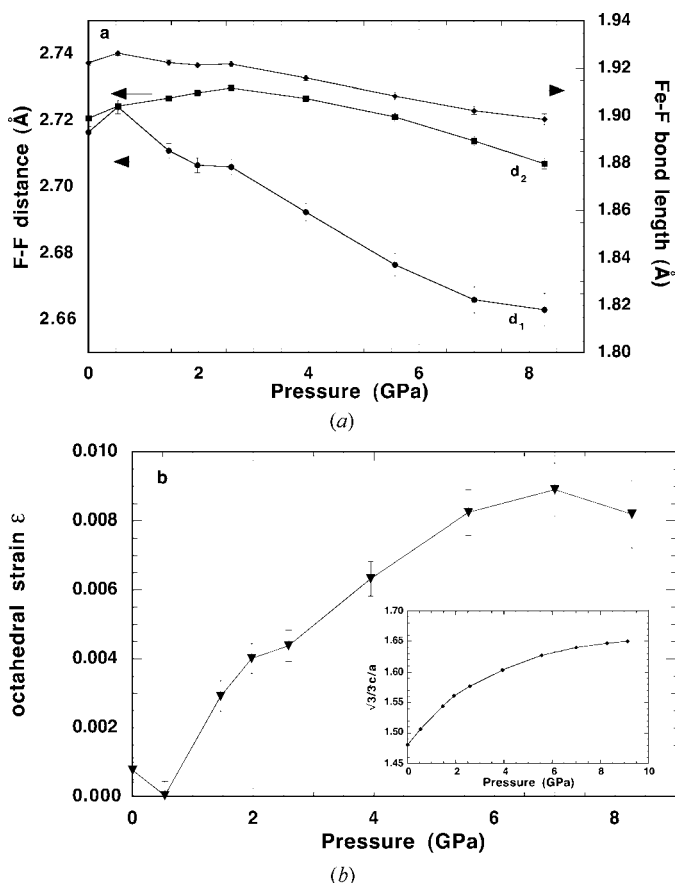
Figure 4
The Fe—F bond length (♦), F—F distances (d_1 ●, d_2 ■) (*a*) and octahedral strain ε (▼) (*b*) plotted as a function of the pressure. The octahedral strain is seen to increase up to about 6 GPa and remains almost constant above this pressure. The increased octahedral strain reflects an elongation of the octahedra along the *c* axis. Solid lines are guides to the eye. The insert shows the $3^{1/2}c/3a$ ratio plotted as function of the pressure.

Figure 3
The FeF_3 structure at ambient pressure and 8.28 GPa viewed along the *c* axis. Symmetry allows for two independent F—F distances d_1 and d_2 within each CrF_6 octahedron, as marked on the lower figure. The octahedral strain is due to an elongation of the octahedra along the *c* axis with $d_1 = 2.663$ (5) Å and $d_2 = 2.707$ (2) Å at 8.28 GPa. The hexagonal unit cell is shown with solid lines.

Figure 5
Fe–F—Fe angle (●) and rotation angle φ (■) of the octahedra plotted as a function of pressure. A structure with hexagonally packed fluoride ions corresponds to an Fe—F—Fe angle of 131.8°. The dashed line is a guide to the eye, while the solid line represents a fit to a power law as described in the text.

strain, ε defined as $\varepsilon = (d_2 - d_1)/(d_2 + d_1)$ and shown in Fig. 4(b) as a function of pressure. ε increases up to a pressure of 5.6 GPa and saturates at an average value of ca 8.4×10^{-3} at higher pressures. The increasing octahedral strain reflects an increasing rhombohedral distortion of the FeF_6 octahedra as they become elongated along the c axis. The increasing octahedral strain is also consistent with the pressure dependence of the c axis described above. Analysis of the results of Sowa & Ahsbahs (1998) for TiF_3 and FeF_3 shows that ε also increases linearly up to about 3 GPa and saturates at values of 1.4×10^{-2} and 6.3×10^{-3} for TiF_3 and FeF_3, respectively. No structural refinement was performed in this high-pressure diffraction study of TiF_3 and FeF_3, and d_1 and d_2 were therefore calculated under the assumption that the metal–fluorine bond length is independent of the pressure. The ε values for these compounds should therefore be considered as lower limits for the octahedral strain, as they will increase if the metal–fluorine bond length is shortened as observed in this study. The pressure-induced octahedral strain was attributed to repulsive interactions between the cations in the cases of FeF_3, TiF_3 and $NaSbF_6$ (Sowa & Ahsbahs, 1998; Sowa, 1997). The Fe—F—Fe bond angle, shown in Fig. 5, decreases from 152.5 (2) to 134.8 (3)°, showing that the F atoms are almost hexagonally close packed at the highest measured pressure of 8.28 GPa (the Fe—F—Fe bond angle is 131.8° in a structure with hexagonally close-packed F atoms). This result again shows that volume reduction is achieved through rotation of the FeF_6 octahedra around the c axis.

The rotation angle φ of the FeF_6 octahedra around the c axis is calculated from the fluorine x coordinates given in Table 1 and shown as a function of pressure in Fig. 5. φ was calculated according to the expression given by Carlson *et al.* (2000). $x = \frac{1}{2}$ corresponds to the cubic $Pm\bar{3}m$ structure ($\varphi = 0°$), while the rhombohedral $R\bar{3}c$ structure with hexagonally close packed F atoms within the basal plane is obtained for $x = 1/3$ or $2/3$ ($\varphi = \pm 30°$). From Table 1 it is seen that x reaches a value of 0.3441 (1) at ca 8.28 GPa (corresponding to $\varphi = 28.5°$), which shows that the F atoms are almost hexagonally close packed
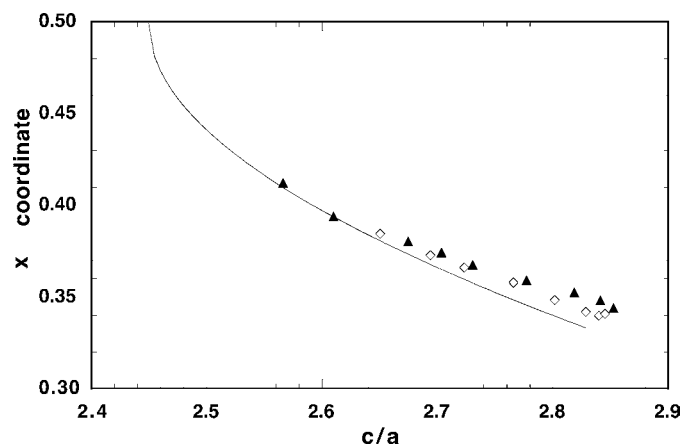
Figure 6
Positional parameter x of the F atoms in FeF_3 (▲) and CrF_3 (◇) *versus* axial ratio c/a. The solid line corresponds to the parameters for an ideal $8/3/c2$ sphere packing in the space group $R\bar{3}c$ as explained in the text.

within the basal plane at this pressure. The $3^{1/2}c/3a$ ratio for an $R\bar{3}c$ structure with hexagonally close packed F atoms corresponds to the conventional c/a ratio for a hexagonal sphere packing, which is 1.633. The insert of Fig. 4(b) shows that $3^{1/2}c/3a$ reaches the value of 1.633 at 6.3 GPa, which is very close to the pressure at which the rhombohedral strain ε saturates, and increases to a value of 1.650 (9) at 9.13 GPa. The fact that $3^{1/2}c/3a$ exceeds 1.633 indicates that the F atoms are becoming slightly squeezed in the ab plane above 6.3 GPa, although x is slightly larger than 1/3. The proximity to hexagonal close packing of the F atoms at the highest measured pressure suggests that the bulk modulus of FeF_3 should increase considerably at higher pressures. However, the accessible pressure range was not large enough to observe an abrupt enhancement of the bulk modulus as was observed at 38 GPa for the $R\bar{3}c$ phase of ReO_3 (Jørgensen *et al.*, 2000).

The pressure dependence of φ is shown in Fig. 5, and it is seen that φ obeys the power law $\varphi \propto (P - P_c)^{\beta}$, with $\beta = 0.139$ (5) and $P_c = -0.20$ (3) GPa over the entire range of measured pressures. A similar analysis of the data for FeF_3 and TiF_3 reported by Sowa & Ahsbahs (1998) yielded $\beta = 0.19$ (1) for both compounds, while $\beta = 0.121$ (9) was found for CrF_3 (Jørgensen *et al.*, 2004). Furthermore, the rotation angle of the $Nb(O,F)_6$ octahedra in NbO_2F was found to obey the above-described power law with $\beta = 0.21$ (1) or 0.14 (1) depending on the method of calculation (Carlson *et al.*, 2000). Several perovskite compounds undergo temperature- or pressure-induced structural phase transitions in which the rotation angle of the octahedra is the order parameter. The pressure or temperature dependence of the low-symmetry phase of these compounds resembles the compression of FeF_3 as the $R\bar{3}c$ structure of this compound can be derived from a hypothetical cubic $Pm\bar{3}m$ phase by rotation of the FeF_6 octahedra around one of the cubic body diagonals. The rotation angle φ is then playing the role of the order parameter. The above-mentioned exponents for CrF_3, FeF_3 and TiF_3 are surprisingly low in comparison with exponents obtained for other perovskite compounds undergoing structural phase transitions in which the rotation angle of the octahedra is the order parameter, as discussed by Jørgensen *et al.* (2004).

The compression of CrF_3 and FeF_3 are compared and described in terms of deformation of the $8/3/c2$ sphere packing in Fig. 6. The $8/3/c2$ sphere packing may, in space group $R\bar{3}c$, be deformed without losing contacts if the following condition is fulfilled (Sowa, 1997)

$$x = 1/2 \pm [c^2/(72\,a^2) - 1/12]^{1/2}. \qquad (2)$$

The limiting cases are the cubic ReO_3 structure type and hexagonal close packing of the spheres. The ReO_3 structure type is obtained for $x = 1/2$ and $c/a = 6^{1/2} \simeq 2.449$. Each sphere has eight contacts in this case. Hexagonal close packing is obtained for $x = 1/3$ and $c/a = 8^{1/2} \simeq 2.828$, and the number of contacts per sphere has in this case increased to the limiting number of 12. From Fig. 6 it is seen that FeF_3 is described by the sphere packing model at the two lowest measured pressures (lowest c/a values). The deviation from the theoretical curve increases at higher pressures. CrF_3 shows a smaller

deviation from the theoretical curve and this compound is therefore better described by the sphere packing model. However, both compounds show larger values of c/a than 2.828, which is the maximum value that can be obtained for an $8/3/c2$ packing of hard spheres in space group $R\bar{3}c$. The large values of c/a reflect the octahedral strain which develops in both compounds at high pressure.

4. Conclusion

FeF_3 is a relatively soft compound, with bulk modulus $B_o = 14\,(1)$ GPa. The present high-pressure neutron powder diffraction study has shown that compression of FeF_3 takes place through rotation of the FeF_6 octahedra around the c axis, with the result that the F atoms were found to be almost hexagonally close packed at ca 8 GPa. No structural phase transitions were observed within the investigated pressure range.

The rotation angle φ of the FeF_6 octahedra obeys the relationship $\varphi \propto (P - P_c)^{\beta}$, with $\beta = 0.139\,(5)$ and $P_c = -0.20\,(3)$ GPa. The FeF_6 octahedra undergo only small deformations during compression, and the changes in the Fe—F bond lengths and the short and long F—F distances within the octahedra are found to be minor (1.2, 2.0 and 0.50%, respectively). Nevertheless, the FeF_6 octahedra were seen to develop a small but significant rhombohedral strain during compression as they become elongated along the c axis.

Finally, it has been shown that the arrangement of the F atoms in FeF_3 and CrF_3 during compression is reasonably well described by the deformation of a sphere packing of type $8/3/c2$.

References

Besson, J. M., Nelmes, R. J., Hamel, G., Loveday, J. S., Weill, G. & Hull, S. (1992). *Physica B*, **180–181**, 907–910.
Carlson, S., Larsson, A.-K. & Rohrer, F. E. (2000). *Acta Cryst.* B**56**, 189–196.
Decker, D. L. (1971). *J. Appl. Phys.* **42**, 3239–3244.
Fischer, W. (1973). *Z. Kristallogr.* **138**, 129–146.
Grosse, L. & Hoppe, R. (1987). *Z. Anorg. Allg. Chem.* **552**, 123–131.
Hepworth, M. A., Jack, K. H., Peacock, R. D. & Westland, G. J. (1957). *Acta Cryst.* **10**, 63–69.
Herzig, P. & Zemann, J. (1993). *Z. Kristallogr.* **205**, 85–97.
Jørgensen, J.-E., Marshall, W. G. & Smith, R. I. (2004). *Acta Cryst.* B**60**, 669–673.
Jørgensen, J.-E., Olsen, J. S. & Gerward, L. (2000). *J. Appl. Cryst.* **33**, 279–284.
Larson, A. C. & Von Dreele, R. B. (1987). Report No. LAUR 86-748. Los Alamos National Laboratory, New Mexico, USA.
Leblanc, M., Pannetier, J., Ferey, G. & de Pape, R. (1985). *Rev. Chim. Miner.* **22**, 107–114.
Lösch, R., Hebecker, Ch. & Ranft, Z. (1982). *Z. Anorg. Allg. Chem.* **491**, 199–202.
Marshall, W. G. & Francis, D. J. (2002). *J. Appl. Cryst.* **35**, 122–125.
Meisel, K. (1932). *Z. Anorg. Allg. Chem.* **207**, 121–128.
Sowa, H. (1997). *Acta Cryst.* B**53**, 25–31.
Sowa, H. & Ahsbahs, H. (1998). *Acta Cryst.* B**54**, 578–584.